1 The properties of gases

1A The perfect gas

Answers to discussion questions

1A.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 upon 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.

Solutions to exercises

1A.1(b) The perfect gas law [1A.5] 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.

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

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

So $\boxed{\text{no}}$, the sample would not exert a pressure of 2.0 bar.

1A.2(b) Boyle's law [1A.4a] applies.

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

Solve for the initial pressure:

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

(ii) The original pressure in Torr is

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

1A.3(b) The relation between pressure and temperature at constant volume can be derived from the perfect gas law, $pV = nRT$ [1A.5]

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

The final pressure, then, ought to be

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

1A.4(b) According to the perfect gas law [1.8], one can compute the amount of gas from pressure, temperature, and volume.

$$pV = nRT$$

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

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

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

1A.5(b) The total pressure is the external pressure plus the hydrostatic pressure [1A.1], making the total pressure

$p = p_{\text{ex}} + \rho gh$.

Let p_{ex} be the pressure at the top of the straw and p the pressure on the surface of the liquid (atmospheric pressure). Thus the pressure difference is

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

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

1A.6(b) The pressure in the apparatus is given by

$p = p_{\text{ex}} + \rho gh$ [1A.1]

where p_{ex} = 760 Torr = 1 atm = 1.013×10^5 Pa,

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

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

1A.7(b) Rearrange the perfect gas equation [1A.5] 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 upon 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.

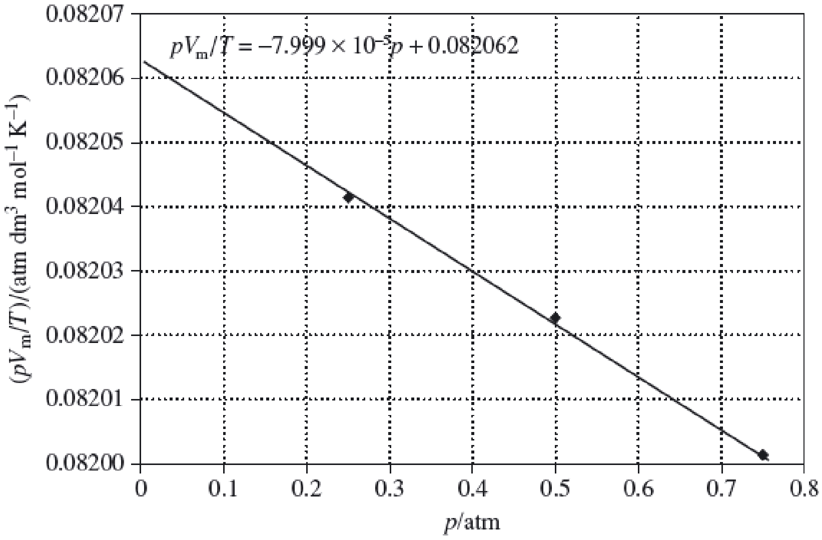
Draw up the following table:

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

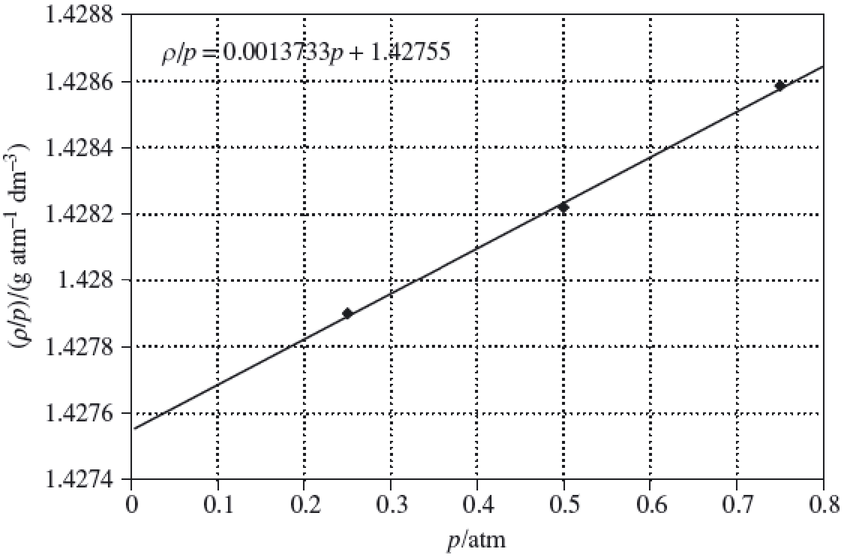
From Figure 1A.1(a), $R = \lim\limits_{p\to 0}\left(\dfrac{pV_{\text{m}}}{T}\right) = \boxed{0.082\ 062\text{ dm}^3\text{ atm K}^{-1}\text{ mol}^{-1}}$

Figure 1A.1

(a)



(b)



From Figure 1A.1(b), $\lim_{p\to 0}\left(\frac{\rho}{p}\right) = 1.427\ 55\ \text{g dm}^{-3}\ \text{atm}^{-1}$

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

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

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

1A.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 relation into the perfect gas law [1A.5] yields

$$pV_m = RT \qquad \text{so} \qquad \frac{pM}{\rho} = RT$$

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.

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

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

The number of atoms per molecule is

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

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

1A.9(b) Use the perfect gas equation [1A.5] to compute the amount; then convert to mass.

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

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

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

so $$n=\frac{(1.49\times10^{3}\ \text{Pa})\times(250\ \text{m}^{3})}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(23+273)\ \text{K}}=151\ \text{mol}$$

and $$m=(151\ \text{mol})\times(18.0\ \text{g mol}^{-1})=2.72\times10^{3}\ \text{g}=\boxed{2.72\ \text{kg}}$$

1A.10(b) **(i)** 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, eqn. 1A.5)

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

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

$$n_{\text{Ne}}=\frac{0.225\ \text{g}}{20.18\ \text{g mol}^{-1}}=1.11\overline{5}\times10^{-2}\ \text{mol}$$

Thus

$$V=\frac{1.11\overline{5}\times10^{-2}\ \text{mol}\times8.3145\ \text{Pa m}^{3}\ \text{K}^{-1}\ \text{mol}^{-1}\times300\ \text{K}}{8.87\times10^{3}\ \text{Pa}}=3.14\times10^{-3}\ \text{m}^{3}=\boxed{3.14\ \text{dm}^{3}}$$

(ii) The total pressure is determined from the total amount of gas, $n=n_{\text{CH}_4}+n_{\text{Ar}}+n_{\text{Ne}}$.

$$n_{\text{CH}_4}=\frac{0.320\ \text{g}}{16.04\ \text{g mol}^{-1}}=1.99\overline{5}\times10^{-2}\ \text{mol}\quad n_{\text{Ar}}=\frac{0.175\ \text{g}}{39.95\ \text{g mol}^{-1}}=4.38\times10^{-3}\ \text{mol}$$

$$n=\left(1.99\overline{5}+0.438+1.11\overline{5}\right)\times10^{-2}\text{mol}=3.55\times10^{-2}\ \text{mol}$$

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

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

1A.11(b) This exercise uses the formula, $M=\dfrac{\rho RT}{p}$, which was developed and used in Exercise 1A.8(b). First the density must first be calculated.

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

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

1A.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:

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

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

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

which is close to the accepted value of –273C.

1A.13(b) **(i)** Mole fractions are

$$x_{\text{N}}=\frac{n_{\text{N}}}{n_{\text{total}}}[1\text{A}.9]=\frac{2.5\ \text{mol}}{(2.5+1.5)\ \text{mol}}=\boxed{0.63}$$

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

According to the perfect gas law

$$p_{\text{tot}}V=n_{\text{tot}}RT$$

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

(ii) The partial pressures are

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

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

(iii) $$p = p_{\text{H}} + p_{\text{N}}[\text{1A.10}] = (2.5+1.5)\text{ atm} = \boxed{4.0\text{ atm}}$$

Solutions to problems

1A.2 Solving for n from the perfect gas equation [1A.5] 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 relation, 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.

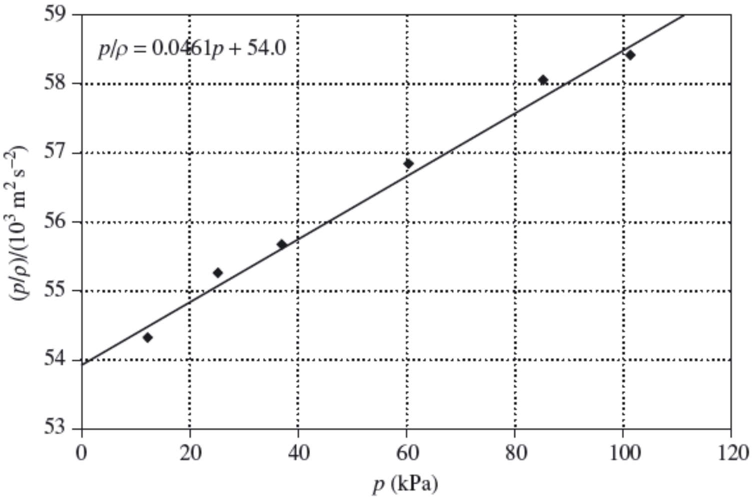
p/(kPa)	12.223	25.20	36.97	60.37	85.23	101.3
ρ/(kg m^{-3})	0.225	0.456	0.664	1.062	1.468	1.734
$\frac{p/\rho}{10^3\text{ m}^2\text{ s}^{-2}}$	54.3	55.3	55.7	56.8	58.1	58.4

Bear in mind that 1 kPa = 10^3 kg m^{-1} s^{-2}.

$\frac{p}{\rho}$ is plotted in Figure 1A.2. A straight line fits the data rather well. The extrapolation to $p = 0$ yields an intercept of $54.0\times10^3\text{ m}^2\text{ s}^{-2}$. 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 1A.2



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

1A.4 The mass of displaced gas is ρV, where V is the volume of the bulb and ρ is the density of the displaced gas. The balance condition for the two gases is

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

which implies that $\rho = \rho'$. Because [Problem 1.2] $\rho = \dfrac{pM}{RT}$

the balance condition is $pM = p'M'$,

which implies that $M' = \dfrac{p}{p'} \times M$

This relation 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.

1A.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

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

$p(H_2) = x(H_2)p = \boxed{0}$
$p(N_2) = x(N_2)p = 0.20 \times 1.66\ \text{atm} = \boxed{0.33\ \text{atm}}$
$p(NH_3) = x(NH_3)p = 0.80 \times 1.66\ \text{atm} = \boxed{1.33\ \text{atm}}$

1A.8 The perfect gas law is $pV = nRT$ so $n = \dfrac{pV}{RT}$

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

$$\frac{n}{V}=\frac{1.12\times10^{-3}\ \text{mol}}{(1.00\,\text{dm}^2)\times(40\times10^3\ \text{m})\times(10\,\text{dm m}^{-1})}=\boxed{2.8\times10^{-9}\ \text{mol}\,\text{dm}^{-3}}$$

and $$\frac{n}{V}=\frac{4.46\times10^{-4}\ \text{mol}}{(1.00\,\text{dm}^2)\times(40\times10^3\ \text{m})\times(10\,\text{dm m}^{-1})}=\boxed{1.1\times10^{-9}\ \text{mol}\,\text{dm}^{-3}}$$

respectively.

1A.10 The perfect gas law [1A.5] can be rearranged to $n=\dfrac{pV}{RT}$

The volume of the balloon is $V=\dfrac{4\pi}{3}r^3=\dfrac{4\pi}{3}\times(3.0\ \text{m})^3=11\bar{3}\ \text{m}^3$

(a) $$n=\frac{(1.0\,\text{atm})\times(11\bar{3}\times10^3\,\text{dm}^3)}{(0.08206\ \text{dm}^3\ \text{atm mol}^{-1}\ \text{K}^{-1})\times(298\,\text{K})}=\boxed{4.6\bar{2}\times10^3\,\text{mol}}$$

(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:

$$m=m(\text{H}_2)=nM(\text{H}_2)=(4.6\bar{2}\times10^3\,\text{mol})\times(2.02\,\text{g mol}^{-1})=9.3\bar{3}\times10^3\ \text{g}$$

$$\text{Mass of displaced air}=(11\bar{3}\,\text{m}^3)\times(1.22\,\text{kg m}^{-3})=1.3\bar{8}\times10^2\ \text{kg}$$

Therefore, the mass of the maximum payload is

$$13\bar{8}\,\text{kg}-9.3\bar{3}\,\text{kg}=\boxed{1.3\times10^2\ \text{kg}}$$

(c) For helium, $m=nM(\text{He})=(4.6\bar{2}\times10^3\,\text{mol})\times(4.00\,\text{g mol}^{-1})=18\,\text{kg}$

The maximum payload is now $13\bar{8}\,\text{kg}-18\,\text{kg}=\boxed{1.2\times10^2\ \text{kg}}$

1A.12 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) $$\frac{n(\text{CCl}_3\text{F})}{V}=\frac{(261\times10^{-12})\times(1.0\,\text{atm})}{(0.08206\,\text{dm}^3\,\text{atm K}^{-1}\text{mol}^{-1})\times(10+273)\,\text{K}}=\boxed{1.1\times10^{-11}\,\text{mol}\,\text{dm}^{-3}}$$

and $$\frac{n(\text{CCl}_2\text{F}_2)}{V}=\frac{(509\times10^{-12})\times(1.0\,\text{atm})}{(0.08206\,\text{dm}^3\,\text{atm K}^{-1}\text{mol}^{-1})\times(10+273)\,\text{K}}=\boxed{2.2\times10^{-11}\,\text{mol}\,\text{dm}^{-3}}$$

(b) $$\frac{n(\text{CCl}_3\text{F})}{V}=\frac{(261\times10^{-12})\times(0.050\,\text{atm})}{(0.08206\,\text{dm}^3\ \text{atm K}^{-1}\text{mol}^{-1})\times(200\,\text{K})}=\boxed{8.0\times10^{-13}\,\text{mol}\,\text{dm}^{-3}}$$

and $$\frac{n(\text{CCl}_2\text{F}_2)}{V}=\frac{(509\times10^{-12})\times(0.050\,\text{atm})}{(0.08206\,\text{dm}^3\,\text{atm K}^{-1}\text{mol}^{-1})\times(200\,\text{K})}=\boxed{1.6\times10^{-12}\,\text{mol}\,\text{dm}^{-3}}$$

1B The kinetic model

Answers to discussion questions

1B.2 The formula for the mean free path [eqn 1B.13] is

$$\lambda=\frac{kT}{\sigma p}$$

In a container of constant volume, the mean free path is directly proportional to temperature and inversely proportional to pressure. The former dependence can be rationalized by noting that the faster the molecules travel, the farther on average they go between collisions. The latter also makes sense in that the lower the pressure, the less frequent are collisions, and therefore the further the average distance between collisions. Perhaps more fundamental than either of these considerations are dependences on size. As pointed out in the text, the ratio T/p is directly proportional to volume for a perfect gas, so the average distance between collisions is directly proportional to the size of the container holding a set number of gas molecules. Finally, the mean free path is inversely proportional to the size of the molecules as given by the collision cross section (and therefore inversely proportional to the square of the molecules' radius).

Solutions to exercises

1B.1(b) The mean speed is [1B.8]

$$v_{\text{mean}} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

The mean translational kinetic energy is

$$\langle E_{\text{k}}\rangle = \langle \tfrac{1}{2}mv^2\rangle = \tfrac{1}{2}m\langle v^2\rangle = \tfrac{1}{2}mv_{\text{rms}}^2 = \frac{m}{2}\left(\frac{3RT}{M}\right)[\text{1B.3}] = \frac{3kT}{2}$$

The ratios of species 1 to species 2 at the same temperature are

$$\frac{v_{\text{mean},1}}{v_{\text{mean},2}} = \left(\frac{M_2}{M_1}\right)^{1/2} \quad \text{and} \quad \frac{\langle E_{\text{k}}\rangle_1}{\langle E_{\text{k}}\rangle_2} = 1$$

(i) $$\frac{v_{\text{mean,H}_2}}{v_{\text{mean,Hg}}} = \left(\frac{200.6}{4.003}\right)^{1/2} = \boxed{7.079}$$

(ii) The mean translation kinetic energy is independent of molecular mass and depends upon 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.

1B.2(b) The root mean square speed [1B.3] is

$$v_{\text{rms}} = \left(\frac{3RT}{M}\right)^{1/2}$$

For CO_2 the molar mass is

$M = (12.011 + 2\times15.9994)\times10^{-3}\ \text{kg mol}^{-1} = 44.010\times10^{-3}\ \text{kg mol}^{-1}$

so $$v_{\text{rms}} = \left(\frac{3(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(20+273)\ \text{K}}{44.01\times10^{-3}\ \text{kg mol}^{-1}}\right)^{1/2} = \boxed{408\ \text{m s}^{-1}}$$

For He

$$v_{\text{rms}} = \left(\frac{3(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(20+273)\ \text{K}}{4.003\times10^{-3}\ \text{kg mol}^{-1}}\right)^{1/2} = \boxed{1.35\times10^{3}\ \text{m s}^{-1}} = \boxed{1.35\ \text{km s}^{-1}}$$

1B.3(b) The Maxwell-Boltzmann distribution of speeds [1B.4] is

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

and the fraction of molecules that have a speed between v and $v+dv$ is $f(v)dv$. The fraction of molecules to have a speed in the range between v_1 and v_2 is, therefore, $\int_{v_1}^{v_2} f(v)\,dv$. If the range is relatively small, however, such that $f(v)$ is nearly constant over that range, the integral may be approximated by $f(v)\Delta v$, where $f(v)$ is evaluated anywhere within the range and $\Delta v = v_2 - v_1$. Thus, we have, with $M = 44.010\times10^{-3}$ kg mol^{-1} [Exericse 1B.2(b)],

$$\int_{v_1}^{v_2} f(v)dv \approx f(v)\Delta v = 4\pi\left(\frac{44.010\times10^{-3}\text{kg mol}^{-1}}{2\pi(8.3145\ \text{J K}^{-1}\text{mol}^{-1})(400\ \text{K})}\right)^{3/2}(402.5\ \text{m s}^{-1})^2$$

$$\times \exp\left(-\frac{(44.010\times10^{-3}\ \text{kg mol}^{-1})(402.5\ \text{m s}^{-1})^2}{2(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(400\ \text{K})}\right)\times(405-400)\ \text{m s}^{-1}$$

$= \boxed{0.0107}$, just over 1%

1B.4(b) The most probable, mean, and mean relative speeds are, respectively

$$v_{\text{mp}} = \left(\frac{2RT}{M}\right)^{1/2}\ [\text{1B.9}] \qquad v_{\text{mean}} = \left(\frac{8RT}{\pi M}\right)^{1/2}\ [\text{1B.8}] \qquad v_{\text{rel}} = \left(\frac{8RT}{\pi\mu}\right)^{1/2}\ [\text{1B.10b}]$$

The temperature is $T = (20+273)\ \text{K} = 293\ \text{K}$.

so $$v_{\text{mp}} = \left(\frac{2(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(293\ \text{K})}{2\times1.008\times10^{-3}\ \text{kg mol}^{-1}}\right)^{1/2} = \boxed{1.55\times10^3\ \text{m s}^{-1}}$$

and $$v_{\text{mean}} = \left(\frac{8(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(293\ \text{K})}{\pi(2\times1.008\times10^{-3}\ \text{kg mol}^{-1})}\right)^{1/2} = \boxed{1.75\times10^3\ \text{m s}^{-1}}$$

For many purposes, air can be considered as a gas with an average molar mass of 29.0 g mol^{-1} . In that case, the reduced molar mass [1B.10b] is

$$\mu = \frac{M_\text{A}M_\text{B}}{M_\text{A}+M_\text{B}} = \frac{(29.0\ \text{g mol}^{-1})(2\times1.008\ \text{g mol}^{-1})}{(29.0+2\times1.008)\ \text{g mol}^{-1}} = 1.88\ \text{g mol}^{-1}$$

and $$v_{\text{rel}} = \left(\frac{8(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(293\ \text{K})}{\pi(1.88\times10^{-3}\ \text{kg mol}^{-1})}\right)^{1/2} = \boxed{1.81\times10^3\ \text{m s}^{-1}}$$

Comment. One computes the average molar mass of air just as one computes the average molar mass of an isotopically mixed element, namely by taking an average of the species that have different masses weighted by their abundances.

Comment. Note that v_{rel} and v_{mean} are very nearly equal. This is because the reduced mass between two very dissimilar species is nearly equal to the mass of the lighter species (in this case, H_2).

1B.5(b) **(i)** $$v_{\text{mean}} = \left(\frac{8RT}{\pi M}\right)^{1/2}[\text{1B.8}] = \left(\frac{8(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298\ \text{K})}{\pi(2\times14.007\times10^{-3}\ \text{kg mol}^{-1})}\right)^{1/2} = \boxed{475\ \text{m s}^{-1}}$$

(ii) The mean free path [1B.13] is

$$\lambda = \frac{kT}{\sigma p} = \frac{kT}{\pi d^2 p} = \frac{(1.381\times10^{-23}\ \text{J K}^{-1})(298\ \text{K})}{\pi(395\times10^{-12}\ \text{m})^2(1\times10^{-9}\ \text{Torr})}\times\frac{1\ \text{Torr}}{133.3\ \text{Pa}}$$

$$= \boxed{6.\bar{3}\times10^4\ \text{m}} = \boxed{6\bar{3}\ \text{km}}$$

The mean free path is much larger than the dimensions of the pumping apparatus used to generate the very low pressure.

(iii) The collision frequency is related to the mean free path and relative mean speed by [1B.12]

$$\lambda = \frac{v_{\text{rel}}}{z} \quad \text{so} \qquad z = \frac{v_{\text{rel}}}{\lambda} = \frac{2^{1/2}v_{\text{mean}}}{\lambda}\ [\text{1B.10a}]$$

$$z = \frac{2^{1/2}(475\ \text{m s}^{-1})}{6.\bar{3}\times10^4\ \text{m}} = \boxed{1.\bar{1}\times10^{-2}\ \text{s}^{-1}}$$

1B.6(b) The collision diameter is related to the collision cross section by

$\sigma = \pi d^2$ so $\quad d = (\sigma/\pi)^{1/2} = (0.36\ \text{nm}^2/\pi)^{1/2} = 0.34\ \text{nm}$.

The mean free path [1B.13] is

$$\lambda = \frac{kT}{\sigma p}$$

Solve this expression for the pressure and set λ equal to 10d:

$$p=\frac{kT}{\sigma\lambda}=\frac{(1.381\times10^{-23}\ \mathrm{J\,K^{-1}})(293\ \mathrm{K})}{0.36\times(10^{-9}\ \mathrm{m})^2(10\times0.34\times10^{-9}\ \mathrm{m})}=3.3\times10^{6}\ \mathrm{J\,m^{-3}}=\boxed{3.3\ \mathrm{MPa}}$$

Comment. This pressure works out to 33 bar (about 33 atm), conditions under which the assumption of perfect gas behavior and kinetic model applicability at least begins to come into question.

1B.7(b) The mean free path [1B.13] is

$$\lambda=\frac{kT}{\sigma p}=\frac{(1.381\times10^{-23}\ \mathrm{J\,K^{-1}})(217\ \mathrm{K})}{0.43\times(10^{-9}\ \mathrm{m})^2(12.1\times10^{3}\ \mathrm{Pa\,atm^{-1}})}=\boxed{5.8\times10^{-7}\ \mathrm{m}}$$

Solutions to problems

1B.2 The number of molecules that escape in unit time is the number per unit time that would have collided with a wall section of area A equal to the area of the small hole. This quantity is readily expressed in terms of Z_W, the collision flux (collisions per unit time with a unit area), given in eqn 19A.6. That is,

$$\frac{\mathrm{d}N}{\mathrm{d}t}=-Z_\mathrm{W}A=\frac{-Ap}{(2\pi mkT)^{1/2}}$$

where p is the (constant) vapour pressure of the solid. The change in the number of molecules inside the cell in an interval Δt is therefore $\Delta N=-Z_\mathrm{W}A\Delta t$, and so the mass loss is

$$\Delta w=m\Delta N=-Ap\left(\frac{m}{2\pi kT}\right)^{1/2}\Delta t=-Ap\left(\frac{M}{2\pi RT}\right)^{1/2}\Delta t$$

Therefore, the vapour pressure of the substance in the cell is

$$p=\left(\frac{-\Delta w}{A\Delta t}\right)\times\left(\frac{2\pi RT}{M}\right)^{1/2}$$

For the vapour pressure of germanium

$$p=\left(\frac{43\times10^{-9}\ \mathrm{kg}}{\pi(0.50\times10^{-3}\ \mathrm{m})(7200\ \mathrm{s})}\right)\times\left(\frac{2\pi(8.3145\ \mathrm{J\,K^{-1}\ mol^{-1}})(1273\ \mathrm{K})}{72.64\times10^{-3}\ \mathrm{kg\,mol^{-1}}}\right)^{1/2}$$

$$=7.3\times10^{-3}\ \mathrm{Pa}=\boxed{7.3\ \mathrm{mPa}}$$

1B.4 We proceed as in Justification 1B.2 except that, instead of taking a product of three one-dimensional distributions in order to get the three-dimensional distribution, we make a product of two one-dimensional distributions.

$$f(v_x,v_y)\mathrm{d}v_x\mathrm{d}v_y=f(v_x^2)f(v_y^2)\mathrm{d}v_x dv_y=\left(\frac{m}{2\pi kT}\right)\mathrm{e}^{-mv^2/2kT}\mathrm{d}v_x\mathrm{d}v_y$$

where $v^2=v_x^2+v_y^2$. The probability $f(v)\mathrm{d}v$ that the molecules have a two-dimensional speed, v, in the range v to $v+\mathrm{d}v$ is the sum of the probabilities that it is in any of the area elements $\mathrm{d}v_x\mathrm{d}v_y$ in the circular shell of radius v. The sum of the area elements is the area of the circular shell of radius v and thickness $\mathrm{d}v$ which is $\pi(v+\mathrm{d}v)^2-\pi v^2=2\pi v\mathrm{d}v$. Therefore,

$$f(v)=\boxed{\left(\frac{m}{kT}\right)v\mathrm{e}^{-mv^2/2kT}}=\boxed{\left(\frac{M}{RT}\right)v\mathrm{e}^{-Mv^2/2RT}}\quad\left[\frac{M}{R}=\frac{m}{k}\right]$$

The mean speed is determined as

$$v_\mathrm{mean}=\int_0^\infty vf(v)\,\mathrm{d}v=\left(\frac{m}{kT}\right)\int_0^\infty v^2\mathrm{e}^{-mv^2/2kT}\,\mathrm{d}v$$

Using integral G.3 from the Resource Section yields

$$v_\mathrm{mean}=\left(\frac{m}{kT}\right)\times\left(\frac{\pi^{1/2}}{4}\right)\times\left(\frac{2kT}{m}\right)^{3/2}=\boxed{\left(\frac{\pi kT}{2m}\right)^{1/2}}=\boxed{\left(\frac{\pi RT}{2M}\right)^{1/2}}$$

1B.6 The distribution [1B.4] is

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 \mathrm{e}^{-Mv^2/2RT} \, .$$

The proportion of molecules with speeds less than v_{rms} is

$$P = \int_0^{v_{\mathrm{rms}}} f(v)\,\mathrm{d}v = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} \int_0^{v_{\mathrm{rms}}} v^2 \mathrm{e}^{-Mv^2/2RT}\,\mathrm{d}v$$

Defining $a \equiv R/2RT$,

$$P = 4\pi\left(\frac{a}{\pi}\right)^{3/2} \int_0^{v_{\mathrm{rms}}} v^2 \mathrm{e}^{-av^2}\,\mathrm{d}v = -4\pi\left(\frac{a}{\pi}\right)^{3/2} \frac{\mathrm{d}}{\mathrm{d}a} \int_0^{v_{\mathrm{rms}}} \mathrm{e}^{-av^2}\,\mathrm{d}v$$

Defining $\chi^2 \equiv av^2$. Then, $\mathrm{d}v = a^{-1/2}\mathrm{d}\chi$ and

$$P = -4\pi\left(\frac{a}{\pi}\right)^{3/2} \frac{\mathrm{d}}{\mathrm{d}a}\left\{\frac{1}{a^{1/2}} \int_0^{v_{\mathrm{rms}}a^{1/2}} \mathrm{e}^{-\chi^2}\,\mathrm{d}\chi\right\}$$

$$= -4\pi\left(\frac{a}{\pi}\right)^{3/2}\left\{-\frac{1}{2}\left(\frac{1}{a}\right)^{3/2} \int_0^{v_{\mathrm{rms}}a^{1/2}} \mathrm{e}^{-\chi^2}\,\mathrm{d}\chi + \left(\frac{1}{a}\right)^{1/2} \frac{\mathrm{d}}{\mathrm{d}a} \int_0^{v_{\mathrm{rms}}a^{1/2}} \mathrm{e}^{-\chi^2}\,\mathrm{d}\chi\right\}$$

Then we use the error function [Integral G.6]:

$$\int_0^{v_{\mathrm{rms}}a^{1/2}} \mathrm{e}^{-\chi^2}\,\mathrm{d}\chi = \left(\pi^{1/2}/2\right)\mathrm{erf}(v_{\mathrm{rms}}a^{1/2}) \, .$$

$$\frac{\mathrm{d}}{\mathrm{d}a} \int_0^{v_{\mathrm{rms}}a^{1/2}} \mathrm{e}^{-\chi^2}\,\mathrm{d}\chi = \left(\frac{\mathrm{d}v_{\mathrm{rms}}a^{1/2}}{\mathrm{d}a}\right) \times (\mathrm{e}^{-av_{\mathrm{rms}}^2}) = \frac{1}{2}\left(\frac{c}{a^{1/2}}\right)\mathrm{e}^{-av_{\mathrm{rms}}^2}$$

where we have used $\frac{\mathrm{d}}{\mathrm{dz}}\int_0^z f(y)\,\mathrm{d}y = f(z)$

Substituting and cancelling we obtain $P = \mathrm{erf}(v_{\mathrm{rms}}a^{1/2}) - \left(2v_{\mathrm{rms}}a^{1/2}/\pi^{1/2}\right)\mathrm{e}^{-av_{\mathrm{rms}}^2}$

Now $\quad v_{\mathrm{rms}} = \left(\frac{3RT}{M}\right)^{1/2}$ $\quad$ so $\quad v_{\mathrm{rms}}a^{1/2} = \left(\frac{3RT}{M}\right)^{1/2} \times \left(\frac{M}{2RT}\right)^{1/2} = \left(\frac{3}{2}\right)^{1/2}$

and $\quad P = \mathrm{erf}\left(\sqrt{\frac{3}{2}}\right) - \left(\frac{6}{\pi}\right)^{1/2}\mathrm{e}^{-3/2} = 0.92 - 0.31 = \boxed{0.61}$

Therefore,

(a) $1 - P = \boxed{39\%}$ have a speed greater than the root mean square speed.

(b) $P = \boxed{61\%}$ of the molecules have a speed less than the root mean square speed.

(c) For the proportions in terms of the mean speed v_{mean}, replace v_{rms} by

$$v_{\mathrm{mean}} = \left(8kT/\pi m\right)^{1/2} = \left(8/3\pi\right)^{1/2} v_{\mathrm{rms}} \qquad \text{so} \qquad v_{\mathrm{mean}}a^{1/2} = 2/\pi^{1/2} \, .$$

Then $\quad P = \mathrm{erf}(v_{\mathrm{mean}}a^{1/2}) - \left(2v_{\mathrm{mean}}a^{1/2}/\pi^{1/2}\right) \times (\mathrm{e}^{-av_{\mathrm{mean}}^2})$

$$= \mathrm{erf}\left(2/\pi^{1/2}\right) - \left(4/\pi\right)\mathrm{e}^{-4/\pi} = 0.889 - 0.356 = \boxed{0.533}$$

That is, $\boxed{53\%}$ of the molecules have a speed less than the mean, and $\boxed{47\%}$ have a speed greater than the mean.

1B.8 The average is obtained by substituting the distribution (eqn 1B.4) into eqn 1B.7:

$$\langle v^n \rangle = \int_0^\infty v^n f(v)\,\mathrm{d}v = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} \int_0^\infty v^{n+2}\mathrm{e}^{-Mv^2/2RT}\,\mathrm{d}v$$

For even values of *n*, use Integral G.8:

$$\langle v^n \rangle = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} \frac{(n+1)!!}{2^{\left(\frac{n+4}{2}\right)}}\left(\frac{2RT}{M}\right)^{\left(\frac{n+2}{2}\right)}\left(\frac{2\pi RT}{M}\right)^{1/2} = (n+1)!!\left(\frac{RT}{M}\right)^{\left(\frac{n}{2}\right)}$$

where $\quad (n+1)!! = 1 \times 3 \times 5 \ldots \times (n+1)$

Thus $\quad \langle v^n \rangle^{1/n} = \boxed{\left\{(n+1)!!\left(\frac{RT}{M}\right)\right\}^{1/2}} \qquad$ even n

For odd values of n, use Integral G.7:

$$\langle v^n\rangle = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\frac{\left(\frac{n+1}{2}\right)!}{2}\left(\frac{2RT}{M}\right)^{\left(\frac{n+3}{2}\right)} = \frac{2}{\pi^{1/2}}\left(\frac{2RT}{M}\right)^{n/2}$$

Thus $$\langle v^n\rangle^{1/n} = \left\{\frac{2}{\pi^{1/2}}\left(\frac{2RT}{M}\right)^{n/2}\right\}^{1/n} = \boxed{\frac{2^{1/n}}{\pi^{1/2n}}\left(\frac{2RT}{M}\right)^{1/2}} \qquad \text{odd } n$$

Question. Show that these expressions reduce to v_{mean} and v_{rms} for $n = 1$ and 2 respectively.

1B.10 Dry atmospheric air is 78.08% N_2, 20.95% O_2, 0.93% Ar, 0.04% 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. (Linear molecules can rotate in two dimensions, contributing two “quadratic terms” of rotational energy, or kT by the equipartition theorem [Topic B.3(b)]. The rotational energy density is given by

$$\rho_{\text{R}} = \frac{E_{\text{R}}}{V} = \frac{0.9906N\langle\varepsilon^{\text{R}}\rangle}{V} = \frac{0.9906NkT}{V} = 0.9906p$$

$$= 0.9906(1.013\times10^5\ \text{Pa}) = 1.004\times10^5\ \text{J m}^{-3} = 0.1004\ \text{J cm}^{-3}$$

The total energy density is translational plus rotational (vibrational energy contributing negligibly):

$$\rho_{\text{tot}} = \rho_{\text{T}} + \rho_{\text{R}} = 0.15\ \text{J cm}^{-3} + 0.10\ \text{J cm}^{-3} = \boxed{0.25\ \text{J cm}^{-3}}$$

1B.12 The fraction of molecules (call it F) between speeds a and b is given by

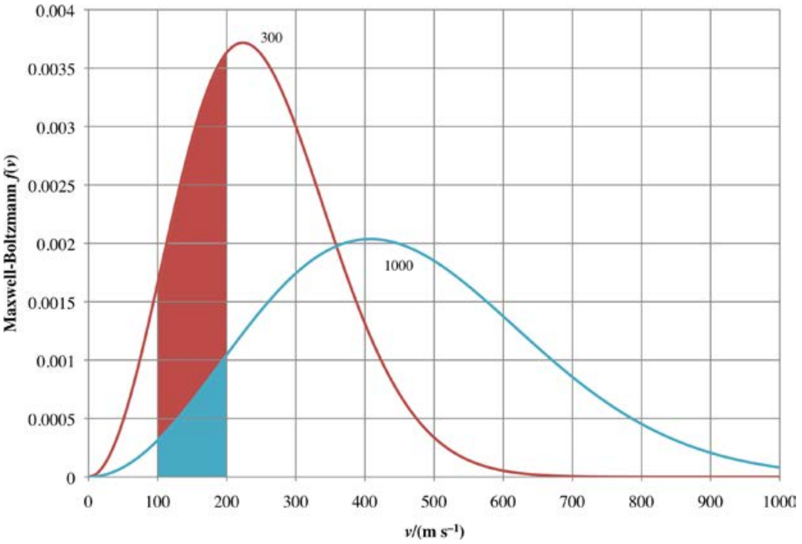
$$F(a,b) = \int_a^b f(v)\,\mathrm{d}v$$

where $f(v)$ is given by eqn 1B.4. This integral can be approximated by a sum over a discrete set of velocity values. For convenience, let the velocities v_i be evenly spaced within the interval such that $v_{i+1} = v_{\text{i}} + \Delta v$:

$$F(a,b) \approx \sum f(v_i)\Delta v$$

On a spreadsheet or other mathematical software, make a column of velocity values and then a column for $f(v)$ [1B.4] at 300 K and at 1000 K. Figure 1B.1 shows $f(v)$ plotted against v for these two temperatures. Each curve is labeled with the numerical value of T/K, and each is shaded under the curve between the speeds of 100 and 200 m s^{-1}. $F(a,b)$ is simply the area under the curve between $v = a$ and $v = b$. One should take some care to avoid double counting at the edges of the interval, that is, not including both endpoints of the interval with full weight. example, beginning the sum with the area under the curve at those speeds. Using a spreadsheet that evaluates $f(v)$ at 5-m s^{-1} intervals, and including points at both 100 and 200 m s^{-1} with half weight, $F(100\ \text{m s}^{-1}, 200\ \text{m s}^{-1}) \approx \boxed{0.281}$ at 300 K and $\boxed{0.066}$ at 1000 K.

Figure 1B.1



1C Real gases

Answers to discussion questions

1C.2 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, though supercritical fluids have both liquid and vapour characteristics.

1C.4 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 behavior 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

1C.1(b) The van der Waals equation [1C.5a] is

$$p = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$$

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

1C.2(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 $$b = 0.0426\ \mathrm{dm^3\ mol^{-1}} \times \frac{10^{-3}\ \mathrm{m^3}}{\mathrm{dm^3}} = \boxed{4.26\times10^{-5}\ \mathrm{m^3\ mol^{-1}}}$$

1C.3(b) The compression factor Z is [1C.1]

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

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

(ii) The molar volume is

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

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

Since $V_{\mathrm{m}} > V_{\mathrm{m}}^{\mathrm{o}}$ $\boxed{\text{repulsive}}$ forces dominate.

1C.4(b) **(i)** According to the perfect gas law

$$V_{\mathrm{m}}^{\mathrm{o}} = \frac{RT}{p} = \frac{(8.3145\ \mathrm{J\,K^{-1}\ mol^{-1}})\times(298.15\,\mathrm{K})}{(200\,\mathrm{bar})\times(10^5\ \mathrm{Pa\,bar^{-1}})}\times\left(\frac{1\ \mathrm{dm}}{10^{-1}\ \mathrm{m}}\right)^3 = \boxed{0.124\ \mathrm{dm^3\ mol^{-1}}}$$

(ii) The van der Waals equation [1C.5b] is a cubic equation in V_{m}. Cubic equations can be solved analytically. However, this approach is cumbersome, so we proceed as in Example 1C.1. The van der Waals equation is rearranged to the cubic form

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

or $\quad x^3 - \left(b + \dfrac{RT}{p}\right)x^2 + \left(\dfrac{a}{p}\right)x - \dfrac{ab}{p} = 0 \qquad$ with $\qquad x = V_{\mathrm{m}}/(\mathrm{dm^3\ mol^{-1}})$.

It will be convenient to have the pressure in atm:

$$200\ \mathrm{bar}\times\frac{1\ \mathrm{atm}}{1.013\ \mathrm{bar}} = 197.\overline{4}\ \mathrm{atm}$$

The coefficients in the equation are

$$b + \frac{RT}{p} = (3.183\times10^{-2}\ \mathrm{dm^3\ mol^{-1}}) + \frac{(0.08206\ \mathrm{dm^3\ atm\ mol^{-1}\ K^{-1}})\times(298.15\ \mathrm{K})}{197.\overline{4}\ \mathrm{atm}}$$

$$= (3.183\times10^{-2} + 0.123\overline{9})\ \mathrm{dm^3\ mol^{-1}} = 0.155\overline{8}\ \mathrm{dm^3\ mol^{-1}}$$

$$\frac{a}{p} = \frac{1.360\ \mathrm{dm^6\ atm\ mol^{-2}}}{197.\overline{4}\ \mathrm{atm}} = 6.89\times10^{-3}\ \mathrm{dm^6\ mol^{-2}}$$

$$\frac{ab}{p} = \frac{(1.360\ \mathrm{dm^6\ atm\,mol^{-2}})\times(3.183\times10^{-2}\ \mathrm{dm^3\ mol^{-1}})}{197.\overline{4}\ \mathrm{atm}} = 2.19\overline{3}\times10^{-4}\ \mathrm{dm^9\ mol^{-3}}$$

Thus, the equation to be solved is $x^3 - 0.155\overline{8}x^2 + (6.89\times10^{-3})x - (2.19\overline{3}\times10^{-4}) = 0$.

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

$x = 0.112 \qquad$ and $\qquad V_{\mathrm{m}} = \boxed{0.112\ \mathrm{dm^3\ mol^{-1}}}$.

The perfect-gas value is about 15 percent greater than the van der Waals result.

1C.5(b) The molar volume is obtained by solving $Z = \dfrac{pV_{\mathrm{m}}}{RT}$ [1C.2], for V_{m} , which yields

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

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

(ii) An approximate value of B can be obtained from eqn 1C.3b by truncation of the series expansion after the second term, B/V_{m}, in the series. Then,

$$B = V_{\mathrm{m}}\left(\frac{pV_{\mathrm{m}}}{RT} - 1\right) = V_{\mathrm{m}}\times(Z-1)$$

$$= (1.0\overline{6}\ \mathrm{dm^3\ mol^{-1}})\times(0.86-1) = \boxed{-0.15\ \mathrm{dm^3\ mol^{-1}}}$$

1C.6(b) Equations 1C.6are solved for b and a, respectively, and yield

$b = V_{\mathrm{c}}/3$ and $\qquad a = 27b^2p_{\mathrm{c}} = 3V_{\mathrm{c}}^2p_{\mathrm{c}}$.

Substituting the critical constants

$$b = \frac{148\ \mathrm{cm^3\ mol^{-1}}}{3} = 49.3\ \mathrm{cm^3\ mol^{-1}} = 0.0493\ \mathrm{dm^3\ mol^{-1}}$$

and $\quad a = 3\times(0.148\ \text{dm}^3\ \text{mol}^{-1})^2 \times (48.20\,\text{atm}) = 3.17\ \text{dm}^6\ \text{atm}\,\text{mol}^{-2}$

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

$$T_\text{c} = \frac{8a}{27Rb}$$

If we use T_c along with V_c as above, we would arrive at the same value of b along with

$$a = \frac{27RbT_\text{c}}{8} = \frac{9RV_\text{c}T_\text{c}}{8}$$

$$= \frac{9(0.08206\ \text{dm}^3\ \text{atm mol}^{-1}\ \text{K}^{-1})(0.148\ \text{dm}^3\ \text{mol}^{-1})(305.4\ \text{K})}{8}$$

$$= 4.17\ \text{dm}^6\ \text{atm}\,\text{mol}^{-2}$$

Or we could use T_c along with p_c. In that case, we can solve the pair of equations for a and b by first setting the two expressions for a equal to each other:

$$a = 27b^2 p_\text{c} = \frac{27RbT_\text{c}}{8}$$

Solving the resulting equation for b yields

$$b = \frac{RT_\text{c}}{8p_\text{c}} = \frac{(0.08206\ \text{dm}^3\ \text{atm mol}^{-1}\ \text{K}^{-1})(305.4\ \text{K})}{8(48.20\ \text{atm})} = 0.06499\ \text{dm}^3\ \text{mol}^{-1}$$

and then

$$a = 27(0.06499\ \text{dm}^3\ \text{mol}^{-1})^2(48.20\ \text{atm}) = 5.497\ \text{dm}^6\ \text{atm mol}^{-2}$$

These results are summarized in the following table

Using	$a/\text{dm}^6\ \text{atm mol}^{-2}$	$b/\text{dm}^3\ \text{mol}^{-1}$
V_c & p_c	3.17	0.0493
V_c & T_c	4.17	0.0493
p_c & T_c	5.497	0.06499

One way of selecting best values for these parameters would be to take the mean of the three determinations, namely $a = \boxed{4.28\ \text{dm}^6\ \text{atm mol}^{-2}}$ and $b = \boxed{0.0546\ \text{dm}^3\ \text{mol}^{-1}}$.

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

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

$$r = \frac{1}{2}\left(\frac{3(0.0546\ \text{dm}^3\ \text{mol}^{-1})}{4\pi(6.022\times10^{23}\ \text{mol}^{-1})}\right)^{1/3} = 1.39\times10^{-9}\ \text{dm} = \boxed{0.139\ \text{nm}}$$

1C.7(b) The Boyle temperature, T_B, is the temperature at which the virial coefficient $B = 0$. In order to express T_B in terms of a and b, the van der Waals equation [1C.5b] must be recast into the form of the virial equation.

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

Factoring out $\dfrac{RT}{V_\text{m}}$ yields $p = \dfrac{RT}{V_\text{m}}\left\{\dfrac{1}{1-b/V_\text{m}} - \dfrac{a}{RTV_\text{m}}\right\}$

So long as $b/V_\text{m} < 1$, the first term inside the brackets can be expanded using

$(1-x)^{-1} = 1 + x + x^2 + \ldots,$

which gives

$$p = \frac{RT}{V_\text{m}}\left\{1 + \left(b - \frac{a}{RT}\right)\times\left(\frac{1}{V_\text{m}}\right) + \cdots\right\}$$

We can now identify the second virial coefficient as $B = b - \dfrac{a}{RT}$

At the Boyle temperature

$$B = 0 = b - \frac{a}{RT_{\mathrm{B}}} \quad \text{so} \qquad T_{\mathrm{B}} = \frac{a}{bR} = \frac{27T_{\mathrm{c}}}{8}$$

(i) From Table 1C.3, $a = 4.484\ \mathrm{dm^6\ atm\ mol^{-2}}$ and $b = 0.0434\ \mathrm{dm^3\ mol^{-1}}$. Therefore,

$$T_{\mathrm{B}} = \frac{(4.484\ \mathrm{dm^6\ atm\ mol^{-2}})}{(0.08206\ \mathrm{L\ atm\ mol^{-1}\ K^{-1}}) \times (0.0434\ \mathrm{dm^3\ mol^{-1}})} = \boxed{1259\,\mathrm{K}}$$

(ii) As in Exercise 1C.6(b),

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

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

1C.8(b) States that have the same reduced pressure, temperature, and volume [1C.8] are said to correspond. The reduced pressure and temperature for N_2 at 1.0 atm and 25°C are [Table 1C.2]

$$p_{\mathrm{r}} = \frac{p}{p_{\mathrm{c}}} = \frac{1.0\,\mathrm{atm}}{33.54\,\mathrm{atm}} = 0.030 \quad \text{and} \quad T_{\mathrm{r}} = \frac{T}{T_{\mathrm{c}}} = \frac{(25+273)\,\mathrm{K}}{126.3\,\mathrm{K}} = 2.36$$

The corresponding states are

(i) For H_2S (critical constants obtained from *NIST Chemistry WebBook*)

$T = 2.36(373.3\ \mathrm{K}) = \boxed{881\ \mathrm{K}}$

$p = 0.030(89.7\ \mathrm{atm}) = \boxed{2.67\ \mathrm{atm}}$

(ii) For CO_2

$T = 2.36(304.2\ \mathrm{K}) = \boxed{718\ \mathrm{K}}$

$p = 0.030(72.9\ \mathrm{atm}) = \boxed{2.2\ \mathrm{atm}}$

(iii) For Ar

$T = 2.36(150.7\ \mathrm{K}) = \boxed{356\ \mathrm{K}}$

$p = 0.030(48.0\ \mathrm{atm}) = \boxed{1.4\ \mathrm{atm}}$

1C.9(b) The van der Waals equation [1C.5b] is

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

which can be solved for b

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

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

The compression factor is

$$Z = \frac{pV_{\mathrm{m}}}{RT}[1\mathrm{C}.2] = \frac{(4.0\times10^{6}\ \mathrm{Pa}) \times (4.00\times10^{-4}\ \mathrm{m^3\ mol^{-1}})}{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (288\,\mathrm{K})} = \boxed{0.67}$$

Solutions to problems

1C.2 From the definition of Z [1C.1] and the virial equation [1C.3b], Z may be expressed in virial form as

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

Since $V_\mathrm{m} = \dfrac{RT}{p}$ (by assumption of approximate perfect gas behavior), $\dfrac{1}{V_\mathrm{m}} = \dfrac{p}{RT}$; hence upon substitution, and dropping terms beyond the second power of $\left(\dfrac{1}{V_\mathrm{m}}\right)$

$$\begin{aligned}
Z &= 1 + B\left(\frac{p}{RT}\right) + C\left(\frac{p}{RT}\right)^2 \\
&= 1 + (-21.7\times10^{-3}\,\mathrm{dm^3\,mol^{-1}})\times\left(\frac{100\,\mathrm{atm}}{(0.08206\ \mathrm{dm^3\ atm\ mol^{-1}\ K^{-1}})\times(273\,\mathrm{K})}\right) \\
&\quad +(1.200\times10^{-3}\,\mathrm{dm^6\,mol^{-2}})\times\left(\frac{100\,\mathrm{atm}}{(0.08206\ \mathrm{dm^3\ atm\ mol^{-1}\ K^{-1}})\times(273\,\mathrm{K})}\right)^2 \\
&= 1 - 0.0968 + 0.0239 = \boxed{0.927} \\
V_\mathrm{m} &= (0.927)\left(\frac{RT}{p}\right) \\
&= (0.927)\left(\frac{(0.08206\ \mathrm{dm^3\ atm\ mol^{-1}\ K^{-1}})(273\ \mathrm{K})}{100\ \mathrm{atm}}\right) = \boxed{0.208\ \mathrm{dm^3}}
\end{aligned}$$

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?

1C.4 Since $B'(T_\mathrm{B}) = 0$ at the Boyle temperature [Topic 1.3b]: $B'(T_\mathrm{B}) = a + b\mathrm{e}^{-c/T_\mathrm{B}^2} = 0$

Solving for T_B: $$T_\mathrm{B} = \left\{\frac{-c}{\ln\left(\dfrac{-a}{b}\right)}\right\}^{1/2} = \left\{\frac{-(1131\,\mathrm{K}^2)}{\ln\left(\dfrac{-(-0.1993\,\mathrm{bar}^{-1})}{(0.2002\,\mathrm{bar}^{-1})}\right)}\right\}^{1/2} = \boxed{5.0\times10^2\ \mathrm{K}}$$

1C.6 From Table 1C.4 $T_\mathrm{c} = \left(\dfrac{2}{3}\right)\times\left(\dfrac{2a}{3bR}\right)^{1/2}$, $p_\mathrm{c} = \left(\dfrac{1}{12}\right)\times\left(\dfrac{2aR}{3b^3}\right)^{1/2}$

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

Thus $$T_\mathrm{c} = \left(\frac{2}{3}\right)\times\left(\frac{12p_\mathrm{c}b}{R}\right) = \left(\frac{8}{3}\right)\times\left(\frac{p_\mathrm{c}V_\mathrm{c}}{R}\right)$$

$$= \left(\frac{8}{3}\right)\times\left(\frac{(40\ \mathrm{atm})\times(160\times10^{-3}\ \mathrm{dm^3\ mol^{-1}})}{0.08206\ \mathrm{dm^3\ atm\ mol^{-1}\ K^{-1}}}\right) = \boxed{21\bar{0}\,\mathrm{K}}$$

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

$$b = N_\mathrm{A}\left(\frac{4\pi(2r)^3}{3}\right) \quad \text{so} \quad r = \frac{1}{2}\left(\frac{3b}{4\pi N_\mathrm{A}}\right)^{1/3} \ [\text{Exercise 1C.6(b)}] = \frac{1}{2}\left(\frac{V_\mathrm{c}}{4\pi N_\mathrm{A}}\right)^{1/3}$$

$$r = \frac{1}{2}\left(\frac{160\ \mathrm{cm^3\ mol^{-1}}}{4\pi(6.022\times10^{23}\ \mathrm{mol^{-1}})}\right)^{1/3} = 1.38\times10^{-8}\ \mathrm{cm} = \boxed{0.138\ \mathrm{nm}}$$

1C.8 Substitute the van der Waals equation [1C.5b] into the definition of the compression factor [1C.2]

$$Z = \frac{pV_{\mathrm{m}}}{RT} = \frac{1}{\left(1-\frac{b}{V_{\mathrm{m}}}\right)} - \frac{a}{RTV_{\mathrm{m}}} \quad \text{[Exercise 1C.7(a)]}$$

which upon expansion of $\left(1-\frac{b}{V_{\mathrm{m}}}\right)^{-1} = 1+\frac{b}{V_{\mathrm{m}}}+\left(\frac{b}{V_{\mathrm{m}}}\right)^2+\cdots$ yields

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

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

$$\frac{a}{RTV_{\mathrm{m}}} > \frac{b}{V_{\mathrm{m}}}+\left(\frac{b}{V_{\mathrm{m}}}\right)^2+\cdots$$

can Z be less than one. If we ignore terms beyond $\frac{b}{V_{\mathrm{m}}}$, 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.

1C.10 The Dieterici equation is

$$p = \frac{RT\mathrm{e}^{-a/RTV_{\mathrm{m}}}}{V_{\mathrm{m}}-b} \quad \text{[Table 1C.4]}$$

At the critical point the derivatives of p with respect to V_{m} equal zero along the isotherm defined by $T = T_{\mathrm{c}}$. This means that $(\partial p/\partial V_{\mathrm{m}})_T = 0$ and $(\partial^2 p/\partial V_{\mathrm{m}}^2)_T = 0$ at the critical point.

$$\left(\frac{\partial p}{\partial V_{\mathrm{m}}}\right)_T = p\left\{\frac{aV_{\mathrm{m}}-ab-RTV_{\mathrm{m}}^2}{V_{\mathrm{m}}^2(V_{\mathrm{m}}-b)(RT)}\right\}$$

and

$$\left(\frac{\partial^2 p}{\partial V_{\mathrm{m}}^2}\right)_T = \left(\frac{\partial p}{\partial V_{\mathrm{m}}}\right)_T\left\{\frac{aV_{\mathrm{m}}-ab-RTV_{\mathrm{m}}^2}{V_{\mathrm{m}}^2(V_{\mathrm{m}}-b)(RT)}\right\}+p\frac{\left(-2aV_{\mathrm{m}}^2+4V_{\mathrm{m}}ab+RTV_{\mathrm{m}}^3-2ab^2\right)}{\left\{V_{\mathrm{m}}^3\left[(V_{\mathrm{m}}-b)^2(RT)\right]\right\}}$$

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

$$p_{\mathrm{c}} = \frac{RT_{\mathrm{c}}\mathrm{e}^{-a/RT_{\mathrm{c}}V_{\mathrm{c}}}}{V_{\mathrm{c}}-b} \qquad aV_{\mathrm{c}}-ab-RT_{\mathrm{c}}V_{\mathrm{c}}^2 = 0$$

and $\quad -2aV_{\mathrm{c}}^2+4V_{\mathrm{c}}ab+RT_{\mathrm{c}}V_{\mathrm{c}}^3-2ab^2 = 0$

Solving the middle equation for T_{c}, substitution of the result into the last equation, and solving for V_{c} yields the result

$V_{\mathrm{c}} = 2b$ or $\quad b = V_{\mathrm{c}}/2$

(The solution $V_{\mathrm{c}} = b$ is rejected because there is a singularity in the Dieterici equation at the point $V_{\mathrm{m}} = b$.) Substitution of $V_{\mathrm{c}} = 2b$ into the middle equation and solving for T_{c} gives the result

$T_{\mathrm{c}} = a/4bR \quad$ or $\quad a = 2RT_{\mathrm{c}}V_{\mathrm{c}}$

Substitution of $V_{\mathrm{c}} = 2b$ and $T_{\mathrm{c}} = a/4bR$ into the first equation gives

$$p_{\mathrm{c}} = \frac{a\mathrm{e}^{-2}}{4b^2} = \frac{2RT_{\mathrm{c}}\mathrm{e}^{-2}}{V_{\mathrm{c}}}$$

The equations for V_{c}, T_{c}, p_{c} are substituted into the equation for the critical compression factor [1C.7] to give

$$Z_{\mathrm{c}} = \frac{p_{\mathrm{c}}V_{\mathrm{c}}}{RT_{\mathrm{c}}} = 2\mathrm{e}^{-2} = 0.2707\,.$$

This is significantly lower than the critical compression factor that is predicted by the van der Waals equation: $Z_{\mathrm{c}}(\mathrm{vdW}) = p_{\mathrm{c}}V_{\mathrm{c}}/RT_{\mathrm{c}} = 3/8 = 0.3750$. Experimental values for Z_{c} are summarized in Table 1C.2 where it is seen that the Dieterici equation prediction is often better.

1C.12 $$\frac{pV_\mathrm{m}}{RT}=1+B'p+C'p^2+\cdots\ [1C.3a]$$

$$\frac{pV_\mathrm{m}}{RT}=1+\frac{B}{V_\mathrm{m}}+\frac{C}{V_\mathrm{m}^2}+\cdots\ [1C.3b]$$

Thus $$B'p+C'p^2+\cdots=\frac{B}{V_\mathrm{m}}+\frac{C}{V_\mathrm{m}^2}+\cdots$$

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

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

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

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

1C.14 Write $V_\mathrm{m}=f(T,p)$; then $\mathrm{d}V_\mathrm{m}=\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p\mathrm{d}T+\left(\frac{\partial V_\mathrm{m}}{\partial p}\right)_T\mathrm{d}p$

Restricting the variations of T and p to those which 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 $$\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_P=\frac{RV_\mathrm{m}^2+bV_\mathrm{m}}{V_\mathrm{m}RT+2pV_\mathrm{m}^2-2RTV_\mathrm{m}}=\boxed{\frac{RV_\mathrm{m}+b_\mathrm{m}}{2pV_\mathrm{m}-RT}}$$

1C.16 $Z=\frac{V_\mathrm{m}}{V_\mathrm{m}^\circ}$ [1C.1], 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 $Z=\frac{10b}{9b}=\boxed{\frac{10}{9}=1.11}$

1C.18 The virial equation is

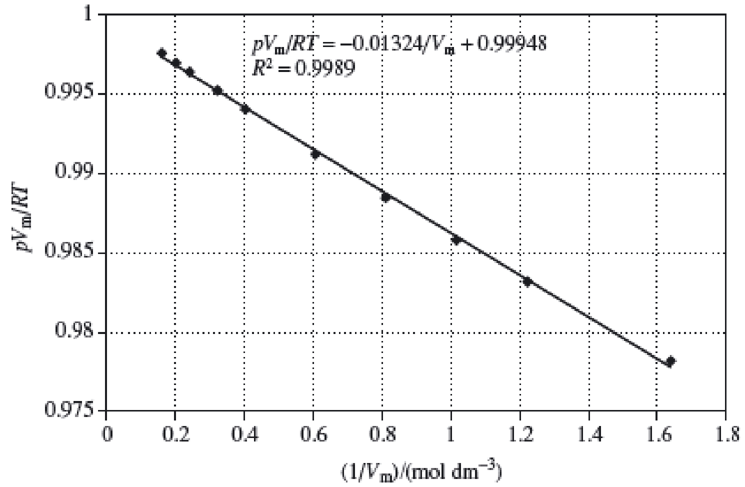
$$pV_\mathrm{m}=RT\left(1+\frac{B}{V_\mathrm{m}}+\frac{C}{V_\mathrm{m}^2}+\cdots\right)[1C.3b]$$

or $$\frac{pV_\mathrm{m}}{RT} = 1 + \frac{B}{V_\mathrm{m}} + \frac{C}{V_\mathrm{m}^2} + \cdots$$

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

p/MPa	V_m/(dm^3 mol^{-1})	$(1/V_\mathrm{m})$/(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

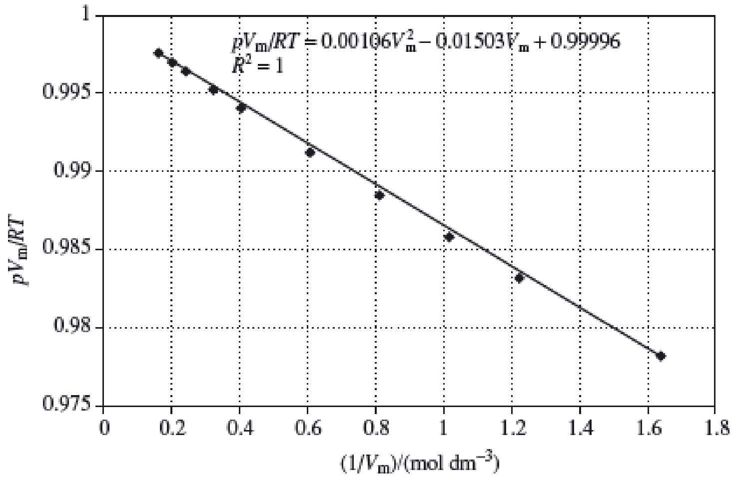
Figure 1C.1(a)



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

(b) A quadratic function fits the data somewhat better (Figure 1C.1(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 1C.1(b)



$$B = \boxed{-1.503\times10^{-2}\ \text{dm}^3\ \text{mol}^{-1}} \qquad \text{and} \qquad C = \boxed{-1.06\times10^{-3}\ \text{dm}^6\ \text{mol}^{-2}}$$

1C.20 The perfect gas equation [1A.5] gives

$$V_\text{m} = \frac{RT}{p} = \frac{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(250\ \text{K})}{150\times10^3\ \text{Pa}} = 0.0139\ \text{m}^3 = 13.9\ \text{dm}^3$$

The van der Waals equation [1C.5b] is a cubic equation in V_m. Cubic equations can be solved analytically. However, this approach is cumbersome, so we proceed as in Example 1C.1. The van der Waals equation is rearranged to the cubic form

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

or $$x^3 - \left(b + \frac{RT}{p}\right)x^2 + \left(\frac{a}{p}\right)x - \frac{ab}{p} = 0 \qquad \text{with} \qquad x = V_\text{m}/(\text{dm}^3\ \text{mol}^{-1})\ .$$

It will be convenient to have the pressure in atm:

$$150\ \text{kPa}\times\frac{1\ \text{atm}}{101.3\ \text{kPa}} = 1.48\overline{1}\ \text{atm}$$

The coefficients in the equation are

$$b + \frac{RT}{p} = (5.42\times10^{-2}\ \text{dm}^3\ \text{mol}^{-1}) + \frac{(0.08206\ \text{dm}^3\ \text{atm mol}^{-1}\ \text{K}^{-1})\times(250\ \text{K})}{1.48\overline{1}\ \text{atm}}$$

$$= (5.42\times10^{-2} + 13.8\overline{5})\ \text{dm}^3\ \text{mol}^{-1} = 13.9\overline{1}\ \text{dm}^3\ \text{mol}^{-1}$$

$$\frac{a}{p} = \frac{6.260\ \text{dm}^6\ \text{atm mol}^{-2}}{1.48\overline{1}\ \text{atm}} = 4.23\ \text{dm}^6\ \text{mol}^{-2}$$

$$\frac{ab}{p} = \frac{(6.260\ \text{dm}^6\ \text{atm mol}^{-2})\times(5.42\times10^{-2}\ \text{dm}^3\ \text{mol}^{-1})}{1.48\overline{1}\ \text{atm}} = 2.29\overline{1}\times10^{-2}\ \text{dm}^9\ \text{mol}^{-3}$$

Thus, the equation to be solved is $x^3 - 13.9\overline{1}x^2 + 4.23x - (2.29\overline{1}\times10^{-2}) = 0$.

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

$x = 13.6$ and $V_\text{m} = \boxed{13.6\ \text{dm}^3\ \text{mol}^{-1}}$.

Taking the van der Waals result to be more accurate, the error in the perfect-gas value is

$$\frac{13.9 - 13.6}{13.6}\times100\% = \boxed{2\%}$$

Assume all gases are perfect unless stated otherwise. Unless otherwise stated, thermochemical data are for 298.15 K.

2 The First Law

2A Internal energy

Answers to discussion questions

2A.2 Work is a precisely defined mechanical concept. It is produced from the application of a force through a distance. The technical definition is based on the realization that both force and displacement are vector quantities and it is the component of the force acting in the direction of the displacement that is used in the calculation of the amount of work, that is, work is the scalar product of the two vectors. In vector notation $w = -\boldsymbol{F}\cdot\boldsymbol{d} = -fd\cos\theta$, where θ is the angle between the force and the displacement. The negative sign is inserted to conform to the standard thermodynamic convention.

Heat is associated with a non-adiabatic process and is defined as the difference between the adiabatic work and the non-adiabatic work associated with the same change in state of the system. This is the formal (and best) definition of heat and is based on the definition of work. A less precise definition of heat is the statement that heat is the form of energy that is transferred between bodies in thermal contact with each other by virtue of a difference in temperature.

The interpretations of heat and work in terms of energy levels and populations is based upon the change in the total energy of a system that arises from a change in the molecular energy levels of a system and from a change in the populations of those levels as explained more fully in Chapter 15 of this text. The statistical thermodynamics of Chapter 15 allows us to express the change in total energy of a system in the following form:

$$N\mathrm{d}\langle\varepsilon\rangle = \sum_i \varepsilon_i \mathrm{d}N_i + \sum_i N_i \mathrm{d}\varepsilon_i$$

The work done by the system in a reversible, isothermal expansion can be identified with the second term on the right of this expression, since there is no change in the populations of the levels which depend only on temperature; hence, the first term on the right is zero. Because the influx of energy as heat does not change the energy levels of a system, but does result in a change in temperature, the second term on the right of the above equation is zero and the heat associated with the process (a constant volume process, with no additional work) can be identified with the first term. The change in populations is due to the change in temperature, which redistributes the molecules over the fixed energy levels.

Solutions to exercises

2A.1(b) See the solution to Exercise 2A.1(a) where we introduced the following equation based on the material of Chapter 15.

$$C_{V,\mathrm{m}} = \tfrac{1}{2}(3 + \nu_\mathrm{R}^* + 2\nu_\mathrm{V}^*)R$$

with a mode active if $T > \theta_\mathrm{M}$ (where M is T, R, or V).

(i) $\mathrm{O_3}: C_{V,\mathrm{m}} = \tfrac{1}{2}(3+3+0)R = 3R$ [experimental = 3.7R]

$$E = 3RT = 3\times 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}} \times 298.15\ \mathrm{K} = \boxed{7.436\ \mathrm{kJ\ mol^{-1}}}$$

(ii) $\mathrm{C_2H_6}: C_{V,\mathrm{m}} = \tfrac{1}{2}(3+3+2\times 1)R = 4R$ [experimental = 6.3R]

$$E = 4RT = 4\times 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}} \times 298.15\ \mathrm{K} = \boxed{9.915\ \mathrm{kJ\ mol^{-1}}}$$

(iii) $SO_2 : C_{V,\mathrm{m}} = \frac{1}{2}(3+3+0)R = 3R$ [experimental = 3.8*R*]

$$E = 3RT = 3\times 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}} \times 298.15\ \mathrm{K} = \boxed{7.436\ \mathrm{kJ\ mol^{-1}}}$$

Consultation of Herzberg references, G. Herzberg, Molecular spectra and Molecular structure, II, Chapters 13 and 14, Van Nostrand, 1945, 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.

2A.2(b) (i) volume, (iii) internal energy, and (iv) density are state functions.

2A.3(b) This is an expansion against a constant external pressure; hence $w = -p_{\mathrm{ex}}\Delta V$ [2A.6]

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

$$\Delta V = (75.0\,\mathrm{cm}^2)\times(25.0\,\mathrm{cm})\times\left(\frac{1\,\mathrm{m}}{100\,\mathrm{cm}}\right)^3 = 1.87\times10^{-3}\ \mathrm{m}^3$$

so $w = -(150\times10^3\ \mathrm{Pa})\times(1.87\times10^{-3}\ \mathrm{m}^3) = \boxed{-281\mathrm{J}}$ as 1 Pa m^3 = 1 J

2A.4(b) For all cases $\Delta U = 0$, since the internal energy of a perfect gas depends only on temperature. From the definition of enthalpy, $H = U + pV$, so $\Delta H = \Delta U + \Delta(pV) = \Delta U + \Delta(nRT)$ (perfect gas). $\Delta H = 0$ as well, at constant temperature for all processes in a perfect gas.

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

$$w = -nRT\ln\left(\frac{V_\mathrm{f}}{V_\mathrm{i}}\right) \quad [2A.9]$$

$$= -(2.00\,\mathrm{mol})\times(8.3145\,\mathrm{J\,K^{-1}\ mol^{-1}})\times 273\,\mathrm{K}\times\ln\frac{20.0\,\mathrm{dm}^3}{5.0\,\mathrm{dm}^3} = \boxed{-6.29\times10^3\ \mathrm{J}}$$

$$q = -w = \boxed{6.29\times10^3\,\mathrm{J}}$$

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

$w = -p_{\mathrm{ex}}\Delta V$ [2A.6]

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

$pV = nRT$

so $$p = \frac{(2.00\,\mathrm{mol})\times(8.3145\mathrm{JK^{-1}mol^{-1}})\times 273\,\mathrm{K}}{20.0\,\mathrm{dm}^3}\times(10\,\mathrm{dm\,m^{-1}})^3 = 2.22\times10^5\ \mathrm{Pa}$$

and $$w = \frac{-(2.22\times10^5\ \mathrm{Pa})\times(20.0-5.0)\,\mathrm{dm}^3}{(10\,\mathrm{dm\,m^{-1}})^3} = \boxed{-3.34\times10^3\ \mathrm{J}}$$

$$q = -w = \boxed{3.34\times10^3\,\mathrm{J}}$$

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

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

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

2A.5(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

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

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

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

2A.6(b) (i) $$w=-p_{\text{ex}}\Delta V=\frac{-(7.7\times10^3\,\text{Pa})\times(2.5\,\text{dm}^3)}{(10\,\text{dm m}^{-1})^3}=\boxed{-19\,\text{J}}$$

(ii) $$w=-nRT\ln\left(\frac{V_\text{f}}{V_\text{i}}\right) \text{ [2A.9]}$$

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

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

Solutions to problems

2A.2 $$w=-p_{\text{ex}}\Delta V \text{ [2A.6]} \qquad V_\text{f}=\frac{nRT}{p_{\text{ex}}}>>V_\text{i}; \quad \text{so} \quad \Delta V\approx V_\text{f}$$

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

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

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

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

2A.4

$$w=-\int_{V_1}^{V_2}p\,\mathrm{d}V=-nRT\int_{V_1}^{V_2}\frac{\mathrm{d}V}{V-nb}+n^2a\int_{V_1}^{V_2}\frac{\mathrm{d}V}{V^2}$$

$$=-nRT\ln\left(\frac{V_2-nb}{V_1-nb}\right)-n^2a\left(\frac{1}{V_2}-\frac{1}{V_1}\right)$$

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

$$w=-nR\times\left(\frac{T}{T_\text{c}}\right)T_\text{c}\times\ln\left(\frac{\frac{V_2}{V_\text{c}}-\frac{nb}{V_\text{c}}}{\frac{V_1}{V_\text{c}}-\frac{nb}{V_\text{c}}}\right)-\left(\frac{n^2a}{V_\text{c}}\right)\times\left(\frac{V_\text{c}}{V_2}-\frac{V_\text{c}}{V_1}\right)$$

$$T_{\mathrm{r}} = \frac{T}{T_{\mathrm{c}}}, \quad V_{\mathrm{r}} = \frac{V}{V_{\mathrm{c}}}, \qquad T_{\mathrm{c}} = \frac{8a}{27Rb}, \quad V_{\mathrm{c}} = 3nb \quad \text{[Table 1C.4]}$$

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

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

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

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

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

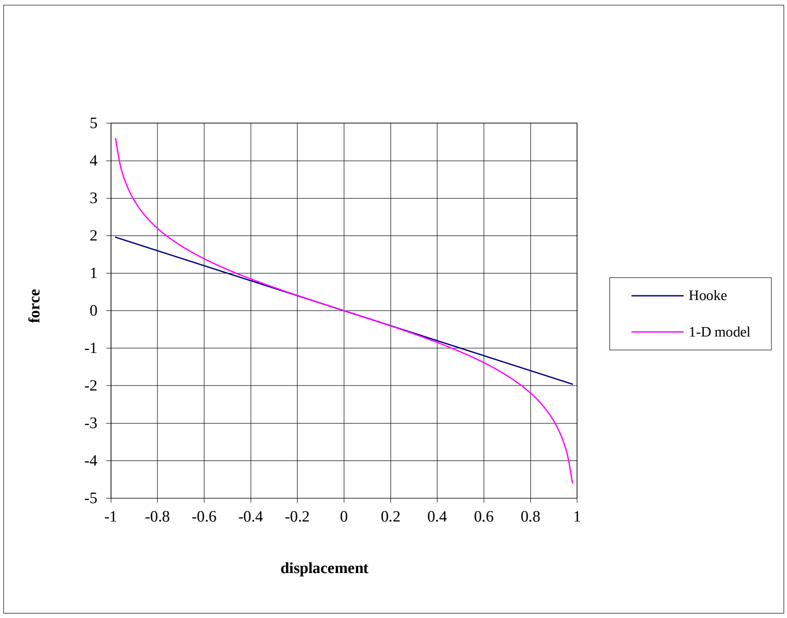
2A.6 One obvious limitation is that the model treats only displacements along the chain, not displacements that take an end away from the chain. (See Fig. 2A.2 in the Student's Solutions Manual)

(a) The displacement is twice the persistence length, so

$x = 2l$, $n = 2$, $\nu = n/N = 2/200 = 1/100$

and $$|F| = \frac{kT}{2l}\ln\left(\frac{1+\nu}{1-\nu}\right) = \frac{(1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}})(298\ \mathrm{K})}{2 \times 45 \times 10^{-9}\ \mathrm{m}}\ln\left(\frac{1.01}{0.99}\right) = \boxed{9.1 \times 10^{-16}\ \mathrm{N}}$$

Figure 2A.1



(b) Fig. 2A.1 displays a plot of force vs. displacement for Hooke's law and for the one-dimensional freely jointed chain. For small displacements the plots very nearly coincide. However, for large displacements, the magnitude of the force in the one-dimensional model grows much faster. In fact, in the one-dimensional model, the magnitude of the force approaches infinity for a finite displacement, namely a displacement the size of the chain itself ($|\nu| = 1$). (For Hooke's law, the force approaches infinity only for infinitely large displacements.)

(c) Work is $\mathrm{d}w = -F\,\mathrm{d}x = \dfrac{kT}{2l}\ln\left(\dfrac{1+\nu}{1-\nu}\right)\mathrm{d}x = \dfrac{kNT}{2}\ln\left(\dfrac{1+\nu}{1-\nu}\right)\mathrm{d}\nu$

This integrates to

$$\begin{aligned} w &= \int_0^{\nu_\mathrm{f}} \frac{kNT}{2}\ln\left(\frac{1+\nu}{1-\nu}\right)\mathrm{d}\nu = \frac{kNT}{2}\int_0^{\nu_\mathrm{f}} [\ln(1+\nu)-\ln(1-\nu)]\mathrm{d}\nu \\ &= \frac{kNT}{2}[(1+\nu)\ln(1+\nu)-\nu+(1-\nu)\ln(1-\nu)+\nu]\Big|_0^{\nu_\mathrm{f}} \\ &= \boxed{\frac{kNT}{2}[(1+\nu_\mathrm{f})\ln(1+\nu_\mathrm{f})+(1-\nu_\mathrm{f})\ln(1-\nu_\mathrm{f})]} \end{aligned}$$

(d) The expression for work is well behaved for displacements less than the length of the chain; however, for $\nu_\mathrm{f} = \pm 1$, we must be a bit more careful, for the expression above is indeterminate at these points. In particular, for expansion to the full length of the chain

$$\begin{aligned} w &= \lim_{\nu\to 1}\frac{kNT}{2}[(1+\nu)\ln(1+\nu)+(1-\nu)\ln(1-\nu)] \\ &= \frac{kNT}{2}\left[(1+1)\ln(1+1)+\lim_{\nu\to 1}(1-\nu)\ln(1-\nu)\right] = \frac{kNT}{2}\left[2\ln 2+\lim_{\nu\to 1}\frac{\ln(1-\nu)}{(1-\nu)^{-1}}\right] \end{aligned}$$

where we have written the indeterminate term in the form of a ratio in order to apply l'Hospital's rule. Focusing on the problematic limit and taking the required derivatives of numerator and denominator yields:

$$\lim_{\nu\to 1}\frac{\ln(1-\nu)}{(1-\nu)^{-1}} = \lim_{\nu\to 1}\frac{-(1-\nu)^{-1}}{(1-\nu)^{-2}} = \lim_{\nu\to 1}[-(1-\nu)] = 0$$

Therefore; $\qquad w = \dfrac{kNT}{2}(2\ln 2) = \boxed{kNT\ln 2}$

2B Enthalpy

Answers to discussion questions

2B.2 See figure 2B.3 of the text. There are two related reasons that can be given as to why C_p is greater than C_V. For ideal gases $C_p - C_V = nR$. For other gases that can be considered roughly ideal the difference is still approximately nR. Upon examination of figure 2B.3, we see that the slope of the curve of enthalpy against temperature is in most cases greater that the slope of the curve of energy against temperature; hence C_p is in most cases greater than C_V.

Solutions to exercises

2B.1(b) $q_p = nC_{p,\mathrm{m}}\Delta T$ [2B.7]

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

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

2B.2(b) (i) At constant pressure, $q = \Delta H$.

$$q=\int C_{\mathrm{p}}\mathrm{d}T=\int_{25+273\,\mathrm{K}}^{100+273\,\mathrm{K}}[20.17+(0.4001)T/\mathrm{K}]\mathrm{d}T\ \mathrm{J\,K^{-1}}$$

$$=\left[(20.17)T+\frac{1}{2}(0.4001)\times\left(\frac{T^2}{\mathrm{K}}\right)\right]_{298\,\mathrm{K}}^{373\,\mathrm{K}}\mathrm{J\,K^{-1}}$$

$$=\left[(20.17)\times(373-298)+\frac{1}{2}(0.4001)\times(373^2-298^2)\right]\mathrm{J}=\boxed{11.6\times10^3\ \mathrm{J}}=\Delta H$$

$$w=-p\Delta V=-nR\Delta T=-(1.00\ \mathrm{mol})\times(8.3145\ \mathrm{J\,K^{-1}\ mol^{-1}})\times(75\ \mathrm{K})=\boxed{-623\ \mathrm{J}}$$

$$\Delta U=q+w=(11.6-0.623)\ \mathrm{kJ}=\boxed{11.0\ \mathrm{kJ}}$$

(ii) The energy and enthalpy of a perfect gas depend on temperature alone. Thus, $\Delta H=\boxed{11.6\,\mathrm{kJ}}$ and $\Delta U=\boxed{11.0\ \mathrm{kJ}}$, as above. At constant volume, $w=\boxed{0}$ and $\Delta U=q$, so $q=\boxed{+11.0\ \mathrm{kJ}}$.

2B.3(b) $\Delta H=q_p=C_p\Delta T$ [2B.2, 2B.7] $=nC_{p,\mathrm{m}}\Delta T$

$$\Delta H=q_p=(2.0\,\mathrm{mol})\times(37.11\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(277-250)\,\mathrm{K}=\boxed{2.0\times10^3\ \mathrm{J\,mol^{-1}}}$$

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

$$\Delta U=2.0\times10^3\ \mathrm{J\,mol^{-1}}-(2.0\,\mathrm{mol})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(277-250)\,\mathrm{K}$$

$$=\boxed{1.6\times10^3\ \mathrm{J\,mol^{-1}}}$$

Solutions to problems

2B.2 In order to explore which of the two proposed equations best fit the data we have used PSI-PLOT®. The parameters obtained with the fitting process to eqn. 2B.8 along with their standard deviations are given in the following table.

parameters	*a*	$b/10^{-3}\ \mathrm{K}^{-1}$	$c/10^{5}\ \mathrm{K}^{2}$
values	28.796	27.89	-1.490
std dev of parameter	0.820	0.91	0.6480

The correlation coefficient is 0.99947. The parameters and their standard deviations obtained with the fitting process to the suggested alternate equation are as follows:

parameters	α	$\beta/10^{-3}\ \mathrm{K}^{-1}$	$\gamma/10^{-6}\ \mathrm{K}^{-2}$
values	24.636	38.18	-6.495
std dev of parameter	0.437	1.45	1.106

The correlation coefficient is 0.99986. It appears that the $\boxed{\text{alternate form for the heat capacity equation fits the data slightly better}}$, but there is very little difference.

2B.4 $$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

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

$\left(\frac{\partial U}{\partial V}\right)_T = 0$ for a perfect gas [Section 2D.2(a)]

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

2C Thermochemistry

Answers to discussion questions

2C.2 The standard state of a substance is the pure substance at a pressure of 1 bar and a specified temperature. The term reference state generally refers to elements and is the thermodynamically most stable state of the element at the temperature of interest. The distinction between standard state and reference state for elements may seem slight but becomes clear for those elements that can exist in more than one form at a specified temperature. So an element can have more than one standard state, one for each form that exists at the specified temperature.

Solutions to exercises

2C.1(b) At constant pressure

$$q = \Delta H = n\Delta_{\text{vap}}H^{\ominus} = (1.75\ \text{mol})\times(43.5\ \text{kJ mol}^{-1}) = \boxed{76.1\ \text{kJ}}$$

and $w = -p\Delta V \approx -pV_{\text{vapor}} = -nRT = -(1.75\ \text{mol})\times(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(260\ \text{K})$

$$w = -3.78\times10^3\ \text{J} = \boxed{-3.78\ \text{kJ}}$$

$$\Delta U = w + q = -3.78 + 76.1 = \boxed{72.3\ \text{kJ}}$$

Comment. Because the vapor is 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.

2C.2(b) The reaction is

$$\mathrm{C_6H_5OH(l) + 7\ O_2(g) \rightarrow\ 6\ CO_2(g) + 3\ H_2O(l)}$$

$$\Delta_c H^{\ominus} = 6\Delta_f H^{\ominus}(\mathrm{CO_2}) + 3\Delta_f H^{\ominus}(\mathrm{H_2O}) - \Delta_f H^{\ominus}(\mathrm{C_6H_5OH}) - 7\Delta_f H^{\ominus}(\mathrm{O_2})$$

$$= [6(-393.51) + 3(-285.83) - (-165.0) - 7(0)]\ \mathrm{kJ\ mol^{-1}} = \boxed{-3053.6\ \mathrm{kJ\ mol^{-1}}}$$

2C.3(b) We need $\Delta_f H^{\ominus}$ for the reaction

(4) $\mathrm{2B(s) + 3H_2(g) \rightarrow B_2H_6(g)}$

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

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

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

2C.4(b) Because $\Delta_f H^{\ominus}(H^+, \mathrm{aq}) = 0$ the whole of $\Delta_f H^{\ominus}$ (HI,aq) is ascribed to $\Delta_f H^{\ominus}(\mathrm{I^-, aq})$. Therefore,

$$\Delta_f H^{\ominus}(\mathrm{I^-, aq}) = \boxed{-55\ \mathrm{kJ/mol^{-1}}}$$

2C.5(b) For anthracene the reaction is

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

$$\Delta_c U^{\ominus} = \Delta_c H^{\ominus} - \Delta n_g RT\ [2B.4], \quad \Delta n_g = -\frac{5}{2}\ \mathrm{mol}$$

$$\Delta_c U^{\ominus} = -7061\ \mathrm{kJ\ mol^{-1}} - \left(-\frac{5}{2} \times 8.3 \times 10^{-3}\mathrm{kJ\ K^{-1}\ mol^{-1}} \times 298\ \mathrm{K}\right)$$

$$= -7055\ \mathrm{kJ\ mol^{-1}}$$

$$|q| = |q_V| = |n\Delta_c U^{\ominus}| = \left(\frac{225 \times 10^{-3}\ \mathrm{g}}{178.23\ \mathrm{g\ mol^{-1}}}\right) \times \left(7055\ \mathrm{kJ\ mol^{-1}}\right)$$

$$= 8.91\ \mathrm{kJ}$$

$$C = \frac{|q|}{\Delta T} = \frac{8.91\ \mathrm{kJ}}{1.35\ \mathrm{K}} = \boxed{6.60\ \mathrm{kJ\ K^{-1}}}$$

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

$$\Delta_c H^{\ominus} = -3054\,\mathrm{kJ\,mol^{-1}}\ [\text{Table 2C.1}]$$

$$\Delta_c U = \Delta_c H - \Delta n_g RT,\ \Delta n_g = -\frac{3}{2}$$

$$= (-3054\,\mathrm{kJ\,mol^{-1}}) + (\tfrac{3}{2}) \times (8.314 \times 10^{-3}\ \mathrm{kJ\ K^{-1}\ mol^{-1}}) \times (298\,\mathrm{K})$$

$$= -3050\,\mathrm{kJ\,mol^{-1}}$$

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

$$\Delta T = \frac{|q|}{C} = \frac{4.37\bar{5}\ \text{kJ}}{6.60\ \text{kJ K}^{-1}} = \boxed{+0.663\ \text{K}}$$

2C.6(b) (a) reaction(3) = (–2) × reaction(1) + reaction(2) and $\Delta n_\mathrm{g} = -1$

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

$$\begin{aligned}\Delta_\mathrm{r}H^\ominus(3) &= (-2)\times\Delta_\mathrm{r}H^\ominus(1) + \Delta_\mathrm{r}H^\ominus(2)\\ &= [(-2)\times(52.96) + (-483.64)]\,\text{kJ mol}^{-1}\\ &= \boxed{-589.56\,\text{kJ mol}^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta_\mathrm{r}U^\ominus &= \Delta_\mathrm{r}H^\ominus - \Delta n_\mathrm{g}RT\\ &= -589.56\ \text{kJ mol}^{-1} - (-3)\times(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\times(298\ \text{K})\\ &= -589.56\ \text{kJ mol}^{-1} + 7.43\ \text{kJ mol}^{-1} = \boxed{-582.13\ \text{kJ mol}^{-1}}\end{aligned}$$

(b) $\Delta_\mathrm{f}H^\ominus$ refers to the formation of one mole of the compound, so

$$\Delta_\mathrm{f}H^\ominus(\text{HI}) = \frac{1}{2}\left(52.96\ \text{kJ mol}^{-1}\right) = \boxed{26.48\ \text{kJ mol}^{-1}}$$

$$\Delta_\mathrm{f}H^\ominus(\text{H}_2\text{O}) = \frac{1}{2}\left(-483.64\ \text{kJ mol}^{-1}\right) = \boxed{-241.82\ \text{kJ mol}^{-1}}$$

2C.7(b) $\Delta_\mathrm{r}H^\ominus = \Delta_\mathrm{r}U^\ominus + RT\Delta n_g$ [2B.4]

$$\begin{aligned}&= -772.7\ \text{kJ mol}^{-1} + (5)\times(8.3145\times10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1})\times(298\ \text{K})\\ &= \boxed{-760.3\ \text{kJ mol}^{-1}}\end{aligned}$$

2C.8(b) The hydrogenation reaction is

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

The reactions and accompanying data which are to be combined in order to yield reaction (1) and $\Delta_\mathrm{r}H^\ominus(T)$ are

$$(2)\ \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(l)} \quad \Delta_\mathrm{c}H^\ominus(2) = -285.83\,\text{kJ mol}^{-1}$$

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

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

$$\text{reaction (1)} = \text{reaction (2)} - \text{reaction (3)} + \text{reaction (4)}$$

Hence, at 298 K:

(i)

$$\begin{aligned}\Delta_\mathrm{r}H^\ominus &= \Delta_\mathrm{c}H^\ominus(2) - \Delta_\mathrm{c}H^\ominus(3) + \Delta_\mathrm{c}H^\ominus(4)\\ &= [(-285.83) - (-1411) + (-1300)]\,\text{kJ mol}^{-1} = \boxed{-175\,\text{kJ mol}^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta_\mathrm{r}U^\ominus &= \Delta_\mathrm{r}H^\ominus - \Delta n_\mathrm{g}RT \quad \text{[2B.4]}; \quad \Delta n_\mathrm{g} = -1\\ &= -175\,\text{kJ mol}^{-1} - (-1)\times(2.48\,\text{kJ mol}^{-1}) = \boxed{-173\,\text{kJ mol}^{-1}}\end{aligned}$$

(ii) At 427 K:

$$\Delta_\mathrm{r}H^\ominus(427\,\text{K}) = \Delta_\mathrm{r}H^\ominus(298\,\text{K}) + \Delta_\mathrm{r}C_p^\ominus(427\,\text{K} - 298\,\text{K}) \qquad \text{[Example 2C.2]}$$

$$\Delta_r C_p = \sum_J \nu_J C^{\ominus}_{p,m}(J)[2C.7c] = C^{\ominus}_{p,m}(C_2H_4,g) - C^{\ominus}_{p,m}(C_2H_2,g) - C^{\ominus}_{p,m}(H_2,g)$$

$$= (43.56 - 43.93 - 28.82)\times10^{-3}\ \mathrm{kJ\,K^{-1}\,mol^{-1}} = -29.19\times10^{-3}\ \mathrm{kJ\,K^{-1}\,mol^{-1}}$$

$$\Delta_r H^{\ominus}(427\ \mathrm{K}) = (-175\ \mathrm{kJ\,mol^{-1}}) - (29.19\times10^{-3}\ \mathrm{kJ\ \ K^{-1}\,mol^{-1}})\times(129\ \mathrm{K})$$

$$= \boxed{-171\ \mathrm{kJ\,mol^{-1}}}$$

2C.9(b) For the reaction $C_{10}H_8(l) + 12O_2(g) \rightarrow 10CO_2(g) + 4H_2O(g)$

$$\Delta_r H^{\ominus} = 10\times\Delta_f H^{\ominus}(CO_2,g) + 4\times\Delta_f H^{\ominus}(H_2O,g) - \Delta_f H^{\ominus}(C_{10}H_8,l)$$

In order to calculate the enthalpy of reaction at 478 K we first calculate its value at 298 K using data in Tables 2C.1 and 2C.2. Note at 298 K naphthalene is a solid. It melts at 80.2 °C = 353.4 K.

$$\Delta_r H^{\ominus}(298\ \mathrm{K}) = 10\times(-393.51\ \mathrm{kJ\,mol^{-1}}) + 4\times(-241.82\ \mathrm{kJ\,mol^{-1}}) - (78.53\ \mathrm{kJ\,mol^{-1}}) = -4980.91\ \mathrm{kJ\,mol^{-1}}$$

Then, using data on the heat capacities and transition enthalpies of all the reacting substances, we can calculate the change in enthalpy, Δ*H*, of each substance as the temperature increases from 298 K to 478 K. The enthalpy of reaction at 478 K can be obtained by adding all these enthalpy changes to the enthalpy of reaction at 298 K. This process is shown below:

$$\Delta_r H^{\ominus}(478\ \mathrm{K}) = \Delta_r H^{\ominus}(298\ \mathrm{K}) + 10\times\Delta H(CO_2,g) + 4\times\Delta H(H_2O,\ g) - \Delta H(C_{10}H_8) - 12\times\Delta H(O_2,g)$$

For $H_2O(g)$, $CO_2(g)$, and $O_2(g)$ we have

$$\Delta_f H^{\ominus}(478\ \mathrm{K}) = \Delta_f H^{\ominus}(298\ \mathrm{K}) + \int_{298\mathrm{K}}^{478\mathrm{K}} C^{\ominus}_{p,m}\mathrm{d}T$$

For naphthalene we have to take into account the change in state from solid to liquid at 80.2 °C = 353.4 K. Then

$$\Delta_f H^{\ominus}(478\ \mathrm{K}) = \Delta_f H^{\ominus}(298\ \mathrm{K}) + \int_{298\mathrm{K}}^{353.4\mathrm{K}} C^{\ominus}_{p,m}\mathrm{d}T + \Delta H_{trs} + \int_{353.4\mathrm{K}}^{478\mathrm{K}} C^{\ominus}_{p,m}\mathrm{d}T$$

We will express the temperature dependence of the heat capacities in the form of the equation given in Problem 2C.7 because data for the heat capacities of the substances involved in this reaction are only available in that form. They are not available for all the substances in the form of the equation of Table 2B.1. We use

$$C^{\ominus}_{p,m} = \alpha + \beta T + \gamma T^2$$

For $H_2O(g)$, $CO_2(g)$, and $O_2(g)$, α, β, and γ values are given in Problem 2C.7. For naphthalene, solid and liquid, γ is zero and the two forms of the heat capacity equation are then identical and we take $\alpha = a$ and $\beta = b$ from Table 2B.1.

$$\Delta_{fus} H^{\ominus}(C_{10}H_8) = 19.01\ \mathrm{kJ\,mol^{-1}}$$

Using the data given in Problem 2C.7 we calculate

$$\Delta H(CO_2,g) = 5.299\ \mathrm{kJ\,mol^{-1}},\ \Delta H(H_2O,\ g) = 6.168\ \mathrm{kJ\,mol^{-1}},\ \text{and}\ \Delta H(O_2,g) = 5.430\ \mathrm{kJ\,mol^{-1}}$$

Using the data from Table 2C.1 we calculate for naphthalene

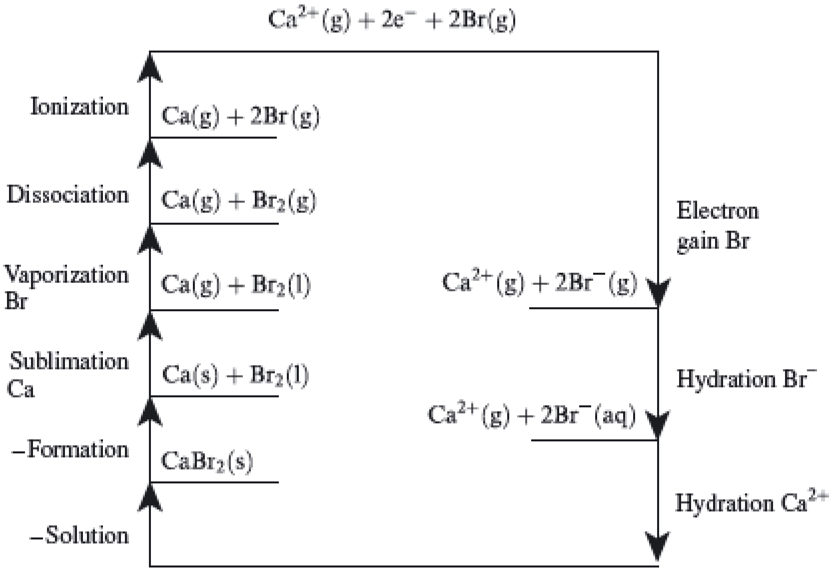
$$\Delta H(C_{10}H_8) = 55.36\ \mathrm{kJ\,mol^{-1}}$$

Collecting all these enthalpy changes we have

$$\Delta_r H^{\ominus}(478\ \mathrm{K}) = \Delta_r H^{\ominus}(298\ \mathrm{K}) + (10\times5.299 + 4\times6.168 - 55.36 - 12\times5.430)\mathrm{kJ\,mol^{-1}} = \boxed{-5023.77\ \mathrm{kJ\,mol^{-1}}}$$

2C.10(b) The cycle is shown in Fig. 2C.1.

Figure 2C.1



$$\begin{aligned}-\Delta_{\text{hyd}}H^\ominus(\text{Ca}^{2+}) &= -\Delta_{\text{soln}}H^\ominus(\text{CaBr}_2) - \Delta_{\text{f}}H^\ominus(\text{CaBr}_2,\text{s}) + \Delta_{\text{sub}}H^\ominus(\text{Ca})\\ &\quad + \Delta_{\text{vap}}H^\ominus(\text{Br}_2) + \Delta_{\text{diss}}H^\ominus(\text{Br}_2) + \Delta_{\text{ion}}H^\ominus(\text{Ca})\\ &\quad + \Delta_{\text{ion}}H^\ominus(\text{Ca}^+) + 2\Delta_{\text{eg}}H^\ominus(\text{Br}) + 2\Delta_{\text{hyd}}H^\ominus(\text{Br}^-)\\ &= [-(-103.1) - (-682.8) + 178.2 + 30.91 + 192.9\\ &\quad +589.7 + 1145 + 2(-331.0) + 2(-289)]\ \text{kJ mol}^{-1}\\ &= \boxed{1684\ \text{kJ mol}^{-1}}\end{aligned}$$

so $\Delta_{\text{hyd}}H^\ominus(\text{Ca}^{2+}) = \boxed{-1684\ \text{kJ mol}^{-1}}$

Solutions to problems

2C.2 $\text{Cr(C}_6\text{H}_6)_2\text{(s)} \rightarrow \text{Cr(s)} + 2\text{C}_6\text{H}_6\text{(g)} \quad \Delta n_{\text{g}} = +2\ \text{mol}$

$$\begin{aligned}\Delta_{\text{r}}H^\ominus &= \Delta_{\text{r}}U^\ominus + 2RT,\ \text{from [2B.4]}\\ &= (8.0\ \text{kJ mol}^{-1}) + (2)\times(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\times(583\ \text{K}) = \boxed{+17.7\ \text{kJ mol}^{-1}}\end{aligned}$$

In terms of enthalpies of formation

$$\Delta_{\text{r}}H^\ominus = (2)\times\Delta_{\text{f}}H^\ominus(\text{benzene, 583 K}) - \Delta_{\text{f}}H^\ominus(\text{metallocene, 583 K})$$

or $\quad \Delta_{\text{r}}H^\ominus(\text{metallocene, 583 K}) = 2\Delta_{\text{f}}H^\ominus(\text{benzene, 583 K}) - 17.7\ \text{kJ mol}^{-1}$

The enthalpy of formation of benzene gas at 583 K is related to its value at 298 K by

$$\begin{aligned}\Delta_{\text{f}}H^\ominus(\text{benzene, 583 K}) &= \Delta_{\text{f}}H^\ominus(\text{benzene, 298 K})\\ &\quad +(T_{\text{b}} - 298\ \text{K})C_{p,\text{m}}(\text{l}) + \Delta_{\text{vap}}H^\ominus + (583\ \text{K} - T_{\text{b}})C_{p,\text{m}}(\text{g})\\ &\quad -6\times(583\ \text{K} - 298\ \text{K})C_{p,\text{m}}(\text{gr}) - 3\times(583\ \text{K} - 298\ \text{K})C_{p,\text{m}}(\text{H}_2,\text{g})\end{aligned}$$

where T_{b} is the boiling temperature of benzene (353 K). We shall assume that the heat capacities of graphite and hydrogen are approximately constant in the range of interest and use their values from Tables 2B.1 and 2B.2.

$$\begin{aligned}\Delta_f H^{\ominus}(\text{benzene}, 583\,\text{K}) &= (49.0\,\text{kJ mol}^{-1}) + (353-298)\,\text{K}\times(136.1\,\text{J K}^{-1}\,\text{mol}^{-1})\\ &\quad + (30.8\,\text{kJ mol}^{-1}) + (583-353)\,\text{K}\times(81.67\,\text{J K}^{-1}\,\text{mol}^{-1})\\ &\quad - (6)\times(583-298)\,\text{K}\times(8.53\,\text{J K}^{-1}\,\text{mol}^{-1})\\ &\quad - (3)\times(583-298)\,\text{K}\times(28.82\,\text{J K}^{-1}\,\text{mol}^{-1})\\ &= \{(49.0)+(7.49)+(18.78)+(30.8)-(14.59)-(24.64)\}\,\text{kJ mol}^{-1}\\ &= +66.8\,\text{kJ mol}^{-1}\end{aligned}$$

Therefore, $\Delta_f H^{\ominus}(\text{metallocene}, 583\,\text{K}) = (2\times 66.8 - 17.7)\,\text{kJ mol}^{-1} = \boxed{+116.0\,\text{kJ mol}^{-1}}$

2C.4 The reaction is

$$C_{60}(s) + 60O_2(g) \rightarrow 60CO_2(g)$$

Because the reaction does not change the number of moles of gas, $\Delta_r H = \Delta_r U$ [2B.4]. Therefore

$$\Delta_c H^{\ominus} = (-36.0334\text{ kJ g}^{-1})\times(60\times 12.011\text{ g mol}^{-1}) = \boxed{-25968\text{ kJ mol}^{-1}}$$

Now relate the enthalpy of combustion to enthalpies of formation and solve for that of C_{60}.

$$\Delta_c H^{\ominus} = 60\Delta_f H^{\ominus}(CO_2) - 60\Delta_f H^{\ominus}(O_2) - \Delta_f H^{\ominus}(C_{60})$$

$$\begin{aligned}\Delta_f H^{\ominus}(C_{60}) &= 60\Delta_f H^{\ominus}(CO_2) - 60\Delta_f H^{\ominus}(O_2) - \Delta_c H^{\ominus}\\ &= [60(-393.51) - 60(0) - (-25968)]\text{ kJ mol}^{-1} = \boxed{2357\text{ kJ mol}^{-1}}\end{aligned}$$

2C.6 **(a)**

$$\begin{aligned}\Delta_r H^{\ominus} &= \Delta_f H^{\ominus}(SiH_2) + \Delta_f H^{\ominus}(H_2) - \Delta_f H^{\ominus}(SiH_4)\\ &= (274 + 0 - 34.3)\text{ kJ mol}^{-1} = \boxed{240\text{ kJ mol}^{-1}}\end{aligned}$$

(b)

$$\begin{aligned}\Delta_r H^{\ominus} &= \Delta_f H^{\ominus}(SiH_2) + \Delta_f H^{\ominus}(SiH_4) - \Delta_f H^{\ominus}(Si_2H_6)\\ &= (274 + 34.3 - 80.3)\text{ kJ mol}^{-1} = \boxed{228\text{ kJ mol}^{-1}}\end{aligned}$$

2C.8 In order to calculate the enthalpy of the protein's unfolding we need to determine the area under the plot of $C_{p,\text{ex}}$ against T, from the baseline value of $C_{p,\text{ex}}$ at T_1, the start of the process, to the baseline value of $C_{p,\text{ex}}$ at T_2, the end of the process. We are provided with an illustration that shows the plot, but no numerical values are provided. Approximate numerical values can be extracted from the plot and then the value of the integral $\Delta H = \int_{T_1}^{T_2} C_{p,\text{ex}}\,\mathrm{d}T$ can be obtained by numerical evaluation of the area under the curve. The first two columns in the table below show the data estimated from the curve, the last column gives the approximate area under the curve from the beginning of the process to the end. The final value, $\boxed{1889\text{ kJ mol}^{-1}}$, is the enthalpy of unfolding of the protein. The four significant figures shown are not really justified because of the imprecise estimation process involved.

$\theta/^{\circ}\mathrm{C}$	$C_{p,\mathrm{ex}}/\mathrm{kJ\ K^{-1}\ mol^{-1}}$	$\Delta H/\mathrm{kJ\ mol^{-1}}$
30	20	0
40	23	215
50	26	460
54	28	567
56	33	626
57	40	663
58	46	706
59	52	755
60	58	810
61	63	870
62	70	937
63	80	1011
64	89	1096
64.5	90	1141
65	85	1185
66	80	1267
67	68	1342
68	60	1405
69	52	1461
70	47	1511
72	41	1598
74	37	1676
80	36	1889

2C.10 **(a)** $q_V = -n\Delta_c U^{\ominus}$; hence

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

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

(i) The complete aerobic oxidation is

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

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

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

(iii) $$\Delta_c H^{\ominus} = 6\Delta_f H^{\ominus}(\mathrm{CO_2,g}) + 6\Delta_f H^{\ominus}(\mathrm{H_2O,l}) - \Delta_f H^{\ominus}(\mathrm{C_6H_{12}O_6,s}) - 6\Delta_f H^{\ominus}(\mathrm{O_2,g})$$

so $$\Delta_f H^{\ominus}(\mathrm{C_6H_{12}O_6,s}) = 6\Delta_f H^{\ominus}(\mathrm{CO_2,g}) + 6\Delta_f H^{\ominus}(\mathrm{H_2O,l}) - 6\Delta_f H^{\ominus}(\mathrm{O_2,g}) - \Delta_c H^{\ominus}$$

$$\Delta_f H^{\ominus}(\mathrm{C_6H_{12}O_6,s}) = [6(-393.51) + 6(-285.83) - 6(0) - (-280\bar{2})]\ \mathrm{kJ\ mol^{-1}}$$
$$= \boxed{-127\bar{4}\ \mathrm{kJ\ mol^{-1}}}$$

(b) The anaerobic glycolysis to lactic acid is

$$\mathrm{C_6H_{12}O_6 \rightarrow 2CH_3CH(OH)COOH}$$

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

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

2D State functions and exact differentials

Answers to discussion questions

2D.2 An inversion temperature is the temperature at which the Joule-Thomson coefficient, μ, changes sign from negative to positive or *vice-versa*. For a perfect gas μ is always zero, thus it cannot have an inversion temperature. As explained in detail in Section 2D.3, the existence of the Joule-Thomson effect depends upon intermolecular attractions and repulsions. A perfect gas has by definition no intermolecular attractions and repulsions, so it cannot exhibit the Joule-Thomson effect.

Solutions to exercises

2D.1(b) Also see exercises E2D.1(a) and E2D.2(a) and their solutions. The internal pressure of a van der Waals gas is $\pi_T = a/V_\mathrm{m}^2$. The molar volume can be estimated from the perfect gas equation:

$$V_\mathrm{m} = \frac{RT}{p} = \frac{0.08206\ \mathrm{dm^3\ atm\ K^{-1}\ mol^{-1}} \times 298\ \mathrm{K}}{1.00\ \mathrm{bar} \times \left(\dfrac{1.000\ \mathrm{atm}}{1.013\ \mathrm{bar}}\right)} = 24.76\ \mathrm{dm^3\ mol^{-1}}$$

$$\pi_T = \frac{a}{V_\mathrm{m}^2} = \frac{6.775\ \mathrm{atm\ dm^6\ mol^{-2}}}{(24.76\ \mathrm{dm^3\ mol^{-1}})^2} = 1.11\times10^{-2}\ \mathrm{atm} = \boxed{11.2\ \mathrm{mbar}}$$

2D.2(b) The internal energy is a function of temperature and volume, $U_\mathrm{m} = U_\mathrm{m}(T,V_\mathrm{m})$, so

$$\mathrm{d}U_\mathrm{m} = \left(\frac{\partial U_\mathrm{m}}{\partial T}\right)_{V_\mathrm{m}} \mathrm{d}T + \left(\frac{\partial U_\mathrm{m}}{\partial V_\mathrm{m}}\right)_T \mathrm{d}V_\mathrm{m} \qquad [\pi_T = (\partial U_\mathrm{m}/\partial V)_T]$$

For an isothermal expansion dT = 0; hence

$$\mathrm{d}U_\mathrm{m} = \left(\frac{\partial U_\mathrm{m}}{\partial V_\mathrm{m}}\right)_T \mathrm{d}V_\mathrm{m} = \pi_T\,\mathrm{d}V_\mathrm{m} = \frac{a}{V_\mathrm{m}^2}\mathrm{d}V_\mathrm{m}$$

$$\Delta U_\mathrm{m} = \int_{V_\mathrm{m,1}}^{V_\mathrm{m,2}} \mathrm{d}U_\mathrm{m} = \int_{V_\mathrm{m,2}}^{V_\mathrm{m,2}} \frac{a}{V_\mathrm{m}^2}\mathrm{d}V_\mathrm{m} = a\int_{1.00\,\mathrm{dm^3\,mol^{-1}}}^{30.00\,\mathrm{dm^3\,mol^{-1}}} \frac{\mathrm{d}V_\mathrm{m}}{V_\mathrm{m}^2} = -\frac{a}{V_\mathrm{m}}\Bigg|_{1.00\,\mathrm{dm^3\,mol^{-1}}}^{30.00\,\mathrm{dm^3\,mol^{-1}}}$$

$$= -\frac{a}{30.00\,\mathrm{dm^3\,mol^{-1}}} + \frac{a}{1.00\,\mathrm{dm^3\,mol^{-1}}} = \frac{29.00a}{30.00\,\mathrm{dm^3\,mol^{-1}}} = 0.9667a\,\mathrm{dm^{-3}\,mol}$$

From Table 1C.3, a = 1.337 dm^6 atm mol^{-1}

$$\Delta U_\mathrm{m} = (0.9667\,\mathrm{mol\,dm^3}) \times (1.337\,\mathrm{atm\,dm^6\,mol^{-2}})$$

$$= (1.292\overline{4}\,\mathrm{atm\,dm^3\,mol^{-1}}) \times (1.01325\times10^5\ \mathrm{Pa\,atm^{-1}}) \times \left(\frac{1\mathrm{m^3}}{10^3\,\mathrm{dm^3}}\right)$$

$$= 131.0\,\mathrm{Pa\,m^3\,mol^{-1}} = \boxed{131.0\ \mathrm{J\,mol^{-1}}}$$

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

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

Thus

$$q=\int_{1.00\,\mathrm{dm^3\,mol^{-1}}}^{30.00\,\mathrm{dm^3\,mol^{-1}}}\left(\frac{RT}{V_\mathrm{m}-b}\right)\mathrm{d}V_\mathrm{m}=RT\ln(V_\mathrm{m}-b)\Big|_{1.00\,\mathrm{dm^3\,mol^{-1}}}^{30.00\,\mathrm{dm^3\,mol^{-1}}}$$

$$=(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})\times\ln\left(\frac{30.00-3.20\times10^{-2}}{1.00-3.20\times10^{-2}}\right)=\boxed{+8.50\bar{5}\,\mathrm{kJ\,mol^{-1}}}$$

and $w=-q+\Delta U_\mathrm{m}=-(850\bar{5}\,\mathrm{J\,mol^{-1}})+(131\,\mathrm{J\,mol^{-1}})=\boxed{-837\bar{4}\,\mathrm{J\,mol^{-1}}}=\boxed{-8.37\,\mathrm{kJ\,mol^{-1}}}$

2D.3(b) The expansion coefficient is

$$\alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p=\frac{V'(3.7\times10^{-4}\,\mathrm{K^{-1}}+2\times1.52\times10^{-6}\,T\,\mathrm{K^{-2}})}{V}$$

$$=\frac{V'[3.7\times10^{-4}+2\times1.52\times10^{-6}(T/\mathrm{K})]\,\mathrm{K^{-1}}}{V'[0.77+3.7\times10^{-4}(T/\mathrm{K})+1.52\times10^{-6}(T/\mathrm{K})^2]}$$

$$=\frac{[3.7\times10^{-4}+2\times1.52\times10^{-6}(310)]\,\mathrm{K^{-1}}}{0.77+3.7\times10^{-4}(310)+1.52\times10^{-6}(310)^2}=\boxed{1.27\times10^{-3}\,\mathrm{K^{-1}}}$$

2D.4(b) Isothermal compressibility is

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

A density increase of 0.10 per cent means $\Delta V/V=-0.0010$. So the additional pressure that must be applied is

$$\Delta p=\frac{0.0010}{2.21\times10^{-6}\,\mathrm{atm^{-1}}}=\boxed{4.\bar{5}\times10^2\,\mathrm{atm}}$$

2D.5(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 which must be supplied to maintain constant temperature is ΔH in the following relationship

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

$$\Delta H=-(41.2\,\mathrm{J\,atm^{-1}\,mol^{-1}})\times(10.0\,\mathrm{mol})\times(-75\,\mathrm{atm})=\boxed{30.\bar{9}\times10^3\,\mathrm{J}}$$

Solutions to problems

2D.2

$$c_\mathrm{s}=\left(\frac{\gamma RT}{M}\right)^{1/2},\quad\gamma=\frac{C_{p,\mathrm{m}}}{C_{V,\mathrm{m}}},\qquad C_{p,\mathrm{m}}=C_{V,\mathrm{m}}+R$$

(a)

$$C_{V,\mathrm{m}}=\tfrac{1}{2}R(3+\nu_\mathrm{R}^*+2\nu_\mathrm{V}^*)=\tfrac{1}{2}R(3+2)=\tfrac{5}{2}R$$

$$C_{p,\mathrm{m}}=\tfrac{5}{2}R+R=\tfrac{7}{2}R$$

$$\gamma=\frac{7}{5}=1.40;\quad\text{hence}\quad\boxed{c_\mathrm{s}=\left(\frac{1.40RT}{M}\right)^{1/2}}$$

(b)

$$C_{V,\mathrm{m}}=\frac{1}{2}R(3+2)=\frac{5}{2}R,\qquad\gamma=1.40,\qquad\boxed{c_\mathrm{s}=\left(\frac{1.40RT}{M}\right)^{1/2}}$$

(c) $C_{V,\mathrm{m}} = \tfrac{1}{2}R(3+3) = 3R$

$$C_{p,\mathrm{m}} = 3R + R = 4R, \qquad \gamma = \frac{4}{3}, \qquad \boxed{c_\mathrm{s} = \left(\frac{4RT}{3M}\right)^{1/2}}$$

For air, $M \approx 29\,\mathrm{g\,mol^{-1}}, T \approx 298\,\mathrm{K}, \gamma = 1.40$

$$c_\mathrm{s} = \left(\frac{(1.40)\times(2.48\,\mathrm{kJ\,mol^{-1}})}{29\times10^{-3}\,\mathrm{kg\,mol^{-1}}}\right)^{1/2} = \boxed{350\,\mathrm{m\,s^{-1}}}$$

2D.4 **(a)** $V = V(p,T)$; hence, $\boxed{\mathrm{d}V = \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p + \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T}$

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

(b) We use $\alpha = \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_p$ [2D.6] and $\kappa_T = -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial p}\right)_T$ [2D.7] 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:

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

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

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

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

2D.6 $$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V\left(\frac{\partial T}{\partial V}\right)_p}$$ [reciprocal identity, *Mathematical Background* 2]

$$\alpha = \frac{1}{V}\times\frac{1}{\left(\frac{T}{V-nb}\right) - \left(\frac{2na}{RV^3}\right)\times(V-nb)}$$ [Problem 2D.5]

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

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

$$\kappa_T = -\frac{1}{V}\times\frac{1}{\left(\frac{-nRT}{(V-nb)^2}\right)+\left(\frac{2n^2a}{V^3}\right)} \text{[Problem 2D.5]}$$

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

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

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

$$= \left(\frac{\partial T}{\partial p}\right)_V \text{ [Euler chain relation]}$$

$$= \frac{V-nb}{nR} \text{[Problem 2D.5]},$$

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

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

2D.8

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T \text{ [\textit{Justification} 2D.2]}$$

$$\mu = \frac{1}{C_p}\left\{T\left(\frac{\partial V}{\partial T}\right)_p - V\right\} \text{ [See the section below for a derivation of this result]}$$

But $V = \frac{nRT}{p} + nb$ or $\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p}$

Therefore,

$$\mu = \frac{1}{C_p}\left\{\frac{nRT}{p} - V\right\} = \frac{1}{C_p}\left\{\frac{nRT}{p} - \frac{nRT}{p} - nb\right\} = \frac{-nb}{C_p}$$

Since $b > 0$ and $C_p > 0$, we conclude that for this gas $\mu < 0$ or $\left(\frac{\partial T}{\partial p}\right)_H < 0$. This says that when the pressure drops during a Joule–Thomson expansion the temperature must $\boxed{\text{increase}}$.

Derivation of expression for $\left(\frac{\partial H}{\partial p}\right)_T$ follows:

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

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

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

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

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

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

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

2D.10 **(a)** The Joule–Thomson coefficient is related to the given data by

$$\mu = -(1/C_p)(\partial H/\partial p)_T = -(-3.29\times10^3\ \text{J mol}^{-1}\ \text{MPa}^{-1})/(110.0\ \text{J K}^{-1}\ \text{mol}^{-1})$$

$$= \boxed{29.9\ \text{K MPa}^{-1}}$$

(b) The Joule–Thomson coefficient is defined as

$$\mu = (\partial T/\partial p)_H \approx (\Delta T/\Delta p)_H$$

Assuming that the expansion is a Joule–Thomson constant-enthalpy process, we have

$$\Delta T = \mu\Delta p = (29.9\ \text{K MPa}^{-1})\times[(0.5-1.5)\times10^{-1}\ \text{MPa}] = \boxed{-2.99\ \text{K}}$$

2E Adiabatic changes

Answers to discussion questions

2E.2 See Figure 2E.2 of the text and the Interactivity associated with that figure. For an adiabatic change, $\mathrm{d}U = \pi_T\mathrm{d}V + C_V\mathrm{d}T = \mathrm{d}w = -p_{\text{ex}}\mathrm{d}V$ [2A.6, 2D.5]. Thus we see that the heat capacity enters into the calculation of the change in energy of the system that occurs during an adiabatic expansion. For a perfect gas Eqn 2E.3 of the text can be written as $p_\text{f} = \left(\frac{V_\text{i}}{V_\text{f}}\right)^\gamma p_\text{i}$ with $\gamma = \frac{C_p}{C_V}$. Again the heat capacity plays a role.

Solutions to exercises

2E.1(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, $C_{p,\text{m}} = R + C_{V,\text{m}}$. So for CO_2

With vibrations $C_{V,\mathrm{m}}/R = 3\left(\tfrac{1}{2}\right)+2\left(\tfrac{1}{2}\right)+(3\times 4-5)=6.5$ and $\gamma=\dfrac{7.5}{6.5}=\boxed{1.15}$

Without vibrations $C_{V,\mathrm{m}}/R = 3\left(\tfrac{1}{2}\right)+2\left(\tfrac{1}{2}\right)=2.5$ and $\gamma=\dfrac{3.5}{2.5}=\boxed{1.40}$

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.

$$\theta_{\mathrm{R}}=\frac{hc\tilde{B}}{k}=\frac{(6.626\times10^{-34}\ \mathrm{J\,s})\times(2.998\times10^{10}\ \mathrm{cm\,s^{-1}})\times(0.39\,\mathrm{cm^{-1}})}{1.381\times10^{-23}\ \mathrm{J\,K^{-1}}}=0.56\,\mathrm{K} << 298\ \mathrm{K}$$

and therefore rotational contributions cannot be neglected.

2E.2(b) For reversible adiabatic expansion

$$T_{\mathrm{f}}=T_{\mathrm{i}}\left(\tfrac{V_{\mathrm{i}}}{V_{\mathrm{f}}}\right)^{1/c}\ \text{[2E.2a]}$$

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

therefore, the final temperature is

$$T_{\mathrm{f}}=(298.15\,\mathrm{K})\times\left(\frac{500\times10^{-3}\ \mathrm{dm^3}}{2.00\,\mathrm{dm^3}}\right)^{1/3.463}=\boxed{200\,\mathrm{K}}$$

2E.3(b) In an adiabatic process, the initial and final pressures are related by (eqn. 2E.3)

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

Find V_{i} from the perfect gas law:

$$V_{\mathrm{i}}=\frac{nRT_{\mathrm{i}}}{p_{\mathrm{i}}}=\frac{(2.5\ \mathrm{mol})\times(8.31\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(325\ \mathrm{K})}{240\times10^{3}\ \mathrm{Pa}}=0.028\bar{1}\ \mathrm{m^3}$$

so $$V_{\mathrm{f}}=V_{\mathrm{i}}\left(\frac{p_{\mathrm{i}}}{p_{\mathrm{f}}}\right)^{1/\gamma}=(0.028\bar{1}\ \mathrm{m^3})\times\left(\frac{240\ \mathrm{kPa}}{150\ \mathrm{kPa}}\right)^{1/1.67}=\boxed{0.037\bar{2}\ \mathrm{m^3}}$$

Find the final temperature from the perfect gas law:

$$T_{\mathrm{f}}=\frac{p_{\mathrm{f}}V_{\mathrm{f}}}{nR}=\frac{(150\times10^{3}\ \mathrm{Pa})\times(0.037\bar{2}\ \mathrm{m^3})}{(2.5\ \mathrm{mol})\times(8.31\ \mathrm{J\ K^{-1}\ mol^{-1}})}=\boxed{26\bar{9}\ \mathrm{K}}$$

Adiabatic work is (eqn. 2E.1)

$$w=C_V\Delta T=(20.8-8.31)\ \mathrm{J\ K^{-1}\ mol^{-1}}\times2.5\ \mathrm{mol}\times(26\bar{9}-325)\ \mathrm{K}=\boxed{-1.7\times10^{3}\ \mathrm{J}}$$

2E.4(b) Reversible adiabatic work is

$$w=C_V\Delta T\ \text{[2E.1]}=n(C_{p,\mathrm{m}}-R)\times(T_{\mathrm{f}}-T_{\mathrm{i}})$$

where the temperatures are related by

$$T_{\mathrm{f}}=T_{\mathrm{i}}\left(\frac{V_{\mathrm{i}}}{V_{\mathrm{f}}}\right)^{1/c}\ \text{[2E.2a]}\qquad \text{where}\qquad c=\frac{C_{V,\mathrm{m}}}{R}=\frac{C_{p,\mathrm{m}}-R}{R}=2.503$$

$$\text{So } T_\text{f} = \left[(23.0+273.15)\text{K}\right]\times\left(\frac{400\times10^{-3}\text{dm}^3}{2.00\ \text{dm}^3}\right)^{1/2.503} = 156\ \text{K}$$

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

2E.5(b) For reversible adiabatic expansion

$$p_\text{f}V_\text{f}^{\gamma} = p_\text{i}V_\text{i}^{\gamma}\ [2\text{E}.3] \qquad \text{so } p_\text{f} = p_\text{i}\left(\frac{V_\text{i}}{V_\text{f}}\right)^{\gamma} = (97.3\ \text{Torr})\times\left(\frac{400\times10^{-3}\ \text{dm}^3}{5.0\ \text{dm}^3}\right)^{1.3} = \boxed{3.6\ \text{Torr}}$$

Integrated activities

2.2 **(a)** and **(b).** The table below displays computed enthalpies of formation (semi-empirical, PM3 level, PC Spartan Pro$^{\text{TM}}$), enthalpies of combustion based on them (and on experimental enthalpies of formation of H_2O(l) and CO_2(g), –285.83 and –393.51 kJ mol^{-1} respectively), experimental enthalpies of combustion (Table 2.6), and the relative error in enthalpy of combustion.

Compound	$\Delta_\text{f}H^{\ominus}$ / kJ mol^{-1}	$\Delta_\text{c}H^{\ominus}$ / kJ mol^{-1}(calc.)	$\Delta_\text{c}H^{\ominus}$ / kJ mol^{-1}(expt.)	% error
CH_4(g)	–54.45	–910.72	–890	2.33
C_2H_6(g)	–75.88	–1568.63	–1560	0.55
C_3H_8(g)	–98.84	–2225.01	–2220	0.23
C_4H_{10}(g)	–121.60	–2881.59	–2878	0.12
C_5H_{12}(g)	–142.11	–3540.42	–3537	0.10

The combustion reactions can be expressed as:

$$\text{C}_n\text{H}_{2n+2}(\text{g}) + \left(\frac{3n+1}{2}\right)\text{O}_2(\text{g}) \rightarrow n\text{CO}_2(g) + (n+1)\,\text{H}_2\text{O(l)}.$$

The enthalpy of combustion, in terms of enthalpies of reaction, is

$$\Delta_\text{c}H^{\ominus} = n\Delta_\text{f}H^{\ominus}(\text{CO}_2) + (n{+}1)\Delta_\text{f}H^{\ominus}(\text{H}_2\text{O}) - \Delta_\text{f}H^{\ominus}(\text{C}_n\text{H}_{2\text{n}+2}),$$

Where we have left out $\Delta_\text{f}H^{\ominus}(\text{O}_2) = 0.$ The % error is defined as:

$$\%\ \text{error} = \frac{\Delta_\text{c}H^{\ominus}(\text{calc}) - \Delta_\text{c}H^{\ominus}(\text{expt.})}{\Delta_\text{c}H^{\ominus}(\text{expt.})}\times100\%$$

The agreement is quite good.

(c) If the enthalpy of combustion is related to the molar mass by

$$\Delta_\text{c}H^{\ominus} = k[M\,/\,(\text{g mol}^{-1})]^n$$

then one can take the natural log of both sides to obtain:

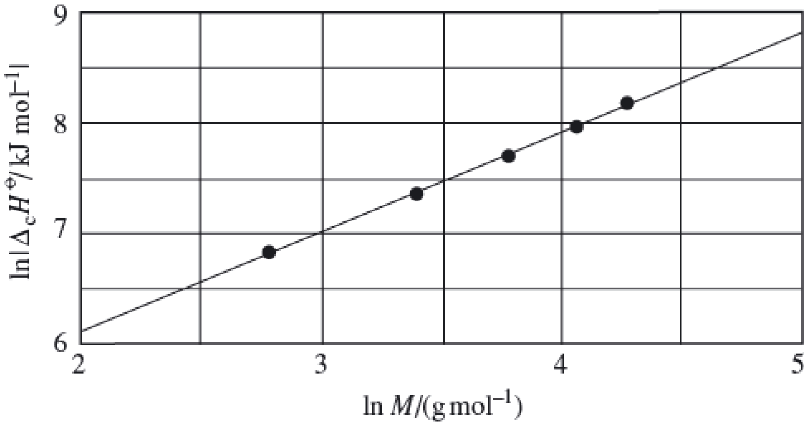
$$\ln\left|\Delta_\text{c}H^{\ominus}\right| = \ln|k| + n\ \ln M\,/\,(\text{g mol}^{-1}).$$

Thus, if one plots ln $\left|\Delta_\text{c}H^{\ominus}\right|$ vs. ln [M / (g mol^{-1})], one ought to obtain a straight line with slope n and y-intercept ln |k|. Draw up the following table:

Compound	$M/(\mathrm{g\ mol^{-1}})$	$\Delta_c H$ / kJ mol^{-1}	$\ln M/(\mathrm{g\ mol^{-1}})$	$\ln\lvert\Delta_c H^{\ominus}$ / kJ mol$^{-1}\rvert$
CH_4(g)	16.04	–910.72	2.775	6.814
C_2H_6(g)	30.07	–1568.63	3.404	7.358
C_3H_8(g)	44.10	–2225.01	3.786	7.708
C_4H_{10}(g)	58.12	–2881.59	4.063	7.966
C_5H_{12}(g)	72.15	–3540.42	4.279	8.172

The plot is shown below in Fig I2.1.

Figure I2.1



The linear least-squares fit equation is:

$$\ln|\Delta_c H^{\ominus}/\mathrm{kJ\,mol^{-1}}| = 4.30 + 0.903\ln M/(\mathrm{g\,mol^{-1}}) \quad R^2 = 1.00$$

These compounds support the proposed relationships, with

$n = \boxed{0.903}$ and $k = -e^{4.30}\ \mathrm{kJ\ mol^{-1}} = \boxed{-73.7\ \mathrm{kJ\ mol^{-1}}}$.

The agreement of these theoretical values of k and n with the experimental values obtained in Problem 2C.3 is rather good.

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

3 The Second and Third Laws

3A Entropy

Answers to discussion questions

3A.2 Everyday experience indicates that the direction of spontaneous change in an isolated system is accompanied by the dispersal of the total energy of the system. For example, for a gas expanding freely and spontaneously into a vacuum, the process is accompanied by a dispersal of energy and matter. It is easy to calculate the increase in the thermodynamic entropy that accompanies this process. For a perfect gas this entropy change is given by the formula $\Delta S = nR\ln\frac{V_\mathrm{f}}{V_\mathrm{i}}$ [eqn. 3A.14], which is clearly positive if V_f is greater than V_i. The molecular interpretation of this thermodynamic result is based on the identification of entropy with molecular disorder. An increase in disorder results from the chaotic dispersal of matter and energy and the only changes that can take place within an isolated system (the universe) are those in which this kind of dispersal occurs. This interpretation of entropy in terms of dispersal and disorder allows for a direct connection of the thermodynamic entropy to the statistical entropy through the Boltzmann formula $S = k\ln W$, where W is the number of microstates, the number of ways in which the molecules of the system can be arranged while keeping the total energy constant. The concept of the number of microstates makes quantitative the more ill-defined qualitative concepts of “disorder” and “the dispersal of matter and energy” used above to give a physical feel for the concept of entropy. A more “disorderly” distribution of energy and matter corresponds to a greater number of microstates associated with the same total energy.

3A.4 The explanation of Trouton’s rule is that $\frac{\Delta_\mathrm{vap}H^\ominus}{T_\mathrm{b}}$ is the standard entropy of vaporization, and we expect a comparable change in volume (with an accompanying comparable change in the number of accessible microstates) whenever an unstructured liquid forms a vapor. Hence, all unstructured liquids can be expected to have similar entropies of vaporization. Liquids that show significant deviations from Trouton’s rule do so on account of strong molecular interactions that restrict molecular motion. As a result there is a greater dispersal of matter and energy when such liquids vaporize. Water is an example of a liquid with strong intermolecular interactions (hydrogen bonding) which tend to organize the molecules in the liquid, hence we expect its entropy of vaporization to be greater than $85\ \mathrm{J\ K^{-1}\ mol^{-1}}$.

Solutions to exercises

3A.1(b) All spontaneous processes are irreversible processes, which implies through eqn. 3A.12, the Clausius inequality, that $\Delta S_\mathrm{tot} = \Delta S_\mathrm{sys} + \Delta S_\mathrm{surr} > 0$, for all spontaneous processes. In this case, $\Delta S_\mathrm{tot} = 10\ \mathrm{J\ K^{-1}} > 0$, so the process $\boxed{\text{may be spontaneous.}}$

3A.2(b) Efficiency, η, is $\frac{\text{work performed}}{\text{heat absorbed}} = \frac{|w|}{q_\mathrm{h}} = \frac{0.71\ \mathrm{kJ}}{2.71\ \mathrm{kJ}} = 0.262$. For an ideal

Heat engine we have $\eta_\mathrm{rev} = 1 - \frac{T_\mathrm{c}}{T_\mathrm{h}}$ [3A.10] $= 0.262 = 1 - \frac{T_\mathrm{c}}{273.16\ \mathrm{K}}$. Solving for T_c, we obtain $\boxed{T_\mathrm{c} = 201.6\ \mathrm{K}}$ as the temperature of the organic liquid.

3A.3(b) Assume that the block is so large that its temperature does not change significantly as a result of the heat transfer. Then

$$\Delta S = \int_i^f \frac{dq_{rev}}{T}\ [3A.2] = \frac{1}{T}\int_i^f dq_{rev}\ [\text{constant } T] = \frac{q_{rev}}{T}$$

$$\text{(a) } \Delta S = \frac{250\times10^3\ \text{J}}{293.15\,\text{K}} = \boxed{853\ \text{J K}^{-1}} \qquad \text{(b) } \Delta S = \frac{250\times10^3\ \text{J}}{373.15\,\text{K}} = \boxed{670\,\text{J K}^{-1}}$$

3A.4(b) $\boxed{CO_2(g)}$ will have the higher standard molar entropy, primarily because ΔS_{fus} and ΔS_{vap} are greater for $CO_2(g)$.

3A.5(b) We use

$$\Delta S = nR\ln\left(\frac{V_f}{V_i}\right)\ [3A.14]$$

$$= \left(\frac{4.00\ \text{g}}{28.0\ \text{g/mol}}\right)\times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}\times\ln\left(\frac{750}{500}\right) = \boxed{0.482\ \text{J K}^{-1}}$$

3A.6(b) Trouton's rule in the form $\Delta_{vap}H^{\ominus} = T_b \times 85\ \text{J K}^{-1}\ \text{mol}^{-1}$ can be used to obtain approximate enthalpies of vaporization. For cyclohexane

$$\Delta_{vap}H^{\ominus} = (273.2+80.7)\text{K}\times 85\ \text{J K}^{-1}\ \text{mol}^{-1} = \boxed{30.1\ \text{kJ/mol}^{-1}}$$

3A.7(b) At 250 K, the entropy is equal to its entropy at 298 K plus ΔS where

$$\Delta S = \int\frac{dq_{rev}}{T} = \int\frac{C_{V,m}\,dT}{T} = C_{V,m}\ln\frac{T_f}{T_i}$$

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

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

3A.8(b) No matter how 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

$$\Delta S_1 = \int\frac{dq_{rev}}{T} = \int\frac{C_{p,m}\,dT}{T} = C_{p,m}\ln\frac{T_f}{T_i}$$

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

and for the second

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

where $q_{rev} = -w = \int p\,dV = nRT\ln\dfrac{V_f}{V_i} = nRT\ \ln\dfrac{p_i}{p_f}$

so $\Delta S_2 = nR\ln\dfrac{p_i}{p_f} = (2.00\,\text{mol})\times(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times\ln\dfrac{1.50\ \text{atm}}{7.00\ \text{atm}} = -25.6\ \text{J K}^{-1}$

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

The heat lost in step 2 was more than the heat gained in step 1, resulting in a net loss of entropy. Or 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 $\Delta S_{\text{total}} > 0$.

3A.9(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,

$$T_{\text{f}} = \frac{1}{2}(100^\circ\text{C} + 25^\circ\text{C}) = 62.\bar{5}^\circ\text{C}$$

The heat capacity of each block is $C = mC_{\text{s}}$ where C_{s} is the specific heat capacity.
So,

$$\Delta H(\text{individual}) = mC_{\text{s}}\Delta T = 10.0\times10^3\ \text{g}\times0.449\ \text{J K}^{-1}\ \text{g}^{-1}\times(\pm37.\bar{5}\ \text{K}) = \pm168\ \text{kJ}$$

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

$$\Delta S = mC_{\text{s}}\ln\left(\frac{T_{\text{f}}}{T_{\text{i}}}\right);\quad 100^\circ\text{C} = 373.2\ \text{K};\ 25^\circ\text{C} = 298.2\ \text{K};\ 62.\bar{5}^\circ\text{C} = 335.\bar{7}\ \text{K}$$

$$\Delta S_1 = (10.0\times10^3\ \text{g})\times(0.449\ \text{J K}^{-1}\ \text{g}^{-1})\times\ln\left(\frac{335.7}{298.2}\right) = 532\ \text{J K}^{-1}$$

$$\Delta S_2 = (10.0\times10^3\ \text{g})\times(0.449\ \text{J K}^{-1}\ \text{g}^{-1})\times\ln\left(\frac{335.7}{373.2}\right) = -475\ \text{J K}^{-1}$$

$$\Delta S_{\text{total}} = \Delta S_1 + \Delta S_2 = \boxed{57\ \text{J K}^{-1}}$$

3A.10(b) **(i)**

$$\Delta S(\text{gas}) = nR\ \ln\left(\frac{V_{\text{f}}}{V_{\text{i}}}\right)[3\text{A}.14] = \left(\frac{21\text{g}}{39.95\ \text{g mol}^{-1}}\right)\times(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ln\frac{4.60\ \text{dm}^3}{1.20\ \text{dm}^3}$$

$$= 5.8\overline{73}\ \text{J K}^{-1} = \boxed{5.9\ \text{J K}^{-1}}$$

$$\Delta S(\text{surroundings}) = -\Delta S(\text{gas}) = \boxed{-5.9\ \text{J K}^{-1}}\ [\text{reversible}]$$

$$\Delta S(\text{total}) = \boxed{0}$$

(ii) $\Delta S(\text{gas}) = \boxed{+5.9\ \text{J K}^{-1}}$ [S is a state function]

$\Delta S(\text{surroundings}) = \boxed{0}$ [no change in surroundings]

$\Delta S(\text{total}) = \boxed{+5.9\ \text{J K}^{-1}}$

(iii) $q_{\text{rev}} = 0$ so $\Delta S(\text{gas}) = \boxed{0}$

$\Delta S(\text{surroundings}) = \boxed{0}$ [No heat is transfered to the surroundings]

$\Delta S(\text{total}) = \boxed{0}$

3A.11(b) (i)

$$\Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{T_{\text{b}}} = \frac{35.27\times10^3\ \text{J mol}^{-1}}{(64.1 + 273.15)\ \text{K}} = +104.5\bar{8}\ \text{J K}^{-1} = \boxed{104.6\ \text{J K}^{-1}}$$

(ii) If vaporization occurs reversibly, as is generally assumed

$$\Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0 \quad\text{so}\quad \Delta S_{\text{sur}} = \boxed{-104.6\ \text{J K}^{-1}}$$

Comment. This calculation has been based on the assumption that the heat capacities remain constant over the range of temperatures involved and that the enthalpy of vaporization at 298.15 K given in Table 3A.2 can be applied to the vaporization at 373.15 K. Neither one of these assumptions are strictly valid. Therefore, the calculated value is only approximate.

3A.12(b) $\Delta S = nC_\mathrm{p}(\mathrm{H_2O,s})\ln\frac{T_\mathrm{f}}{T_\mathrm{i}} + n\frac{\Delta_\mathrm{fus}H}{T_\mathrm{fus}} + nC_\mathrm{p}(\mathrm{H_2O,l})\ln\frac{T_\mathrm{f}}{T_\mathrm{i}} + n\frac{\Delta_\mathrm{vap}H}{T_\mathrm{vap}} + nC_\mathrm{p}(\mathrm{H_2O,g})\ln\frac{T_\mathrm{f}}{T_\mathrm{i}}$

$$n = \frac{15.0\ \mathrm{g}}{18.02\ \mathrm{g\ mol^{-1}}} = 0.832\ \mathrm{mol}$$

$$\begin{aligned}\Delta S &= 0.832\ \mathrm{mol} \times 38.02\ \mathrm{J\ K^{-1}\ mol^{-1}} \times \ln\frac{273.15}{261.15} + 0.832\ \mathrm{mol} \times \frac{6.008\ \mathrm{kJ/mol^{-1}}}{273.15\ \mathrm{K}} \\ &\quad + 0.832\ \mathrm{mol} \times 75.291\ \mathrm{J\ K^{-1}\ mol^{-1}} \times \ln\frac{373.15}{273.15} \\ &\quad + 0.832\ \mathrm{mol} \times \frac{40.657\ \mathrm{kJ/mol^{-1}}}{373.15\ \mathrm{K}} + 0.832\ \mathrm{mol} \times 33.58\ \mathrm{J\ K^{-1}\ mol^{-1}} \times \ln\frac{378.15}{373.15}\end{aligned}$$

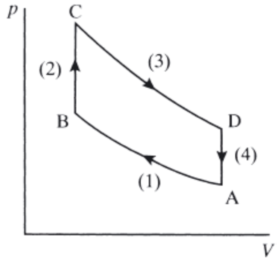
$$\boxed{\Delta S = 130.3\ \mathrm{J\ K^{-1}}}$$

Comment. This calculation was based on the assumption that heat capacities were constant over the range of temperatures involved. This assumption is not strictly valid. Therefore the calculated value is only approximate.

Problems

3A.2 The Otto cycle is represented in Fig. 3.1. Assume one mole of air.

Figure 3A.1



$$\eta = \frac{|w|_\mathrm{cycle}}{|q_2|}\quad [3\mathrm{A}.8]$$

$$w_\mathrm{cycle} = w_1 + w_3 = \Delta U_1 + \Delta U_3\ [q_1 = q_3 = 0] = C_V(T_\mathrm{B} - T_\mathrm{A}) + C_V(T_\mathrm{D} - T_\mathrm{C})$$

$$q_2 = \Delta U_2 = C_V(T_\mathrm{C} - T_\mathrm{B})$$

$$\eta = \frac{|T_\mathrm{B} - T_\mathrm{A} + T_\mathrm{D} - T_\mathrm{C}|}{|T_\mathrm{C} - T_\mathrm{B}|} = 1 - \left(\frac{T_\mathrm{D} - T_\mathrm{A}}{T_\mathrm{C} - T_\mathrm{B}}\right)$$

We know that

$$\frac{T_\mathrm{A}}{T_\mathrm{B}} = \left(\frac{V_\mathrm{B}}{V_\mathrm{A}}\right)^{1/c} \quad \text{and} \quad \frac{T_\mathrm{D}}{T_\mathrm{C}} = \left(\frac{V_\mathrm{C}}{V_\mathrm{D}}\right)^{1/c} \quad [2\mathrm{E}.2\mathrm{a}]$$

Since $V_\mathrm{B} = V_\mathrm{C}$ and $V_\mathrm{A} = V_\mathrm{D}$, $\frac{T_\mathrm{A}}{T_\mathrm{B}} = \frac{T_\mathrm{D}}{T_\mathrm{C}}$, or $T_\mathrm{D} = \frac{T_\mathrm{A}T_\mathrm{C}}{T_\mathrm{B}}$

Then $\quad \eta = 1 - \dfrac{\dfrac{T_\mathrm{A}T_\mathrm{C}}{T_\mathrm{B}} - T_\mathrm{A}}{T_\mathrm{C} - T_\mathrm{B}} = 1 - \dfrac{T_\mathrm{A}}{T_\mathrm{B}}$ or $\boxed{\eta = 1 - \left(\dfrac{V_\mathrm{B}}{V_\mathrm{A}}\right)^{1/c}}$

Given that $C_{p,\mathrm{m}} = {}^7\!/_2R$, we have $C_{V,\mathrm{m}} = {}^5\!/_2R$ [2D.11] and $c = \dfrac{2}{5}$

For $\quad \dfrac{V_\mathrm{A}}{V_\mathrm{B}} = 10,\ \eta = 1 - \left(\dfrac{1}{10}\right)^{2/5} = \boxed{0.47}$

$$\Delta S_1 = \Delta S_3 = \Delta S_{\mathrm{sur},1} = \Delta S_{\mathrm{sur},3} = \boxed{0} \quad \text{[adiabatic reversible steps]}$$

$$\Delta S_2 = C_{V,\mathrm{m}} \ln\left(\frac{T_\mathrm{C}}{T_\mathrm{B}}\right)$$

At constant volume $\left(\dfrac{T_\mathrm{C}}{T_\mathrm{B}}\right) = \left(\dfrac{p_\mathrm{C}}{p_\mathrm{B}}\right) = 5.0$

$$\Delta S_2 = \left(\frac{5}{2}\right) \times (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (\ln 5.0) = \boxed{+33\,\mathrm{J\,K^{-1}}}$$

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

$$\Delta S_4 = -\Delta S_2 \left[\frac{T_\mathrm{C}}{T_\mathrm{D}} = \frac{T_\mathrm{B}}{T_\mathrm{A}}\right] = \boxed{-33\,\mathrm{J\,K^{-1}}}$$

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

3A.4 **(a)** As suggested, relate the work to the temperature-dependent coefficient of performance :

$$|\mathrm{d}w| = \frac{|\mathrm{d}q_\mathrm{c}|}{c} = \frac{|C_p\mathrm{d}T|}{\left(\dfrac{T}{T_\mathrm{h} - T}\right)} = C_p\left|\frac{T_\mathrm{h}\mathrm{d}T}{T} - \mathrm{d}T\right|$$

Integrating yields

$$|w| = C_p\left|T_\mathrm{h}\int_{T_\mathrm{i}}^{T_\mathrm{f}} \frac{\mathrm{d}T}{T} + \int_{T_\mathrm{i}}^{T_\mathrm{f}} \mathrm{d}T\right| = C_p\left|T_\mathrm{h} \ln\frac{T_\mathrm{f}}{T_\mathrm{i}} - (T_\mathrm{f} - T_\mathrm{i})\right| = C_p\left(T_\mathrm{h} \ln\frac{T_\mathrm{i}}{T_\mathrm{f}} - T_\mathrm{i} + T_\mathrm{f}\right)$$

(b) The heat capacity is C_p = (4.184 J K^{-1} g^{-1}) × (250 g) = 1046 J K^{-1}, so the work associated with cooling the water from 293 K to the freezing temperature is

$$|w|_\mathrm{cooling} = 1046\ \mathrm{J\,K^{-1}} \times \left(293\ \mathrm{K} \times \ln\frac{293\ \mathrm{K}}{273\ \mathrm{K}} - 293\ \mathrm{K} + 273\ \mathrm{K}\right) = 748\ \mathrm{J}$$

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

$$|w|_\mathrm{freeze} = \frac{|q_\mathrm{c}|}{c} = \frac{\Delta_\mathrm{fus}H}{\left(\dfrac{T_\mathrm{c}}{T_\mathrm{h} - T_\mathrm{c}}\right)} = \Delta_\mathrm{fus}H\left(\frac{T_\mathrm{h} - T_\mathrm{c}}{T_\mathrm{c}}\right)$$

$$= 6.008 \times 10^3\ \mathrm{J\,mol^{-1}} \times \frac{250\ \mathrm{g}}{18.0\ \mathrm{g\,mol^{-1}}} \times \left(\frac{293 - 273}{273}\right) = 611\bar{3}\ \mathrm{J}$$

The total work is

$$|w|_\mathrm{total} = |w|_\mathrm{cooling} + |w|_\mathrm{freeze} = (748 + 611\bar{3})\ \mathrm{J} = \boxed{6.86 \times 10^3\ \mathrm{J} = 6.86\ \mathrm{kJ}}$$

At the rate of 100 W = 100 J s^{-1}, the refrigerator would freeze the water in

$$t = \frac{6.86 \times 10^3\ \mathrm{J}}{100\ \mathrm{J\,s^{-1}}} = \boxed{68.6\ \mathrm{s}}$$

3A.6 **(a)** Because entropy is a state function $\Delta_{\text{trs}}S(\text{l}\rightarrow\text{s},-5^\circ\text{C})$ may be determined indirectly from the following cycle

$$\begin{tikzcd}
\text{H}_2\text{O}(1,0^\circ\text{C}) \arrow[r, "\Delta_{\text{trs}}S(\text{l}\rightarrow\text{s},0^\circ\text{C})"] & \text{H}_2\text{O}(\text{s},0^\circ\text{C}) \arrow[d, "\Delta S_{\text{s}}"] \\
\text{H}_2\text{O}(1,-5^\circ\text{C}) \arrow[u, "\Delta S_{\text{l}}"] \arrow[r, "\Delta_{\text{trs}}S(\text{l}\rightarrow\text{s},-5^\circ\text{C})"] & \text{H}_2\text{O}(\text{s},-5^\circ\text{C})
\end{tikzcd}$$

Thus $\Delta_{\text{trs}}S(\text{l}\rightarrow\text{s},-5^\circ\text{C}) = \Delta S_{\text{l}} + \Delta_{\text{trs}}S(\text{l}\rightarrow\text{s},0^\circ\text{C}) + \Delta S_{\text{s}}$,

where $\Delta S_{\text{l}} = C_{p,\text{m}}(\text{l})\ln\dfrac{T_{\text{f}}}{T}$ [3A.20; $\theta_{\text{f}} = 0^\circ\text{C}$, $\theta = -5^\circ\text{C}$]

and $\Delta S_{\text{s}} = C_{p,\text{m}}(\text{s})\ln\dfrac{T}{T_{\text{f}}}$

$$\Delta S_{\text{l}} + \Delta S_{\text{s}} = -\Delta C_p \ln\frac{T}{T_{\text{f}}} \quad \text{with } \Delta C_p = C_{p,\text{m}}(\text{l}) - C_{p,\text{m}}(\text{s}) = +37.3\,\text{J K}^{-1}\text{ mol}^{-1}$$

$$\Delta_{\text{trs}}S(\text{l}\rightarrow\text{s},T_{\text{f}}) = \frac{-\Delta_{\text{fus}}H}{T_{\text{f}}} \quad [\text{3A.17}]$$

Thus, $\Delta_{\text{trs}}S(\text{l}\rightarrow\text{s},T) = \dfrac{-\Delta_{\text{fus}}H}{T_{\text{f}}} - \Delta C_p \ln\dfrac{T}{T_{\text{f}}}$

$$\Delta_{\text{trs}}S(\text{l}\rightarrow\text{s},-5^\circ\text{C}) = \frac{-6.01\times10^3\,\text{J mol}^{-1}}{273\text{ K}} - (37.3\,\text{J K}^{-1}\text{ mol}^{-1})\times\ln\frac{268}{273}$$

$$= \boxed{-21.3\,\text{J K}^{-1}\text{ mol}^{-1}}$$

$$\Delta S_{\text{sur}} = \frac{\Delta_{\text{fus}}H(T)}{T}$$

$$\Delta_{\text{fus}}H(T) = -\Delta H_{\text{l}} + \Delta_{\text{fus}}H(T_{\text{f}}) - \Delta H_{\text{s}}$$

$$\Delta H_{\text{l}} + \Delta H_{\text{s}} = C_{p,\text{m}}(\text{l})(T_{\text{f}} - T) + C_{p,\text{m}}(\text{s})(T - T_{\text{f}}) = \Delta C_{\text{p}}(T_{\text{f}} - T)$$

$$\Delta_{\text{fus}}H(T) = \Delta_{\text{fus}}H(T_{\text{f}}) - \Delta C_p(T_{\text{f}} - T)$$

Thus, $\Delta S_{\text{sur}} = \dfrac{\Delta_{\text{fus}}H(T)}{T} = \dfrac{\Delta_{\text{fus}}H(T_{\text{f}})}{T} + \Delta C_p\dfrac{(T - T_{\text{f}})}{T}$

$$\Delta S_{\text{sur}} = \frac{6.01\,\text{kJ mol}^{-1}}{268\text{ K}} + (37.3\,\text{J K}^{-1}\text{ mol}^{-1})\times\left(\frac{268-273}{268}\right)$$

$$= \boxed{+21.7\,\text{J K}^{-1}\text{ mol}^{-1}}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{sur}} + \Delta S = (21.7 - 21.3)\,\text{J K}^{-1}\text{ mol}^{-1} = \boxed{+0.4\,\text{J K}^{-1}\text{ mol}^{-1}}$$

Because $\Delta S_{\text{total}} > 0$, the transition $\text{l}\rightarrow\text{s}$ is spontaneous at –5°C.

(b) A similar cycle and analysis can be set up for the transition liquid $\rightarrow$ vapour at 95°C. However, since the transformation here is to the high temperature state (vapour) from the low temperature state (liquid), which is the opposite of part (a), we can expect that the analogous equations will occur with a change of sign.

$$\Delta_{\text{trs}}S(1\rightarrow\text{g},\,T) = \Delta_{\text{trs}}S(1\rightarrow\text{g},\,T_{\text{b}}) + \Delta C_p \ln\frac{T}{T_{\text{b}}}$$

$$= \frac{\Delta_{\text{vap}}H}{T_{\text{b}}} + \Delta C_p \ln\frac{T}{T_{\text{b}}}, \qquad \Delta C_p = -\,41.9\text{ J K}^{-1}\text{ mol}^{-1}$$

$$\Delta_{\text{trs}}S(1\rightarrow\text{g},\,T) = \frac{40.7\text{ kJ mol}^{-1}}{373\text{ K}} - (41.9\text{ J K}^{-1}\text{ mol}^{-1})\times\ln\left(\frac{368}{373}\right)$$

$$= \boxed{+109.7\text{ J K}^{-1}\text{ mol}^{-1}}$$

$$\Delta S_{\text{sur}} = \frac{-\Delta_{\text{vap}}H(T)}{T} = -\frac{\Delta_{\text{vap}}H(T_{\text{b}})}{T} - \frac{\Delta C_p(T-T_{\text{b}})}{T}$$

$$= \left(\frac{-40.7\ \text{kJ mol}^{-1}}{368\ \text{K}}\right) - (-41.9\ \text{J K}^{-1}\ \text{mol}^{-1}) \times \left(\frac{368-373}{368}\right)$$

$$= \boxed{-111.2\ \text{J K}^{-1}\ \text{mol}^{-1}}$$

$$\Delta S_{\text{total}} = (109.7 - 111.2)\,\text{J K}^{-1}\ \text{mol}^{-1} = \boxed{-1.5\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

Since $\Delta S_{\text{total}} < 0$, the reverse transition, $\text{g} \rightarrow \text{l}$, is spontaneous at 95°C.

3A.8 **(a)** $q(\text{total}) = q(\text{H}_2\text{O}) + q(\text{Cu}) = 0, \text{hence} - q(\text{H}_2\text{O}) = q(\text{Cu})$

$$q(\text{H}_2\text{O}) = n(-\Delta_{\text{vap}}H) + nC_{p,\text{m}}(\text{H}_2\text{O,l}) \times (\theta - 100°\text{C})$$

where θ is the final temperature of the water and copper.

$$q(\text{Cu}) = mC_{\text{s}}(\theta - 0) = mC_{\text{s}}\theta, \quad C_{\text{s}} = 0.385\,\text{J K}^{-1}\text{g}^{-1}\ [C_{\text{s}} = C_{p,\text{m}}/M]$$

Setting $-q(\text{H}_2\text{O}) = q(\text{Cu})$ allows us to solve for θ.

$$n(\Delta_{\text{vap}}H) - nC_{p,\text{m}}(\text{H}_2\text{O,l}) \times (\theta - 100°\text{C}) = mC_{\text{s}}\theta$$

Solving for θ yields:

$$\theta = \frac{n\{\Delta_{\text{vap}}H + C_{p,\text{m}}(\text{H}_2\text{O,l}) \times 100°\text{C}\}}{mC_{\text{s}} + nC_{p,\text{m}}(\text{H}_2\text{O,l})}$$

$$= \frac{(1.00\ \text{mol}) \times (40.656 \times 10^3\ \text{J mol}^{-1} + 75.3\ \text{J°C}^{-1}\ \text{mol}^{-1} \times 100°\text{C})}{2.00 \times 10^3\ \text{g} \times 0.385\ \text{J°C}^{-1}\ \text{g}^{-1} + 1.00\ \text{mol} \times 75.3\ \text{J°C}^{-1}\ \text{mol}^{-1}}$$

$$= 57.0°\text{C} = 330.2\ \text{K}$$

$$q(\text{Cu}) = (2.00 \times 10^3\ \text{g}) \times (0.385\,\text{J K}^{-1}\ \text{g}^{-1}) \times (57.0\,\text{K}) = 4.39 \times 10^4\ \text{J} = \boxed{43.9\ \text{kJ}}$$

$$q(\text{H}_2\text{O}) = \boxed{-43.9\ \text{kJ}}$$

$$\Delta S(\text{total}) = \Delta S(\text{H}_2\text{O}) + \Delta S(\text{Cu})$$

$$\Delta S(\text{H}_2\text{O}) = \frac{-n\Delta_{\text{vap}}H}{T_{\text{b}}}\ [3\text{A}.17] + nC_{p,\text{m}} \ln\left(\frac{T_{\text{f}}}{T_{\text{i}}}\right)\ [3\text{A}.20]$$

$$= -\frac{(1.00\,\text{mol}) \times (40.656 \times 10^3\,\text{J mol}^{-1})}{373.2\,\text{K}}$$

$$+(1.00\,\text{mol}) \times (75.3\,\text{J K}^{-1}\,\text{mol}^{-1}) \times \ln\left(\frac{330.2\,\text{K}}{373.2\,\text{K}}\right)$$

$$= -108.\bar{9}\,\text{J K}^{-1} - 9.22\,\text{J K}^{-1} = \boxed{-118.\bar{1}\,\text{J K}^{-1}}$$

$$\Delta S(\text{Cu}) = mC_{\text{s}} \ln\frac{T_{\text{f}}}{T_{\text{i}}} = (2.00 \times 10^3\ \text{g}) \times (0.385\,\text{J K}^{-1}\ \text{g}^{-1}) \times \ln\left(\frac{330.2\,\text{K}}{273.2\,\text{K}}\right)$$

$$= \boxed{145.\bar{9}\,\text{J K}^{-1}}$$

$$\Delta S(\text{total}) = -118.\bar{1}\,\text{J K}^{-1} + 145.\bar{9}\,\text{J K}^{-1} = \boxed{28\ \text{J K}^{-1}}$$

This process is spontaneous since $\Delta S(\text{surroundings})$ (surroundings) is zero and, hence,

$$\Delta S(\text{universe}) = \Delta S(\text{total}) > 0$$

(b) The volume of the container may be calculated from the perfect gas law.

$$V = \frac{nRT}{p} = \frac{(1.00\,\text{mol}) \times (0.08206\ \text{dm}^3\,\text{atm K}^{-1}\,\text{mol}^{-1}) \times (373.2\ \text{K})}{1.00\ \text{atm}} = 30.6\ \text{dm}^3$$

At 57°C the vapor pressure of water is 130 Torr (*Handbook of Chemistry and Physics*, 81st edition). The amount of water vapor present at equilibrium is then

$$n=\frac{pV}{RT}=\frac{(130\,\text{Torr})\times\left(\dfrac{1\,\text{atm}}{760\,\text{Torr}}\right)\times(30.6\,\text{dm}^3)}{(0.08206\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1})\times(330.2\,\text{K})}=0.193\,\text{mol}$$

This is a substantial fraction of the original amount of water and cannot be ignored. Consequently the calculation needs to be redone taking into account the fact that only a part, n_l, of the vapor condenses into a liquid while the remainder (1.00 mol – n_l) remains gaseous. The heat flow involving water, then, becomes

$$q(\text{H}_2\text{O})=-n_\text{l}\Delta_\text{vap}H+n_\text{l}C_{p,\text{m}}(\text{H}_2\text{O},\text{l})\Delta T(\text{H}_2\text{O})$$
$$+(1.00\,\text{mol}-n_\text{l})C_{p,\text{m}}(\text{H}_2\text{O},\text{g})\Delta T(\text{H}_2\text{O})$$

Because n_l depends on the equilibrium temperature through

$n_\text{l}=1.00\,\text{mol}-\dfrac{pV}{RT}$, where p is the vapor pressure of water, we will have two unknowns (p and T) in the equation $-q(\text{H}_2\text{O})=q(\text{Cu})$. There are two ways out of this dilemma: (1) p may be expressed as a function of T by use of the Clapeyron equation, or (2) by use of successive approximations. Redoing the calculation yields:

$$\theta=\frac{n_\text{l}\Delta_\text{vap}H+n_\text{l}C_{p,\text{m}}(\text{H}_2\text{O},\text{l})\times100°\text{C}+(1.00-n_\text{l})C_{p,\text{m}}(\text{H}_2\text{O},\text{g})\times100°\text{C}}{mC_\text{s}+nC_{p,\text{m}}(\text{H}_2\text{O},\text{l})+(1.00-n_\text{l})C_{p,\text{m}}(\text{H}_2\text{O},\text{g})}$$

With

$$n_\text{l}=(1.00\,\text{mol})-(0.193\,\text{mol})=0.80\overline{7}\,\text{mol}$$

(noting that $C_\text{p,m}(\text{H}_2\text{O,g})$ = 33.6 J mol^{-1} K^{-1} [Table 2C.2]) θ = 47.2°C. At this temperature, the vapor pressure of water is 80.41 Torr, corresponding to

$$n_\text{l}=(1.00\,\text{mol})-(0.123\,\text{mol})=0.87\overline{7}\,\text{mol}$$

This leads to θ = 50.8°C. The successive approximations eventually converge to yield a value of θ = $\boxed{49.9^\circ\text{C}=323.1\,\text{K}}$ for the final temperature. (At this temperature, the vapor pressure is 0.123 bar.) Using this value of the final temperature, the heat transferred and the various entropies are calculated as in part (a).

$$q(\text{Cu})=(2.00\times10^3\,\text{g})\times(0.385\,\text{J}\,\text{K}^{-1}\,\text{g}^{-1})\times(49.9\,\text{K})=\boxed{38.4\text{ kJ}}=-q(\text{H}_2\text{O})$$

$$\Delta S(\text{H}_2\text{O})=\frac{-n\Delta_\text{vap}H}{T_\text{b}}+nC_{p,\text{m}}\ln\left(\frac{T_\text{f}}{T_\text{i}}\right)=\boxed{-119.\overline{8}\,\text{J}\,\text{K}^{-1}}$$

$$\Delta S(\text{Cu})=mC_\text{s}\ln\frac{T_\text{f}}{T_\text{i}}=\boxed{129.\overline{2}\,\text{J}\,\text{K}^{-1}}$$

$$\Delta S(\text{total})=-119.\overline{8}\text{ J K}^{-1}+129.\overline{2}\text{ J K}^{-1}=\boxed{9\text{ J K}^{-1}}$$

3A.10 ΔS depends on only the initial and final states, so we can use $\Delta S=nC_{p,\text{m}}\ln\dfrac{T_\text{f}}{T_\text{i}}$ [3A.20]

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 $n=\dfrac{500\text{ g}}{63.5\text{ g mol}^{-1}}=7.87\text{ mol}$

$$\Delta S=(7.87\text{ mol})\times(24.4\text{ J K}^{-1}\text{ mol}^{-1})\times\ln\left(1+\frac{(1.00\text{ A})^2\times(1000\ \Omega)\times(15.0\text{ s})}{(7.87)\times(24.4\text{ J K}^{-1})\times(293\text{ K})}\right)$$

$$=(192\text{ J K}^{-1})\times(\ln1.27)=\boxed{+45.4\text{ J K}^{-1}}$$

$$[1\ \text{J} = 1\ \text{AVs} = 1\ \text{A}^2\Omega\ \text{s}]$$

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

$$\Delta S(\text{water}) = \frac{q}{T} = \frac{I^2Rt}{T} = \frac{(1.00\ \text{A})^2 \times (1000\ \Omega) \times (15.0\ \text{s})}{293\ \text{K}} = \boxed{+51.2\ \text{J K}^{-1}}$$

3A.12 Let us write Newton's law of cooling as follows:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -A(T - T_s)$$

Where A is a constant characteristic of the system and T_S is the temperature of the surroundings. The negative sign appears because we assume $T > T_\text{S}$. Separating variables

$$\frac{\mathrm{d}T}{T - T_\text{S}} = -A\mathrm{d}t$$, and integrating, we obtain

$$\ln(T - T_\text{S}) = -At + K$$, where K is a constant of integration.

Let T_i be the initial temperature of the system when $t = 0$, then

$$K = \ln(T_\text{i} - T_\text{S})$$

Introducing this expression for K gives

$$\ln\left(\frac{T - T_\text{S}}{T_\text{i} - T_\text{S}}\right) = -At \text{ or } T = T_\text{S} + (T_\text{i} - T_\text{S})\mathrm{e}^{-At}$$

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\left(C\ln\frac{T}{T_\text{i}}\right) = \frac{\mathrm{d}}{\mathrm{d}t}(C\ln T)$$

From the above expression for T, we obtain $\ln T = \ln T_\text{S} - At\ln(T_\text{i} - T_\text{S})$. Substituting ln t we obtain $\boxed{\frac{\mathrm{d}S}{\mathrm{d}t} = -CA\ln(T_\text{i} - T_\text{S})}$, where now T_i can be interpreted as any temperature T during the course of the cooling process.

3B The measurement of entropy

Solutions to exercises

3B.1(b) Use $S_\text{m} = R \ln s$, where s is the number of orientations of about equal energy that the molecule can adopt.

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* the 1,2,4 isomer, and *c* the 1,3,5 isomer.

3B.2(b) **(i)**

$$\Delta_r S^\ominus = S_m^\ominus(\mathrm{Zn^{2+},aq}) + S_m^\ominus(\mathrm{Cu,s}) - S_m^\ominus(\mathrm{Zn,s}) - S_m^\ominus(\mathrm{Cu^{2+},aq})$$
$$= \left[-112.1 + 33.15 - 41.63 + 99.6\right]\,\mathrm{J\,K^{-1}\,mol^{-1}} = \boxed{-21.0\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

(ii)

$$\Delta_r S^\ominus = 12S_m^\ominus(\mathrm{CO_2,g}) + 11S_m^\ominus(\mathrm{H_2O,l}) - S_m^\ominus(\mathrm{C_{12}H_{22}O_{11},s}) - 12S_m^\ominus(\mathrm{O_2,g})$$
$$= \left[(12\times 213.74) + (11\times 69.91) - 360.2 - (12\times 205.14)\right]\,\mathrm{J\,K^{-1}\,mol^{-1}}$$
$$= \boxed{+512.0\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

Solutions to problems

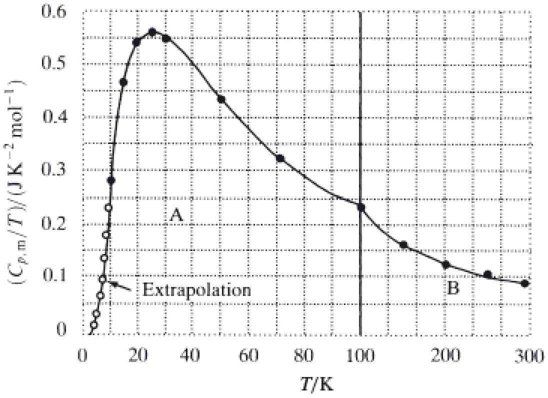
3B.2 $S_m(T) = S_m(0) + \int_0^T \frac{C_{p,m}\,dT}{T}$ [3A.19]

From the data, draw up the following table

T / K	10	15	20	25	30	50
$\frac{C_{p,m}}{T}$ / (J K^{-2} mol^{-1})	0.28	0.47	0.540	0.564	0.550	0.428
T / K	70	100	150	200	250	298
$\frac{C_{p,m}}{T}$ / (J K^{-2} mol^{-1})	0.333	0.245	0.169	0.129	0.105	0.089

Plot $C_{p,m}$ / T against T (Fig. 3B.1). This has been done on two scales. The region 0 to 10 K has been constructed using $C_{p,m} = aT^3$, fitted to the point at T = 10 K, at which $C_{p,m}$ = 2.8 J K^{-1} mol^{-1}, so $a = 2.8\times 10^{-3}\,\mathrm{J\,K^{-4}\,mol^{-1}}$. The area can be determined (primitively) by counting squares. Area A = 38.28 J K^{-1} mol^{-1}. Area B up to 0°C = 25.60 J K^{-1} mol^{-1}; area B up to 25°C = 27.80 J K^{-1} mol^{-1}. Hence

Figure 3B.1



(a) $S_m(273\,\mathrm{K}) = S_m(0) + \boxed{63.88\,\mathrm{J\,K^{-1}\,mol^{-1}}}$

(b) $S_m(298\,\mathrm{K}) = S_m(0) + \boxed{66.08\,\mathrm{J\,K^{-1}\,mol^{-1}}}$

3B.4 $S_m(T) = S_m(0) + \int_0^T \frac{C_{p,m}\,dT}{T}$ [3A.19]

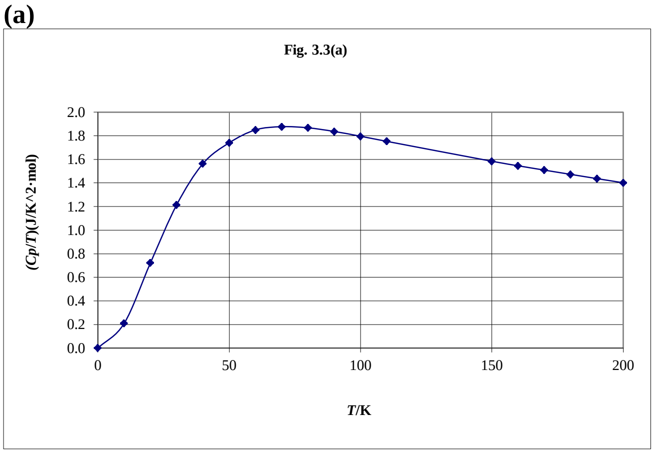
Perform a graphical integration by plotting $C_{p,\mathrm{m}}/T$ against T and determining the area under the curve. Draw up the following table. (The last two columns come from determining areas under the curves described below.)

T / K	$\dfrac{C_{p,\mathrm{m}}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\dfrac{C_{p,\mathrm{m}}/T}{\mathrm{J\,K^{-2}\,mol^{-1}}}$	$\dfrac{S_\mathrm{m}^\ominus - S_\mathrm{m}^\ominus(0)}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\dfrac{H_\mathrm{m}^\ominus - H_\mathrm{m}^\ominus(0)}{\mathrm{kJ\,mol^{-1}}}$
0.00	0.00	0.00	0.00	0.00
10.00	2.09	0.21	0.80	0.01
20.00	14.43	0.72	5.61	0.09
30.00	36.44	1.21	15.60	0.34
40.00	62.55	1.56	29.83	0.85
50.00	87.03	1.74	46.56	1.61
60.00	111.00	1.85	64.62	2.62
70.00	131.40	1.88	83.29	3.84
80.00	149.40	1.87	102.07	5.26
90.00	165.30	1.84	120.60	6.84
100.00	179.60	1.80	138.72	8.57
110.00	192.80	1.75	156.42	10.44
150.00	237.60	1.58	222.91	19.09
160.00	247.30	1.55	238.54	21.52
170.00	256.50	1.51	253.79	24.05
180.00	265.10	1.47	268.68	26.66
190.00	273.00	1.44	283.21	29.35
200.00	280.30	1.40	297.38	32.13

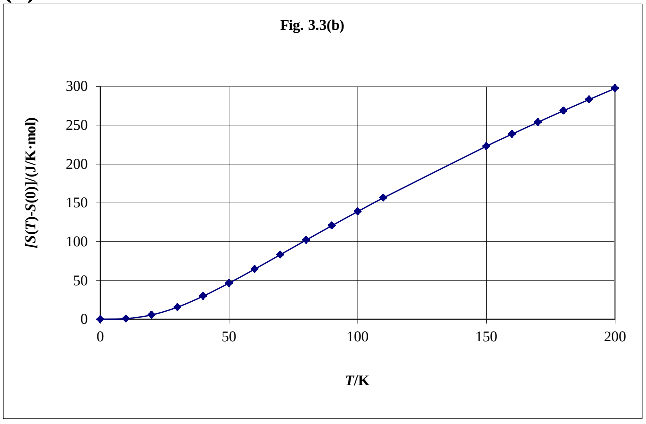
Plot $C_{p,\mathrm{m}}$ against T (Fig. 3B.2(a)). Extrapolate to $T = 0$ using $C_{p,\mathrm{m}} = aT^3$ fitted to the point at $T = 10$ K, which gives $a = 2.09$ mJ K^{-2} mol^{-1}. Determine the area under the graph up to each T and plot S_m against T (Fig. 3B.2(b)).

Figure 3B.2

(a)



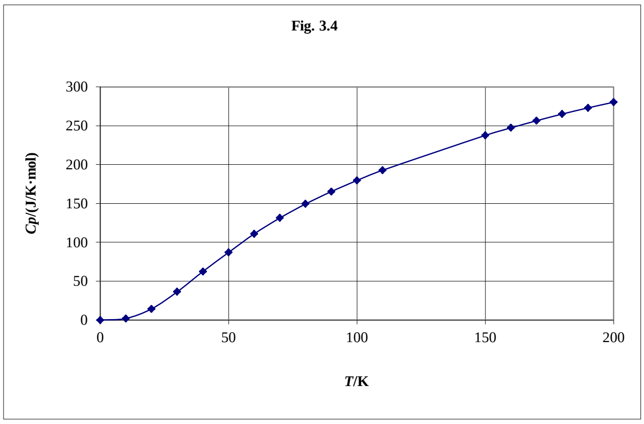
(b)



The molar enthalpy is determined in a similar manner from a plot of $C_{p,\mathrm{m}}$ against T by determining the area under the curve (Fig. 3.4)

$$H_{\mathrm{m}}^{\ominus}(200\,\mathrm{K}) - H_{\mathrm{m}}^{\ominus}(0) = \int_0^{200\,\mathrm{K}} C_{p,\mathrm{m}}\,\mathrm{d}T = \boxed{32.1\ \mathrm{kJ\ mol^{-1}}}$$

Figure 3B.3



3B.6 The entropy at 200 K is calculated from

$$S_{\mathrm{m}}^{\ominus}(200\ \mathrm{K}) = S_{\mathrm{m}}^{\ominus}(100\ \mathrm{K}) + \int_{100\ \mathrm{K}}^{200\ \mathrm{K}} \frac{C_{p,\mathrm{m}}\,\mathrm{d}T}{T}$$

The integrand may be evaluated at each of the data points; the transformed data appear below. The numerical integration can be carried out by a standard procedure such as the trapezoid rule (taking the integral within any interval as the mean value of the integrand times the length of the interval). Programs for performing this integration are readily available for personal computers. Many graphing calculators will also perform this numerical integration.

T / K	100	120	140	150	160	180	200
$C_{p,\mathrm{m}}$ / (J K^{-1} mol^{-1})	23.00	23.74	24.25	24.44	24.61	24.89	25.11
$\dfrac{C_{p,\mathrm{m}}}{T}$ / (J K^{-2} mol^{-1})	0.230	0.1978	0.1732	0.1629	0.1538	0.1383	0.1256

Integration by the trapezoid rule yields

$$S_{\mathrm{m}}^{\ominus}(200\ \mathrm{K}) = (29.79 + 16.81)\ \mathrm{J\ K^{-1}\ mol^{-1}} = \boxed{46.60\ \mathrm{J\ K^{-1}\ mol^{-1}}}$$

Taking $C_{p,\mathrm{m}}$ constant yields

$$S_{\mathrm{m}}^{\ominus}(200\ \mathrm{K}) = S_{\mathrm{m}}^{\ominus}(100\ \mathrm{K}) + C_{p,\mathrm{m}}\ \ln(200\ \mathrm{K}/100\ \mathrm{K})$$

$$= [29.79 + 24.44\ \ln(200\ /100\ \mathrm{K})]\ \mathrm{J\ K^{-1}\ mol^{-1}} = \boxed{46.60\ \mathrm{J\ K^{-1}\ mol^{-1}}}$$

The difference is slight.

3B.8 $S = k \ln W$ [also see Exercises 3B.1(a) and (b)]

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 Exercises 3B.1(a) and (b).

3C Concentrating on the system

Answers to discussion questions

3C.2 All of the thermodynamic properties of a system that we have encountered, *U*, *H*, *S*, *A*, and *G* can be used as the criteria for the spontaneity of a process under specific conditions. The criteria are derived directly from the fundamental relation of thermodynamics which is a combination of the first and second laws, namely

$$-\mathrm{d}U - p_{\mathrm{ext}}\mathrm{d}V + \mathrm{d}w_{\text{non-pV}} + T\mathrm{d}S \ge 0$$

The inequality sign gives the criteria for the spontaneity of a process, the equality gives the criteria for equilibrium.

The specific conditions we are interested in and the criteria that follow from inserting these conditions into the fundamental relation are the following:

(1) Constant *U* and *V*, no work at all

$$\mathrm{d}S_{U,V} \ge 0$$

(2) Constant *S* and *V*, no work at all

$$\mathrm{d}U_{S,V} \le 0$$

(3) Constant S and p, no work at all

$$\mathrm{d}H_{S,p} \le 0$$

(4) Constant *T*

$$\mathrm{d}A_T \le \mathrm{d}w$$

(5) Constant *T* and *V*, only non-*pV* work

$$\mathrm{d}A_{T,V} \le \mathrm{d}w_{\text{non-pV}}$$

(6) Constant *T* and *V*, no work at all

$$\mathrm{d}A_{T,V} \le 0$$

(7) Constant *T* and *p*, $p = p_{\mathrm{ext}}$

$$\mathrm{d}G_{T,p} \le \mathrm{d}w_{\text{non-pV}}$$

(8) Constant *T* and *p*, no non-pV work

$$\mathrm{d}G_{T,p} \le 0$$

Exercises

3C.1(b) (i)

$$\begin{aligned}\Delta_r H^\ominus &= \Delta_f H^\ominus(\mathrm{Zn^{2+}},\mathrm{aq}) - \Delta_f H^\ominus(\mathrm{Cu^{2+}},\mathrm{aq})\\ &= -153.89 - 64.77\ \mathrm{kJ\ mol^{-1}} = -218.66\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

$$\Delta_r G^\ominus = -218.66\ \mathrm{kJ\ mol^{-1}} - (298.15\ \mathrm{K}) \times (-21.0\ \mathrm{J\ K^{-1}\ mol^{-1}}) = \boxed{-212.40\ \mathrm{kJ\ mol^{-1}}}$$

(ii)

$$\Delta_r H^\ominus = \Delta_c H^\ominus = -5645\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta_r G^\ominus = -5645\ \mathrm{kJ\ mol^{-1}} - (298.15\ \mathrm{K}) \times (512.0\ \mathrm{J\ K^{-1}\ mol^{-1}}) = \boxed{-5798\ \mathrm{kJ\ mol^{-1}}}$$

3C.2(b) $\mathrm{CO(g)} + \mathrm{CH_3CH_2OH(l)} \rightarrow \mathrm{CH_3CH_2COOH(l)}$

$$\Delta_r H^\ominus = \sum_{\text{Products}} \nu \Delta_f H^\ominus - \sum_{\text{Reactants}} \nu \Delta_f H^\ominus \ \ [2\mathrm{C}.5]$$

$$\begin{aligned}&= -510.7\ \mathrm{kJ\ mol^{-1}} - (-277.69\ \mathrm{kJ\ mol^{-1}}) - (-110.53\ \mathrm{kJ\ mol^{-1}})\\ &= -122.5\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

$$\Delta_r S^\ominus = \sum_{\text{Products}} \nu S_m^\ominus - \sum_{\text{Reactants}} \nu S_m^\ominus [3\mathrm{B}.2]$$

$$\begin{aligned}&= 191.0\ \mathrm{J\ K^{-1}\ mol^{-1}} - 160.7\ \mathrm{J\ K^{-1}\ mol^{-1}} - 197.67\ \mathrm{J\ K^{-1}\ mol^{-1}}\\ &= -167.4\ \mathrm{J\ K^{-1}\ mol^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta_r G^\ominus &= \Delta_r H^\ominus - T\Delta_r S^\ominus\\ &= -122.5\ \mathrm{kJ\ mol^{-1}} - (298\ \mathrm{K}) \times (-167.4\ \mathrm{J\ K^{-1}\ mol^{-1}})\\ &= \boxed{-72.6\ \mathrm{kJ\ mol^{-1}}}\end{aligned}$$

3C.3(b) $\mathrm{C_3H_8(g)} + 5\mathrm{O_2(g)} \rightarrow 3\mathrm{CO_2(g)} + 4\mathrm{H_2O(l)}$

$$\begin{aligned}\Delta_r G^\ominus &= 3\Delta_f G^\ominus(\mathrm{CO_2},\mathrm{g}) + 4\Delta_f G^\ominus(\mathrm{H_2O},\mathrm{l}) - \Delta_f G^\ominus(\mathrm{C_3H_8},\mathrm{g}) - 0\\ &= 3(-394.36\ \mathrm{kJ\ mol^{-1}}) + 4(-237.13\ \mathrm{kJ\ mol^{-1}}) - 1(-23.49\ \mathrm{kJ\ mol^{-1}})\\ &= -2108.11\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

The maximum non-expansion work is $\boxed{2108.11\ \mathrm{kJ\ mol^{-1}}}$ since $|w_{\mathrm{add}}| = |\Delta G|$

3C.4(b) (a)

$$\begin{aligned}\Delta_r G^\ominus &= \Delta_f G^\ominus(\mathrm{Zn^{2+}},\mathrm{aq}) - \Delta_f G^\ominus(\mathrm{Cu^{2+}},\mathrm{aq})\\ &= -147.06 - 65.49\ \mathrm{kJ\ mol^{-1}} = \boxed{-212.55\ \mathrm{kJ\ mol^{-1}}}\end{aligned}$$

(b)

$$\begin{aligned}\Delta_r G^\ominus &= 12\Delta_f G^\ominus(\mathrm{CO_2},\mathrm{g}) + 11\Delta_f G^\ominus(\mathrm{H_2O},\mathrm{l}) - \Delta_f G^\ominus(\mathrm{C_{12}H_{22}O_{11}},\mathrm{s}) - 12\Delta_f G^\ominus(\mathrm{O_2},\mathrm{g})\\ &= \left[12 \times (-394.36) + 11 \times (-237.13) - (-1543) - 12 \times 0\right]\mathrm{kJ\ mol^{-1}} = \boxed{-5798\ \mathrm{kJ\ mol^{-1}}}\end{aligned}$$

Comment. In each case these values of $\Delta_r G^\ominus$ agree closely with the calculated values in Exercise 3C.1(b).

3C.5(b) The formation reaction of glycine is

$$2\mathrm{C(gr)} + \mathrm{O_2(g)} + \tfrac{1}{2}\mathrm{N_2(g)} + \tfrac{5}{2}\mathrm{H_2(g)} \rightarrow \mathrm{NH_2CH_2COOH(s)}$$

The combustion reaction is

$$\mathrm{NH_2CH_2COOH(s)} + \tfrac{7}{2}\mathrm{O_2(g)} \rightarrow 2\mathrm{CO_2(g)} + \tfrac{5}{2}\mathrm{H_2O(l)} + \tfrac{1}{2}\mathrm{N_2(g)}$$

$$\Delta_c H = 2\Delta_f H^{\ominus}(\mathrm{CO_2,g}) + \tfrac{5}{2}\Delta_f H^{\ominus}(\mathrm{H_2O,1}) - \Delta_f H^{\ominus}(\mathrm{NH_2CH_2COOH(s)})$$

$$\begin{aligned}\Delta_f H^{\ominus}(\mathrm{NH_2CH_2COOH(s)}) &= 2\Delta_f H^{\ominus}(\mathrm{CO_2,g}) + \tfrac{5}{2}\Delta_f H^{\ominus}(\mathrm{H_2O,1}) - \Delta_c H(\mathrm{NH_2CH_2COOH(s)})\\ &= -2\times 393.51\ \mathrm{kJ\ mol^{-1}} + (\tfrac{5}{2})\times(-285.83\ \mathrm{kJ\ mol^{-1}}) - (-969\ \mathrm{kJ\ mol^{-1}})\\ &= -532.\bar{6}\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta_f S^{\ominus} &= S_m^{\ominus}(\mathrm{NH_2CH_2COOH(s)}) - 2\times S_m^{\ominus}(\mathrm{C,gr}) - S_m^{\ominus}(\mathrm{O_2,g}) - \tfrac{1}{2}\times S_m^{\ominus}(\mathrm{N_2,g}) - \tfrac{5}{2}\times S_m^{\ominus}(\mathrm{H_2,g})\\ &= 103.5\,\mathrm{J\,K^{-1}\ mol^{-1}} - 2\times 5.740\,\mathrm{J\,K^{-1}\ mol^{-1}} - (205.138\,\mathrm{J\,K^{-1}\ mol^{-1}})\\ &\quad -\tfrac{1}{2}\times 191.61\,\mathrm{J\,K^{-1}\ mol^{-1}} - \tfrac{5}{2}\times(130.684\,\mathrm{J\,K^{-1}\ mol^{-1}})\\ &= -535.6\bar{3}\,\mathrm{J\,K^{-1}\ mol^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta_f G^{\ominus} &= \Delta_f H^{\ominus} - T\ \Delta_f S^{\ominus}\\ &= -532.\bar{6}\ \mathrm{kJ\ mol^{-1}} - (298.15\ \mathrm{K})\times(-535.6\bar{3}\ \mathrm{J\,K^{-1}\ mol^{-1}})\\ &= \boxed{-373\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

Solutions to problems

3C.2 Begin with the partition function of an oscillator [See Chapter 15].

$$q = \frac{1}{1-\mathrm{e}^{-x}},\quad x = \frac{\theta_V}{T} = hc\tilde{\nu}\beta = \hbar\omega\beta$$

The molar internal energy, molar entropy, and molar Helmholtz energy are obtained from the partition function as follows:

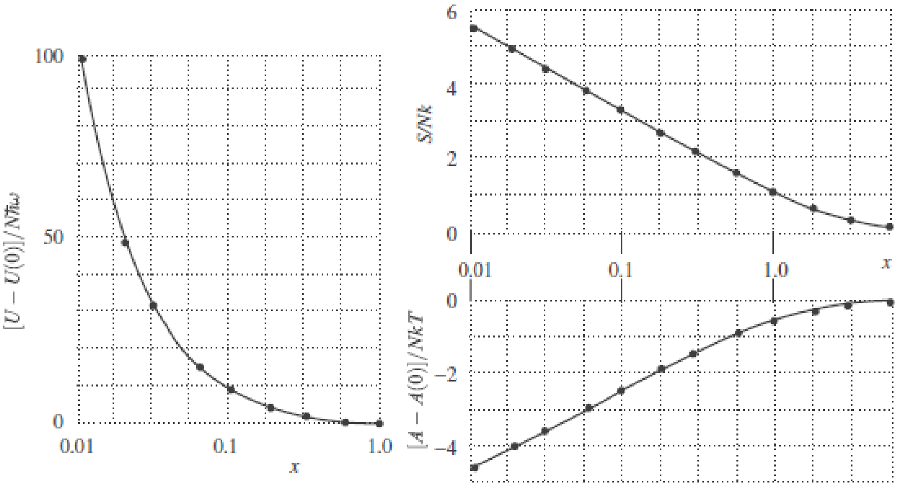
$$U - U(0) = -\frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V = -N(1-e^{-x})\frac{\mathrm{d}}{\mathrm{d}\beta}(1-e^{-x})^{-1} = \frac{N\hbar\omega\mathrm{e}^{-x}}{1-\mathrm{e}^{-x}} = \boxed{\frac{N\hbar\omega}{\mathrm{e}^{x}-1}}$$

$$\begin{aligned}S &= \frac{U-U(0)}{T} + nR\ln q = \frac{Nkx\mathrm{e}^{-x}}{1-\mathrm{e}^{-x}} - Nk\ln(1-\mathrm{e}^{-x})\\ &= \boxed{Nk\left(\frac{x}{\mathrm{e}^{x}-1} - \ln(1-\mathrm{e}^{-x})\right)}\end{aligned}$$

$$A - A(0) = G - G(0) = -nRT\ln q = \boxed{NkT\ \ln(1-\mathrm{e}^{-x})}$$

The functions are plotted in Fig. 3C.1.

Figure 3C.1



3D Combining the First and Second Laws

Answers to discussion questions

3D.2 The relation $(\partial G/\partial p)_T = V$, eqn 3D.8, shows that the Gibbs function of a system increases with p at constant T in proportion to the magnitude of its volume. This makes good sense when one considers the definition of G, which is $G = U + pV - TS$. Hence, G is expected to increase with p in proportion to V when T is constant.

Solutions to exercises

3D.1(b) $\Delta G = nRT\ln\left(\dfrac{p_\mathrm{f}}{p_\mathrm{i}}\right)$ [3D.14] $= nRT\ln\left(\dfrac{V_\mathrm{i}}{V_\mathrm{f}}\right)$ [Boyle's law]

$$\Delta G = (6.0\times10^{-3}\ \mathrm{mol})\times(8.314\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(298\ \mathrm{K})\times\ln\left(\frac{52}{122}\right) = \boxed{-13\ \mathrm{J}}$$

3D.2(b) $\left(\dfrac{\partial G}{\partial T}\right)_p = -S$ [3D.8]; hence $\left(\dfrac{\partial G_\mathrm{f}}{\partial T}\right)_p = -S_\mathrm{f}$, and $\left(\dfrac{\partial G_\mathrm{i}}{\partial T}\right)_p = -S_\mathrm{i}$

$$\Delta S = S_\mathrm{f} - S_\mathrm{i} = -\left(\frac{\partial G_\mathrm{f}}{\partial T}\right)_p + \left(\frac{\partial G_\mathrm{i}}{\partial T}\right)_p = -\left(\frac{\partial(G_\mathrm{f} - G_\mathrm{i})}{\partial T}\right)_p$$

$$= -\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\frac{\partial}{\partial T}\left(-73.1\ \mathrm{J} + 42.8\ \mathrm{J}\times\frac{T}{\mathrm{K}}\right)$$

$$= \boxed{-42.8\ \mathrm{J\,K^{-1}}}$$

3D.3(b) We will assume that the volume and molar volume of water changes little over the range of pressures given and that, therefore, equation 3D.13 which applies to incompressible substances can be used to solve this exercise. The change in Gibbs energy for this sample is then given by

$$\Delta G = nV_\mathrm{m}\Delta p\ [3\mathrm{D}.13] = V\Delta p$$

$$\Delta G = (100\ \text{cm}^3) \times \left(\frac{1\text{m}^3}{10^6\ \text{cm}^3}\right) \times 400\ \text{kPa} = 40\ \text{Pa m}^3 = \boxed{+40\,\text{J}}$$

In order to calculate the change in Gibbs energy per mole we calculate the molar volume

$$V_\text{m} = \frac{M}{\rho(\text{density})} = \frac{18.02\ \text{g mol}^{-1}}{0.997\ \text{g cm}^{-3}} \times \frac{10^{-6}\,\text{m}^3}{\text{cm}^3} = 1.81 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1}\text{,then}$$

$$\Delta G_\text{m} = V_\text{m}\Delta p\ [3\text{D}.13] = 1.81 \times 10^{-5}\ \text{m}^3\text{mol}^{-1} \times 400\ \text{kPa} \times \frac{10^3\,\text{Pa}}{\text{kPa}} = \boxed{7.2\ \text{J mol}^{-1}}$$

3D.4(b)

$$\Delta G_\text{m} = RT\ln\left(\frac{p_\text{f}}{p_\text{i}}\right) = \left(8.314\,\text{J K}^{-1}\,\text{mol}^{-1}\right) \times \left(500\,\text{K}\right) \times \ln\left(\frac{100.0\ \text{kPa}}{50.0\ \text{kPa}}\right)$$
$$= \boxed{+2.88\,\text{kJ mol}^{-1}}$$

Solutions to problems

3D.2 The Gibbs–Helmholtz equation [3D.9] may be recast into an analogous equation involving ΔG and ΔH, since

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = \left(\frac{\partial G_\text{f}}{\partial T}\right)_p - \left(\frac{\partial G_\text{i}}{\partial T}\right)_p$$

and $\Delta H = H_\text{f} - H_\text{i}$

Thus, $$\left(\frac{\partial}{\partial T}\frac{\Delta_\text{r} G^\ominus}{T}\right)_p = -\frac{\Delta_\text{r} H^\ominus}{T^2}$$

$$\text{d}\left(\frac{\Delta_\text{r} G^\ominus}{T}\right) = \left(\frac{\partial}{\partial T}\frac{\Delta_\text{r} G^\ominus}{T}\right)_p \text{d}T[\text{constant pressure}] = -\frac{\Delta_\text{r} H^\ominus}{T^2}\text{d}T$$

$$\Delta\left(\frac{\Delta_\text{r} G^\ominus}{T}\right) = -\int_{T_\text{c}}^{T} \frac{\Delta_\text{r} H^\ominus\,\text{d}T}{T^2}$$

$$\approx -\Delta_\text{r} H^\ominus \int_{T_\text{c}}^{T} \frac{\text{d}T}{T^2} = \Delta_\text{r} H^\ominus \left(\frac{1}{T} - \frac{1}{T_\text{c}}\right) \quad [\Delta_\text{r} H^\ominus \text{ assumed constant}]$$

Therefore, $$\frac{\Delta_\text{r} G^\ominus(T)}{T} - \frac{\Delta_\text{r} G^\ominus(T_\text{c})}{T_\text{c}} \approx \Delta_\text{r} H^\ominus \left(\frac{1}{T} - \frac{1}{T_\text{c}}\right)$$

and so

$$\Delta_\text{r} G^\ominus(T) = \frac{T}{T_\text{c}}\Delta_\text{r} G^\ominus(T_\text{c}) + \left(1 - \frac{T}{T_\text{c}}\right)\Delta_\text{r} H^\ominus(T_\text{c})$$
$$= \tau\Delta_\text{r} G^\ominus(T_\text{c}) + (1-\tau)\Delta_\text{r} H^\ominus(T_\text{c}) \quad \text{where} \quad \tau = \frac{T}{T_\text{c}}$$

For the reaction

$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g}) \quad \Delta_\text{r} G^\ominus = 2\Delta_\text{f} G^\ominus(\text{NH}_3,\text{g})$$

(a) At 500 K, $\tau = \frac{500}{298} = 1.67\overline{8}$,

so

$$\Delta_\text{r} G^\ominus(500\,\text{K}) = \{(1.67\overline{8}) \times 2 \times (-16.45) + (1 - 1.67\overline{8}) \times 2 \times (-46.11)\}\,\text{kJ mol}^{-1}$$
$$\boxed{= -7\,\text{kJ mol}^{-1}}$$

(b) At 1000 K, $\tau = \dfrac{1000}{298} = 3.35\overline{6}$,

so

$$\Delta_r G^{\ominus}(1000\,\mathrm{K}) = \{(3.35\overline{6}) \times 2 \times (-16.45) + (1 - 3.35\overline{6}) \times 2 \times (-46.11)\}\,\mathrm{kJ\,mol^{-1}}$$

$$\boxed{= +107\,\mathrm{kJ\,mol^{-1}}}$$

3D.4 $\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial p}{\partial T}\right)_V$ [Table 3D.1]

(a) For a van der Waals gas

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

Hence, $\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial p}{\partial T}\right)_V = \boxed{\dfrac{R}{V_\mathrm{m} - b}}$

(b) For a Dieterici gas

$$p = \frac{RT\mathrm{e}^{-a/RTV_m}}{V_\mathrm{m} - b}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \boxed{\frac{R\left(1 + \dfrac{a}{RV_\mathrm{m}T}\right)\mathrm{e}^{-a/RV_\mathrm{m}T}}{V_\mathrm{m} - b}}$$

For an isothermal expansion,

$$\Delta S = \int_{V_\mathrm{i}}^{V_\mathrm{f}} \mathrm{d}S = \int_{V_\mathrm{i}}^{V_\mathrm{f}} \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V$$

so we can simply compare $\left(\dfrac{\partial S}{\partial V}\right)_T$ expressions for the three gases. For a perfect gas,

$$p = \frac{nRT}{V} = \frac{RT}{V_\mathrm{m}} \quad \text{so} \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V_\mathrm{m}}$$

$\left(\dfrac{\partial S}{\partial V}\right)_T$ is certainly greater for a van der Waals gas than for a perfect gas, for the denominator is smaller for the van der Waals gas. To compare the van der Waals gas to the Dieterici gas, we assume that both have the same parameter *b*. (That is reasonable, for *b* is an excluded volume in both equations of state.) In that case,

$$\left(\frac{\partial S}{\partial V}\right)_{T,\mathrm{Die}} = \frac{R\left(1 + \dfrac{a}{RV_\mathrm{m}T}\right)\mathrm{e}^{-a/RV_\mathrm{m}T}}{V_\mathrm{m} - b} = \left(\frac{\partial S}{\partial V}\right)_{T,\mathrm{vdW}} \left(1 + \frac{a}{RV_\mathrm{m}T}\right)\mathrm{e}^{-a/RV_\mathrm{m}T}$$

Now notice that the additional factor in $\left(\dfrac{\partial S}{\partial V}\right)_{T,\mathrm{Die}}$ has the form $(1+x)\mathrm{e}^{-x}$, where $x > 0$. This factor is always less than 1. Clearly $(1+x)\mathrm{e}^{-x} < 1$ for large *x*, for then the exponential dominates. But $(1+x)\mathrm{e}^{-x} < 1$ even for small *x*, as can be seen by using the power series expansion for the exponential: $(1+x)(1-x+x^2/2+\ldots) = 1 - x^2/2 + \ldots$ So $\left(\dfrac{\partial S}{\partial V}\right)_{T,\mathrm{Die}} < \left(\dfrac{\partial S}{\partial V}\right)_{T,\mathrm{vdW}}$ To summarize, for isothermal expansions:

$$\boxed{\Delta S_\mathrm{vdW} > \Delta S_\mathrm{Die}} \text{ and } \boxed{\Delta S_\mathrm{vdW} > \Delta S_\mathrm{perfect}}$$

The comparison between a perfect gas and a Dieterici gas depends on particular values of the constants *a* and *b* and on the physical conditions.

3D.6 **(a)** $\alpha = \left(\dfrac{1}{V}\right) \times \left(\dfrac{\partial V}{\partial T}\right)_p; \qquad \kappa_T = -\left(\dfrac{1}{V}\right) \times \left(\dfrac{\partial V}{\partial p}\right)_T$

(1) $$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad \text{[Maxwell relation]}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial p}{\partial V}\right)_T \text{[Euler chain relation, \textit{Mathematical Background} 2]}$$

$$= -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T}\text{[reciprocal identity, \textit{Mathematical Background} 2]}$$

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

$$\left(\frac{\partial V}{\partial S}\right)_p = \left(\frac{\partial T}{\partial p}\right)_S \quad \text{[Maxwell relation]}$$

$$\left(\frac{\partial T}{\partial p}\right)_S = -\left(\frac{\partial T}{\partial S}\right)_p\left(\frac{\partial S}{\partial p}\right)_T \text{[Euler chain]} = -\frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p}\text{[reciprocal]}$$

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

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T \quad \text{and} \quad \mathrm{d}S = \frac{\mathrm{d}q_{\text{rev}}}{T} = \frac{\mathrm{d}H}{T} = \frac{C_p\,\mathrm{d}T}{T} \quad [\mathrm{d}q_p = \mathrm{d}H]$$

Therefore, $\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$ and $\left(\frac{\partial V}{\partial S}\right)_p = \boxed{\frac{\alpha TV}{\mathrm{C}_p}}$

(2) $$\left(\frac{\partial p}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S \quad \text{[Maxwell relation]}$$

$$-\left(\frac{\partial T}{\partial V}\right)_S = \frac{1}{\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial V}{\partial S}\right)_T}\text{[Euler chain]} = \frac{\left(\frac{\partial S}{\partial V}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_V} \text{ [reciprocal]}$$

$$= \frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial S}{\partial U}\right)_V\left(\frac{\partial U}{\partial T}\right)_V} \text{ [Maxwell relation]} = \frac{-\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial U}\right)_V\left(\frac{\partial U}{\partial T}\right)_V}\text{[Euler chain relation]}$$

$$= \frac{-\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial U}{\partial S}\right)_V}{\left(\frac{\partial V}{\partial p}\right)_T\left(\frac{\partial U}{\partial T}\right)_V} \text{ [reciprocal identity, twice]} = \boxed{\frac{\alpha T}{\kappa_T C_V}} \quad \left[\left(\frac{\partial U}{\partial S}\right)_V = T\right]$$

(b) $$\mu_{\mathrm{J}} = \left(\frac{\partial T}{\partial V}\right)_U \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\mu_{\mathrm{J}}C_V = \left(\frac{\partial T}{\partial V}\right)_U\left(\frac{\partial U}{\partial T}\right)_V = \frac{-1}{\left(\frac{\partial V}{\partial U}\right)_T}\text{[Euler chain relation]}$$

$$= -\left(\frac{\partial U}{\partial V}\right)_T \text{[reciprocal identity]} = p - T\left(\frac{\partial p}{\partial T}\right)_V \text{[3D.6]}$$

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

Therefore, $\boxed{\mu_{\mathrm{J}} C_V = p - \frac{\alpha T}{\kappa_T}}$

3D.8 $\pi_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$ [3D.6]

$A = -kT\ln Q$ [Chapter 15] $\qquad p = -\left(\frac{\partial A}{\partial V}\right)_T = kT\left[\frac{\partial \ln Q}{\partial V}\right]_T$

$Q = \frac{q^N}{N!}$ then $p = \frac{NkT}{q}\left(\frac{\partial q}{\partial V}\right)_T$

Substitute this expression for p into eqn. 3D.6. We obtain after differentiating p with respect to T at constant V

$$\boxed{\pi_T = \frac{NkT^2}{q}\frac{\partial}{\partial T}\left(\frac{\partial q}{\partial V}\right)_T}$$

3D.10 The Gibbs–Helmholtz equation is

$$\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right) = -\frac{\Delta H}{T^2}$$

so for a small temperature change

$$\Delta\left(\frac{\Delta_{\mathrm{r}}G^{\ominus}}{T}\right) = \frac{\Delta_{\mathrm{r}}H^{\ominus}}{T^2}\Delta T \quad \text{and} \quad \frac{\Delta_{\mathrm{r}}G_2^{\ominus}}{T_2} = \frac{\Delta_{\mathrm{r}}G_1^{\ominus}}{T_1} - \frac{\Delta_{\mathrm{r}}H^{\ominus}}{T^2}\Delta T$$

so $$\int \mathrm{d}\frac{\Delta_{\mathrm{r}}G^{\ominus}}{T} = -\int\frac{\Delta_{\mathrm{r}}H^{\ominus}\mathrm{d}T}{T^2} \quad \text{and} \quad \frac{\Delta_{\mathrm{r}}G_{190}^{\ominus}}{T_{190}} = \frac{\Delta_{\mathrm{r}}G_{220}^{\ominus}}{T_{220}} + \Delta_{\mathrm{r}}H^{\ominus}\left(\frac{1}{T_{190}} - \frac{1}{T_{220}}\right)$$

$$\Delta_{\mathrm{r}}G_{190}^{\ominus} = \Delta_{\mathrm{r}}G_{220}^{\ominus}\frac{T_{190}}{T_{220}} + \Delta_{\mathrm{r}}H^{\ominus}\left(1 - \frac{T_{190}}{T_{220}}\right)$$

For the monohydrate

$$\Delta_r G_{190}^{\ominus} = (46.2\,\mathrm{kJ\,mol^{-1}}) \times \left(\frac{190\,\mathrm{K}}{220\,\mathrm{K}}\right) + (127\,\mathrm{kJ\,mol^{-1}}) \times \left(1 - \frac{190\,\mathrm{K}}{220\,\mathrm{K}}\right),$$

$$\Delta_r G_{190}^{\ominus} = \boxed{57.2\,\mathrm{kJ\,mol^{-1}}}$$

For the dihydrate

$$\Delta_r G_{190}^{\ominus} = (69.4\,\mathrm{kJ\,mol^{-1}}) \times \left(\frac{190\,\mathrm{K}}{220\,\mathrm{K}}\right) + (188\,\mathrm{kJ\,mol^{-1}}) \times \left(1 - \frac{190\,\mathrm{K}}{220\,\mathrm{K}}\right),$$

$$\Delta_r G_{190}^{\ominus} = \boxed{85.6\,\mathrm{kJ\,mol^{-1}}}$$

For the trihydrate

$$\Delta_r G_{190}^{\ominus} = (93.2\,\mathrm{kJ\,mol^{-1}}) \times \left(\frac{190\,\mathrm{K}}{220\,\mathrm{K}}\right) + (237\,\mathrm{kJ\,mol^{-1}}) \times \left(1 - \frac{190\,\mathrm{K}}{220\,\mathrm{K}}\right),$$

$$\Delta_r G_{190}^{\ominus} = \boxed{112.8\,\mathrm{kJ\,mol^{-1}}}$$

Integrated activities

3.2 For a thorough discussion of the relationship between the thermodynamic and statistical definitions of entropy, see Section 3A. We will not repeat all of that discussion here and will merely summarize the main points.

The thermodynamic entropy is defined in terms of the quantity $\mathrm{d}S = \frac{\mathrm{d}q_{\mathrm{rev}}}{T}$ where $\mathrm{d}q_{\mathrm{rev}}$ is the infinitesimal quantity of energy supplied as heat to the system reversibly at a temperature T.

The statistical entropy is defined in terms of the Boltzmann formula for the entropy: $S = k\ln W$ where k is the Boltzmann constant and W is the number of microstates, the total number of ways in which the molecules of the system can be arranged to achieve the same total energy of the system. These two definitions turn out to be equivalent provided the thermodynamic entropy is taken to be zero at $T = 0$.

The concept of the number of microstates makes quantitative the ill-defined qualitative concepts of 'disorder' and 'dispersal of matter and energy' that are used widely to introduce the concept of entropy: a more 'disorderly' distribution of energy and matter corresponds to a greater number of microstates associated with the same total energy. The more molecules that can participate in the distribution of energy, the more microstates there are for a given total energy and the greater the entropy than when the energy is confined to a smaller number of molecules.

The molecular interpretation of entropy given by the Boltzmann formula also suggests the thermodynamic definition. At high temperatures where the molecules of a system can occupy a large number of available energy levels, a small additional transfer of energy as heat will cause only a small change in the number of accessible energy levels, whereas at low temperatures the transfer of the same quantity of heat will increase the number of accessible energy levels and microstates significantly. Hence, the change in entropy upon heating will be greater when the energy is transferred to a cold body than when it is transferred to a hot body. This argument suggests that the change in entropy should be inversely proportional to the temperature at which the transfer takes place as in indicated in the thermodynamic definition.

4 Physical transformations of pure substances

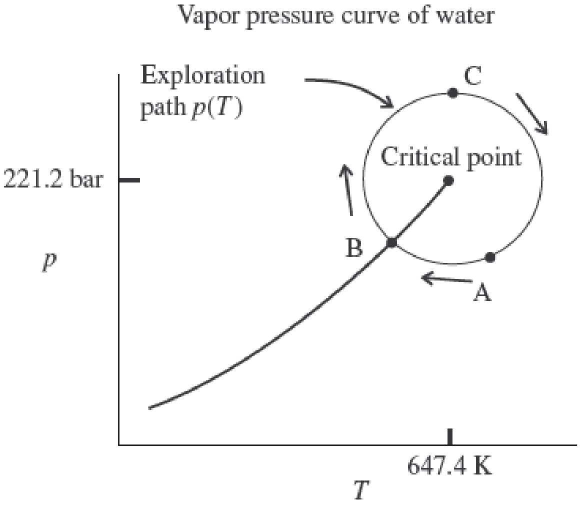
4A Phase diagrams of pure substances

Answers to discussion questions

4A.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 is 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 Topic 4B.1(c).

4A.4

Figure 4A.1



Refer to Figure 4A.1. 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 $p(T)$. Upon 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.

Solutions to Exercises

4A.1(b) The phase rule (eqn 4A.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 and 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.

4A.2(b) For pure substances (one-component systems), the chemical potential is the molar Gibbs energy:

$$\mathrm{d}G = (\mu_2 - \mu_1)\mathrm{d}n$$

so $\Delta G = (\mu_2 - \mu_1)n = (-8.3\ \mathrm{kJ\ mol^{-1}})(0.15\times10^{-3}\ \mathrm{mol}) = +1.2\times10^{-3}\ \mathrm{kJ} = \boxed{1.2\ \mathrm{J}}$.

4A.3(b) Use the phase rule (eqn 4A.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.

4B Phase diagrams of pure substances

Answers to discussion questions

4B.2 See Topic 4B.1(b). The mathematical reason can be seen in eqn 4B.2,

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_\mathrm{m}$$

Because $V_\mathrm{m} > 0$ for all pure substances, the slope of the change in chemical potential with respect to change in pressure is positive: chemical potential increases with increasing pressure. See also the answer to Discussion question 4A.2, which addresses why the chemical potential changes even in incompressible substances.

4B.4 See Topic 4B.3 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 4B.9 through 4B.12 of the text.

Solutions to Exercises

4B.1(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 (exactly 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:

$$\mu_{\text{liquid}}(T_{\text{norm}},p_{\text{norm}}) = \mu_{\text{gas}}(T_{\text{norm}},p_{\text{norm}})$$

Equations 4B.1 and 4B.2 show how the chemical potential changes with temperature and pressure, so for small changes we can write

$$\mathrm{d}\mu = \left(\frac{\partial \mu}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial \mu}{\partial p}\right)_T \mathrm{d}p = -S_{\text{m}}\mathrm{d}T + V_{\text{m}}\mathrm{d}p$$

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 3A.17):

$$\Delta T \approx \frac{V_{\text{m,gas}}\Delta p}{\Delta_{\text{vap}}S} = \frac{RT\Delta p}{p\Delta_{\text{vap}}S} = \frac{RT_{\text{b}}^2\Delta p}{p\Delta_{\text{vap}}H} = \frac{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(373\ \text{K})^2(1325\ \text{Pa})}{(10^5\ \text{Pa})(40.656\times10^3\ \text{J})}$$

$$= \boxed{0.38\ \text{K}}$$

That is, the normal boiling temperature is 0.38 K higher than the standard boiling temperature.

4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature

$$\mathrm{d}\mu = \left(\frac{\partial \mu}{\partial T}\right)_p \mathrm{d}T = -S_{\text{m}}\mathrm{d}T$$

so $$\Delta\mu = -\int S_{\text{m}}\,\mathrm{d}T = -S_{\text{m}}\Delta T = -53\ \text{J K}^{-1}\ \text{mol}^{-1}\times(1000-100)\ \text{K}$$

$$= \boxed{4.8\times10^4\ \text{J mol}^{-1}} = \boxed{48\ \text{kJ mol}^{-1}}$$

4B.3(b) Equation 4B.2 shows how the chemical potential changes with pressure

$$\mathrm{d}\mu = \left(\frac{\partial \mu}{\partial p}\right)_T \mathrm{d}p = V_{\text{m}}\mathrm{d}p = \frac{M}{\rho}\mathrm{d}p$$

so $$\Delta\mu = \int \frac{M}{\rho}\mathrm{d}p = \frac{M}{\rho}\Delta p = \frac{78.11\ \text{g mol}^{-1}}{0.879\ \text{g cm}^{-3}}\times(10\times10^6-100\times10^3)\ \text{Pa}\times\frac{1\ \text{m}^3}{10^6\ \text{cm}^3}$$

$$= \boxed{8.8\times10^2\ \text{J mol}^{-1}} = \boxed{0.088\ \text{kJ mol}^{-1}}$$

Note: we assumed that the sample is incompressible.

4B.4(b) The effect on vapour pressure of a change in applied external pressure on a liquid is given by eqn 4B.3:

$$p = p^*\mathrm{e}^{V_{\text{m}}(\text{l})\Delta P/RT}\ .$$

For liquid naphthalene, the molar volume is

$$V_{\text{m}} = \frac{M}{\rho} = \frac{118.16\ \text{g mol}^{-1}}{0.962\ \text{g cm}^{-3}} = 122.8\ \text{cm}^3\ \text{mol}^{-1}$$

so $$\frac{V_{\text{m}}(\text{l})\Delta P}{RT} = \frac{122.8\ \text{cm}^3\ \text{mol}^{-1}\times(15\times10^6-1.0\times10^5)\ \text{Pa}}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}\times368\ \text{K}}\times\frac{1\ \text{m}^3}{10^6\ \text{cm}^3} = 0.598$$

and $$p = p^*\mathrm{e}^{V_{\text{m}}(\text{l})\Delta P/RT} = (2.0\ \text{kPa})\mathrm{e}^{0.598} = \boxed{3.6\ \text{kPa}}\ .$$

4B.5(b) Use the Clapeyron equation (eqn 4B.5a)

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\text{trs}}S}{\Delta_{\text{trs}}V}$$

Assume that $\Delta_{\text{fus}}S$ and $\Delta_{\text{fus}}T$ are independent of temperature:

$$\Delta_{\text{fus}}S = \Delta_{\text{fus}}V \times \left(\frac{\mathrm{d}p}{\mathrm{d}T}\right) \approx \Delta_{\text{fus}}V \times \frac{\Delta p}{\Delta T}$$

$$\Delta_{\text{fus}}S = (152.6\,\text{cm}^3\,\text{mol}^{-1} - 142.0\,\text{cm}^3\,\text{mol}^{-1}) \times \frac{(1.2\times10^6\,\text{Pa} - 1.01\times10^5\,\text{Pa})}{429.26\,\text{K} - 427.15\,\text{K}}$$

$$= (10.6\,\text{cm}^3\,\text{mol}^{-1}) \times \left(\frac{1\,\text{m}^3}{10^6\,\text{cm}^3}\right) \times (5.21\times10^5\,\text{Pa K}^{-1})$$

$$= 5.52\,\text{Pa m}^3\,\text{K}^{-1}\,\text{mol}^{-1} = \boxed{+5.5\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

At the melting temperature

$$\Delta_{\text{fus}}H = T_{\text{f}}\Delta_{\text{fus}}S = (427.15\,\text{K}) \times (5.5\overline{2}\,\text{J K}^{-1}\,\text{mol}^{-1}) = \boxed{+2.4\,\text{kJ mol}^{-1}}$$

4B.6(b) On the assumption that the vapour is a perfect gas and that $\Delta_{\text{vap}}H$ is independent of temperature, we may write [4B.11]

$$p = p^*\mathrm{e}^{-\chi}, \quad \chi = \left(\frac{\Delta_{\text{vap}}H}{R}\right) \times \left(\frac{1}{T} - \frac{1}{T^*}\right), \quad \ln\frac{p^*}{p} = \chi$$

$$\frac{1}{T} = \frac{1}{T^*} + \frac{R}{\Delta_{\text{vap}}H}\ln\frac{p^*}{p}$$

$$= \frac{1}{293.2\,\text{K}} + \frac{8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}}{32.7\times10^3\,\text{J mol}^{-1}} \times \ln\left(\frac{58.0}{66.0}\right) = 3.37\overline{8}\times10^{-3}\,\text{K}^{-1}$$

Hence $T = \dfrac{1}{3.37\overline{8}\times10^{-3}\,\text{K}^{-1}} = 296\,\text{K} = \boxed{23°\text{C}}$

4B.7(b) Integrating the Clausius-Clapeyron eqation (4B.10) yields an expression for $\ln p$:

$$\int \mathrm{d}\ \ln p = \int \frac{\Delta_{\text{vap}}H}{RT^2}\,\mathrm{d}T$$

so $\quad \ln p = \text{constant} - \dfrac{\Delta_{\text{vap}}H}{RT}$

Therefore, $\Delta_{\text{vap}}H = 3036.8\,\text{K} \times R = 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1} \times (3036.8\,\text{K}) = \boxed{+25.25\,\text{kJ mol}^{-1}}$

4B.8(b) **(i)** The indefinitely integrated form of eqn 4B.10 is used as in Exercise 4B.7(b).

$$\ln p = \text{constant} - \frac{\Delta_{\text{vap}}H}{RT}, \quad \text{or} \quad \log p = \text{constant} - \frac{\Delta_{\text{vap}}H}{2.303\,RT}$$

Thus $\quad \Delta_{\text{vap}}H = 1625\,\text{K} \times R \times 2.303 = 1625\,\text{K} \times 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1} \times 2.303$

$$= \boxed{31.11\,\text{kJ mol}^{-1}}$$

(ii) The normal boiling point corresponds to p = 1.000 atm = 760 Torr,

so $\quad \log 760 = 8.750 - \dfrac{1625\ \text{K}}{T}$

and $\quad T = \dfrac{1625\ \text{K}}{8.750 - \log 760} = \boxed{276.9\ \text{K}}$

4B.9(b) $\quad \Delta T \approx \dfrac{\Delta_{\text{fus}}V}{\Delta_{\text{fus}}S} \times \Delta p$ [4B.5a and Exercise 4B.5(a)]

$$\approx \frac{T_{\text{f}}\Delta_{\text{fus}}V}{\Delta_{\text{fus}}H} \times \Delta p = \frac{T_{\text{f}}M\Delta p}{\Delta_{\text{fus}}H} \times \Delta\left(\frac{1}{\rho}\right) \quad [V_{\text{m}} = M/\rho]$$

Normal freezing point is T_{f} = (273.15 – 3.65) K = 269.50 K at a pressure of 1 atm, which is about 0.1 MPa. Thus, to the nearest MPa, Δp = 100 MPa = 1.00×10^8 Pa

$$\Delta T \approx \frac{269.50\,\mathrm{K}\times 46.1\,\mathrm{g\,mol^{-1}}\times(1.00\times10^{8}\ \mathrm{Pa})}{8.68\times10^{3}\,\mathrm{J\,mol^{-1}}}\times\left(\frac{1}{0.789\,\mathrm{g\,cm^{-3}}}-\frac{1}{0.801\,\mathrm{g\,cm^{-3}}}\right)$$

$$\approx 2.7\ \mathrm{K}$$

Therefore, at 100 MPa, T_{f} = (269.50+2.7) K = $\boxed{272.2\ \mathrm{K}}$ or $\boxed{-1.0^{\circ}\mathrm{C}}$.

4B.10(b) The rate of loss of mass of water may be expressed as

$$\frac{\mathrm{d}m}{\mathrm{d}t}=\frac{\mathrm{d}}{\mathrm{d}t}(nM) \quad \text{where} \quad n=\frac{q}{\Delta_{\mathrm{vap}}H}$$

Thus $$\frac{\mathrm{d}n}{\mathrm{d}t}=\frac{\mathrm{d}q/\mathrm{d}t}{\Delta_{\mathrm{vap}}H}=\frac{(0.87\times10^{3}\ \mathrm{W\,m^{-2}})\times(10^{4}\ \mathrm{m^{2}})}{44.0\times10^{3}\ \mathrm{J\,mol^{-1}}}=20\bar{0}\ \mathrm{mol\,s^{-1}}$$

and $$\frac{\mathrm{d}m}{\mathrm{d}t}=(200\ \mathrm{mol\ s^{-1}})\times(18.02\,\mathrm{g\,mol^{-1}})=\boxed{3.6\ \mathrm{kg\,s^{-1}}}$$

4B.11(b) The equilibrium vapour pressure of ice at –5°C is 0.40 kPa Therefore, the frost would sublime. A partial pressure of $\boxed{0.40\ \text{kPa or more}}$ would ensure that the frost remains.

4B.12(b) **(i)** According to Trouton's rule (eqn 3A.17)

$$\Delta_{\mathrm{vap}}H\approx 85\,\mathrm{J\,K^{-1}\,mol^{-1}}\times T_{\mathrm{b}}=85\,\mathrm{J\,K^{-1}\,mol^{-1}}\times 342.2\,\mathrm{K}=\boxed{29.1\,\mathrm{kJ\,mol^{-1}}}$$

(ii) Use the integrated form of the Clausius–Clapeyron equation (eqn 4B.11) rearranged to

$$\ln\left(\frac{p_2}{p_1}\right)=\frac{\Delta_{\mathrm{vap}}H}{R}\times\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

At T_1 = 342.2 K, p_1 = 1.000 atm [normal boiling point]; thus at 25°C

$$\ln\left(\frac{p_2}{1.000\ \mathrm{atm}}\right)=\left(\frac{2.91\times10^{4}\ \mathrm{J\,mol^{-1}}}{8.3145\ \mathrm{J\,K^{-1}\ mol^{-1}}}\right)\times\left(\frac{1}{342.2\ \mathrm{K}}-\frac{1}{298.2\ \mathrm{K}}\right)=-1.51$$

and $p_2 = \mathrm{e}^{-1.51}$ atm = $\boxed{0.22\ \mathrm{atm}}$.

At 60°C, $$\ln\left(\frac{p_2}{1.000\ \mathrm{atm}}\right)=\left(\frac{2.91\times10^{4}\ \mathrm{J\,mol^{-1}}}{8.3145\ \mathrm{J\,K^{-1}\ mol^{-1}}}\right)\times\left(\frac{1}{342.2\ \mathrm{K}}-\frac{1}{333.2\ \mathrm{K}}\right)=-0.276$$

and $p_2 = \mathrm{e}^{-0.276}$ atm = $\boxed{0.76\ \mathrm{atm}}$.

4B.13(b) $$\Delta T = T_{\mathrm{f}}(10\,\mathrm{MPa})-T_{\mathrm{f}}(0.1\,\mathrm{MPa})=\frac{T_{\mathrm{f}}\Delta pM}{\Delta_{\mathrm{fus}}H}\Delta\left(\frac{1}{\rho}\right) \quad \text{[Exercise 4B.9(b)]}$$

$$\Delta T=\left(\frac{(273.15\,\mathrm{K})\times 9.9\times10^{6}\ \mathrm{Pa}\times 18.0\,\mathrm{g\,mol^{-1}}}{6.01\times10^{3}\ \mathrm{J\,mol^{-1}}}\right)$$

$$\times\left(\frac{1}{0.998\ \mathrm{g\ cm^{-3}}}-\frac{1}{0.915\ \mathrm{g\ cm^{-3}}}\right)=-0.74\,\mathrm{K}$$

T_{f}(10 MPa) = (273.15 – 0.74) K = $\boxed{272.41\ \mathrm{K}}$.

4B.14(b) $\Delta_{\mathrm{vap}}H = \Delta_{\mathrm{vap}}U + \Delta_{\mathrm{vap}}(pV)$ = 43.5 kJ mol^{-1}

$\Delta_{\mathrm{vap}}(pV) = p\Delta_{\mathrm{vap}}V = p(V_{\mathrm{gas}} - V_{\mathrm{liq}}) \approx pV_{\mathrm{gas}} = RT$ [perfect gas]

$\Delta_{\mathrm{vap}}(pV) \approx (8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (352\ \mathrm{K}) = 2.93\times10^{3}\ \mathrm{J\ mol^{-1}}$

$$\text{Fraction}=\frac{\Delta_{\mathrm{vap}}(pV)}{\Delta_{\mathrm{vap}}H}=\frac{2.93\,\mathrm{kJ\,mol^{-1}}}{43.5\,\mathrm{kJ\,mol^{-1}}}=\boxed{0.0673}=6.73\,\text{per cent}$$

Solutions to problems

4B.2 Use the definite integral form of the Clausius–Clapeyron equation [Exercise 4B.12(b)].

$$\ln\left(\frac{p_2}{p_1}\right)=\frac{\Delta_{\mathrm{vap}}H}{R}\times\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

At T_1 = (273.15 – 29.2) K = 244.0 K (normal boiling point), p_1 = 1.000 atm; thus at 40°C

$$\ln\left(\frac{p_2}{1.000\ \text{atm}}\right) = \left(\frac{20.25\times10^3\ \text{J mol}^{-1}}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}\right)\times\left(\frac{1}{244.0\,\text{K}} - \frac{1}{313.2\,\text{K}}\right) = 2.205$$

and $\quad p_2 = 1.000\ \text{atm} \times e^{2.205} = \boxed{9.07\ \text{atm}}$

Comment. Three significant figures are not really warranted in this answer because of the approximations employed.

4B.4 **(a)** $$\left(\frac{\partial\mu(\text{l})}{\partial T}\right)_p - \left(\frac{\partial\mu(\text{s})}{\partial T}\right)_p = -S_\text{m}(\text{l}) + S_\text{m}(\text{s}) = -\Delta_\text{fus}S = \frac{-\Delta_\text{fus}H}{T_\text{f}}\ \ [4\text{B}.12]$$

$$= \frac{-6.01\times10^3\ \text{J mol}^{-1}}{273.15\,\text{K}} = \boxed{-22.0\ \text{J K}^{-1}\text{mol}^{-1}}$$

(b) $$\left(\frac{\partial\mu(\text{g})}{\partial T}\right)_p - \left(\frac{\partial\mu(\text{l})}{\partial T}\right)_p = -S_\text{m}(\text{g}) + S_\text{m}(\text{l}) = -\Delta_\text{vap}S = \frac{-\Delta_\text{vap}H}{T_\text{b}}$$

$$= \frac{-40.6\times10^3\ \text{J mol}^{-1}}{373.15\,\text{K}} = \boxed{-108.8\ \text{J K}^{-1}\ \text{mol}^{-1}}$$

(c) $\quad \mu(\text{l},-5°\text{C}) - \mu(\text{s},-5°\text{C}) = \mu(\text{l},-5°\text{C}) - \mu(\text{l},0°\text{C}) - \{\mu(\text{s},-5°\text{C}) - \mu(\text{s},0°\text{C})\}$

because $\mu(\text{l},0°\text{C}) = \mu(\text{s},0°\text{C})$

Thus $\quad \mu(\text{l},-5°\text{C}) - \mu(\text{s},-5°\text{C}) = \Delta\mu(\text{l}) - \Delta\mu(\text{s})$

where $\Delta\mu$ is the difference in chemical potential of a given phase at –5°C compared to that at normal freezing temperature.

$$\Delta\mu \approx \left(\frac{\partial\mu}{\partial T}\right)_p \Delta T = -S_\text{m}\Delta T\ \ [4\text{B}.1]$$

so $\quad \{\mu(\text{l},-5°\text{C}) - \mu(\text{l},0°\text{C})\} - \{\mu(\text{s},-5°\text{C}) - \mu(\text{s},0°\text{C})\} = -\Delta_\text{fus}S\,\Delta T$

$$\mu(\text{l},-5°\text{C}) - \mu(\text{s},-5°\text{C}) = -(+22.0\,\text{J K}^{-1}\,\text{mol}^{-1})\times(-5\,\text{K}) = \boxed{+11\bar{0}\ \text{J mol}^{-1}}$$

Since $\mu(\text{l},-5°\text{C}) > \mu(\text{s},-5°\text{C})$, there is a thermodynamic tendency to freeze.

4B.6 $$\frac{\text{d}p}{\text{d}T} = \frac{\Delta_\text{fus}S}{\Delta_\text{fus}V}[4\text{B}.5\text{a}] = \frac{\Delta_\text{fus}H}{T\Delta_\text{fus}V}\ \ [4\text{B}.6]$$

Thus $\quad \text{d}T = \dfrac{T\Delta_\text{fus}V}{\Delta_\text{fus}H}\text{d}p$.

Integrate both sides:

$$\Delta T = \int_{T_\text{f,top}}^{T_\text{f,bot}}\text{d}T = \int_{p_\text{top}}^{p_\text{bot}}\frac{T_\text{m}\Delta_\text{fus}V}{\Delta_\text{fus}H}\,\text{d}p = \frac{T_\text{m}\Delta_\text{fus}V}{\Delta_\text{fus}H}\Delta p\ \ \text{[assuming the integrand is constant]}$$

Now $\quad \Delta p = p_\text{bot} - p_\text{top} = \rho g h$;

so $\quad \Delta T = \dfrac{T_\text{m}\rho g h\Delta_\text{fus}V}{\Delta_\text{fus}H}$

$$= \frac{(234.3\text{K})\times(13.6\,\text{g cm}^{-3})\times(9.81\,\text{m s}^{-2})\times(10.0\,\text{m})\times(0.517\,\text{cm}^3\,\text{mol}^{-1})}{2.292\times10^3\ \text{J mol}^{-1}}\times\frac{1\ \text{kg}}{10^3\ \text{g}}$$

$$= 0.071\,\text{K}$$

Therefore, the freezing point changes to $\boxed{234.4\ \text{K}}$

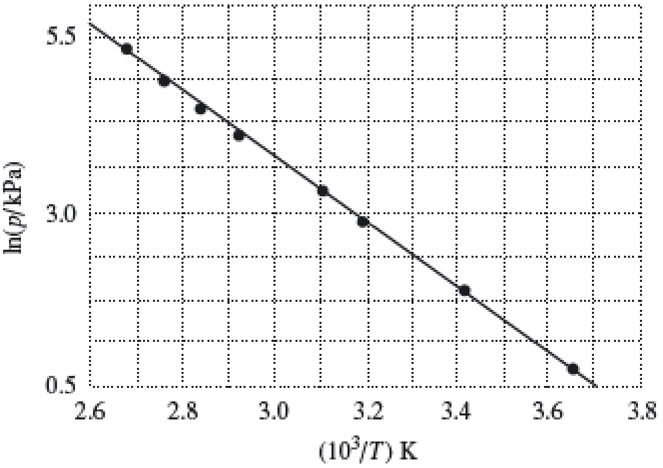
4B.8 Integrating the Clausius-Clapeyron eqation [4B.10] yields an expression for ln p:

$$\ln p = \text{constant} - \frac{\Delta_\text{vap}H}{RT}$$

Therefore, plot ln p against $1/T$ and identify $-\Delta_\text{vap}H/R$ as the slope of the plot. Construct the following table

θ/°C	0	20	40	50	70	80	90	100
T / K	273	293	313	323	343	353	363	373
1000 K / T	3.66	3.41	3.19	3.10	2.92	2.83	2.75	2.68
ln (p / kPa)	0.652	1.85	2.87	3.32	4.13	4.49	4.83	5.14

Figure 4B.1



The points are plotted in Figure 4B.1. The slope is –4569 K, so

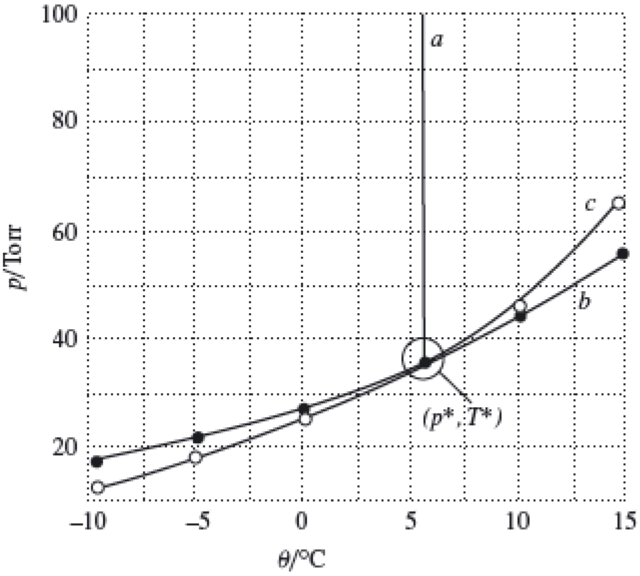
$$\frac{-\Delta_{\text{vap}}H}{R} = -4569\,\text{K}, \quad \text{or} \quad \Delta_{\text{vap}}H = \boxed{+38.0\text{ kJ mol}^{-1}}$$

The normal boiling point occurs at p = 1 atm = 101.3 kPa, or at ln(p/kPa) = 4.618, which from the figure corresponds to 1000 K/T = 2.80. Therefore, T_b = $\boxed{357\text{ K }(84°\text{C})}$ The accepted value is 83°C.

4B.10 The slope of the solid–vapour coexistence curve is given by

$$\frac{dp}{dT} = \frac{\Delta_{\text{sub}}H}{T\Delta_{\text{sub}}V} \text{ [analogous to 4B.9] so } \Delta_{\text{sub}}H = T\Delta_{\text{sub}}V\frac{dp}{dT}$$

Figure 4B.2



The slope can be obtained by differentiating an equation fit to the coexistence curve (Figure 4B.2). 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

$$p/\text{Pa} = 2.659\times10^{-10}\,e^{0.1687T/\text{K}}$$

so $$\frac{\mathrm{d}p}{\mathrm{d}T} = (2.659\times10^{-10}\ \mathrm{Pa})\times(0.1687\ \mathrm{K}^{-1})\times \mathrm{e}^{0.1687T/\mathrm{K}} = 4.41\,\mathrm{Pa\,K}^{-1}\ \text{ at 150 K.}$$

The change in volume is essentially the volume of the vapour

$$V_\mathrm{m} = \frac{RT}{p} = \frac{(8.3145\ \mathrm{J\,K^{-1}\ mol^{-1}})\times(150\ \mathrm{K})}{(2.659\times10^{-10}\ \mathrm{Pa})\times \mathrm{e}^{0.1687\times150}} = 47.7\,\mathrm{m}^3$$

So $$\Delta_\mathrm{sub}H^\ominus = (150\,\mathrm{K})\times(47.7\,\mathrm{m}^3)\times 4.41\,\mathrm{Pa\,K}^{-1} = 3.16\times10^4\ \mathrm{J\,mol}^{-1} = \boxed{31.6\,\mathrm{kJ\,mol}^{-1}}$$

4B.12 $\mathrm{d}H = C_p\mathrm{d}T + V\,\mathrm{d}p$ implies $\mathrm{d}\Delta H = \Delta C_p\mathrm{d}T + \Delta V\,\mathrm{d}p$,

where Δ signifies a difference between phases. Along a phase boundary dp and dT are related by

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H}{T\Delta V}\ \ [\text{4B.6 or 4B.9}]$$

Therefore,

$$\mathrm{d}\Delta H = \left(\Delta C_p + \Delta V\times\frac{\Delta H}{T\Delta V}\right)\mathrm{d}T = \left(\Delta C_p + \frac{\Delta H}{T}\right)\mathrm{d}T \quad\text{and}\quad \frac{\mathrm{d}\Delta H}{\mathrm{d}T} = \Delta C_p + \frac{\Delta H}{T}$$

Then, since

$$\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\Delta H}{T}\right) = \frac{1}{T}\frac{\mathrm{d}\Delta H}{\mathrm{d}T} - \frac{\Delta H}{T^2} = \frac{1}{T}\left(\frac{\mathrm{d}\Delta H}{\mathrm{d}T} - \frac{\Delta H}{T}\right)$$

substituting the first result gives

$$\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\Delta H}{T}\right) = \frac{\Delta C_p}{T}$$

Therefore,

$$\mathrm{d}\left(\frac{\Delta H}{T}\right) = \frac{\Delta C_p\,\mathrm{d}T}{T} = \boxed{\Delta C_p\ \mathrm{d\,In}\ T}$$

4B.14 Equation 4B.3 gives the vapour pressure of a liquid under an additional applied pressure ΔP:

$$p = p^*\mathrm{e}^{V_\mathrm{m}(\mathrm{l})\Delta P/RT}$$

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

$$V_\mathrm{m}(\mathrm{l}) = M/\rho$$

Substituting into eqn. 4B.3 yields

$$\boxed{p = p^*\mathrm{e}^{Mgd/RT}}$$

For a 10-m column of water at 25°C,

$$\frac{Mgd}{RT} = \frac{(18.02\times10^{-3}\ \mathrm{kg\,mol^{-1}})\times(9.81\ \mathrm{m\,s^{-2}})\times(10\ \mathrm{m})}{(8.3145\ \mathrm{J\,K^{-1}\ mol^{-1}})\times(298\ \mathrm{K})} = 7.1\times10^{-4}$$

so $$\frac{p}{p^*} = \mathrm{e}^{7.1\times10^{-4}} \approx 1 + 7.1\times10^{-4}$$

That is, the fractional increase in vapor pressure is $\boxed{7.1\times10^{-4}}$ or $\boxed{0.071\text{ per cent}}$.

4B.16 In each phase the slopes of curves of chemical potential plotted against temperature are

$$\left(\frac{\partial\mu}{\partial T}\right)_p = -S_\mathrm{m}\ \ [4.1]$$

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, though 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 upon the substance.

4B.18 $S = S(T,p)$

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial S}{\partial p}\right)_T \mathrm{d}p$$

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \text{ [Problem 4B.16]} \qquad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \text{ [Table 3D.1]} = -\alpha V_\mathrm{m}$$

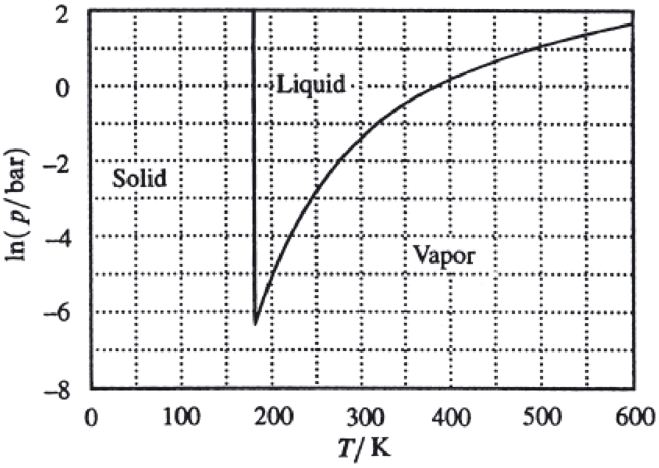
$$\mathrm{d}q_\mathrm{rev} = T\ \mathrm{d}S = C_p\,\mathrm{d}T - T\left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p$$

$$C_S = \left(\frac{\partial q}{\partial T}\right)_S = C_p - TV\alpha\left(\frac{\partial p}{\partial T}\right)_S = \boxed{C_p - \alpha V \times \frac{\Delta_\mathrm{trs}H}{\Delta_\mathrm{trs}V}} \text{ [4B.6]}$$

Integrated activities

4.2 **(a)** The phase diagram is shown in Figure I4.1.

Figure I4.1



(b) The standard melting point is the temperature at which solid and liquid are in equilibrium at 1 bar. That temperature can be found by solving the equation of the solid–liquid coexistence curve for the temperature:

$$1 = p_3/\mathrm{bar} + 1000(5.60+11.727x)x\ .$$

Put the equation into standard form:

$$11727x^2 + 5600x + (4.362\times10^{-7} - 1) = 0$$

The quadratic formula yields

$$x = \frac{-5600 \pm \left\{(5600)^2 - 4\times11727\times(-1)\right\}^{1/2}}{2\times11727} = \frac{-1 \pm \left(1+\frac{4\times11727}{5600^2}\right)^{1/2}}{2\times\left(\frac{11727}{5600}\right)}$$

The square root is rewritten to make it clear that the square root is of the form $\left\{1+a\right\}^{1/2}$, with $|a|= 1$; thus the numerator is approximately $-1+\left(1+\frac{1}{2}a\right)=\frac{1}{2}a$, and the whole expression reduces to

$$x \approx 1/5600 = 1.79\times10^{-4}\ .$$

Thus, the melting point is

$$T = (1+x)T_3 = (1.000179)\times(178.15\ \mathrm{K}) = \boxed{178.18\ \mathrm{K}}.$$

(c) The standard boiling point is the temperature at which the liquid and vapour are in equilibrium at 1 bar. That temperature can be found by solving the equation of the liquid–vapour coexistence curve for the temperature. This equation is too complicated to solve analytically, but not difficult to solve numerically with a spreadsheet. The calculated answer is $y = 0.6459$,

so $\quad T = 0.6459 \times 593.95\ \text{K} = \boxed{383.6\ \text{K}}$.

(d) The slope of the liquid–vapour coexistence curve is given by

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\text{vap}}H}{T\Delta_{\text{vap}}V}\ [\text{4B.9}] \text{ so } \Delta_{\text{vap}}H = T\Delta_{\text{vap}}V\frac{\mathrm{d}p}{\mathrm{d}T}$$

The slope can be obtained by differentiating the equation for the coexistence curve.

$$\frac{\mathrm{d}p}{\mathrm{d}T} = p\frac{\mathrm{d}\ln p}{\mathrm{d}T} = p\frac{\mathrm{d}\ln p}{\mathrm{d}y}\frac{\mathrm{d}y}{\mathrm{d}T}$$

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \left(\frac{10.413}{y^2} - 15.996 + 2(14.015)y - 3(5.0120)y^2 - (1.70)\times(4.7224)\times(1-y)^{0.70}\right)$$
$$\times\left(\frac{p}{T_{\text{c}}}\right)$$

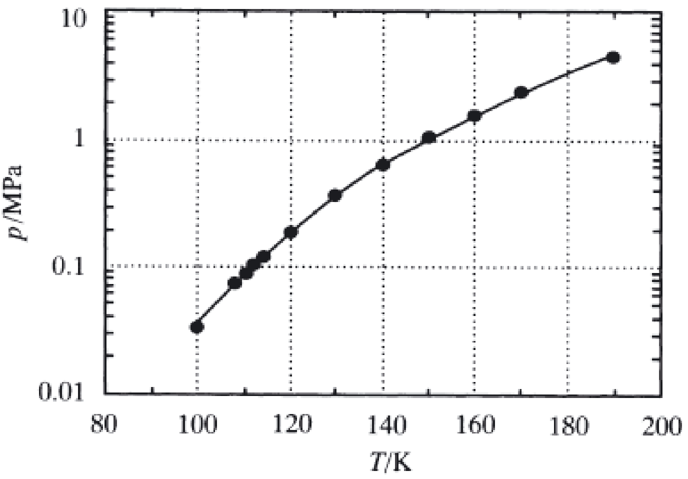
Substituting the value of y at the boiling point yields,

$$\frac{\mathrm{d}p}{\mathrm{d}T} = 2.848\times10^{-2}\ \text{bar K}^{-1} = 2.848\ \text{kPa K}^{-1}$$

and $\quad \Delta_{\text{vap}}H = (383.6\ \text{K})\times\left(\frac{(30.3-0.12)\ \text{dm}^3\ \text{mol}^{-1}}{1000\ \text{dm}^3\ \text{m}^{-3}}\right)\times(2.848\ \text{kPa K}^{-1}) = \boxed{33.0\ \text{kJ mol}^{-1}}$

4.4 **(a)** The phase boundary is plotted in Figure I4.2.

Figure I4.2



(b) The standard boiling point is the temperature at which the liquid is in equilibrium with the standard pressure of 1 bar (0.1 MPa). Interpolation of the plotted points gives $T_{\text{b}} = \boxed{112\ \text{K}}$.

(c) The slope of the liquid–vapor coexistence curve is given by

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\text{vap}}H}{T\Delta_{\text{vap}}V}\ [\text{4B.9}] \quad \text{so} \quad \Delta_{\text{vap}}H = (T\Delta_{\text{vap}}V)\frac{\mathrm{d}p}{\mathrm{d}T}$$

The slope can be obtained graphically or by fitting the points nearest the boiling point. Then

$$\frac{\mathrm{d}p}{\mathrm{d}T} = 8.14\times10^{-3}\ \text{MPa K}^{-1}$$

so $\quad \Delta_{\text{vap}}H = (112\ \text{K})\times\left(\frac{(8.89-0.0380)\ \text{dm}^3\ \text{mol}^{-1}}{1000\ \text{dm}^3\ \text{m}^{-3}}\right)\times(8.14\ \text{kPa K}^{-1}) = \boxed{8.07\ \text{kJ mol}^{-1}}$

5 Simple mixtures

5A The thermodynamic description of mixtures

Answers to discussion questions

5A.2 As noted in Topic 5A.1(b), $dG = dw_{\text{add,max}}$ (where w_{add} stands for additional (non-expansion) work) for systems at constant temperature and pressure. Therefore [5A.8]

$$dw_{\text{add,max}} = \mu_A dn_A + \mu_B dn_B + \ldots$$

Thus non-expansion work can arise from the changing composition of a system. Physically, it should not be surprising that at least *energy* can be changed by changing composition, by a chemical reaction transforming a species into one that is more or less favored energetically. In an electrochemical cell, where the reaction takes place at two distinct sites, the electrical work of transporting charge between the electrodes can be traced to changes in composition as products are formed from reactants.

5A.4 See Topic 5A.3(a). In both cases, the vapor pressure of a component in a solution is proportional to its concentration (mole fraction) in the solution, at least in the limit of low concentration:

$$p_J \propto x_J$$

If the proportionality constant is the component's vapor pressure as a pure substance, then Raoult's law is a good approximation [5A.21]. Substitution of Raoult's law into eqn 5A.20 for the chemical potential yields eqn 5A.22:

$$\mu_A = \mu_A^* + RT \ln x_A$$

If Raoult's law applies to both or all components of a mixture over a large range of composition, then we call the solution ideal. If, on the other hand, only the solvent obeys Raoult's law, and it may only obey it in the limit of mole fractions close to 1, we call the solution ideal-dilute if the solutes obey Henry's law [5A.23]. Substitution of Henry's law into eqn 5A.20 for solutes yields eqn 5E.8:

$$\mu_B = \mu_B^{\ominus} + RT \ln x_B \qquad \text{where} \qquad \mu_B^{\ominus} = \mu_B^* + RT \ln \frac{K_B}{p_B^*} \quad [5E.7]$$

Solutions to exercises

5A.1(b) The partial molar volume is

$$V_J = \left(\frac{\partial V}{\partial n_J}\right)_{p,T,n'} [5A.1] = \left(\frac{dv}{dx}\right)\left(\frac{dV}{dv}\right)\left(\frac{dx}{dn_J}\right)$$

Right away we see that $V_A = \boxed{0}$ because V is independent of n_A [$dx/dn_A = 0$]

$$V_B = (-22.5749 + 2\times 0.56892x + 3\times 0.01023x^2 + 4\times 0.00234x^3)\left(\frac{\text{cm}^3}{\text{mol}}\right)$$

$$= \boxed{(-22.5749 + 1.13784x + 0.03069x^2 + 0.00936x^3)\ \text{cm}^3\ \text{mol}^{-1}}$$

5A.2(b) Let A stand for water and B for $MgSO_4(aq)$

$$V_J = \left(\frac{\partial V}{\partial n_J}\right)_{p,T,n'} [5A.1] = \left(\frac{dv}{dx}\right)\left(\frac{dV}{dv}\right)\left(\frac{\partial x}{\partial n_J}\right)_{n'}$$

Now $\quad x = \dfrac{b}{b^{\ominus}} = \dfrac{n_B}{n_A M_A b^{\ominus}} \qquad$ so $\qquad \left(\dfrac{\partial x}{\partial n_B}\right)_{n_A} = \dfrac{1}{n_A M_A b^{\ominus}}$

and $\quad V_B = 2\times 34.69\times (x - 0.070)\dfrac{\text{cm}^3}{n_A M_A b^{\ominus}}$

Evaluate this expression for $b = 0.050$ mol kg^{-1} ($x = 0.050$), recalling that the original expression for v applies for 1.000 kg of water (*i.e.*, for $n_A M_A = 1.000$ kg). The result is $V_B = \boxed{-1.4\ \text{cm}^3\ \text{mol}^{-1}}$.

The total volume consisting of 0.050 mol of $MgSO_4$ and 1.000 kg (55.49 mol) water is

$$V = 1001.21 + 34.69 \times (0.050\text{–}0.070)^2 = 1001.23\ \text{cm}^3 .$$

The total volume is also equal to

$V = V_A n_A + V_B n_B$ [5A.3] .

Therefore, $V_A = \dfrac{V - V_B n_B}{n_A} = \dfrac{1001.21\ \text{cm}^3 - (-1.4\ \text{cm}^3) \times (0.050\ \text{mol})}{55.49\ \text{mol}} = \boxed{18.\overline{04}\ \text{cm}^3\ \text{mol}^{-1}}$

Question. V_A is essentially the same as the molar volume of pure water, but clearly V_B is not even approximately the molar volume of pure solid $MgSO_4$. What meaning can be ascribed to a negative partial molar volume?

5A.3(b) Use the Gibbs-Duhem equation [5A.13], replacing infinitesimal changes in chemical potential ($\mathrm{d}\mu_J$) with small finite changes ($\delta\mu_J$)

$$\delta\mu_B \approx -\frac{n_A}{n_B}\delta\mu_A = -\frac{0.22 n_B}{n_B} \times (-15\ \text{J mol}^{-1}) = \boxed{+3.3\ \text{J mol}^{-1}}$$

5A.4(b) The Gibbs energy of mixing perfect gases is

$\Delta_{\text{mix}}G = nRT(x_A \ln x_A + x_B \ln x_B)$ [5A.16] $= pV(x_A \ln x_A + x_B \ln x_B)$ [perfect gas law]

Because the compartments are of equal size, each contains half of the gas; therefore,

$$\Delta_{\text{mix}}G = (pV) \times \left(\frac{1}{2}\ln\frac{1}{2} + \frac{1}{2}\ln\frac{1}{2}\right) = -pV \ln 2$$

$$= -(100 \times 10^3\ \text{Pa}) \times (250\,\text{cm}^3)\left(\frac{1\text{m}^3}{10^6\ \text{cm}^3}\right) \times \ln 2 = -17.3\ \text{Pa m}^3 = \boxed{-17.3\ \text{J}}$$

$$\Delta_{\text{mix}}S = -nR(x_A \ln x_A + x_B \ln x_B)\ [5A.17] = \frac{-\Delta_{\text{mix}}G}{T} = \frac{+17.3\ \text{J}}{273\ \text{K}} = \boxed{+0.635\ \text{J K}^{-1}}$$

5A.5(b) $\Delta_{\text{mix}}S = -nR\sum_J x_J \ln x_J$ [5A.17]

We need mole fractions:

$$x_J = \frac{n_J}{\sum_J n_J}$$

Since we have mass percentages, 100.0 g is a convenient sample size. The amounts of each component are

$$n_{N_2} = 75.52\ \text{g} \times \frac{1\ \text{mol}}{2 \times 14.007\ \text{g}} = 2.696\ \text{mol}$$

$$n_{O_2} = 23.15\ \text{g} \times \frac{1\ \text{mol}}{2 \times 15.999\ \text{g}} = 0.7235\ \text{mol}$$

$$n_{Ar} = 1.28\ \text{g} \times \frac{1\ \text{mol}}{39.95\ \text{g}} = 0.0320\ \text{mol}$$

$$n_{CO_2} = 0.046\ \text{g} \times \frac{1\ \text{mol}}{(12.011 + 2 \times 15.999)\ \text{g}} = 0.0010\overline{5}\ \text{mol}$$

The mole fractions are

$$x_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{O_2} + n_{Ar} + n_{CO_2}} = \frac{2.696\ \text{mol}}{(2.696 + 0.7235 + 0.0320 + 0.0010\overline{5})\ \text{mol}} = 0.7809$$

Similarly, $x_{O_2} = 0.2096$, $x_{Ar} = 0.00928$, and $x_{CO_2} = 0.00030$.

Once we have mole fractions, the convenient sample size is for a total of one mole of gas:

$$\Delta_{\text{mix}}S = -R\sum_J x_J \ln x_J = -R\{(0.7809 \ln 0.7809) + (0.2096 \ln 0.2096)$$

$$+(0.00928 \ln 0.00928) + (0.00030 \ln 0.00030)\}$$

$$= 0.5665R = +4.710\ \text{J K}^{-1}\ \text{mol}^{-1}$$

From the data in Exercise 5A.5(a), the entropy of mixing was

$$\Delta_{\text{mix}}S = -R\sum_J x_J \ln x_J$$

$$= -R\{(0.781 \ln 0.781) + (0.210 \ln 0.210) + (0.0094 \ln 0.0094)\}$$

$$= 0.565R = +4.70\ \text{J K}^{-1}\ \text{mol}^{-1}$$

So the difference is

$$\Delta_{\text{mix}}S(\text{b}) - \Delta_{\text{mix}}S(\text{a}) = \boxed{0.001\overline{5}R} = \boxed{+0.01\overline{2}\ \text{J K}^{-1}\ \text{mol}^{-1}}$$

Comment. We can readily see that the data in this exercise (b) includes the CO_2 term, which contributes $-R(0.00030 \ln 0.00030) = 0.0025R$ to the entropy of mixing—more than the total difference. The fact that the mole fractions of the other components are slightly smaller in part (b) to make room for the small amount of CO_2 partly offsets the direct CO_2 term itself.

5A.6(b) Let 12 refer to 1,2-dimethylbenzene and 13 to 1,3-dimethylbenzene. Because the two components are structurally similar, we assume Raoult's Law [5A.21] applies.

$$p_{\text{total}} = p_{12} + p_{13} = x_{12}p_{12}^* + x_{13}p_{13}^* = (0.500)(20 + 18)\ \text{kPa} = 19\ \text{kPa}.$$

The mole fractions in the vapor phase are the ratios of partial to total pressure:

$$x_{12,\text{vap}} = \frac{p_{12}}{p_{\text{total}}} = \frac{x_{\text{liq},12}p_{12}^*}{p_{\text{total}}} = \frac{(0.500)(20\ \text{kPa})}{19\ \text{kPa}} = \boxed{0.53} \quad \text{and} \quad x_{\text{vap},13} = \boxed{0.47}$$

5A.7(b) Total volume $V = n_AV_A + n_BV_B = n(x_AV_A + x_BV_B)$, where $n = n_A + n_B$
Total mass $m = n_AM_A + n_BM_B = n\{x_AM_A + (1-x_A)M_B\}$

So

$$n = \frac{m}{x_A M_A + (1 - x_A)M_B}$$

$$= \frac{1.000 \times 10^3\ \text{g}}{(0.3713) \times (241.1\ \text{g mol}^{-1}) + (1 - 0.3713) \times (198.2\ \text{g mol}^{-1})} = 4.670\ \text{mol}$$

$$V = n(x_AV_A + x_BV_B)$$

and

$$= (4.670\ \text{mol}) \times \{(0.3713) \times (188.2) + (1 - 0.3713) \times (176.14)\}\ \text{cm}^3\ \text{mol}^{-1}$$

$$= \boxed{843.5\ \text{cm}^3}$$

5A.8(b) Let W denote water and E ethanol. The total volume of the solution is

$$V = n_WV_W + n_EV_E$$

We are given V_E, we need to determine n_W and n_E in order to solve for V_W, for

$$V_W = \frac{V - n_EV_E}{n_W}$$

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 per cent of this mass water and 20 per cent ethanol, so the moles of each component are

$$n_W = \frac{(0.80) \times (96.87\ \text{g})}{18.02\ \text{g mol}^{-1}} = 4.3\ \text{mol} \ \text{ and } \ n_E = \frac{(0.20) \times (96.87\ \text{g})}{46.07\ \text{g mol}^{-1}} = 0.42\ \text{mol}^{-1}\ .$$

$$V_W = \frac{V - n_EV_E}{n_W} = \frac{100\ \text{cm}^3 - (0.42\ \text{mol}) \times (52.2\ \text{cm}^3\ \text{mol}^{-1})}{4.3\ \text{mol}} = \boxed{18\ \text{cm}^3\ \text{mol}^{-1}}$$

5A.9(b) Henry's law is [5A.23] $p_B = x_BK_B$, so check whether p_B / x_B is equal to a constant (K_B)

x	0.010	0.015	0.020
p/kPa	82.0	122.0	166.1
(p/kPa) / x	8.2×10^3	8.1×10^3	8.3×10^3

Hence, $K_B = p / x = \boxed{8.2\times10^3\ \text{kPa}}$ (average value).

5A.10(b) Refer to *Brief Illustration* 5A.4 and use the Henry's Law constant from Table 5A.1. Henry's law in terms of molal concentration is $p_B = b_BK_B$. So the molal solubility of methane in benzene at 25°C in equilibrium with 1.0 bar of methane is

$$b_{CH_4} = \frac{p_{CH_4}}{K_{CH_4}} = \frac{100\ \text{kPa}}{44.4 \times 10^3\ \text{kPa kg mol}^{-1}} = 2.2\overline{5} \times 10^{-3}\ \text{mol kg}^{-1}$$

To find the molar solubility, we assume that the density of the solution is the same as that of pure benzene, given at a nearby temperature (20°C) in Table 0.1:

$$[CH_4] = b_{CH_4}\rho_{\text{benzene}} = 2.2\overline{5} \times 10^{-3}\ \text{mol kg}^{-1} \times 0.879\ \text{kg dm}^{-3} = \boxed{2.0 \times 10^{-3}\ \text{mol dm}^{-3}}$$

5A.11(b) With concentrations expressed in molalities, Henry's law [5A.23] becomes $p_B = b_BK_B$.

Solving for b_B, the molality, we have $b_B = \frac{p_B}{K} = \frac{x_B p_{\text{total}}}{K}$,

where p_{total} = 1 atm = 101.3 kPa

For N_2, $K = 1.56\times10^5$ kPa kg mol^{-1} [Table 5A.1]

$$b = \frac{0.78\times 101.3\ \text{kPa}}{1.56\times 10^5\ \text{kPa kg mol}^{-1}} = \boxed{5.1\times 10^{-4}\ \text{mol kg}^{-1}}$$

For O_2, $K = 7.92\times10^4$ kPa kg mol^{-1} [Table 5A.1]

$$b = \frac{0.21\times 101.3\ \text{kPa}}{7.92\times 10^4\ \text{kPa kg mol}^{-1}} = \boxed{2.7\times 10^{-4}\ \text{mol kg}^{-1}}$$

5A.12(b) As in Exercise 5A.11(b), we have

$$b_B = \frac{p_B}{K} = \frac{2.0\times 101.3\ \text{kPa}}{3.01\times 10^3\ \text{kPa kg mol}^{-1}} = 0.067\ \text{mol kg}^{-1}$$

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 $\boxed{0.067\ \text{mol dm}^{-3}}$.

Solutions to problems

5A.2 $C = 1$; hence, according to the phase rule (eqn 4A.1) $F = C - P + 2 = 3 - P$

Since the tube is sealed there will always be some gaseous compound in equilibrium with the condensed phases. Thus when liquid begins to form upon melting, $P = 3$ (s, l, and g) and $F = 0$, corresponding to a definite melting temperature. At the transition to a normal liquid, $P = 3$ (l, l′, and g) as well, so again $F = 0$.

5A.4 Letting B stand for $CuSO_4$(aq), the partial molar volume of the dissolved salt is

$$V_B = \left(\frac{\partial V}{\partial n_B}\right)_{n_A} \quad [5A.1]$$

We will determine V_B by plotting V against n_B while holding n_A constant. We can find the volume from the density:

$$\rho = \frac{m_A + m_B}{V} \qquad \text{so} \qquad V = \frac{m_A + m_B}{\rho}.$$

The data include the composition of the solution expressed as mass percent. (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 percent). 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

$$n_B = \frac{m_B}{M_B}$$

such that $\frac{m_B}{m_A + m_B}\times 100 = w$.

Solve for m_B:

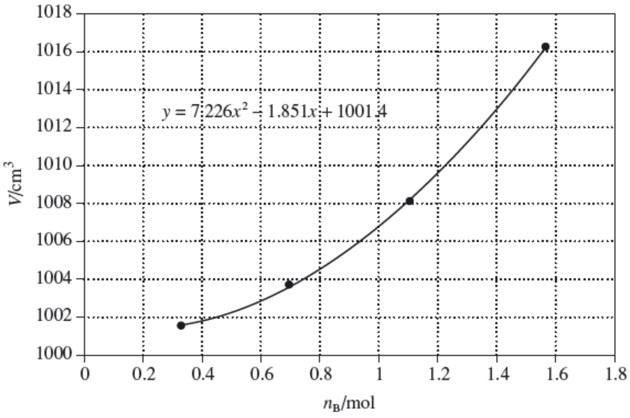
$$m_B = \frac{w m_A}{100 - w}.$$

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
ρ/(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/(cm^3 mol^{-1})	2.91	8.21	14.13	20.78

A plot V against n_B is shown in Figure 5A.1.

Figure 5A.1



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

$$V/\text{cm}^3 = 7.226(n_B/\text{mol})^2 - 1.851(n_B/\text{mol}) + 1001.4\ ,$$

so $$V_B/\text{cm}^3 = \left(\frac{\partial V/\text{cm}^3}{\partial n_B/\text{mol}}\right)_{n_A} = 2\times 7.226\times(n_B/\text{mol}) - 1.851$$

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; however, you should arrive at the same values for V_B.

5A.6 From *Example* 5A.1, we have

$$V_E/(\text{cm}^3\ \text{mol}^{-1}) = 54.6664 - 0.72788x + 0.084468x^2\ ,$$

where $x = n_E/\text{mol}$ mixed with 1.000 kg water. Thus, x is also equal to the numerical value of the molality. To find the minimum in V_E, differentiate it and set the derivative equal to zero:

$$\frac{\text{d}V_E(\text{cm}^3\ \text{mol}^{-1})}{\text{d}x} = -0.72788 + 2\times 0.084468x = 0$$

Thus $$x = \frac{0.72788}{2\times 0.084468} = 4.3086 \qquad \text{so} \qquad b = \boxed{4.3086\ \text{mol kg}^{-1}}$$

This value is consistent with Figure 5A.3 of the main text.

5B The properties of solutions

Answers to discussion question

5B.2 All of the colligative properties result from the lowering of the chemical potential of the solvent due to the presence of the solute. This reduction takes the form $\mu_A = \mu_A^* + RT \ln x_A$ or $\mu_A = \mu_A^* + RT \ln a_A$, depending on whether or not the solution can be considered ideal. The lowering of the chemical potential results in a freezing point depression and a boiling point elevation as illustrated in Figure 5B.6 of the text. Both of these effects can be explained by the lowering of the vapour pressure of the solvent in solution due to the presence of the solute. The solute molecules get in the way of the solvent molecules, reducing their escaping tendency.

Solutions to exercises

5B.1(b) In Exercise 5A.10(b), the Henry's law constant was determined for concentrations expressed in mole fractions; $K_B = 8.2\times10^3$ kPa. Thus the concentration must be converted from molality to mole fraction

m_A = 1000 g, corresponding to $n_A = \dfrac{1000\,\text{g}}{74.1\,\text{g mol}^{-1}} = 13.50\,\text{mol}$

Therefore $x_B = \dfrac{0.25\text{ mol}}{(0.25\,\text{mol}) + (13.50\,\text{mol})} = 0.018$

The pressure is

$p_B = K_B x_B$ [5A.23] = (0.018) × (8.2×10^3 kPa) = $\boxed{1.5\times10^2\text{ kPa}}$.

5B.2(b) We assume that the solvent, 2-propanol, is ideal and obeys Raoult's law [5A.21].

$$x_A\,(\text{solvent}) = \frac{p}{p^*} = \frac{49.62}{50.00} = 0.9924$$

Since $M_A(C_3H_8O)$ = 60.096 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 $n_B = n_A\left(\dfrac{1}{x_A} - 1\right) = 4.16\text{ mol}\times\left(\dfrac{1}{0.9924} - 1\right) = 3.12\times10^{-2}\text{ mol}$

and $M_B = \dfrac{m_B}{n_B} = \dfrac{8.69\text{ g}}{3.12\times10^{-2}\text{ mol}} = \boxed{273\text{ g mol}^{-1}}$

5B.3(b) Let B denote the compound and A the solvent, naphthalene. K_f = 6.94 K kg mol^{-1} [Table 5B.1]

$$M_B = \frac{m_B}{n_B}$$

$n_B = m_A\, b_B$ where $b_B = \dfrac{\Delta T}{K_f}$ [5B.13]

Thus $M_B = \dfrac{m_B K_f}{m_A \Delta T} = \dfrac{(5.00\,\text{g})\times(6.94\text{ K kg mol}^{-1})}{(0.250\,\text{kg})\times(0.780\,\text{K})} = \boxed{178\text{ g mol}^{-1}}$

5B.4(b) From the osmotic pressure, compute the concentration, and from the concentration the freezing point. According to the van't Hoff equation [5B.16], 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 [5B.13] includes the molality *b* rather than the molarity [B]. In dilute solutions, the two concentration measures are readily related:

$$b = \frac{n_B}{m_A} \approx \frac{n_B}{V_{\text{soln}}\rho_{\text{soln}}} = \frac{[\text{B}]}{\rho_{\text{soln}}} = \frac{\Pi}{RT\rho_{\text{soln}}}$$

The freezing point depression is

$\Delta T = K_f b \approx \dfrac{K_f \Pi}{RT\rho_{\text{soln}}}$ where K_f = 1.86 K mol^{-1} kg [Table 5B.1]

The density of a dilute aqueous solution is approximately that of water:

$\rho \approx$ 1.0 g cm^{-3} =1.0×10^3 kg m^{-3}

So $\Delta T \approx \dfrac{(1.86\,\text{K kg mol}^{-1})\times(99\times10^3\text{ Pa})}{(8.3145\text{ J K}^{-1}\text{ mol}^{-1})\times(288\,\text{K})\times(10^3\text{ kg m}^{-3})} = 0.077\,\text{K}$

Therefore, the solution will freeze at about $\boxed{-0.077°\text{C}}$.

5B.5(b) $\Delta_{\text{mix}}G = nRT\sum_J x_J \ln x_J$ [5A.16] and

$$\Delta_{\text{mix}}S = -nR\sum_J x_J \ln x_J \text{ [5A.17]} = \frac{-\Delta_{\text{mix}}G}{T}$$

$n = 2.00$ mol and $x_{\text{hexane}} = x_{\text{heptane}} = 0.500$

Therefore,

$$\Delta_{\text{mix}}G = (2.00\ \text{mol}) \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K}) \times 2 \times (0.500\ \ln 0.500)$$

$$= -3.43 \times 10^{3}\ \text{J} = \boxed{-3.43\ \text{kJ}}$$

and $\Delta_{\text{mix}}S = \dfrac{-\Delta_{\text{mix}}G}{T} = \dfrac{+3.43 \times 10^{3}}{298\ \text{K}} = \boxed{+11.5\ \text{J K}^{-1}}$

For an ideal solution, $\Delta_{\text{mix}}H = \boxed{0}$, just as it is for a mixture of perfect gases [5A.18]. It can be demonstrated from

$$\Delta_{\text{mix}}H = \Delta_{\text{mix}}G + T\Delta_{\text{mix}}S = \Delta_{\text{mix}}G + T\left(\frac{-\Delta_{\text{mix}}G}{T}\right) = 0$$

5B.6(b) **(i)** Benzene and ethylbenzene form nearly ideal solutions, so.

$\Delta_{\text{mix}}S = -nRT(x_A \ln x_A + x_B \ln x_B)$ [5A.17]

We need to differentiate eqn 5A.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

$\Delta_{\text{mix}}S = -nRT\{x_A \ln x_A + (1-x_A)\ln(1-x_A)\}$

This gives $\left(\text{using } \dfrac{\text{d}\ln x}{\text{d}x} = \dfrac{1}{x}\right)$

$$\frac{\text{d}\Delta_{\text{mix}}S}{\text{d}x_A} = -nR\{\ln x_A + 1 - \ln(1-x_A) - 1\} = -nR\ln\frac{x_A}{1-x_A}$$

which is zero when $x_A = \boxed{\frac{1}{2}}$. Hence, the maximum entropy of mixing occurs for the preparation of a mixture that contains equal mole fractions of the two components.

(ii) Because entropy of mixing is maximized when $n_E = n_B$ (changing to notation specific to Benzene and Ethylbenzene)

$$\frac{m_E}{M_E} = \frac{m_B}{M_B}$$

This makes the mass ratio

$$\frac{m_B}{m_E} = \frac{M_B}{M_E} = \frac{78.11\ \text{g mol}^{-1}}{106.17\ \text{g mol}^{-1}} = \boxed{0.7357}$$

5B.7(b) The ideal solubility in terms of mole fraction is given by eqn 5B.15:

$$\ln x_{\text{Pb}} = \frac{\Delta_{\text{fus}}H}{R} \times \left(\frac{1}{T_f} - \frac{1}{T}\right)$$

$$= \left(\frac{5.2 \times 10^{3}\ \text{J mol}^{-1}}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}\right) \times \left(\frac{1}{600.\text{K}} - \frac{1}{553\text{K}}\right) = -0.089$$

Therefore, $x_{\text{Pb}} = e^{-0.089} = 0.92$.

$$x_{\text{Pb}} = \frac{n_{\text{Pb}}}{n_{\text{Bi}} + n_{\text{Pb}}} \quad \text{implying that} \quad n_{\text{Pb}} = \frac{n_{\text{Bi}}x_{\text{Pb}}}{1-x_{\text{Pb}}} = \frac{m_{\text{Bi}}}{M_{\text{Bi}}} \times \frac{x_{\text{Pb}}}{1-x_{\text{Pb}}}$$

Hence the amount of lead that dissolves in 1 kg of bismuth is

$$n_{\text{Pb}} = \frac{1000\ \text{g}}{209\ \text{g mol}^{-1}} \times \frac{0.92}{1-0.92} = \boxed{52\ \text{mol}}$$

or, in mass units, $m_{\text{Pb}} = n_{\text{Pb}} \times M_{\text{Pb}} = 52\ \text{mol} \times 207\ \text{g mol}^{-1} = 1.1 \times 10^{4}\ \text{g} = \boxed{11\ \text{kg}}$.

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 5B.15 ought to be considered suggestive at best, rather than quantitative.

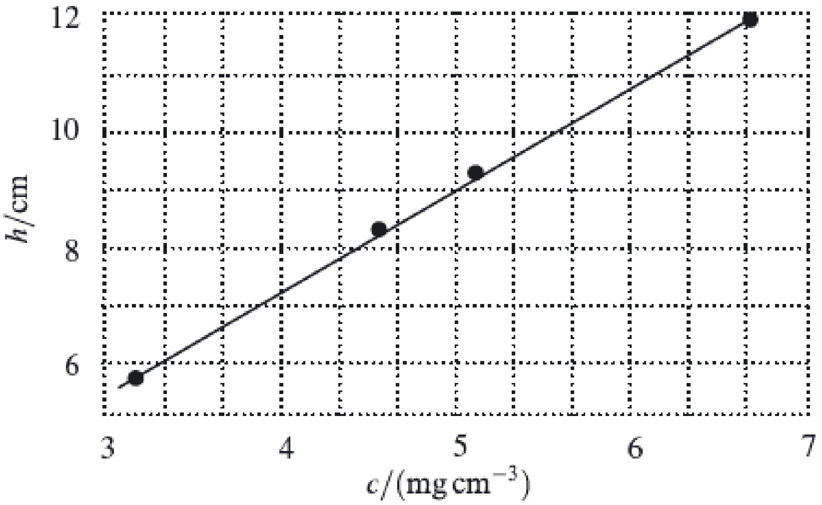
5B.8(b) The best value of the molar mass is obtained from values of the data extrapolated to zero concentration, since it is under this condition that the van't Hoff equation (5B.16) applies.

$$\Pi V = n_B RT \qquad \text{so} \qquad \Pi = \frac{mRT}{MV} = \frac{cRT}{M} \text{ where } c = m/V.$$

But the osmotic pressure is also equal to the hydrostatic pressure

$$\Pi = \rho g h \text{ [1A.1]} \qquad \text{so} \qquad h = \left(\frac{RT}{\rho g M}\right)c$$

Figure 5B.1



Hence, plot h against c and identify the slope as $\frac{RT}{\rho g M}$. Figure 5B.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,

$$M = \frac{RT}{(\rho g) \times (1.78 \times 10^{-2} \text{ m}^4 \text{ kg}^{-1})}$$
$$= \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293 \text{K})}{(1.000 \times 10^3 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2}) \times (1.78 \times 10^{-2} \text{ m}^4 \text{ kg}^{-1})} = \boxed{14.0 \text{ kg mol}^{-1}}$$

5B.9(b) In an ideal dilute solution the solvent (CCl_4, A) obeys Raoult's law [5A.21] and the solute (Br_2, B) obeys Henry's law [5A.23]; hence

$$p_A = x_A p^* = (0.934) \times (23 \text{ kPa}) = \boxed{21.\bar{5} \text{ kPa}}$$
$$p_B = x_B K_B = (0.066) \times (73 \text{ kPa}) = \boxed{4.8 \text{ kPa}}$$
$$p_{\text{total}} = (21.\bar{5} + 4.8) \text{ kPa} = \boxed{26.\bar{3} \text{ kPa}}$$

The composition of the vapour in equilibrium with the liquid is

$$y_A = \frac{p_A}{p_{\text{total}}} = \frac{21.\bar{5} \text{ kPa}}{23.\bar{3} \text{ kPa}} = \boxed{0.82} \qquad \text{and} \qquad y_B = \frac{p_B}{p_{\text{total}}} = \frac{4.8 \text{ kPa}}{23.\bar{3} \text{ kPa}} = \boxed{0.18}$$

5B.10(b) Let subscript 12 denote the 1,2 isomer and 13 the 1,3 isomer. Assume that the structurally similar liquids obey Raoult's law [5A.21]. The partial pressures of the two liquids sum to 19 kPa.

$$p_{13} + p_{12} = p = x_{13}p_{13}^* + x_{12}p_{12}^* = x_{13}p_{13}^* + (1-x_{13})p_{12}^*$$

Solve for x_{13}:

$$x_{13} = \frac{p - p_{12}^*}{p_{13}^* - p_{12}^*} = \frac{(19-20) \text{ kPa}}{(18-20) \text{ kPa}} = \boxed{0.5}$$

and $x_{12} = 1 - 0.5 = \boxed{0.5}$.

The vapour phase mole fractions are given by eqn 1A.8:

$$y_{13} = \frac{p_{13}}{p} = \frac{x_{13}p_{13}^{\ *}}{p} = \frac{(0.5)\times 18 \text{ kPa}}{19 \text{ kPa}} = \boxed{0.4\overline{7}}$$

and $$y_{12} = \frac{x_{12}p_{12}^{\ *}}{p} = \frac{(0.5)\times 20.0 \text{ kPa}}{50.7 \text{ kPa}} = \boxed{0.5\overline{3}} \, .$$

5B.11(b) The partial vapour pressures are given by Raoult's law [5A.21]:

$p_A = x_Ap_A^*$ and $p_B = x_Bp_B^* = (1–x_B)p_B^*$.

Eqn 1A.8 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:

$$x_A p_A^* + (1-x_A)p_B^* = \frac{x_A p_A^*}{y_A}$$

$$x_A\left(p_A^* - p_B^* - \frac{p_A^*}{y_A}\right) = -p_B^*$$

$$x_A = \frac{p_B^*}{p_B^* + \dfrac{p_A^*}{y_A} - p_A^*} = \frac{82.1 \text{ kPa}}{\left(82.1 + \dfrac{68.8}{0.621} - 68.8\right) \text{ kPa}} = \boxed{0.662}$$

and $x_B = 1 – x_A = 1 – 0.662 = \boxed{0.338}$.

The total vapour pressure is

$p_{\text{total}} = x_Ap_A^* + x_Bp_B^* = 0.662 \times 68.8 \text{ kPa} + 0.338 \times 82.1 \text{ kPa} = \boxed{73.3 \text{ kPa}}$.

5B.12(b) **(i)** If the solution is ideal, then the partial vapour pressures are given by Raoult's law [5A.21]:

$p_A° = x_Ap_A^* = 0.4217 \times 110.1 \text{ kPa} = 46.4 \text{ kPa}$

and $p_B° = x_Bp_B^* = (1–x_B)p_B^* = (1–0.4217) \times 76.5 \text{ kPa} = 44.2 \text{ kPa}$.

(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 $\boxed{\text{solution is not ideal}}$.

(ii) 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

$$y_A = y_A° = \frac{p_A°}{p_A° + p_B°} = \frac{46.4 \text{ kPa}}{(46.4 + 44.2) \text{ kPa}} = \boxed{0.512}$$

and $$y_B = y_B° = \frac{p_B°}{p_A° + p_B°} = \frac{44.2 \text{ kPa}}{(46.4 + 44.2) \text{ kPa}} = \boxed{0.488} \, .$$

By Eqn. 1A.8, the actual partial vapour pressures would then be

$p_A = y_Ap_{\text{total}} = 0.512 \times 101.3 \text{ kPa} = \boxed{51.9 \text{ kPa}}$

and $p_B = y_Bp_{\text{total}} = 0.488 \times 101.3 \text{ kPa} = \boxed{49.4 \text{ kPa}}$.

To find the activity coefficients, note that

$$\gamma_A = \frac{p_A}{x_A p_A^*} = \frac{p_A}{p_A°} = \frac{51.9 \text{ kPa}}{46.4 \text{ kPa}} = 1.117 \qquad \text{and} \qquad \gamma_B = \frac{49.4 \text{ kPa}}{44.2 \text{ kPa}} = 1.117$$

Comment. Assuming that the actual proportions of the vapours are the same as the ideal proportions begs the question (*i.e.*, arrives at the answer by assumption rather than calculation). The assumption is not unreasonable, though. It is equivalent to assuming that the activity coefficients of the two components are equal (when in principle they could be different). The facts that the difference between ideal and actual total pressure is relatively small (on the order of 10%), that non-ideal behavior is due to the **interaction** of the two components, and that the two components are present in comparable quantities combine to suggest that the error we make in making this assumption is fairly small.

5B.13(b) **(i)** If the solution is ideal, then the partial vapour pressures are given by Raoult's law [5A.21]:

$p_B = x_B p_B^* = 0.50 \times 9.9\text{ kPa} = 4.95\text{ kPa}$

$p_T = x_T p_T^* = 0.50 \times 2.9\text{ kPa} = 1.45\text{ kPa}$

The total pressure is

$p_{\text{total}} = p_B + p_T = (4.95 + 1.45)\text{ kPa} = \boxed{6.4\text{ kPa}}$.

(ii) 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 $$y_T = \frac{p_T}{p_{\text{total}}} = \frac{1.45\text{ kPa}}{6.4\text{ kPa}} = \boxed{0.23}$$

(iii) 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

$p_B = x_B p_B^* = 0.23 \times 9.9\text{ kPa} = 2.24\text{ kPa} = p_T$ [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.

Solutions to problems

5B.2 The apparent molality is

$$b_{\text{app}} = \frac{\Delta T}{K_f}\ [5B.13] = \frac{0.0703\text{ K}}{1.86\text{ K/(mol kg}^{-1})} = 0.0378\text{ mol kg}^{-1}$$

Since the solution molality is nominally 0.0096 mol kg^{-1} in $Th(NO_3)_4$, each formula unit supplies $\frac{0.0378}{0.0096} \approx \boxed{4\text{ ions}}$. (More careful data, as described in the original reference gives 5 to 6 ions.)

5B.4 **(a)** Let V_1^* be the molar volume of *pure* propionic acid and V_1 be its *partial* molar volume in the mixture (and V_2^* and V_2 the analogous quantities for oxane). The volume of an ideal mixture is additive

$V^{\text{ideal}} = n_1 V_1^* + n_2 V_2^*$,

so the volume of a real mixture is

$V = V^{\text{ideal}} + V^E$.

We have an expression for excess molar volume in terms of mole fractions. To compute partial molar volumes, we need an expression for the excess volume as a function of moles

$$V^E = (n_1 + n_2)V_m^E = \frac{n_1 n_2}{n_1 + n_2}\left(a_0 + \frac{a_1(n_1 - n_2)}{n_1 + n_2}\right)$$

so $$V = n_1 V_1^* + n_2 V_2^* + \frac{n_1 n_2}{n_1 + n_2}\left(a_0 + \frac{a_1(n_1 - n_2)}{n_1 + n_2}\right)$$

The partial molar volume of propionic acid is

$$V_1 = \left(\frac{\partial V}{\partial n_1}\right)_{n_2} = V_1^* + \frac{a_0 n_2^2}{(n_1 + n_2)^2} + \frac{a_1(3n_1 - n_2)n_2^2}{(n_1 + n_2)^3} = \boxed{V_1^* + a_0 x_2^2 + a_1(3x_1 - x_2)x_2^2}$$

That of oxane is

$$V_2 = \left(\frac{\partial V}{\partial n_2}\right)_{n_1} = V_2^* + \frac{a_0 n_1^2}{(n_1 + n_2)^2} + \frac{a_1(n_1^3 - 3n_1^2 n_2^2)}{(n_1 + n_2)^3} = \boxed{V_2^* + a_0 x_1^2 + a_1(x_1 - 3x_2)x_1^2}$$

(b) We need the molar volumes of the pure liquids

$$V_1^* = \frac{M_1}{\rho_1} = \frac{74.08\ \text{g mol}^{-1}}{0.97174\ \text{g cm}^{-3}} = 76.23\ \text{cm}^3\ \text{mol}^{-1}$$

and $$V_2^* = \frac{M_2}{\rho_2} = \frac{86.13\ \text{g mol}^{-1}}{0.86398\ \text{g cm}^{-3}} = 99.69\ \text{cm}^3\ \text{mol}^{-1}$$

In an equimolar mixture, the partial molar volume of propionic acid is

$$V_1 = 76.23 + (-2.4697)\times(0.5)^2 + (0.0608)\times\{3(0.5) - 0.5\}\times(0.5)^2\ \text{cm}^3\ \text{mol}^{-1}$$
$$= \boxed{75.63\ \text{cm}^3\ \text{mol}^{-1}}$$

and that of oxane is

$$V_2 = 99.69 + (-2.4697)\times(0.5)^2 + (0.0608)\times\{0.5 - 3(0.5)\}\times(0.5)^2\ \text{cm}^3\ \text{mol}^{-1}$$
$$= \boxed{99.06\ \text{cm}^3\ \text{mol}^{-1}}$$

5B.6 In this mixture, $x = 0.250$, so

$$G^{\text{E}} = RT(0.250)(1–0.250)\{0.4857–0.1077(0.500–1)+0.0191(0.500–1)^2\} = 0.1021RT$$

Therefore, since

$$\Delta_{\text{mix}}G = \Delta_{\text{mix}}G^{\text{ideal}} + nG^{\text{E}} = nRT(x_{\text{A}} \ln x_{\text{A}} + x_{\text{B}} \ln x_{\text{B}}) + nG^{\text{E}}\ [\text{5B.5 and 5A.16}]$$
$$\Delta_{\text{mix}}G = nRT(0.250 \ln 0.250 + 0.750 \ln 0.750) + 0.1021nRT = –0.460nRT$$
$$\Delta_{\text{mix}}G = –0.460 \times 4.00\ \text{mol} \times 8.3145\ \text{J mol}^{-1}\ \text{K}^{-1} \times 303.15\ \text{K} = \boxed{–4.64\ \text{kJ mol}^{-1}}\ .$$

5B.8 $$\mu_{\text{A}} = \left(\frac{\partial G}{\partial n_{\text{A}}}\right)_{n_{\text{B}}} [\text{5A.4}] = \mu_{\text{A}}^{\text{ideal}} + \left(\frac{\partial}{\partial n_{\text{A}}}(nG^{\text{E}})\right)_{n_{\text{B}}} [\text{5B.5}] \quad \text{where} \quad \mu_{\text{A}}^{\text{ideal}} = \mu_{\text{A}}^* + RT\ln x_{\text{A}}\ [\text{5A.22}]$$

$$\left(\frac{\partial nG^{\text{E}}}{\partial n_{\text{A}}}\right)_{n_{\text{B}}} = G^{\text{E}} + n\left(\frac{\partial G^{\text{E}}}{\partial n_{\text{A}}}\right)_{n_{\text{B}}} = G^{E} + n\left(\frac{\partial x_{\text{A}}}{\partial n_{\text{A}}}\right)_{n_{\text{B}}}\left(\frac{\partial G^{\text{E}}}{\partial x_{\text{A}}}\right)_{n_{\text{B}}}$$

where $$\left(\frac{\partial x_{\text{A}}}{\partial n_{\text{A}}}\right)_{n_{\text{B}}} = \frac{\partial}{\partial n_{\text{A}}}\left(\frac{n_{\text{A}}}{n_{\text{A}}+n_{\text{B}}}\right) = \frac{1}{n_{\text{A}}+n_{\text{B}}} - \frac{n_{\text{A}}}{(n_{\text{A}}+n_{\text{B}})^2} = \frac{n_{\text{B}}}{(n_{\text{A}}+n_{\text{B}})^2} = \frac{x_{\text{B}}}{n_{\text{A}}+n_{\text{B}}} = \frac{x_{\text{B}}}{n}$$

Hence $$\left(\frac{\partial nG^{\text{E}}}{\partial n_{\text{A}}}\right)_{n_{\text{B}}} = G^{\text{E}} + x_{\text{B}}\left(\frac{\partial G^{\text{E}}}{\partial x_{\text{A}}}\right)_{n_{\text{B}}} = gRTx_{\text{A}}(1-x_{\text{A}}) + (1-x_{\text{A}})gRT(1-2x_{\text{A}})$$

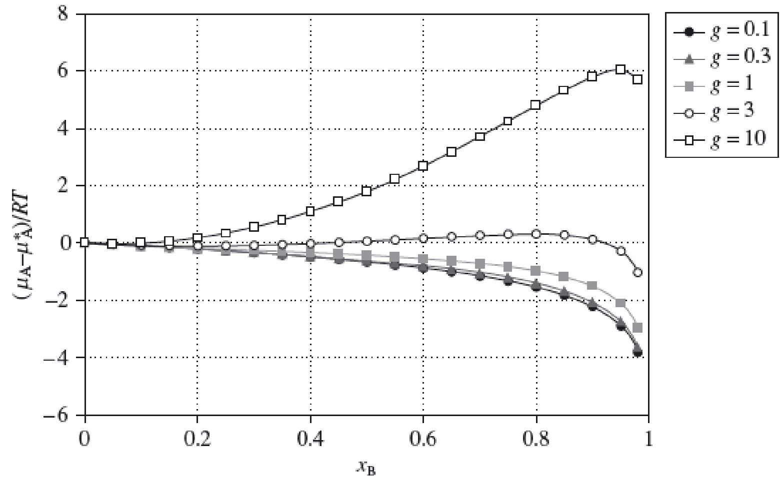
After expanding and collecting terms, we arrive at

$$\left(\frac{\partial nG^{\text{E}}}{\partial n_{\text{A}}}\right)_{n_{\text{B}}} = gRT(1-x_{\text{A}})^2 = gRTx_{\text{B}}^2$$

Therefore, $\mu_{\text{A}} = \boxed{\mu_{\text{A}}^* + RT\ln x_{\text{A}} + gRTx_{\text{B}}^2}$

This function is plotted for several values of the parameter g in Figure 5B.2.

Figure 5B.2



5B.10 By the van't Hoff equation [5B.16]

$$\Pi = [\mathrm{B}]RT = \frac{cRT}{M}$$

Division by the standard acceleration of free fall, g, gives

$$\frac{\Pi}{g} = \frac{c(R/g)T}{M}$$

(a) This expression may be written in the form

$$\Pi' = \frac{cR'T}{M}$$

which has the same form as the van't Hoff equation, but the unit of osmotic pressure (Π') is now

$$\frac{\text{force / area}}{\text{length / time}^2} = \frac{(\text{mass length})/(\text{area time}^2)}{\text{length / time}^2} = \frac{\text{mass}}{\text{area}}$$

This ratio can be specified in g cm^{-2}. Likewise, the constant of proportionality (R') would have the units of R/g.

$$\frac{\text{energy}\,\mathrm{K}^{-1}\,\mathrm{mol}^{-1}}{\text{length / time}^2} = \frac{(\text{mass length}^2/\text{time}^2)\,\mathrm{K}^{-1}\,\mathrm{mol}^{-1}}{\text{length / time}^2} = \text{mass length}\,\mathrm{K}^{-1}\,\mathrm{mol}^{-1}$$

This result may be specified in $\boxed{\mathrm{g\ cm\ K^{-1}\ mol^{-1}}}$.

$$R' = \frac{R}{g} = \frac{8.314\,47\,\mathrm{J\,K^{-1}\,mol^{-1}}}{9.806\,65\,\mathrm{m\,s^{-2}}}$$

$$= 0.847\,840\,\mathrm{kg\,m\,K^{-1}\,mol^{-1}}\left(\frac{10^3\,\mathrm{g}}{\mathrm{kg}}\right)\times\left(\frac{10^2\,\mathrm{cm}}{\mathrm{m}}\right)$$

$$= \boxed{84\,784.0\,\mathrm{g\,cm\,K^{-1}\,mol^{-1}}}$$

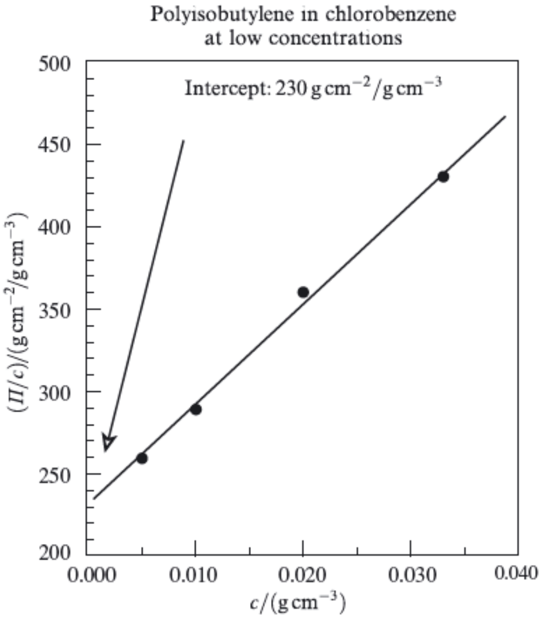
In the following we will drop the primes giving

$$\Pi = \frac{cRT}{M}$$

and use the Π units of g cm^{-2} and the R units g cm K^{-1} mol^{-1}.

(b) By extrapolating the low concentration plot of Π/c versus c (Figure 5B.3(a)) to $c = 0$ we find the intercept 230 g cm^{-2}/(g cm^{-3}). In this limit the van't Hoff equation is valid so

Figure 5B.3(a)

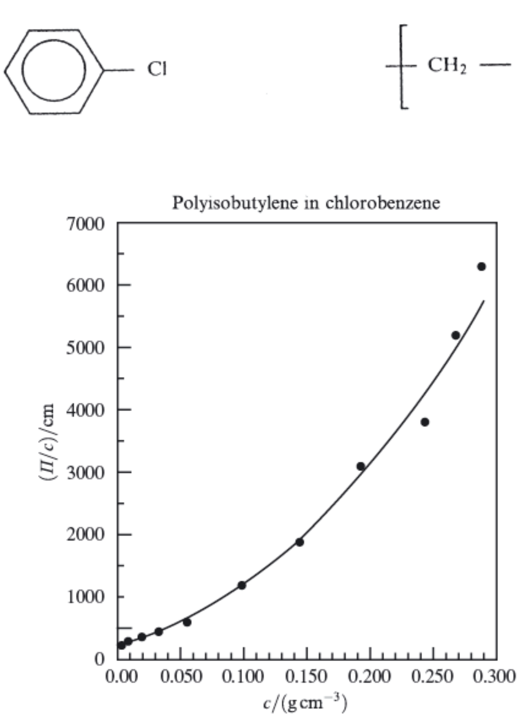


$$\frac{RT}{M} = \text{intercept} \quad \text{or} \quad M = \frac{RT}{\text{intercept}}$$

$$M = \frac{RT}{\text{intercept}} = \frac{(84\,784.0\ \text{g cm K}^{-1}\ \text{mol}^{-1}) \times (298.15\ \text{K})}{(230\ \text{g cm}^{-2})/(\text{g cm}^{-3})} = \boxed{1.1\times 10^{5}\ \text{g mol}^{-1}}$$

(c) The plot of Π / c versus c for the full concentration range (Figure 5B.3(b)) is very nonlinear. We may conclude that the solvent is good. This may be due to the nonpolar nature of both solvent and solute.

Figure 5B.3(b)



(d) The virial analogue to the van’t Hoff equation (eqn. 5B.18) rearranges to

$$\Pi / c = (RT / M)(1 + B'c + C'c^2)$$

Since RT / M has been determined in part (b) by extrapolation to $c = 0$, it is best to determine the second and third virial coefficients with the linear regression fit

$$\frac{(\Pi / c)/(RT / M)^{-1}}{c} = B' + C'c$$

$R = 0.9791$.

$B' = \boxed{21.4\ \text{cm}^3\ \text{g}^{-1}}$; standard deviation = $2.4\ \text{cm}^3\ \text{g}^{-1}$.

$C' = \boxed{211\ \text{cm}^6\ \text{g}^{-2}}$; standard deviation = $15\ \text{cm}^6\ \text{g}^{-2}$.

(e) Using 1/4 for g and neglecting terms beyond the second power, we may write

$$\left(\frac{\Pi}{c}\right)^{1/2} = \left(\frac{RT}{M}\right)^{1/2}\left(1 + \frac{1}{2}B'c\right)$$

We can solve for B' , then $g(B')^2 = C'$.

$$\frac{\left(\frac{\Pi}{c}\right)^{1/2}}{\left(\frac{RT}{M}\right)^{1/2}} - 1 = \frac{1}{2}B'c$$

RT / M has been determined above as 230 g cm^{-2}/(g cm^{-3}). We may analytically solve for B' from one of the data points, say, $\Pi / c = 430\ \text{g cm}^{-2} / \text{g cm}^{-3}$ at $c = 0.033\ \text{g cm}^{-3}$.

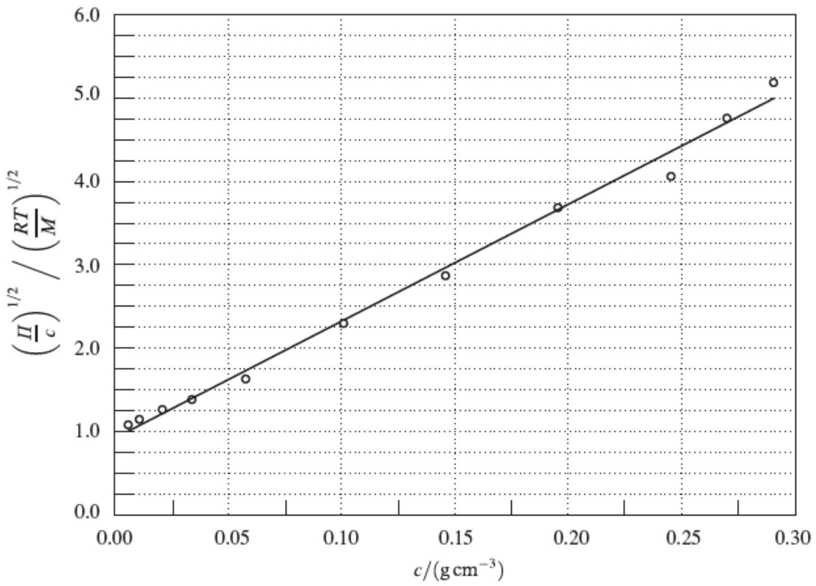
$$\left(\frac{430\ \text{g cm}^{-2} / \text{g cm}^{-3}}{230\ \text{g cm}^{-2} / \text{g cm}^{-3}}\right)^{1/2} - 1 = \frac{1}{2}B' \times (0.033\ \text{g cm}^{-3})$$

$$B' = \frac{2\times(1.367-1)}{0.033\ \text{g cm}^{-3}} = 22\ \text{cm}^3\ \text{g}^{-1}$$

$$C' = g(B')^2 = 0.25\times(22\ \text{cm}^3\ \text{g}^{-1})^2 = 12\overline{3}\ \text{cm}^6\ \text{g}^{-2}$$

Better values of B' and C' can be obtained by plotting $\left(\dfrac{\Pi}{c}\right)^{1/2}\Big/\left(\dfrac{RT}{M}\right)^{1/2}$ against c. This plot is shown in Figure 5B.3(c). The slope is 14 $\text{cm}^3\ \text{g}^{-1}$. B' =2 × slope = $\boxed{28\ \text{cm}^3\ \text{g}^{-1}}$. C' is then $\boxed{19\overline{6}\ \text{cm}^6\ \text{g}^{-2}}$. The intercept of this plot should theoretically be 1.00, but it is in fact 0.916 with a standard deviation of 0.066. The overall consistency of the values of the parameters confirms that g is roughly 1/4 as assumed.

Figure 5B.3(c)

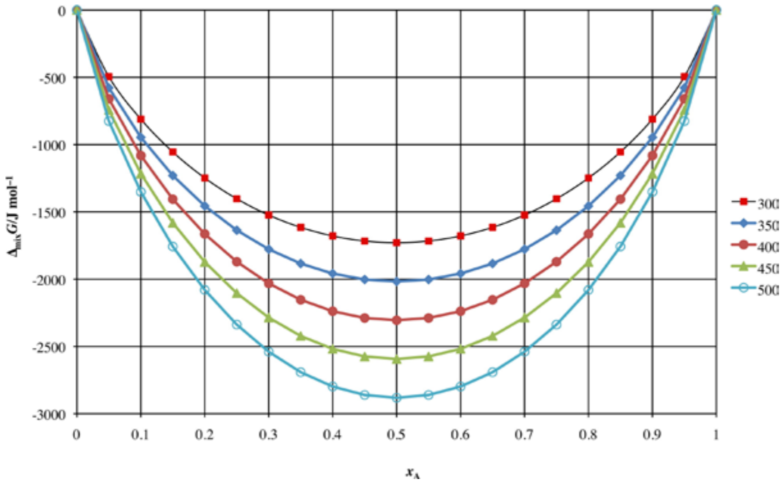


5B.12 The Gibbs energy of mixing an ideal solution is [5A.16]

$$\Delta_{\text{mix}}G = nRT(x_A \ln x_A + x_B \ln x_B)$$

The molar Gibbs energy of mixing is plotted against composition for several temperatures in Fig. 5B.4. The legend shows the temperature in kelvins.

Figure 5B.4



The composition at which the temperature dependence is strongest is the composition at which the function has its largest magnitude, namely $\boxed{x_A = x_B = 0.5}$.

5B.14 The theoretical solubility [5B.15] is

$$\ln x_{\mathrm{B}} = \frac{\Delta_{\mathrm{fus}}H}{R}\left(\frac{1}{T_{\mathrm{f}}} - \frac{1}{T}\right)$$

so $$x_{\mathrm{B}} = \exp\left(\frac{\Delta_{\mathrm{fus}}H}{RT_{\mathrm{f}}}\right)\exp\left(-\frac{\Delta_{\mathrm{fus}}H}{RT}\right)$$

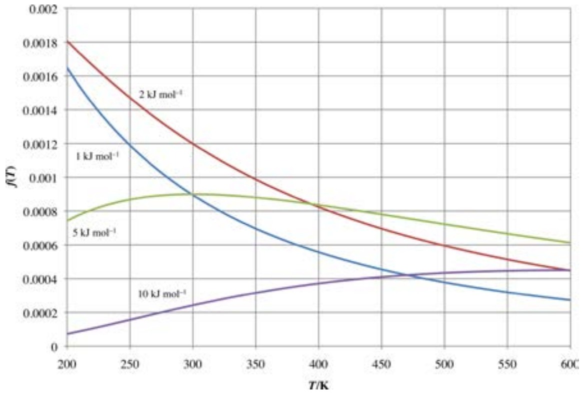
and $$\frac{\mathrm{d}x_{\mathrm{B}}}{\mathrm{d}T} = \boxed{\exp\left(\frac{\Delta_{\mathrm{fus}}H}{RT_{\mathrm{f}}}\right)\exp\left(-\frac{\Delta_{\mathrm{fus}}H}{RT}\right)\times\left(\frac{\Delta_{\mathrm{fus}}H}{RT^2}\right)}$$

This expression can be plotted as a function of temperature for various values of the enthalpy of fusion and the freezing temperature. The dependence on the freezing temperature is relatively uninteresting, though, since it enters into a factor that is independent of temperature, namely $\exp\left(\frac{\Delta_{\mathrm{fus}}H}{RT_{\mathrm{f}}}\right)$

So we will ignore the effect of the freezing temperature and simply plot $\mathrm{d}x_{\mathrm{B}}/\mathrm{d}T$ with this factor divided out. That is, in Figure 5B.5, we plot $f(T)$ vs. T for several values of $\Delta_{\mathrm{fus}}H$ between 1 and 10 kJ mol^{-1}, where

$$f(T) = \exp\left(-\frac{\Delta_{\mathrm{fus}}H}{RT}\right)\times\left(\frac{\Delta_{\mathrm{fus}}H}{RT^2}\right)$$

Figure 5B.5



Note that the function does not appear to consistently as we increase $\Delta_{\mathrm{fus}}H$. This apparent inconsistency would be removed, though, if we plotted over a temperature range that extended back to $T = 0$. The function has a maximum because the exponential factor increases toward a constant value of 1 with increasing temperature while the other factor decreases toward zero. The higher the value of $\Delta_{\mathrm{fus}}H$. the higher the temperature at which $f(T)$ is maximal and the lower the value of that maximum value. For $\Delta_{\mathrm{fus}}H = 1$ or 2 kJ mol^{-1}, the maximum occurs at temperatures lower than those shown and for $\Delta_{\mathrm{fus}}H = 10$ kJ mol^{-1} it occurs at a higher temperature than those shown.

5C Phase diagrams of binary systems

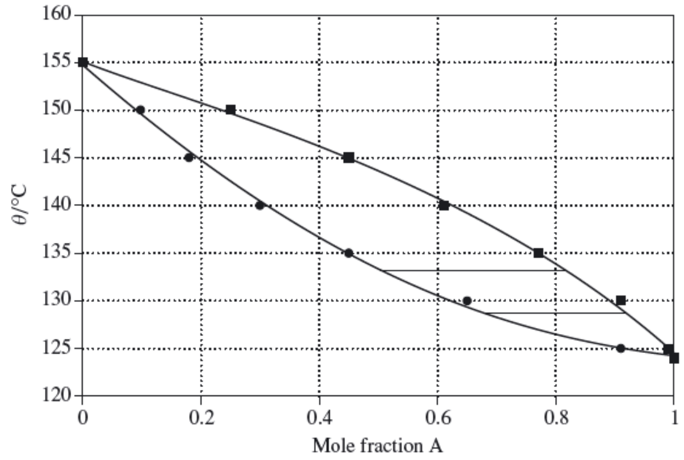
Answers to discussion question

5C.2 A low-boiling azeotrope has a boiling temperature lower than that of either component, so it is easier to get the molecules into the vapor phase than in a “normal” (non-azeotropic) mixture. Therefore, the liquid phase has less favorable intermolecular interactions than in a “normal” mixture, a sign that the components are less attracted to each other in the liquid phase than to molecules of their own kind. These intermolecular interactions are determined by factors such as dipole moment (polarity) and hydrogen bonding. Conversely, a high-boiling azeotrope has a boiling temperature higher than that of either component, so it is more difficult to get the molecules into the vapor phase. This reflects the relatively unusual situation of components that have more favorable intermolecular interactions with each other in the liquid phase than with molecules of their own kind. The concepts of ideal mixtures of liquids (in Topic 5A) and deviations from ideal behavior (in Topics 5B and 5E) will further define the behavior of “normal” (ideal) mixtures.

Solutions to exercises

5C.1(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 5C.1. The phase boundary curves are polynomial fits to the data points.

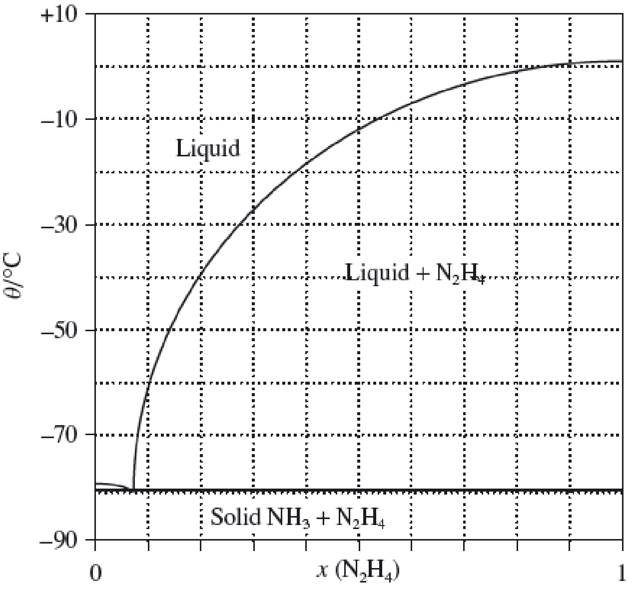
Figure 5C.1



(i) 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 $\boxed{y_A = 0.82}$.
(ii) 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 $\boxed{y_A = 0.91 \text{ (i.e., } y_B = 0.09)}$.

5C.2(b) The phase diagram is shown in Figure 5C.2.

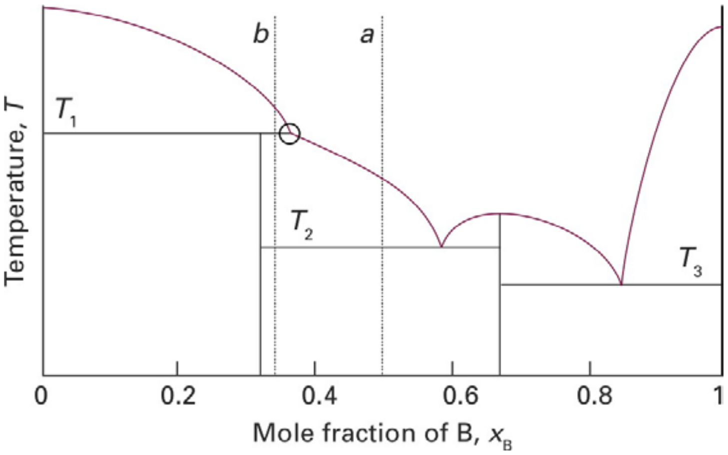
Figure 5C.2



5C.3(b) Refer to the figure given with the exercise. At the lowest temperature shown on the phase diagram, there are two liquid phases, a water-rich phase ($x_B = 0.07$) and a methylpropanol-rich phase ($x_B = 0.88$); the latter phase is about 10 times as abundant as the former (lever rule). On heating, the compositions of the two phases change, the water-rich phase increasing significantly in methylpropanol and the methylpropanol-rich phase more gradually increasing in water. (Note how the composition of the left side of the diagram changes more with temperature than the right.) The relative proportions of the phases continue to be given by the lever rule. Just before the isopleth intersects the phase boundary, the methylpropanol-rich phase ($x_B = 0.84$) is in equilibrium with a vanishingly small water-rich phase ($x_B = 0.3$). Then the phases merge, and the single-phase region is encountered with $x_B = 0.3$.

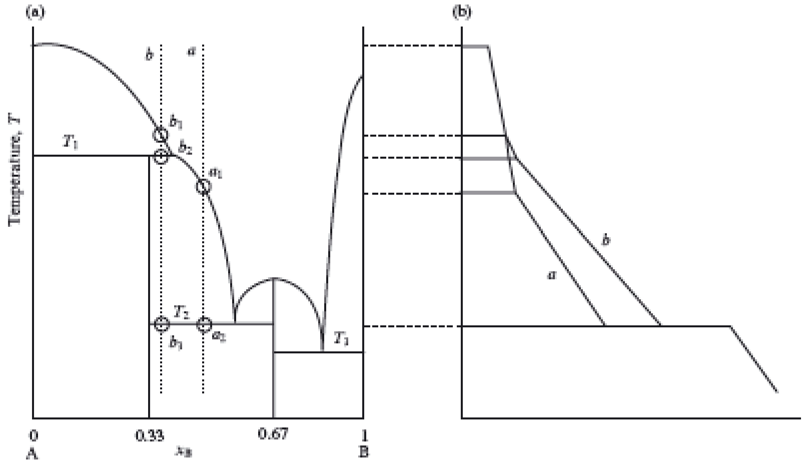
5C.4(b) The feature that indicates incongruent melting (Topic 5C.4(c)) is circled in Figure 5C.3. The incongruent melting point is marked as T_1. The composition of the eutectic is $x_B \approx \boxed{0.58}$ and its melting point is labeled $\boxed{T_2}$.

Figure 5C.3



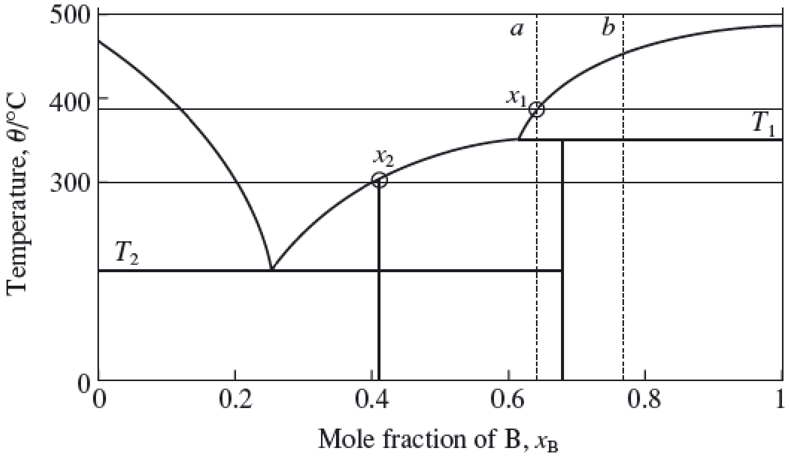
5C.5(b) The cooling curves corresponding to the phase diagram in Figure 5C.4(a) are shown in Figure 5C.4(b). Note the breaks (abrupt change in slope) at temperatures corresponding to points a_1, b_1, and b_2. Also note the eutectic halts at a_2 and b_3.

Figure 5C.4



5C.6(b) Refer to Figure 5C.5. Dotted horizontal lines have been drawn at the relevant temperatures.

Figure 5C.5



(i) At 500°C, the phase diagram shows a single liquid phase at all compositions, so $\boxed{\text{B is soluble in A in all proportions}}$.

(ii) At 390°C, solid B exists in equilibrium with a liquid whose composition is circled and labeled x_1 on Figure 5.11. That composition is $x_\mathrm{B} = x_1 = \boxed{0.63}$.

(iii) At point x_2, two phases coexist: solid AB_2 and a liquid mixture of A and B with mole fraction $x_\mathrm{B} = x_2 = 0.41$. 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

$$n_\mathrm{A} = n_\mathrm{a} + n_\mathrm{c} ,$$

and the amount of B is

$$n_\mathrm{B} = 2n_\mathrm{c} .$$

The mole fraction of B is

$$x_\mathrm{B} = x_2 = \frac{n_\mathrm{B}}{n_\mathrm{A} + n_\mathrm{B}} = \frac{2n_\mathrm{c}}{(n_\mathrm{a} + n_\mathrm{c}) + 2n_\mathrm{c}} = \frac{2n_\mathrm{c}}{n_\mathrm{a} + 3n_\mathrm{c}}$$

Rearrange this relationship, collecting terms in n_c on one side and n_a on the other:

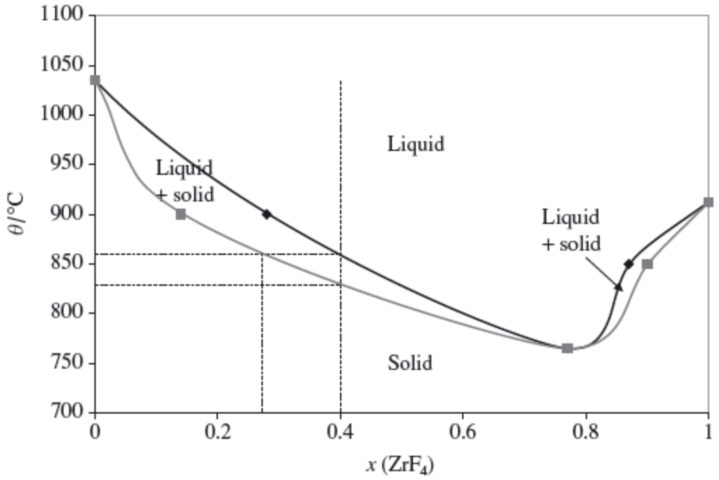
$$n_\mathrm{a}x_2 = n_\mathrm{c}(2–3x_2) .$$

The mole ratio of compound to free A is given by

$$\frac{n_\mathrm{c}}{n_\mathrm{a}} = \frac{x_2}{2 - 3x_2} = \frac{0.41}{2 - 3 \times 0.41} = \boxed{0.53} .$$

5C.7(b) The phase diagram is shown in Figure 5C.6. Point symbols are plotted at the given data points. The lines are schematic at best.

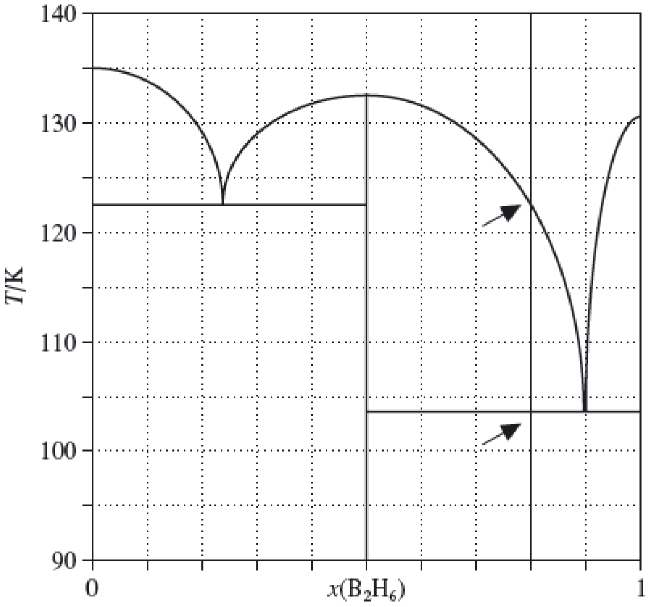
Figure 5C.6



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.

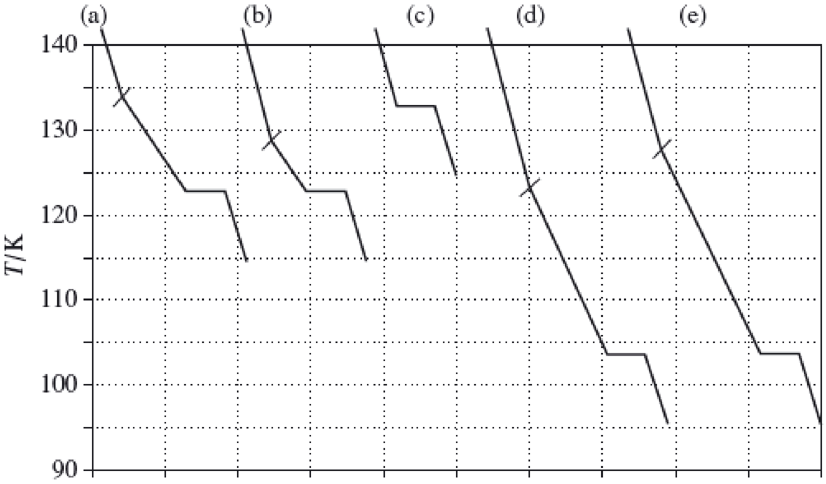
5C.8(b) The phase diagram for this system (Figure 5C.7) is very similar to that for the system methyl ethyl ether and diborane of Exercise 5C.7(a). The regions of the diagram contain analogous substances. The mixture in this Exercise has a diborane mole fraction of 0.80. Follow this isopleth down to 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 5C.7



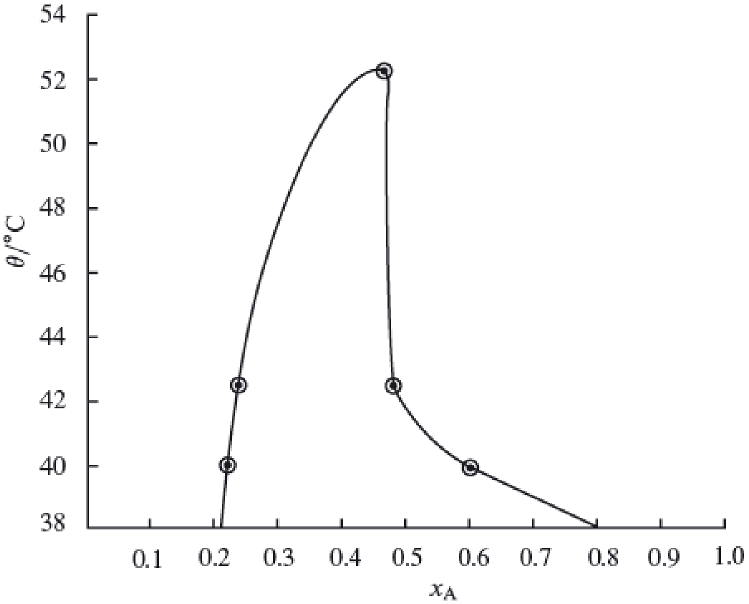
5C.9(b) The cooling curves are sketched in Figure 5C.8. Note the breaks and halts. The breaks correspond to changes in the rate of cooling due to the freezing out of a solid which releases its heat of fusion and thus slows down the cooling process. The halts correspond to the existence of three phases and hence no variance until one of the phases disappears.

Figure 5C.8



5C.10(b) The phase diagram is sketched in Figure 5C.9.

Figure 5C.9

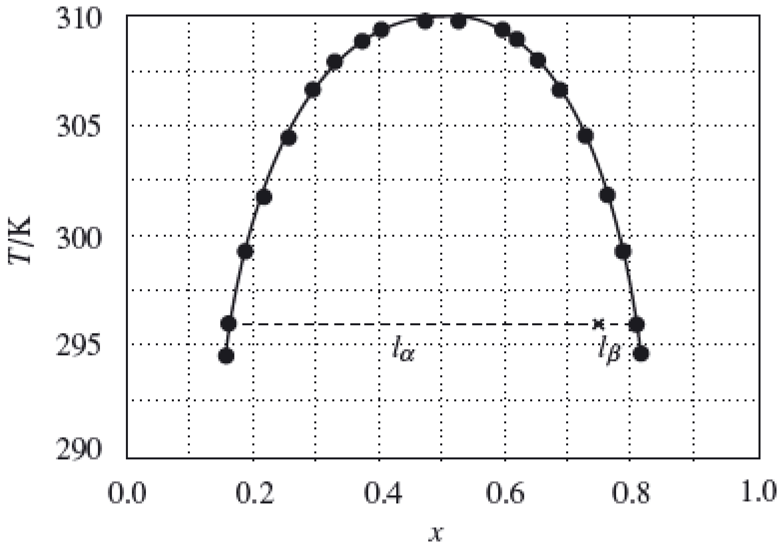


(i) When x_A falls to 0.47, a second liquid phase appears. The amount of new phase increases as x_A falls and the amount of original phase decreases until, at x_A = 0.314, only one liquid remains.
(ii) The mixture has a single liquid phase at all compositions.

Solutions to problems

5C.2 **(a)** The phase diagram is shown in Figure 5C.10.

Figure 5C.10



(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

$$n_\alpha / n_\beta = l_\beta / l_\alpha = (0.804 - 0.750)/(0.750 - 0.168) = \boxed{0.093}$$

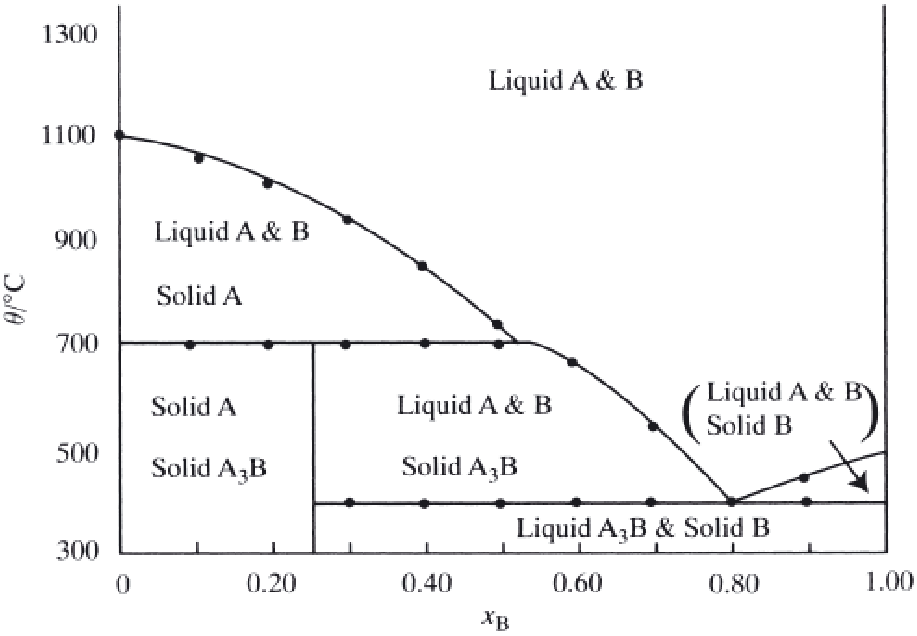
The smooth curve through the data crosses $x = 0.750$ at $\boxed{302.5\text{ K}}$, the temperature at which the heptane-rich phase will vanish.

5C.4 Figure 5C.11 displays the phase diagram. $\boxed{\text{A compound with probable formula } A_3B \text{ exists}}$. It melts incongruently at 700 °C , undergoing the peritectic reaction

$$A_3B(s) \rightarrow A(s) + (A + B,\ l)$$

The proportions of A and B in the product are dependent upon the overall composition and the temperature. A eutectic exists at 400°C and $x_B = 0.83$.

Figure 5C.11



5C.6 The information has been used to construct the phase diagram in Figure 5C.12(a). In $MgCu_2$ the mass percentage of Mg is

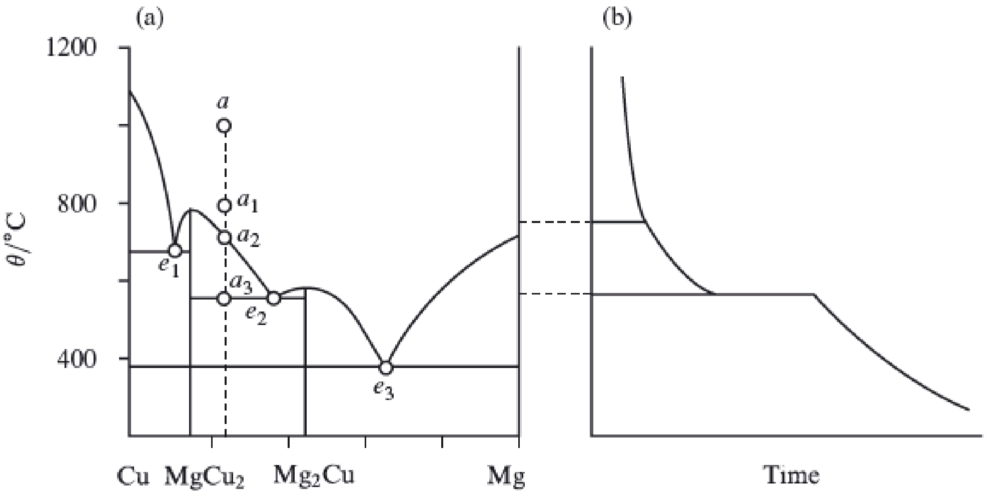
$$(100)\times\frac{24.3}{24.3+127}=\boxed{16}$$

and in Mg_2Cu it is

$$(100)\times\frac{48.6}{48.6+63.5}=\boxed{43}\,.$$

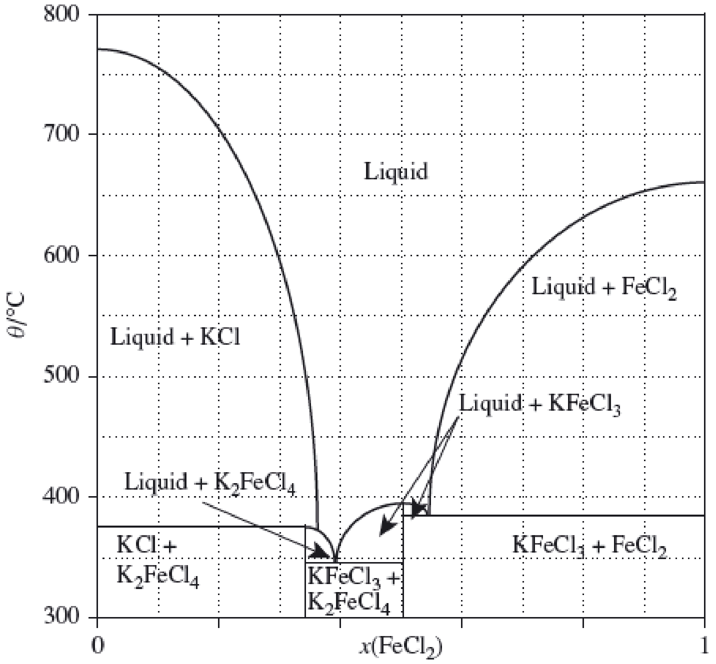
The initial point is a_1, corresponding to a single-phase liquid system. At a_2 (at 720°C) $MgCu_2$ begins to come out of solution and the liquid becomes richer in Mg, moving toward e_2. At a_3 there is solid $MgCu_2$ + liquid of composition e_2 (33 per cent by mass of Mg). This solution freezes without further change. The cooling curve will resemble that shown in Figure 5C.12(b).

Figure 5C.12



5C.8 The data are plotted in Figure 5C.13. At 360°C, $K_2FeCl_4(s)$ appears. The solution becomes richer in $FeCl_2$ until the temperature reaches 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 5C.13



5C.10 Equation 5C.5 is

$$p = \frac{p_A^* p_B^*}{p_A^* + (p_B^* - p_A^*) y_A}$$

First divide both sides by p_A^* to express the pressure in units of p_A^*. Next, divide both numerator and denominator by p_B^* to see if the right hand side can be expressed as a function of the ratio p_A^* / p_B^* rather than of each vapor pressure separately:

$$p / p_A^* = \frac{1}{p_A^* / p_B^* + (1 - p_A^* / p_B^*) y_A}$$

The plot of p / p_A^* vs. y_A at several values of the vapor pressure ratio is shown in Figure 5C.4 of the main text.

5C.12 Equation 5C.7 is

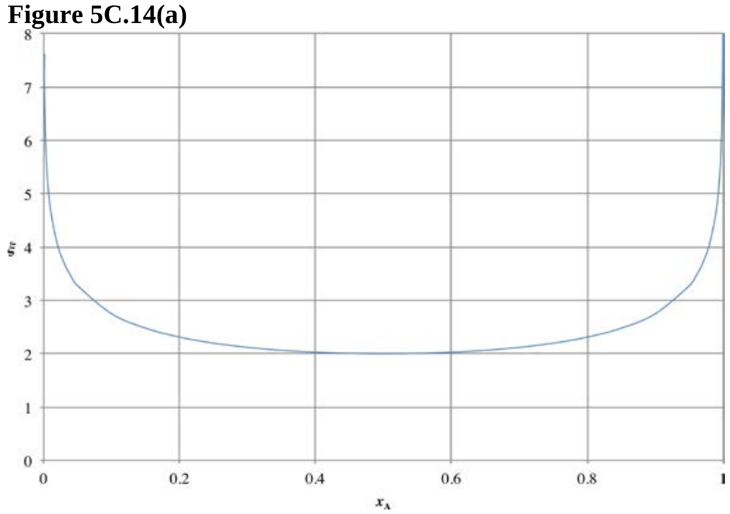
$$\ln \frac{x_A}{1 - x_A} = -\xi(1 - 2x_A) = \xi(2x_A - 1)$$

The simplest way to construct a plot of ξ vs. x_A is to isolate ξ:

$$\xi = \frac{\ln \dfrac{x_A}{1 - x_A}}{2x_A - 1}$$

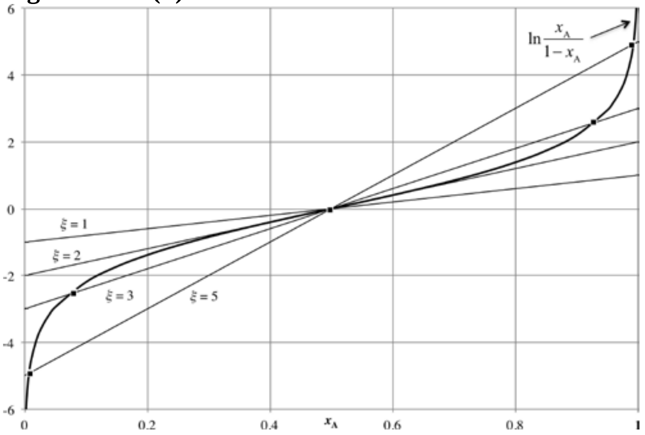
A plot based on this equation is shown in Figure 5C.14(a).

Figure 5C.14(a)



(a) The graphical method described in section 5C.3(b) and illustrated in the main text's Figure 5C.19 is also shown below in Figure 5C.14(b). Here the left-hand side of eqn 5C.7 is plotted as the bold curve, and the lighter lines are the right-hand side for ξ = 1, 2, 3, and 5. Small squares are placed where the curve intersects one of the lines. Note that the curve intersects **every** line at x_A = ½, the composition at which H^E is maximized. For values of $\xi \leq 2$, that is the only point of intersection; for values of $\xi > 2$, there are two additional points of intersection arranged at equal distance from x_A = ½.

Figure 5C.14(b)



The root $x_A = ½$ is unlike the other roots of eqn 5C.7 in several respects. The graphical approach shows that it is a root for all values of ξ. That fact can be confirmed by inspection by substituting $x_A = ½$ into eqn 5C.7, leading to 0 = 0 for any finite value of ξ. For $\xi > 2$, that root of eqn 5C.7 is a maximum in the Gibbs energy, not a minimum, as can be seen in Figure 5C.18 of the main text. However, in the equation obtained by isolating ξ, $x_A = ½$ leads only to $\xi = 2$. That equation yields an indeterminate form for $x_A = ½$, but application of L'Hospital's rule yields

$$\lim_{x\to½}\frac{\ln\dfrac{x_A}{1-x_A}}{2x_A-1}=\lim_{x\to½}\frac{\ln x_A-\ln(1-x_A)}{2x_A-1}=\lim_{x\to½}\frac{x_A^{-1}-(-x_A)^{-1}}{2}=\frac{2+2}{2}=2$$

(b) One method of numerical solution is illustrated by the following cells from a spreadsheet. Set up one column to represent x_A, one for the left-hand side of eqn 5C.7, and one for the right-hand side (with variable). From the cells shown here, it is apparent that $\ln\frac{x_A}{1-x_A}<7(2x_A-1)$ when x_A = 0.9980 or 0.9985, but $\ln\frac{x_A}{1-x_A}>7(2x_A-1)$ when x_A = 0.9990. Therefore, the value of x_A when the two sides were equal lies somewhere between 0.9985 and 0.9990, or, to three decimal places, at 0.999. Therefore, a root of eqn 5C.7 when ξ = 7 is x_A = 0.999.

x	ln(x/(1-x))	7(2x–1)
0.998	6.213	6.972
0.9985	6.501	6.979
0.999	6.907	6.986

5D Phase diagrams of ternary systems

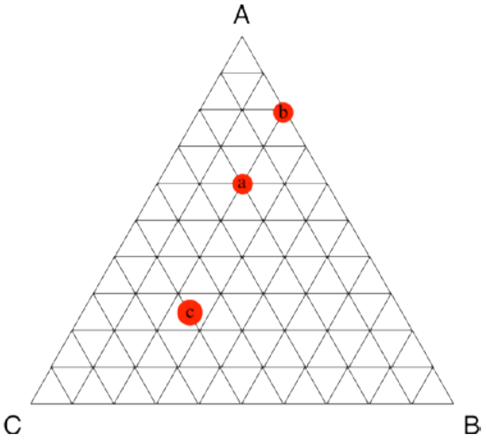
Answers to discussion question

5D.2 The lever rule [5C.6] applies in a ternary system, but with an important caveat. The tie lines along which the rule applies are experimentally determined, not necessarily horizontal lines or lines parallel to any edge of the triangular diagram. Thus the lever rule applies, but as a practical matter it can be used only in the vicinity of plotted tie lines. (By contrast, recall that the lever rule in a binary phase diagram could be applied within a two-phase region simply by drawing a horizontal line to the appropriate phase boundaries.) See Topic 5D.2(a) and Figure 5D.4 of the main text.

Solutions to exercises

5D.1(b) The ordered triples (x_A, x_B, x_C) are plotted in Figure 5D.1. The vertices of the triangular phase diagram are labeled for the component that is pure at that vertex. For example, the top of the diagram is pure A: (1, 0, 0). As a reminder, at the edge opposite a labeled vertex, that component’s mole fraction is zero. For example, the base of the diagram represents compositions $(0, x_B, x_C)$.

Figure 5D.1



5D.2(b) Note that the compositions are given in mass percentages, not mole percentages, so we simply convert to moles before plotting. Assume a convenient sample size, such as 100 g, making the numerical values of the mass percentages equal to masses in grams:

(i) NaCl: $$33\ \text{g} \times \frac{1\ \text{mol}}{58.44\ \text{g}} = 0.56\overline{5}\ \text{mol}$$

$Na_2SO_4 \cdot 10H_2O$: $$33\ \text{g} \times \frac{1\ \text{mol}}{322.21\ \text{g}} = 0.10\overline{2}\ \text{mol}$$

H_2O: $$34\ \text{g} \times \frac{1\ \text{mol}}{18.016\ \text{g}} = 1.8\overline{9}\ \text{mol}$$

To get mole fractions, divide these amounts by the total amount of 2.55 mol:

$$x(\text{NaCl}) = \frac{0.56\overline{5}\ \text{mol}}{2.55\ \text{mol}} = 0.22$$

$x(Na_2SO_4 \cdot 10H_2O) = 0.040$ $x(H_2O) = 0.74$

This composition is point a in Figure 5D.2.

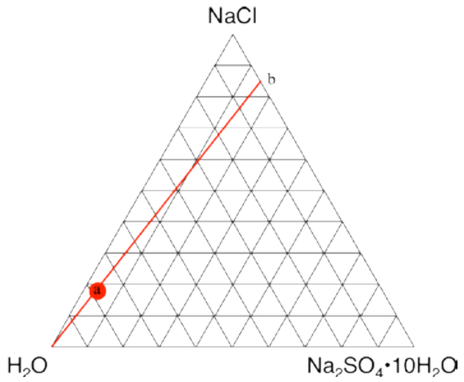
(ii) We want to plot a line representing equal masses of salt with varying amounts of water. One point on that line has no water. Compute the mole fractions that correspond to the amounts of salt computed in part (a) with no water. In that case, the total amount is:

$$n_{\text{total}} = (0.56\overline{5} + 0.10\overline{2})\ \text{mol} = 0.66\overline{7}\ \text{mol}$$

so $x(\text{NaCl}) = \dfrac{0.56\overline{5}\ \text{mol}}{0.66\overline{7}\ \text{mol}} = 0.85$ and $x(Na_2SO_4 \cdot 10H_2O) = 0.15$

Plot this point on the edge opposite the vertex labeled H_2O. The other extreme has the salts in the same proportions, but in amounts negligible compared to that of water, so the other end of this line lies at the vertex labeled H_2O. The line is labeled b on Figure 5D.2, and note that it goes through point (a) as it must.

Figure 5D.2



5D.3(b) First convert to moles and find composition by mole fraction.

H_2O (W): $$55.0\ \text{g} \times \frac{1\ \text{mol}}{18.016\ \text{g}} = 3.05\ \text{mol}$$

$CHCl_3$ (C): $$8.8\ \text{g} \times \frac{1\ \text{mol}}{119.4\ \text{g}} = 0.074\ \text{mol}$$

CH_3COOH (A): $$3.7\ \text{g} \times \frac{1\ \text{mol}}{60.05\ \text{g}} = 0.062\ \text{mol}$$

To get mole fractions, divide these amounts by the total amount of 3.19 mol:

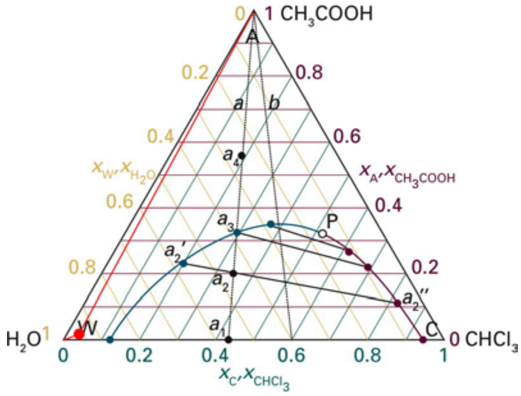
$$x_W = \frac{3.05\ \text{mol}}{3.19\ \text{mol}} = 0.958 \qquad x_C = 0.023 \qquad x_A = 0.019$$

This point is plotted in Figure 5D.3; it is very close to the label W in the original Figure 5D.4 of the main text. $\boxed{\text{One phase}}$ is present, since our point lies outside the phase-boundary arc (to the left of it).

(i) If water is added to our mixture, the composition changes from our point along the very short line connecting it to the vertex labeled W. The system remains in a single phase.

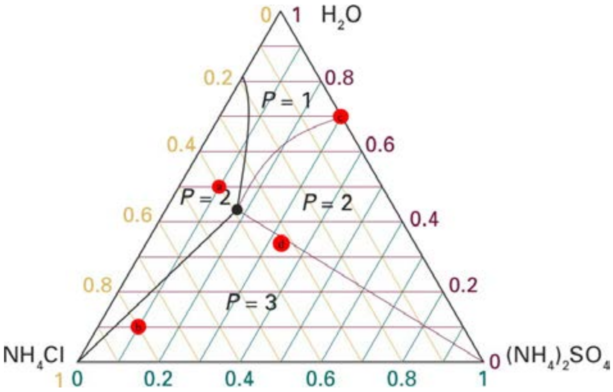
(ii) If acetic acid is added to our mixture, the composition changes from our point along the line connecting it to the vertex labeled A. The system remains in a single phase.

Figure 5D.3



5D.4(b) The phase diagram showing the four given compositions is shown in Figure 5D.4.

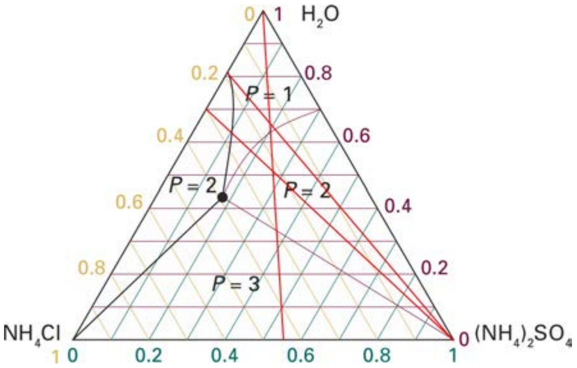
Figure 5D.4



Point (a) is in a $\boxed{\text{two-phase}}$ region and point (b) in a $\boxed{\text{three-phase}}$ region. Point (c) is practically in a $\boxed{\text{single-phase}}$ region; that is, it is on the border between a single-phase and a two-phase region, so there would be a vanishingly small amount of a second phase present. Finally, point (d), for which all three components are present in nearly equal amounts, is in a $\boxed{\text{three-phase region}}$ (although very near the border with a two-phase region).

5D.5(b) **(i)** Note the line in Figure 5D. 5 that runs from the water-NH_4Cl edge near $x(NH_4Cl) = 0.2$ (the point that represents a saturated aqueous solution of NH_4Cl) to the $(NH_4)_2SO_4$ vertex. Traveling along that line from the edge to the vertex represents adding $(NH_4)_2SO_4$ to a saturated aqueous solution of NH_4Cl. Note that it traverses the single-phase region at first. That is, the added $(NH_4)_2SO_4$ dissolves and does not cause NH_4Cl to precipitate out. If one starts with saturated aqueous NH_4Cl with solid NH_4Cl in excess, then the starting point is a bit further down on the water-NH_4Cl edge, for example at $x(NH_4Cl) = 0.3$. Adding $(NH_4)_2SO_4$ to such a solution would take one from that point to the $(NH_4)_2SO_4$ vertex. Initially, the system remains in the two-phase region, but eventually a single-phase region is reached. Note that the line intersects the single-phase region at a higher NH_4Cl-water ratio and even a higher overall $x(NH_4Cl)$ than that of saturated aqueous NH_4Cl. (That is, there is not only more NH_4Cl relative to water at that intersection point, but NH_4Cl is a larger fraction of the saturated **three**-component solution than it was in the saturated **two**-component system of water and NH_4Cl.) So here too, the effect of adding $(NH_4)_2SO_4$ is to make additional NH_4Cl dissolve, at least at first.

Figure 5D.5



(ii) First convert to moles for a convenient sample size, such as 100 g, and find composition by mole fraction.

NH_4Cl: $$25\text{ g}\times\frac{1\text{ mol}}{53.49\text{ g}} = 0.46\overline{7}\text{ mol}$$

$(NH_4)_2SO_4$: $$75\text{ g}\times\frac{1\text{ mol}}{132.15\text{ g}} = 0.56\overline{8}\text{ mol}$$

To get mole fractions, divide these amounts by the total amount of 1.03 mol:

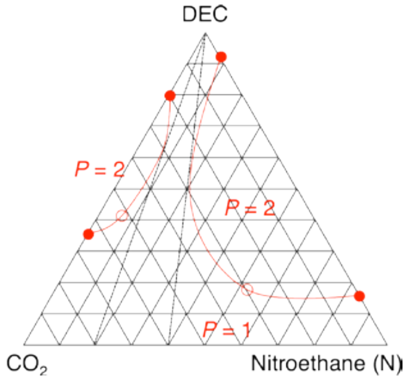
$$x(NH_4Cl) = \frac{0.46\overline{7}\text{ mol}}{1.03\text{ mol}} = 0.45 \qquad x((NH_4)_2SO_4) = 0.55$$

So the system’s starting point is on the baseline of the triangle, and the path it traverses joins the initial point on the baseline to the H_2O vertex. As soon as water is introduced, a third (saturated aqueous) phase is formed in equilibrium with two solid phases. As more water is added, one of the solid phases disappears, and the two remaining phases consist of a saturated aqueous phase and a solid rich in $(NH_4)_2SO_4$. Eventually, as still more water is added, that solid phase also disappears, leaving a single aqueous phase at $x(H_2O) \geq 0.63$.

Solutions to problem

5D.2 **(i)** The phase diagram is shown in Figure 5D.6.

Figure 5D.6



(ii) Lines from the baseline (the CO_2-nitroethane edge) to the DEC vertex represent compositions obtained by adding DEC to a CO_2-nitroethane mixture. Such lines that avoid two-phase regions represent compositions of CO_2 and nitroethane to which addition of DEC can cause no phase separation. The range of such CO_2-nitroethane compositions can be found by drawing lines from the DEC vertex to the baseline **tangent** to the two-phase arcs. On Figure 5.26, the dashed lines are tangent to the two two-phase regions, and they intersect the baseline at $\boxed{x = 0.2 \text{ and } x = 0.4}$ (where x is mole fraction of nitroethane). So binary CO_2-nitroethane compositions between these would show no phase separation if DEC is added to them in any amount. (Keep in mind, though, that the phase boundaries here are sketched, not plotted, so the tangent lines are only approximate.)

5E Activities

Answers to discussion question

5E.2 Raoult’s law [5A.21] assumes that the vapor pressure of a solvent in solution (or of a liquid in a mixture of liquids) is simply its pure-substance vapor pressure multiplied by its mole fraction in the mixture. That is, it assumes that the intermolecular interactions that produce equilibrium between pure liquid and vapor are unchanged except for the fact that only a fraction of the molecules in the liquid are molecules of the species of interest. In effect, Raoult’s law predicts vapor pressure based on pure-liquid vapor pressure and composition (mole fraction):

$$p_A = p_A{}^* x_A$$

For real solutions, on the other hand, we modify Raoult’s law to say, in effect, whatever the vapor pressure ***really*** is, let us use that to define an “effective” mole fraction. Raoult’s law implies

$$\frac{p_A}{p_A^*} = x_A$$

We modify this relationship to define activity:

$$\frac{p_A}{p_A^*} = a_A \quad [5E.2]$$

Solutions to exercises

5E.1(b) Let A = water and B = solute.

$$a_A = \frac{p_A}{p_A^*} \; [5E.2] = \frac{0.02239 \text{ atm}}{0.02308 \text{ atm}} = \boxed{0.9701}$$

$$\gamma_A = \frac{a_A}{x_A} [5E.4] \text{ and } x_A = \frac{n_A}{n_A + n_B}$$

$$n_A = \frac{920 \text{ g}}{18.02 \text{ g mol}^{-1}} = 51.1 \text{ mol} \qquad n_B = \frac{122 \text{ g}}{241 \text{ g mol}^{-1}} = 0.506 \text{ mol}$$

So $x_A = \dfrac{51.1}{51.1 + 0.506} = 0.990$ and $\gamma_A = \dfrac{0.9701}{0.990} = \boxed{0.980}$

5E.2(b) From eqn 1A.8 (partial pressures) and y_A we can compute the partial pressures:

$$y_A = \frac{p_A}{p_A + p_B} = \frac{p_A}{101.3 \text{ kPa}} = 0.314$$

So $p_A = 101.3 \text{ kPa} \times 0.314 = 31.8 \text{ kPa}$

and $p_B = 101.3 \text{ kPa} - 31.8 \text{ kPa} = 69.5 \text{ kPa}$

$$a_A = \frac{p_A}{p_A^*} \; [5E.2] = \frac{31.8 \text{ kPa}}{73.0 \text{ kPa}} = \boxed{0.436} \quad \text{and} \quad a_B = \frac{p_B}{p^*_B} = \frac{69.5 \text{ kPa}}{92.1 \text{ kPa}} = \boxed{0.755}$$

$$\gamma_A = \frac{a_A}{x_A} \; [5E.4] = \frac{0.436}{0.220} = \boxed{1.98} \quad \text{and} \quad \gamma_B = \frac{a_B}{x_B} = \frac{0.755}{0.780} = \boxed{0.967}$$

5E.3(b) The biological standard state is defined as pH 7, which implies $a_{H^+} = 10^{-7}$. All other activities in the biological standard state are unity, just as in the chemical standard state; in the chemical standard state, $a_{H^+} = 1 = 10^0$ as well (which implies pH 0). As a result, the biological standard molar Gibbs function for H^+ is lower than that of the chemical standard by 7 *RT* ln 10 [5E.16], which is equal to 39.96 kJ mol^{-1} at 25°C [*Brief illustration* 5E.3]. For the given reaction, the standard Gibbs energy is

$$\Delta G^{\ominus} = \Delta_f G^{\ominus}(B) + 4\Delta_f G^{\ominus}(H^+) - 2\Delta_f G^{\ominus}(A)$$

The biological standard is

$$\begin{aligned}\Delta G^{\oplus} &= \Delta_f G^{\oplus}(B) + 4\Delta_f G^{\oplus}(H^+) - 2\Delta_f G^{\oplus}(A) \\ &= \Delta_f G^{\ominus}(B) + 4\{\Delta_f G^{\ominus}(H^+) - 39.96 \text{ kJ mol}^{-1}\} - 2\Delta_f G^{\ominus}(A)\end{aligned}$$

Comparing the two, we have

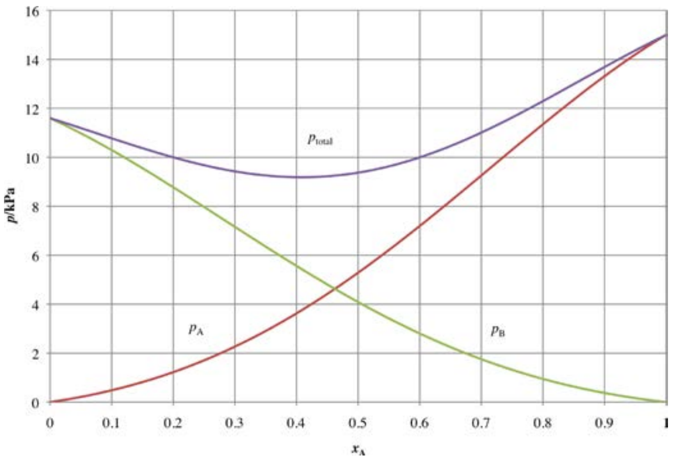
$$\Delta G^{\oplus} - \Delta G^{\ominus} = -4 \times 39.96 \text{ kJ mol}^{-1} = \boxed{-159.84 \text{ kJ mol}^{-1}}$$

5E.4(b) The partial pressures of both components are given by eqn 5E.19

$$p_J = p_J^* x_J e^{\xi(1-x_J)^2}$$

The total pressure is the sum of the two partial pressures. The vapor-pressure diagram is plotted in Figure 5E.1.

Figure 5E.1



Comment. The figure shows that upon adding the other component to either pure component, the vapor pressure falls (as is evident from the fact that the total pressure decreases as one moves from either edge of the graph). This is consistent with the physical interpretation given in Topic 5E.3: negative ξ corresponds to exothermic mixing, reflecting favorable interactions between the components.

Solutions to problems

5E.2 $$\phi = -\frac{x_A}{x_B}\ln a_A = -\frac{\ln a_A}{r} \qquad \text{(a)}$$

Therefore, $\mathrm{d}\phi = -\frac{1}{r}\mathrm{d}\ln a_A + \frac{1}{r^2}\ln a_A \mathrm{d}r$

and $$\mathrm{d}\ln a_A = \frac{1}{r}\ln a_A \mathrm{d}r - r\mathrm{d}\phi . \qquad \text{(b)}$$

Now the Gibbs–Duhem equation [5A.12a], implies

$$x_A\mathrm{d}\mu_A + x_B\mathrm{d}\mu_B = 0 .$$

Since $\mu = \mu^* + RT\ln a$,

$$x_A\,\mathrm{d}\ln a_A + x_B\,\mathrm{d}\ln a_B = 0 .$$

Therefore $\mathrm{d}\ln a_B = -\frac{x_A}{x_B}\mathrm{d}\ln a_A = -\frac{\mathrm{d}\ln a_A}{r} = -\frac{1}{r^2}\ln a_A\ \mathrm{d}r + \mathrm{d}\phi$ [from (b)]

$$= \frac{\phi}{r}\mathrm{d}r + \mathrm{d}\phi \text{ [from (a)]} = \phi\ \mathrm{d}\ln r + \mathrm{d}\phi$$

Subtract d ln r from both sides, to obtain

$$\mathrm{d}\ln\frac{a_B}{r} = (\phi - 1)\mathrm{d}\ln r + \mathrm{d}\phi = \frac{(\phi-1)}{r}\mathrm{d}r + \mathrm{d}\phi .$$

Integrate both sides of the equality from pure A (where $r = 0$) to an arbitrary composition:

$$\int \mathrm{d}\ln\frac{a_B}{r} = \int\frac{(\phi-1)}{r}\mathrm{d}r + \int\mathrm{d}\phi$$

The lower limit of the left-hand integral is:

$$\lim_{r\to 0}\ln\left(\frac{a_B}{r}\right) = \lim_{r\to 0}\ln\left(\frac{\gamma_B x_B}{r}\right) = \lim_{r\to 0}\ln(\gamma_B x_A) = \ln 1 = 0 ,$$

leaving the desired expression

$$\ln\frac{a_B}{r} = \boxed{\phi - \phi(0) + \int_0^r\left(\frac{\phi-1}{r}\right)\mathrm{d}r}$$

5E.4 The partial pressure compared to its pure substance value, according to eqn 5E.19, is

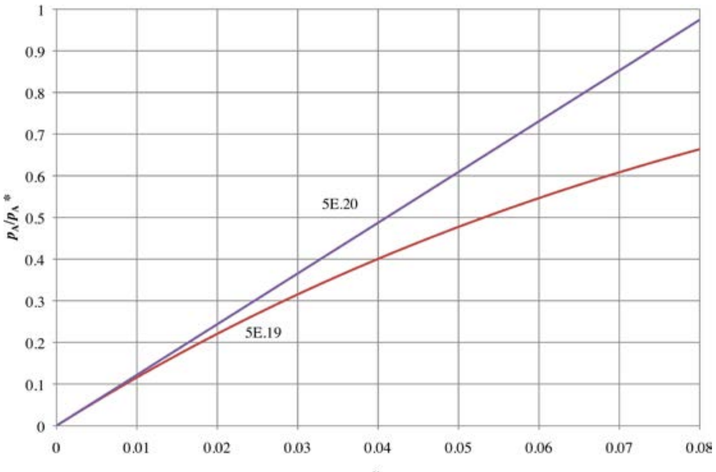
$$p_A / p_A^* = x_A \mathrm{e}^{\xi(1-x_A)^2}$$

For small x_A, this becomes approximately [5E.20]

$$p_A / p_A^* \approx x_A \mathrm{e}^{\xi}$$

Certainly one would not expect this expression to hold over the entire range of compositions. In fact, the two equations differ pretty quickly, particularly for relatively large values of ξ. These two equations are plotted against x_A in Figure 5E.2.

Figure 5E.2



At $x_A > \boxed{0.019}$, eqn 5E.20 exceeds 5E.19 by more than 10 per cent.

5F The activities of ions

Answers to discussion question

5F.2 The Debye-Hückel theory of electrolyte solutions formulates deviations from ideal behavior (essentially, deviations due to electrostatic interactions) in terms of the work of charging the ions. The assumption is that the solute particles would behave ideally if they were not charged, and the difference in chemical potential between real and ideal behavior amounts to the work of putting electrical charges onto the ions. (Recall [Topic 3C.1(e)] that the Gibbs function is associated with maximum non-expansion work.) To find the work of charging, the distribution of ions must be found, and that is done using the shielded Coulomb potential [5F.15], which takes into account the ionic strength of the solution and the dielectric constant of the solvent. Details of the derivation are found in Topic 5F.2 (particularly in the *Justifications*). The Debye-Hückel limiting law [5F.19b] (valid only for dilute solutions because of some truncated series expansions) gives a mean ionic activity coefficient that depends on the charges of the ions involved, the ionic strength of the solution, and on a constant [5F.20] that takes into account solvent properties and temperature.

Solutions to exercises

5F.1(b) The definition of ionic strength is

$$I = \frac{1}{2}\sum_i \left(\frac{b_i}{b^\ominus}\right) z_i^2 \quad [5F.9]$$

and if b is the molal concentration of an M_pX_q salt, the molal concentrations of the ions are

$b_M = p \times b$ and $b_X = q \times b$.

Hence $I = \frac{1}{2}(pz_+^2 + qz_-^2)\left(\frac{b}{b^\ominus}\right)$

For $K_3[Fe(CN)_6]$ $I = \frac{1}{2}(3\times 1^2 + 1\times 3^2)\left(\frac{b}{b^\ominus}\right) = 6\left(\frac{b}{b^\ominus}\right)$

For KCl and NaBr (and any other compound of monovalent ions)

$$I = \frac{1}{2}(1\times 1 + 1\times 1)\left(\frac{b}{b^{\ominus}}\right) = \left(\frac{b}{b^{\ominus}}\right)$$

Thus, for this mixture

$$I = I(\mathrm{K_3[Fe(CN)_6]}) + I(\mathrm{KCl}) + I(\mathrm{NaBr})$$

$$= 6\left(\frac{b(\mathrm{K_3[Fe(CN)_6]})}{b^{\ominus}}\right) + \frac{b(\mathrm{KCl})}{b^{\ominus}} + \frac{b(\mathrm{NaBr})}{b^{\ominus}}$$

$$= (6)\times(0.040) + (0.030) + (0.050) = \boxed{0.320}$$

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 [5F.9].

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.

5F.2(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 5F.1(b).) Therefore, the ionic strengths of the added salts must be 0.890.

(i) 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

$$(0.500\ \mathrm{kg}) \times (0.890\ \mathrm{mol\ kg^{-1}}) \times (101.11\ \mathrm{g\ mol^{-1}}) = \boxed{45.0\ \mathrm{g}}\ .$$

(ii) For $Ba(NO_3)_2$ $\quad I = \frac{1}{2}(1\times 2^2 + 2\times 1^2)\left(\frac{b}{b^{\ominus}}\right)$ [5F.9] $= 3\left(\frac{b}{b^{\ominus}}\right)$

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

$$(0.500\ \mathrm{kg}) \times (0.297\ \mathrm{mol\ kg^{-1}}) \times (261.32\ \mathrm{g\ mol^{-1}}) = \boxed{38.8\ \mathrm{g}}\ .$$

5F.3(b) The solution is dilute, so use the Debye–Hückel limiting law.

$\log \gamma_\pm = -|z_+z_-|\, AI^{1/2}$ [5F.8]

$$I = \frac{1}{2}\sum_i \left(\frac{b_i}{b^{\ominus}}\right) z_i^2 [5F.9] = \frac{1}{2}\{(0.020\times 1^2) + (0.020\times 1^2) + (0.035\times 2^2) + (2\times 0.035\times 1^2)\}$$

$$= 0.125$$

For NaCl:

$\log \gamma_\pm = -1\times 1\times 0.509\times(0.125)^{1/2} = -0.180$ so $\gamma_\pm = \boxed{0.66}$.

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?

5F.4(b) The extended Debye–Hückel law [5F.11a] 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 / (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 $B = \boxed{1.3}$.

Solutions to problem

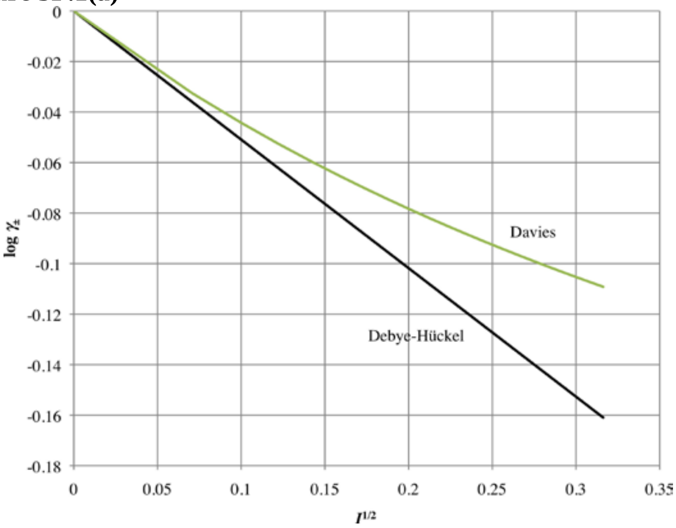
5F.2 Specialized to 1,1 electrolytes, the Davies equation with $C = 0$ and Debye-Hückel limiting law are, respectively

$$\log \gamma_\pm = -\frac{AI^{1/2}}{1+BI^{1/2}} \text{ [5F.11b]} \qquad \text{and}$$

$$\log \gamma_\pm = -0.509 I^{1/2} \text{[5F.8]} = -0.509 \left(\frac{b}{b^\ominus}\right)^{1/2} \text{ [5F.9]}$$

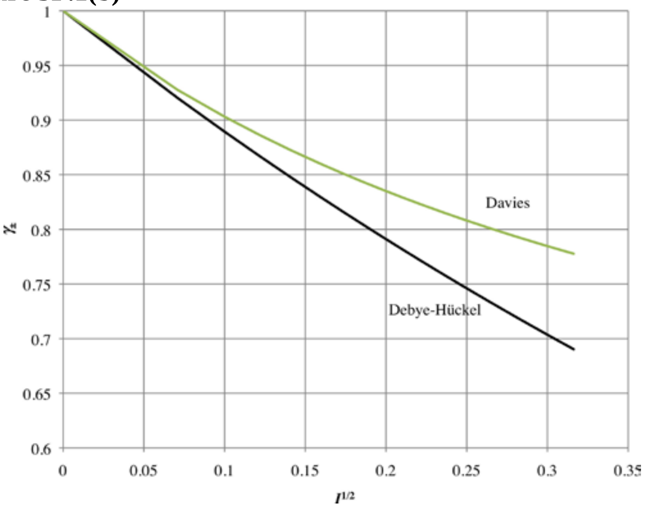
Figure 5F.1(a) shows a plot of log $\gamma_\pm$ vs. $I^{1/2}$ for both equations.

Figure 5F.1(a)



It is clear that the values plotted differ by about 50% at the right side of the figure; however, note that the values plotted are log $\gamma_\pm$ and not $\gamma_\pm$. Figure 5F.1(b) shows a plot of $\gamma_\pm$ vs. $I^{1/2}$ for both equations. Toward the right side of this graph, one can see that the values plotted differ by about 10%. To be exact, for $I < \boxed{0.086}$, the limiting law predicts activity coefficients within 10% of those predicted by the extended law.

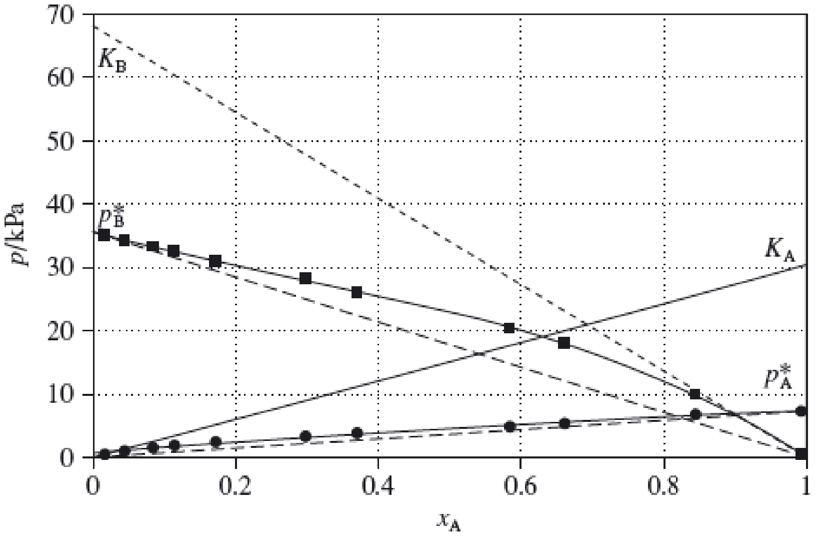
Figure 5F.1(b)



Integrated activities

5.2 The data are plotted in Figure I5.1. The dotted lines correspond to Henry's law vapour pressures and the dashed lines to Raoult's law; the solid curves represent the experimental data.

Figure I5.1



On a Raoult's law basis, $a = \frac{p}{p^*}$ [5E.2] and $a = \gamma x$ [5E.4], so $\gamma = \frac{p}{xp^*}$. On a Henry's law basis, $a = \frac{p}{K}$ [5E.10], so $\gamma = \frac{p}{xK}$. The vapour pressures of the pure components are not given in the table of data, so we extrapolate the experimental data to obtain p^*_A = 7.3 kPa and p^*_B = 35.6 kPa. The Henry's law constant for benzene is determined by extrapolating the low-B data to x_B = 1, *i.e.*, to x_A = 0. (The Henry's law constant for acetic acid can also be determined by extrapolating the low-A data to x_A = 1) The values obtained are K_B = 68.1 kPa and K_A = 30.3 kPa. Then draw up the following table based on the partial pressures given in the data.

x_A	0.016	0.0439	0.0835	0.1138	0.1714
p_A/kPa	0.484	0.967	1.535	1.89	2.45
p_A/kPa	35.05	34.29	33.28	32.64	30.9
a_A(R)	0.066	0.132	0.210	0.259	0.336 [p_A/p^*_A]
a_B(R)	0.985	0.963	0.935	0.917	0.868 [p_B/p^*_B]
γ_A(R)	4.144	3.017	2.518	2.275	1.958 [$p_A/x_Ap^*_A$]
γ_B(R)	1.001	1.007	1.020	1.035	1.048 [$p_B/x_Bp^*_B$]
a_B(H)	0.515	0.504	0.489	0.479	0.454 [p_B/K_B]
γ_B(H)	0.523	0.527	0.533	0.541	0.548 [p_B/x_BK_B]

x_A	0.2973	0.3696	0.5834	0.6604	0.8437	0.9931
p_A/kPa	3.31	3.83	4.84	5.36	6.76	7.29
p_A/kPa	28.16	26.08	20.42	18.01	10	0.47
a_A(R)	0.453	0.525	0.663	0.734	0.926	0.999
a_B(R)	0.791	0.733	0.574	0.506	0.281	0.013
γ_A(R)	1.525	1.420	1.136	1.112	1.098	1.006
γ_B(R)	1.126	1.162	1.377	1.490	1.797	1.913
a_B(H)	0.414	0.383	0.300	0.264	0.147	0.007
γ_B(H)	0.588	0.607	0.720	0.779	0.939	1.000

G^E is defined [5B.5] as

$$G^E = \Delta_{mix}G - \Delta_{mix}G^{ideal} = nRT(x_A \ln a_A + x_B \ln a_B) - nRT(x_A \ln x_A + x_B \ln x_B)$$

and with $a = \gamma x$

$$G^E = nRT(x_A \ln \gamma_A + x_B \ln \gamma_B)\ .$$

For n = 1, we can draw up the following table from the information above and

$$RT = 8.3145\ \text{J mol}^{-1}\ \text{K}^{-1} \times 323\ \text{K} = 2.69\times10^3\ \text{J mol}^{-1} = 2.69\ \text{kJ mol}^{-1}.$$

x_A	0.016	0.0439	0.0835	0.1138	0.1714
x_A ln γ_A	0.023	0.0485	0.077	0.094	0.115
x_b ln γ_B(R)	0.001	0.0071	0.018	0.030	0.038

G^E / kJ mol^{-1}	0.0626	0.1492	0.256	0.332	0.413

x_A	0.2973	0.3696	0.5834	0.6604	0.8437	0.9931
$x_A \ln \gamma_A$	0.125	0.129	0.075	0.070	0.079	0.006
$x_b \ln \gamma_B$(R)	0.083	0.095	0.133	0.135	0.092	0.004
G^E / kJ mol^{-1}	0.560	0.602	0.558	0.551	0.457	0.027

Question. In this problem both A and B were treated as solvents, but only B as a solute. Extend the table by including a row for γ_A(H).

5.4 $p_A = a_A p_A^*$ [5E.2] $= \gamma_A x_A p_A^*$ [5E.4]

so $$\gamma_A = \frac{p_A}{x_A p_A^*} = \frac{y_A p}{x_A p_A^*}$$

Sample calculation at 80 K:

$$\gamma(O_2) = \frac{0.11 \times 100\,\text{kPa}}{0.34 \times 225\,\text{Torr}} \times \left(\frac{760\,\text{Torr}}{101.325\,\text{kPa}}\right) = 1.079$$

Summary

T/K	77.3	78	80	82	84	86	88	90.2
$\gamma(O_2)$	—	0.877	1.079	1.039	0.995	0.993	0.990	0.987

To within the experimental uncertainties the solution appears to be ideal ($\gamma = 1$). The low value at 78 K may be caused by nonideality; however, the larger relative uncertainty in $y(O_2)$ is probably the origin of the low value.

A temperature–composition diagram is shown in Figure I5.2(a). The near ideality of this solution is, however, best shown in the pressure–composition diagram of Figure I5.2(b). The liquid line is essentially a straight line as predicted for an ideal solution.

Figure I5.2(a)

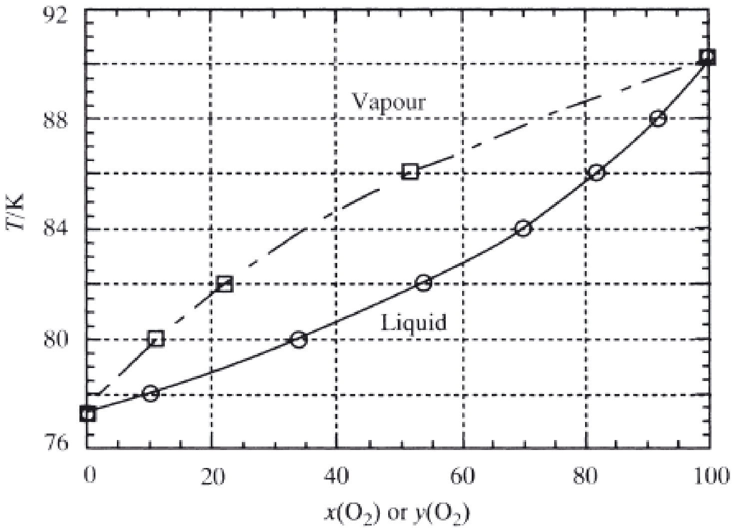
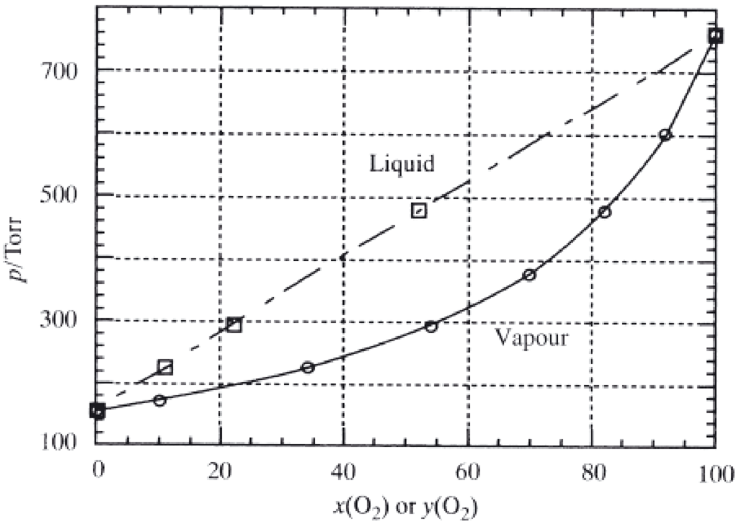


Figure I5.2(b)



5.6 The Gibbs-Duhem equation applies to any partial molar quantity, so we start, as in Example 5A.2, with

$$n_A \, dV_A + n_B \, dV_B = 0$$

Hence $\quad dV_B = -\frac{n_A}{n_B} dV_A$

Therefore, by integration,

$$V_B(x_A, x_B) - V_B(0,1) = \int_{V_B(0,1)}^{V_B(x_A,x_B)} dV_B = -\int_{V_A(0,1)}^{V_A(x_A,x_B)} \frac{n_A}{n_B} dV_A = -\int_{V_A(0,1)}^{V_A(x_A,x_B)} \frac{n x_A \, dV_A}{n(1-x_A)}$$

The notation V_B^* means the molar volume of pure B, which is the same as the partial molar volume of B when $x_B = 1$. Therefore,

$$V_B(x_A, x_B) = V_B^* - \int_{V_A(0,1)}^{V_A(x_A,x_B)} \frac{x_A \, dV_A}{1-x_A} .$$

We must now plot $x_A/(1 - x_A)$ against V_A and estimate the integral. That means we must first find the partial molar volumes of chloroform (V_A) that corresponds to various chloroform mole fractions (x_A). At constant temperature and pressure,

$$V_A = \left(\frac{\partial V}{\partial n_A}\right)_{n_B} [5A.1] = \left(\frac{\partial (nV_m)}{\partial (nx_A)}\right)_{n_B} \quad \text{where } n = n_A + n_B \text{ is the total number of moles.}$$

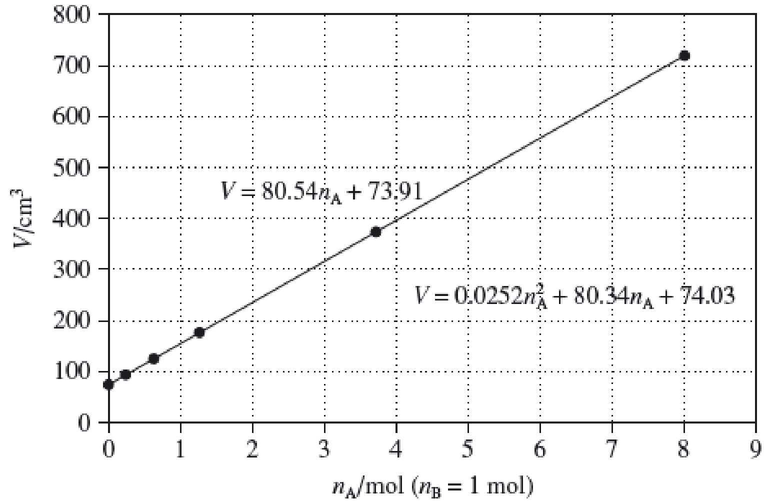
Thus, V_A is the tangent line to the curve of a plot of V vs. n_A for a constant value of n_B. For convenience, let $n_B = 1$ mol. Then we can draw up a table of V, n, and n_A values using the V_m, x_A data given and the relationship

$$x_A = \frac{n_A}{n} = \frac{n_A}{n_A + 1 \text{ mol}} .$$

Solving for n_A yields $\quad n_A = \frac{x_A}{1-x_A} \times 1 \text{ mol}$

x_A	0	0.194	0.385	0.559	0.788	0.889	1
$V_m/(\text{cm}^3\ \text{mol}^{-1})$	73.99	75.29	76.5	77.55	79.08	79.82	80.67
n_A/mol	0	0.241	0.626	1.268	3.717	8.009	
n/mol	1	1.241	1.626	2.268	4.717	9.009	
V/cm^3	73.99	93.41	124.4	175.9	373.0	719.1	

Figure I5.3(a)



In Figure I5.3(a), we plot V against n_A. Both linear and quadratic fits to the data are shown. The data fit a straight line quite well; however, the slope of a straight line is constant, which would imply V_A is constant (at 80.54 cm^3 mol^{-1}) over this range of compositions. We require some variation in V_A, so we use the quadratic fit,

$$V/\text{cm}^3 = 0.0252(n_A/\text{mol})^2 + 80.34(n_A/\text{mol}) + 74.03\ ,$$

which leads to

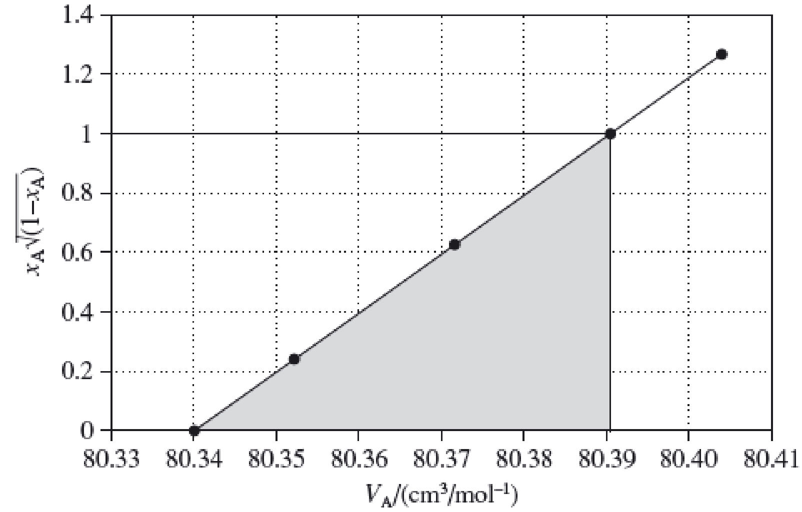
$$V_A = \left(\frac{\partial V}{\partial n_A}\right)_{n_B} = \{2 \times 0.0252(n_A\ /\ \text{mol}) + 80.34\}\ \text{cm}^3\ \text{mol}^{-1}$$

Finally, we can draw up the table, including $x_A = 0.500$

x_A	0	0.194	0.385	0.500	0.559	0.788	0.889
V_A/(cm^3 mol^{-1})	80.34	80.35	80.37	80.39	80.40	80.53	80.74

For the present purpose we integrate up to $V_A(0.5,0.5) = 84.39$ cm^3 mol^{-1}.

Figure I5.3(b)



The points are plotted in Figure I5.3(b), and the area required is 0.025 cm^3 mol^{-1}. Hence,

$$V_B(0.5,0.5) = 73.99\ \text{cm}^3\ \text{mol}^{-1} - 0.025\ \text{cm}^3\ \text{mol}^{-1} = \boxed{73.96\ \text{cm}^3\ \text{mol}^{-1}}.$$

Comment. The integral derived at the start of this problem is most useful for computing the partial molar quantity of one component given that of the other. In this case, the data given were overall molar volumes, from which we had to compute V_A before we could apply the integral to compute V_B. In such a case, it would have been easier to compute V_B directly in the same way we computed V_A.

5.8 In this case it is convenient to rewrite the Henry's law expression as

$$\text{mass of N}_2 = p_{N_2} \times \text{ mass of H}_2\text{O } \times K_{N_2}$$

(1) At $p_{N_2} = 0.78 \times 4.0\ \text{atm} = 3.1\ \text{atm}$

$$\text{mass of } N_2 = 3.1\ \text{atm} \times 100\ \text{g } H_2O\ \times 0.18\ \mu\text{g } N_2 / (\text{g } H_2O\ \text{atm}) = \boxed{56\ \mu\text{g } N_2}$$

(2) At $p_{N_2} =\ 0.78$ atm, mass of $N_2\ = \boxed{14\ \mu\text{g } N_2}$

(3) In fatty tissue the increase in N_2 concentration from 1 atm to 4 atm is

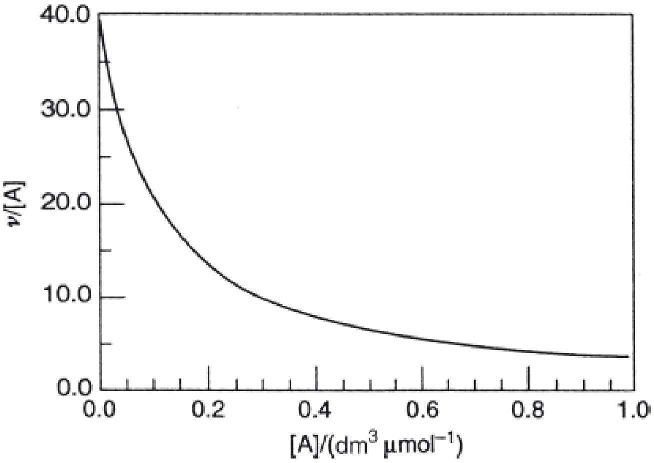
$$4 \times (56 - 14)\mu\text{g } N_2 = \boxed{1.7{\times}10^2\ \mu\text{g } N_2}$$

5.10 **(a)** The sum has just one term, so

$$\frac{v}{[A]_{out}} = \frac{NK}{1 + K[A]_{out}} = \frac{4.0 \times 10^7\ \text{dm}^3\ \text{mol}^{-1}}{1 + (1.0 \times 10^7\ \text{dm}^3\ \text{mol}^{-1})[A]_{out}} = \frac{40\ \text{dm}^3\ \mu\text{mol}^{-1}}{1 + (10\ \text{dm}^3\ \mu\text{mol}^{-1})[A]_{out}}$$

The plot is shown in Figure I5.4(a).

Figure I5.4(a)



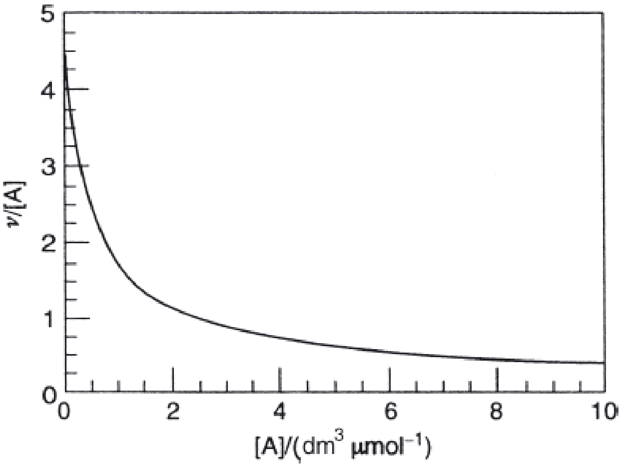
(b) There are two terms in the sum here

$$\frac{v}{[A]_{out}} = \frac{4 \times (1 \times 10^5\ \text{dm}^3\ \text{mol}^{-1})}{1 + (1 \times 10^5\ \text{dm}^3\ \text{mol}^{-1}) \times [A]_{out}} + \frac{2 \times (2 \times 10^6\ \text{dm}^3\ \text{mol}^{-1})}{1 + (2 \times 10^6\ \text{dm}^3\ \text{mol}^{-1}) \times [A]_{out}}$$

$$= \frac{0.4\ \text{dm}^3\ \mu\text{mol}^{-1}}{1 + (0.1\ \text{dm}^3\ \mu\text{mol}^{-1}) \times [A]_{out}} + \frac{4\ \text{dm}^3\ \mu\text{mol}^{-1}}{1 + (2\ \text{dm}^3\ \mu\text{mol}^{-1}) \times [A]_{out}}$$

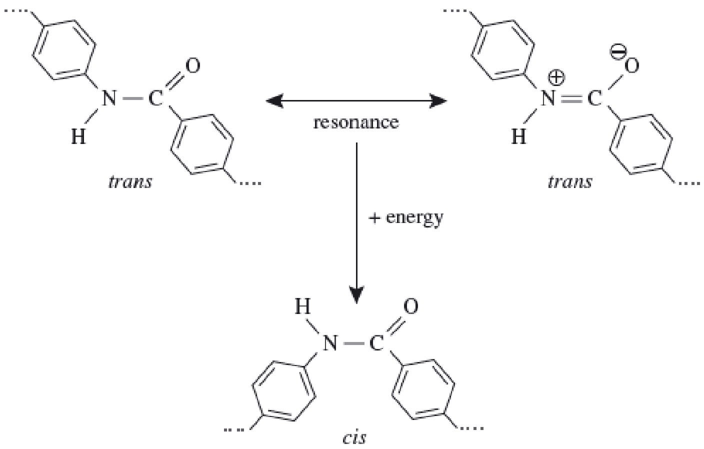
The plot is shown in Figure I5.4(b).

Figure I5.4(b)



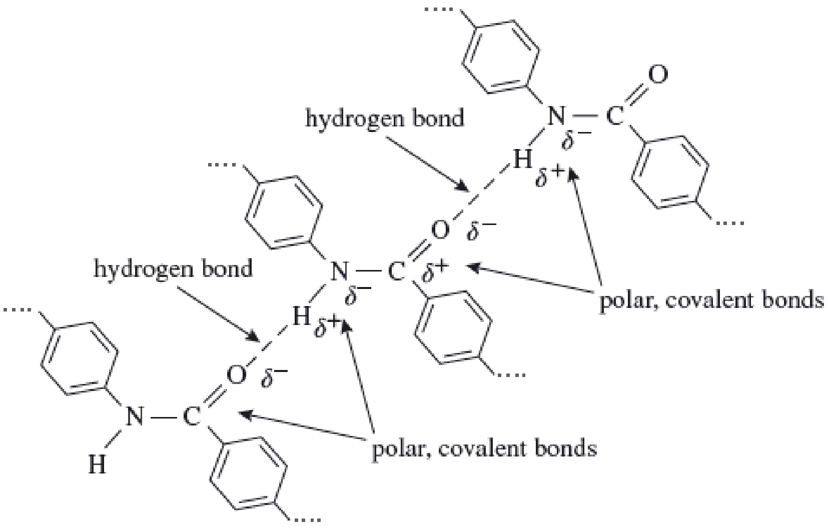
5.12 Kevlar is a polyaromatic amide. Phenyl groups provide aromaticity and a planar, rigid structure. The amide group is expected to be like the peptide bond that connects amino acid residues within protein molecules. This group is also planar because resonance produces partial double bond character 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 I5.5(a).

Figure I5.5(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 I5.5(b).

Figure I5.5(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

6A The equilibrium constant

Answers to discussion questions

6A.2 Eqn 5E.9, in the form of the following expression, provides the general definition of the **activity** for species J, a_J: $\mu_J = \mu_J^{\ominus} + RT\ln a_J$ [5E.9] 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 eqns 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 upon T alone; $p^{\ominus} \equiv 1$ bar.)
Real Gas: $a_J = \gamma_J\, p_J/p^{\ominus}$ ($\mu_J^{\ominus}$ depends upon T alone.)
Ideal solutions: $a_J = x_J$
Ideal-dilute solutions: $a_B = [\mathrm{B}]/c^{\ominus}$ where $c^{\ominus} \equiv 1\ \mathrm{mol\ dm^{-3}}$
Solvent A of a non-ideal solution: $a_A = \gamma_A x_A$
Solute B of a non-ideal solution: $a_B = \gamma_B[\mathrm{B}]/c^{\ominus}$

Solutions to exercises

6A.1(b) $2\,\mathrm{A} \rightarrow \mathrm{B}$

$n_J = n_J(0) + \nu_J\Delta\xi$ where ξ is the extent of reaction; ν_J is negative for reactants and positive for products.

$n_A = 1.75\ \mathrm{mol} - 2\times(0.30\ \mathrm{mol}) = \boxed{1.15\ \mathrm{mol}}$

$n_B = 0.12\ \mathrm{mol} + 1\times(0.30\ \mathrm{mol}) = \boxed{0.42\ \mathrm{mol}}$

6A.2(b) $2\,\mathrm{A} \rightarrow \mathrm{B}$ $\quad \Delta_r G = -2.41\ \mathrm{kJ\ mol^{-1}}$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} \quad [6\mathrm{A}.1]$$

With the approximation that $\left(\frac{\partial G}{\partial \xi}\right)_{p,T} \simeq \frac{\Delta G}{\Delta \xi}$, which is valid when $\Delta\xi$ is very small, we find that

$$\Delta G \simeq \Delta_r G \times \Delta\xi$$
$$\simeq \left(-2.41\ \mathrm{kJ\ mol^{-1}}\right)\times\left(+0.051\ \mathrm{mol}\right) = \boxed{-0.12\ \mathrm{kJ}}$$

6A.3(b) $2\,\mathrm{NO_2(g)} \rightarrow \mathrm{N_2O_4(g)}$ $\quad \Delta_r G^{\ominus} = -4.73\ \mathrm{kJ\ mol^{-1}}$

$$\Delta_r G = \Delta_r G^{\ominus} + RT \ln Q \quad [6A.10]$$
$$= \left(-4.73 \text{ kJ mol}^{-1}\right) + \left(2.4790 \text{ kJ mol}^{-1}\right) \times \ln Q \qquad \text{at 298.15 K}$$

The above equation is used to calculate $\Delta_r G$ values at the given Q values in the following table.

Part	Q	ln$Q$	$\Delta_r G$ / kJ mol^{-1}
(i)	0.10	−2.303	−10.44
(ii)	1.0	0	−4.73
(iii)	10	2.303	+0.979
(iv)	100	4.605	+6.69

The above equation also indicates that a plot of ln$Q$ against $\Delta_r G$ should be linear so points ii and iii, which straddle $\Delta_r G = 0$, can be used to perform a linear interpolation to find K from our equilibrium knowledge that ln$Q$ = ln$Q_{\text{equilibrium}}$ = ln$K$ when $\Delta_r G = 0$. Performing the linear interpolation:

$$\ln Q = \ln Q_{\text{ii}} + \left(\frac{\ln Q_{\text{iii}} - \ln Q_{\text{ii}}}{\Delta_r G_{\text{iii}} - \Delta_r G_{\text{ii}}}\right) \times \left(\Delta_r G - \Delta_r G_{\text{ii}}\right)$$
$$= 0 + \left(\frac{2.303 - 0}{0.979 - (-4.73)}\right) \times \left(\frac{\Delta_r G}{\text{kJ mol}^{-1}} - (-4.73)\right)$$
$$= 0.4034 \times \left(\frac{\Delta_r G}{\text{kJ mol}^{-1}} + 4.73\right)$$

Thus,

$$\ln K = 0.4034 \times (0 + 4.73)$$
$$= 1.908$$
$$K = \mathrm{e}^{1.908} = \boxed{6.74} \text{ from a two-point interpolation}$$

The two-point interpolation is in agreement with the result given by eqn 6A.8:

$$K = \mathrm{e}^{-\Delta_r G^{\ominus}/RT} \quad [6A.8]$$
$$= \mathrm{e}^{-\left(-4.73\times 10^{3} \text{ J mol}^{-1}\right)/\left\{\left(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}\right)\times(298.15 \text{ K})\right\}}$$
$$= 6.74$$

6A.4(b) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ T = 298.15 K, p = 1 bar = $p^{\ominus}$, α = 0.201 at equilibrium

We draw up the following equilibrium table (Example 6A.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	$\dfrac{(1-\alpha)p}{1+\alpha}$	$\dfrac{2\alpha p}{1+\alpha}$

$$K = \left(\prod_{\text{J}} a_{\text{J}}^{\nu_{\text{J}}}\right)_{\text{equilibrium}} [6A.13] = \left(\prod_{\text{J}} \left(p_{\text{J}} / p^{\ominus}\right)^{\nu_{\text{J}}}\right)_{\text{equilibrium}} \qquad \text{(perfect gas assumption)}$$

$$= \frac{\left(p_{NO_2} / p^{\ominus}\right)^2}{p_{N_2O_4} / p^{\ominus}} = \frac{p_{NO_2}{}^2}{p_{N_2O_4}\, p^{\ominus}} = \frac{\left(\dfrac{2\alpha p}{1+\alpha}\right)^2}{\left(\dfrac{(1-\alpha)p}{1+\alpha}\right) p^{\ominus}}$$

$$= \frac{4p}{p^{\ominus}}\left\{\frac{\alpha^2}{(1-\alpha)\times(1+\alpha)}\right\} = 4\left\{\frac{(0.201)^2}{(1-0.201)\times(1+0.201)}\right\}$$

$$= \boxed{0.168}$$

6A.5(b) (i) $Br_2(g) \rightleftharpoons 2\ Br(g)$ $\quad T = 1600\ K$, $p = 1\ \text{bar} = p^{\ominus}$, $\alpha = 0.24$ at equilibrium

We draw up the following equilibrium table (Example 6A.2).

	$Br_2(g)$	$Br(g)$
Amount at equilibrium	$(1-\alpha)n$	$2\alpha n$
Mole fraction	$\frac{1-\alpha}{1+\alpha}$	$\frac{2\alpha}{1+\alpha}$
Partial pressure	$\frac{(1-\alpha)p}{1+\alpha}$	$\frac{2\alpha p}{1+\alpha}$

$$K = \left(\prod_J a_J^{\nu_J}\right)_{\text{equilibrium}} [6A.13] = \left(\prod_J \left(p_J / p^{\ominus}\right)^{\nu_J}\right)_{\text{equilibrium}} \quad \text{(perfect gas assumption)}$$

$$= \frac{\left(p_{Br}/p^{\ominus}\right)^2}{p_{Br_2}/p^{\ominus}} = \frac{p_{Br}{}^2}{p_{Br_2}\,p^{\ominus}} = \frac{\left(\frac{2\alpha p}{1+\alpha}\right)^2}{\left(\frac{(1-\alpha)p}{1+\alpha}\right)p^{\ominus}}$$

$$= \frac{4p}{p^{\ominus}}\left\{\frac{\alpha^2}{(1-\alpha)\times(1+\alpha)}\right\} = 4\left\{\frac{(0.24)^2}{(1-0.24)\times(1+0.24)}\right\}$$

$$= \boxed{0.24\bar{4}} \text{ at 1600 K}$$

(ii) $$\ln K_2 = \ln K_1 - \frac{\Delta_r H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad [6A.22]$$

$$\ln K_{2000\ K} = \ln K_{1600\ K} - \frac{\Delta_r H^{\ominus}}{R}\left(\frac{1}{2000\ K} - \frac{1}{1600\ K}\right)$$

$$= \ln\left(0.24\bar{4}\right) - \left(\frac{+112\times10^3\ J\ mol^{-1}}{8.3145\ J\ K^{-1}\ mol^{-1}}\right)\times\left(\frac{1}{2000\ K} - \frac{1}{1600\ K}\right) = 0.27\bar{3}$$

$$K_{2000\ K} = e^{0.27\bar{3}} = \boxed{1.3}$$

As expected, the temperature increase causes a shift to the right when the reaction is endothermic.

6A.6(b) $CH_4(g) + 3\ Cl_2(g) \rightleftharpoons CHCl_3(l) + 3\ HCl(g)$

(i) Using data tables of the text *Resource section* at 25°C, we find

$$\Delta_r G^{\ominus} = \Delta_f G^{\ominus}(CHCl_3, l) + 3\ \Delta_f G^{\ominus}(HCl, g) - \Delta_f G^{\ominus}(CH_4, g)$$

$$= (-73.66\ KJ\ mol^{-1}) + (3)\times(-95.30\ KJ\ mol^{-1}) - (-50.72\ KJ\ mol^{-1})$$

$$= \boxed{-308.84\ kJ\ mol^{-1}}$$

$$\Delta_r H^{\ominus} = \Delta_f H^{\ominus}(CHCl_3, l) + 3\ \Delta_f H^{\ominus}(HCl, g) - \Delta_f H^{\ominus}(CH_4, g)$$

$$= (-134.47\ kJ\ mol^{-1}) + (3)\times(-92.31\ kJ\ mol^{-1}) - (-74.81\ kJ\ mol^{-1})$$

$$= -336.59\ kJ\ mol^{-1} \quad \text{[Used in part (ii)]}$$

$$\ln K = \frac{-\Delta_r G^{\ominus}}{RT}[6A.14] = \frac{-\left(-308.84\times10^{3}\,\mathrm{J\,mol^{-1}}\right)}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298.15\,\mathrm{K})} = 124.6$$

$$K = \mathrm{e}^{124.6} = \boxed{1.30\times10^{54}}$$

(ii) $$\ln K_2 = \ln K_1 - \frac{\Delta_r H^{\ominus}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \quad [6A.22]$$

$$\ln K_{50°\mathrm{C}} = \ln K_{25°\mathrm{C}} - \frac{\Delta_r H^{\ominus}}{R}\left(\frac{1}{323.15\ \mathrm{K}}-\frac{1}{298.15\ \mathrm{K}}\right)$$

$$= \ln\left(1.30\times10^{54}\right) - \left(\frac{-336.59\times10^{3}\ \mathrm{J\ mol^{-1}}}{8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}}\right)\times\left(\frac{1}{323.15\ \mathrm{K}}-\frac{1}{298.15\ \mathrm{K}}\right) = 114.\bar{1}$$

$$K_{50°\mathrm{C}} = \mathrm{e}^{114.\bar{1}} = \boxed{3.57\times10^{49}}$$

As expected, the temperature increase causes a shift to the left when the reaction is exothermic.

$$\Delta_r G^{\ominus} = -RT\ln K \quad [6A.14]$$

$$\Delta_r G^{\ominus}_{50°\mathrm{C}} = -\left(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}\right)\times\left(323.15\ \mathrm{K}\right)\ln\left(3.57\times10^{49}\right) = \boxed{-307\ \mathrm{kJ\ mol^{-1}}}$$

6A.7(b) $3\ N_2(g) + H_2(g) \rightarrow 2\ HN_3(g)$ For this gas phase reaction $\Delta\nu = \sum_{\mathrm{J}} \nu_{\mathrm{J}} = 2-3-1=-2$

$$K = \left(\prod_{\mathrm{J}} a_{\mathrm{J}}^{\nu_{\mathrm{J}}}\right)_{\text{equilibrium}} [6A.13] = \left(\prod_{\mathrm{J}}\left(\gamma_{\mathrm{J}} p_{\mathrm{J}}/p^{\ominus}\right)^{\nu_{\mathrm{J}}}\right)_{\text{equilibrium}} = \left(\prod_{\mathrm{J}}\gamma_{\mathrm{J}}^{\nu_{\mathrm{J}}}\right)_{\text{equilibrium}}\left(\prod_{\mathrm{J}}\left(p_{\mathrm{J}}/p^{\ominus}\right)^{\nu_{\mathrm{J}}}\right)_{\text{equilibrium}}$$

$$= K_\gamma K_p \quad \text{where} \quad K_\gamma = \left(\prod_{\mathrm{J}}\gamma_{\mathrm{J}}^{\nu_{\mathrm{J}}}\right)_{\text{equilibrium}} \quad \text{and } K_p = \left(\prod_{\mathrm{J}}\left(p_{\mathrm{J}}/p^{\ominus}\right)^{\nu_{\mathrm{J}}}\right)_{\text{equilibrium}}$$

Let us assume that the gases are perfect gases. Then, the activity coefficients equal 1 and $K_\gamma = 1$. Additionally, $p_{\mathrm{J}} = n_{\mathrm{J}}RT/V = [\mathrm{J}]RT$. Substitution gives

$$K = K_p = \left(\prod_{\mathrm{J}}\left([\mathrm{J}]RT/p^{\ominus}\right)^{\nu_{\mathrm{J}}}\right)_{\text{equilibrium}} = \left(\prod_{\mathrm{J}}\left([\mathrm{J}]/c^{\ominus}\right)^{\nu_{\mathrm{J}}}\right)_{\text{equilibrium}}\left(\prod_{\mathrm{J}}\left(c^{\ominus}RT/p^{\ominus}\right)^{\nu_{\mathrm{J}}}\right)_{\text{equilibrium}}$$

$$= K_c\left(c^{\ominus}RT/p^{\ominus}\right)^{\Delta\nu} \quad \text{where} \quad K_c = \left(\prod_{\mathrm{J}}\left([\mathrm{J}]/c^{\ominus}\right)^{\nu_{\mathrm{J}}}\right)_{\text{equilibrium}}$$

$$K = K_c\times\left(c^{\ominus}RT/p^{\ominus}\right)^{-2} \qquad \text{because } \Delta\nu = -2 \text{ for this reaction}$$

Since $c^{\ominus}R/p^{\ominus} = 0.0831451\ \mathrm{K^{-1}}$, this expression may be written in the form

$$\boxed{K = \left(144.653\ \mathrm{K}^2\right)\times K_c/T^2}$$

Anhydrous hydrogen azide, HN_3, boils at 36°C and decomposes explosively. A dilute solution can be handled safely.

6A.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	$0.178\bar{2}$	$0.030\bar{9}$	$0.116\bar{3}$	$0.674\bar{5}$	$0.999\bar{9}$

(i) Mole fractions are given in the table.

(ii) $$K_x = \prod_{\mathrm{J}} x_{\mathrm{J}}^{\nu_{\mathrm{J}}}$$

$$K_x=\frac{(0.116\overline{3})\times(0.674\overline{5})^2}{(0.178\overline{2})\times(0.030\overline{9})}=\boxed{9.61}$$

(iii) $p_J=x_Jp$. Assuming the gases are perfect, $a_J=p_J/p^{\ominus}$, so

$$K=\frac{(p_C/p^{\ominus})\times(p_D/p^{\ominus})^2}{(p_A/p^{\ominus})\times(p_B/p^{\ominus})}=K_x\left(\frac{p}{p^{\ominus}}\right)=K_x\quad \text{when } p=1.00\text{ bar}$$

$$K=K_x=\boxed{9.61}$$

(iv) $\Delta_rG^{\ominus}=-RT\ln K=-(8.3145\text{ J K}^{-1}\text{ mol}^{-1})\times(298\text{ K})\times\ln(9.61)=\boxed{-5.61\text{ kJ mol}^{-1}}$

6A.9(b) The formation reaction is: U(s) + $^3/_2$ H_2(g) $\rightleftharpoons$ UH_3(s).

$$K=\frac{1}{a^{3/2}_{H_2(g)}}=\left(\frac{p^{\ominus}}{p_{H_2}}\right)^{3/2}\quad (a_{U(s)}=a_{UH_3(s)}=1\text{ and, assuming perfect gas behavior, }a_{H_2(g)}=p_{H_2}/p^{\ominus}.)$$

$$=\left(\frac{10^5\text{ Pa}}{139\text{ Pa}}\right)^{3/2}=1.93\times10^4$$

$$\Delta_rG^{\ominus}=-RT\ln K\ \text{[6A.14]}$$

$$=-\left(8.3145\text{ J K}^{-1}\text{ mol}^{-1}\right)\times\left(500\text{ K}\right)\times\ln\left(1.93\times10^4\right)$$

$$=\boxed{-41.0\text{ kJ mol}^{-1}}$$

6A.10(b) P(s,wh) + $^3/_2$ H_2(g) → PH_3(g) $\quad\Delta_fG^{\ominus}=+13.4\text{ kJ mol}^{-1}$

$$\Delta_fG=\Delta_fG^{\ominus}+RT\ln Q\ \text{[6A.10]}\quad \text{where}\quad Q=\prod_J a_J^{\nu_J}\ \text{[6A.12b]}$$

$$=\Delta_fG^{\ominus}+RT\ln\frac{p_{PH_3}/p^{\ominus}}{\left(p_{H_2}/p^{\ominus}\right)^{3/2}}\quad\text{[Perfect gas assumption]}$$

$$=\left(+13.4\text{ kJ mol}^{-1}\right)+\left(8.3145\times10^{-3}\text{ kJ K}^{-1}\text{ mol}^{-1}\right)\times\left(298.15\text{ K}\right)\times\ln\left(\frac{0.60}{1^{3/2}}\right)$$

$$=\boxed{+12.1\text{ kJ mol}^{-1}}$$

Since $\Delta_fG>0$, the spontaneous direction of reaction is $\boxed{\text{toward the elements in their standard states}}$.

6A.11(b) $PbI_2(s)\rightleftharpoons PbI_2(aq)\qquad K_s=1.4\times10^{-8}$

$$\Delta_rG^{\ominus}=-RT\ \ln K_s$$

$$=-(8.3145\text{ J K}^{-1}\text{ mol}^{-1})\times(298.15\text{ K})\times\ln\left(1.4\times10^{-8}\right)=+44.8\text{ kJ mol}^{-1}$$

$$=\Delta_fG^{\ominus}(PbI_2,aq)-\Delta_fG^{\ominus}(PbI_2,s)$$

$$\Delta_fG^{\ominus}(PbI_2,aq)=\Delta_rG^{\ominus}+\Delta_fG^{\ominus}(PbI_2,s)$$

$$=\left(44.8-173.64\right)\text{ kJ mol}^{-1}=\boxed{-128.8\text{ kJ mol}^{-1}}$$

Solutions to problems

6A.2 $\Delta_rG^{\ominus}(H_2CO,g)=\Delta_rG^{\ominus}(H_2CO,l)+\Delta_{vap}G^{\ominus}(H_2CO,l)$ where $\Delta_rG^{\ominus}(H_2CO,l)=+28.95\text{ kJ mol}^{-1}$

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

$$\Delta_{\text{vap}}G^{\ominus} = -RT\ln K(\text{vap}) = -RT\ln\frac{p}{p^{\ominus}}$$

$$= -(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(298\ \text{K})\times\ln\left(\frac{2.000\ \text{bar}}{1\ \text{bar}}\right) = -1.72\ \text{kJ mol}^{-1}$$

Therefore, for the reaction $\text{CO(g)}+\text{H}_2\text{(g)} \rightleftharpoons \text{H}_2\text{CO(g)}$,

$$\Delta_r G^{\ominus} = \{(+28.95)+(-1.72)\}\ \text{kJ mol}^{-1} = +27.23\ \text{kJ mol}^{-1}$$

Hence, $K = e^{(-27.23\times10^3\ \text{J mol}^{-1})/(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(298\ \text{K})} = e^{-10.99} = \boxed{1.69\times10^{-5}}$.

6A.4‡ A reaction proceeds spontaneously if its reaction Gibbs function is negative.

$$\Delta_r G = \Delta_r G^{\ominus} + RT\ln Q \quad [6A.10]$$

Note that under the given conditions, $RT = 1.58\ \text{kJ mol}^{-1}$

(i) $\Delta_r G/(\text{kJ mol}^{-1}) = \{\Delta_r G^{\ominus}(\text{i}) - RT\ln p_{\text{H}_2\text{O}}\}/\text{kJ mol}^{-1} = -23.6 - 1.58\ln(1.3\times10^{-7})$

$= +1.5$

(ii) $\Delta_r G/(\text{kJ mol}^{-1}) = \{\Delta_r G^{\ominus}(\text{ii}) - RT\ln p_{\text{H}_2\text{O}}\,p_{\text{HNO}_3}\}/(\text{kJ mol}^{-1})$

$= -57.2 - 1.58\ln\left[(1.3\times10^{-7})\times(4.1\times10^{-10})\right]$

$= +2.0$

(iii) $\Delta_r G/(\text{kJ mol}^{-1}) = \{\Delta_r G^{\ominus}(\text{iii}) - RT\ln p_{\text{H}_2\text{O}}{}^2\,p_{\text{HNO}_3}\}/(\text{kJ mol}^{-1})$

$= -85.6 - 1.58\ln[(1.3\times10^{-7})^2\times(4.1\times10^{-10})]$

$= -1.3$

(iv) $\Delta_r G/(\text{kJ mol}^{-1}) = \{\Delta_r G^{\ominus}(\text{iv}) - RT\ln p_{\text{H}_2\text{O}}{}^3\,p_{\text{HNO}_3}\}/(\text{kJ mol}^{-1})$

$= -112.8 - 1.58\ln[(1.3\times10^{-7})^3\times(4.1\times10^{-10})]$

$= -3.5$

So both the dihydrate and trihydrate form spontaneously from the vapour. Does one convert spontaneously into the other? Consider the reaction

$$\text{HNO}_3\cdot2\text{H}_2\text{O(s)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{HNO}_3\cdot3\text{H}_2\text{O(s)}$$

which may be considered as reaction(iv) – reaction(iii). $\Delta_r G$ for this reaction is

$$\Delta_r G = \Delta_r G(\text{iv}) - \Delta_r G(\text{iii}) = -2.2\ \text{kJ mol}^{-1}.$$

We conclude that the dihydrate converts spontaneously to the $\boxed{\text{trihydrate}}$, the most stable solid (at least of the four we considered).

6B The response to equilibria to the conditions

Answers to discussion questions

6B.2 (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, Δ*v*, between the sums of the number of moles of gases on the product and reactant sides of the balanced chemical reaction equation.

$$\Delta v = \sum_{\text{J}} v_{\text{J}} = \sum_{\text{J=product gases}} v_{\text{J}} - \sum_{\text{J=reactant gases}} |v_{\text{J}}|$$

The requirement of an unchanged equilibrium constant implies that the side with the smaller number of moles of gas be favored as pressure increases. To see this, we examine the general reaction equation $0=\sum_{\mathrm{J}} \nu_{\mathrm{J}}\mathrm{J}$ [6A.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,

$$a_{\mathrm{J(gas)}} = p_{\mathrm{J}}/p^{\ominus} = x_{\mathrm{J}}p/p^{\ominus}$$

where x_{J} is the mole fraction of gaseous species J. Substitution into eqn 6A.13 and simplification yields a useful equation.

$$K=\left(\prod_{\mathrm{J}} a_{\mathrm{J}}^{\nu_{\mathrm{J}}}\right)_{\text{equilibrium}} = \left(\prod_{\mathrm{J}} x_{\mathrm{J}}^{\nu_{\mathrm{J}}}\left(p/p^{\ominus}\right)^{\nu_{\mathrm{J}}}\right)_{\text{equilibrium}}$$

$$=\left(\prod_{\mathrm{J}} x_{\mathrm{J}}^{\nu_{\mathrm{J}}}\right)_{\text{equilibrium}}\left(\prod_{\mathrm{J}}\left(p/p^{\ominus}\right)^{\nu_{\mathrm{J}}}\right)_{\text{equilibrium}} = \left(\prod_{\mathrm{J}} x_{\mathrm{J}}^{\nu_{\mathrm{J}}}\right)_{\text{equilibrium}}\left(p/p^{\ominus}\right)^{\Delta\nu}$$

$$=K_x\left(p/p^{\ominus}\right)^{\Delta\nu} \quad \text{where} \quad K_x=\left(\prod_{\mathrm{J}} x_{\mathrm{J}}^{\nu_{\mathrm{J}}}\right)_{\text{equilibrium}}$$

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 upon temperature alone, the concentration ratio K_x depends upon both temperature and pressure. Solving for K_x provides an equation that directly indicates its pressure dependence.

$$K_x=K\left(p/p^{\ominus}\right)^{-\Delta\nu}$$

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 upon 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), $K_x=K\left(p/p^{\ominus}\right)^{|\Delta\nu|}$. 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 reestablish 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), $K_x=K\left(p/p^{\ominus}\right)^{-|\Delta\nu|}$. Because p is raised to a negative power in this case, the concentrations now shift to the reactant side to reestablish equilibrium when an increase in pressure has stressed the reaction equilibrium.

(2) Response to change in temperature. The **van 't Hoff equation**, $\dfrac{\mathrm{d}\ln K}{\mathrm{d}T}=\dfrac{\Delta_{\mathrm{r}}H^{\ominus}}{RT^2}$ [6B.2(a)], shows that K decreases with increasing temperature when the reaction is exothermic (i.e., $\Delta_{\mathrm{r}}H^{\ominus} < 0$); thus the reaction shifts to the left. The opposite occurs in endothermic reactions (i.e., $\Delta_{\mathrm{r}}H^{\ominus} > 0$). See text Section 6B.2 for a more detailed discussion.

Solutions to exercises

6B.1(b) At $1120\,\mathrm{K},\ \Delta_{\mathrm{r}}G^{\ominus}=+22\times10^{3}\ \mathrm{J\ mol^{-1}}$

$$\ln K_1(1120\text{K}) = -\frac{\Delta_r G^\ominus}{RT}\ [6\text{A}.14] = -\frac{(22\times10^3\ \text{J mol}^{-1})}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(1120\ \text{K})} = -2.3\overline{63}$$

$$K = \text{e}^{-2.3\overline{63}} = 9.\overline{41}\times10^{-2}$$

$$\ln K_2 = \ln K_1 - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\ [6\text{B}.4]$$

Solve for T_2 at $\ln K_2 = 0$ ($K_2 = 1$).

$$\frac{1}{T_2} = \frac{R\ \ln K_1}{\Delta_r H^\ominus} + \frac{1}{T_1} = \frac{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(-2.3\overline{63})}{(125\times10^3\ \text{J mol}^{-1})} + \frac{1}{1120\ \text{K}} = 7.3\overline{6}\times10^{-4}$$

$$T_2 = \boxed{1.4\times10^3\ \text{K}}$$

6B.2(b) $\ln K = A + \frac{B}{T} + \frac{C}{T^3}$ where $A = -2.04$, $B = -1176$ K, and $C = 2.1\times10^7\ \text{K}^3$

At 450 K:

$$\Delta_r G^\ominus = -RT\ln K\ [6\text{A}.14] = RT\times\left(A+\frac{B}{T}+\frac{C}{T^3}\right)$$

$$= -\left(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}\right)\times(450\ \text{K})\times\left(-2.04-\frac{1176\ \text{K}}{450\ \text{K}}+\frac{2.1\times10^7\ \text{K}^3}{(450\ \text{K})^3}\right)$$

$$= +16.6\ \text{kJ mol}^{-1}$$

$$\Delta_r H^\ominus = -R\frac{\text{d}\ln K}{\text{d}(1/T)}\ [6\text{B}.2(\text{b})]$$

$$= -R\frac{\text{d}}{\text{d}(1/T)}\left(A+\frac{B}{T}+\frac{C}{T^3}\right) = -R\times\left(B+\frac{3C}{T^2}\right)$$

$$= -\left(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}\right)\times\left\{\left(-1176\ \text{K}\right)+3\times\frac{2.1\times10^7\ \text{K}^3}{\left(450\ \text{K}\right)^2}\right\} = \boxed{+7.19\ \text{kJ mol}^{-1}}$$

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$$

$$\Delta_r S^\ominus = \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T} = \frac{7.19\ \text{kJ mol}^{-1} - 16.6\ \text{kJ mol}^{-1}}{450\ \text{K}} = \boxed{-20.9\ \text{J K}^{-1}\ \text{mol}^{-1}}$$

6B.3(b) $CH_3OH(g) + NOCl(g) \rightarrow HCl(g) + CH_3NO_2(g)$ For this gas phase reaction $\Delta\nu = \sum_J \nu_J = 0$

$$K = \left(\prod_J a_J^{\nu_J}\right)_{\text{equilibrium}} [6\text{A}.13] = \left(\prod_J\left(\gamma_J p_J / p^\ominus\right)^{\nu_J}\right)_{\text{equilibrium}} = \left(\prod_J \gamma_J^{\nu_J}\right)_{\text{equilibrium}}\left(\prod_J\left(p_J / p^\ominus\right)^{\nu_J}\right)_{\text{equilibrium}}$$

$$= K_\gamma K_p \quad \text{where} \quad K_\gamma = \left(\prod_J \gamma_J^{\nu_J}\right)_{\text{equilibrium}} \quad \text{and } K_p = \left(\prod_J\left(p_J / p^\ominus\right)^{\nu_J}\right)_{\text{equilibrium}}$$

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

$$K = K_p = \left(\prod_J\left(x_J p / p^\ominus\right)^{\nu_J}\right)_{\text{equilibrium}} = \left(\prod_J x_J^{\nu_J}\right)_{\text{equilibrium}}\left(\prod_J\left(p / p^\ominus\right)^{\nu_J}\right)_{\text{equilibrium}}$$

$$= K_x\left(p / p^\ominus\right)^{\Delta\nu} \quad \text{where} \quad K_x = \left(\prod_J x_J^{\nu_J}\right)_{\text{equilibrium}}$$

For this reaction:

$$K = K_x\times\left(p / p^\ominus\right)^0 = K_x \quad \text{because } \Delta\nu = 0$$

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 upon changing the pressure equals $\boxed{\text{zero}}$ for this reaction.

6B.4(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \quad K = 1.69\times10^{-3}$ at 2300 K

Initial modes: $n_{N_2} = \dfrac{5.0 \text{ g}}{28.013 \text{ g mol}^{-1}} = 0.17\overline{85} \text{ mol}$

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	$\left(n_{N_2} - z\right)/n$	$\left(n_{O_2} - z\right)/n$	$2z/n$	1

$$K = K_x\left(\frac{p}{p^{\ominus}}\right)^{\Delta\nu} = K_x \quad \text{(Because } \Delta\nu = \sum_J \nu_J = 0 \text{ for this reaction. See Exercise 6B.3(a) or (b))}$$

$$K = \frac{(2z)^2}{\left(n_{N_2} - z\right)\times\left(n_{O_2} - z\right)}$$

$$\left(1 - \tfrac{4}{K}\right)z^2 - nz + n_{N_2}n_{O_2} = 0$$

$$z = \frac{n \pm \sqrt{n^2 - 4\left(1 - \tfrac{4}{K}\right)n_{N_2}n_{O_2}}}{2\left(1 - \tfrac{4}{K}\right)}$$

$$= \frac{0.2410 \pm \sqrt{0.2410^2 - 4\left(1 - \tfrac{4}{1.69\times10^{-3}}\right)(0.1785)(0.0625)}}{2\left(1 - \tfrac{4}{1.69\times10^{-3}}\right)}$$

$$= -2.223\times10^{-3} \text{ or } 2.121\times10^{-3}$$

$$= 2.121\times10^{-3} \text{ because the negative value is non-physical.}$$

$$x_{NO} = \frac{2z}{n} = \frac{2(2.121\times10^{-3})}{0.24\overline{1}} = \boxed{1.8\times10^{-2}}$$

6B.5(b) $\ln\dfrac{K_2}{K_1} = -\dfrac{\Delta_r H^{\ominus}}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$ [6B.4]

$$\Delta_r H^{\ominus} = R\times\left(\frac{1}{T_1} - \frac{1}{T_2}\right)^{-1}\times\ln\left(\frac{K_2}{K_1}\right)$$

$$= \left(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}\right)\times\left(\frac{1}{310 \text{ K}} - \frac{1}{325 \text{ K}}\right)^{-1}\times\ln\left(\frac{K_2}{K_1}\right)$$

$$= \left(55.85 \text{ kJ mol}^{-1}\right)\times\ln\left(\frac{K_2}{K_1}\right)$$

(a) $K_2/K_1 = 2.00$

$$\Delta_r H^{\ominus} = \left(55.85 \text{ kJ mol}^{-1}\right)\times\ln(2.00) = \boxed{38.71 \text{ kJ mol}^{-1}}$$

(b) $K_2/K_1 = 0.500$

$$\Delta_r H^{\ominus} = \left(55.85 \text{ kJ mol}^{-1}\right)\times\ln(0.500) = \boxed{-38.71 \text{ kJ mol}^{-1}}$$

6B.6(b) The reaction is $CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4(s) + 5\ H_2O(g)$.
For the purposes of this exercise we may assume that the required temperature is that temperature at which $K = 1$ at a pressure of 1 bar. For $K = 1$, $\ln K = 0$, and $\Delta_r G^\ominus = 0$.

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus = 0$$

$$T = \frac{\Delta_r H^\ominus}{\Delta_r S^\ominus}$$

We now estimate that the values of both $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ are not too different then the values at 25 °C and calculate each with standard values found in the text *Resource section*.

$$\Delta_r H^\ominus = \sum_J \nu_J \Delta_{f,J} H^\ominus = \{(-771.36) + (5)\times(-241.82) - (-2279.7)\}\ \text{J mol}^{-1} = +299.2\ \text{kJ mol}^{-1}$$

$$\Delta_r S^\ominus = \sum_J \nu_J S_J^\ominus = \{(109) + (5)\times(188.83) - (300.4)\}\ \text{J K}^{-1}\ \text{mol}^{-1} = 752.\overline{8}\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$T \sim \frac{299.2\times10^3\ \text{J mol}^{-1}}{752.8\ \text{J K}^{-1}\ \text{mol}^{-1}} = \boxed{397\ \text{K}}$$

Question: What would the decomposition temperature be for decomposition defined as the state at which $K = ½$?

6B.7(b) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$ Vapor pressures: $p_{427°C} = 608$ kPa and $p_{459°C} = 1115$ kPa
The gases originate from the dissociation of the solid alone so $p_{NH_3} = p_{HCl} = \tfrac{1}{2} p$.

(i) Equilibrium constants

$$K = \left(p_{NH_3}/p^\ominus\right)\times\left(p_{HCl}/p^\ominus\right) \quad \text{[Perfect gas assumption]}$$

$$= \left(\tfrac{1}{2}p/p^\ominus\right)\times\left(\tfrac{1}{2}p/p^\ominus\right)$$

$$= \tfrac{1}{4}\left(p/p^\ominus\right)^2$$

$$K_{427°C} = \tfrac{1}{4}(608\ \text{kPa}/100\ \text{kPa})^2 = \boxed{9.24}$$

$$K_{459°C} = \tfrac{1}{4}(1115\ \text{kPa}/100\ \text{kPa})^2 = 31.08$$

(ii) $\Delta\ G^\ominus = -RT\ln K$ [6A.14]

$$\Delta_r G^\ominus_{427°C} = -\left(8.3145\ \text{J K}^{-1}\text{mol}^{-1}\right)\times(700.15\ \text{K})\times\ln(9.24) = \boxed{-12.9\ \text{kJ mol}^{-1}}$$

(iii) $\ln\dfrac{K_2}{K_1} = -\dfrac{\Delta_r H^\ominus}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$ [6B.4]

$$\Delta_r H^\ominus = R\times\left(\frac{1}{T_1} - \frac{1}{T_2}\right)^{-1}\times\ln\left(\frac{K_2}{K_1}\right)$$

$$= \left(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}\right)\times\left(\frac{1}{700.15\ \text{K}} - \frac{1}{732.15\ \text{K}}\right)^{-1}\times\ln\left(\frac{31.08}{9.24}\right)$$

$$= \boxed{162\ \text{kJ mol}^{-1}}$$

(iv) $\Delta_r S^\ominus = \dfrac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T} = \dfrac{(162\ \text{kJ mol}^{-1}) - (-12.9\ \text{kJ mol}^{-1})}{700.15\ \text{K}} = \boxed{+250\ \text{J K}^{-1}\ \text{mol}^{-1}}$

Solutions to problems

6B.2 $U(s) + \tfrac{3}{2}\ H_2(g) \rightleftharpoons UH_3(s)$

$$K = a_{\mathrm{H_2}}^{-3/2} = (p_{\mathrm{H_2}}/p^{\ominus})^{-3/2} \ \text{[perfect gas]}$$
$$= (p/p^{\ominus})^{-3/2} \qquad [p_{\mathrm{H_2}} = p]$$

$$\Delta_{\mathrm{f}} H^{\ominus} = RT^2\frac{\mathrm{d}\ln K}{\mathrm{d}T}\ \text{[6B.2(a)]} = RT^2\frac{\mathrm{d}}{\mathrm{d}T}\ln\left(p/p^{\ominus}\right)^{-3/2} = -\tfrac{3}{2}RT^2\frac{\mathrm{d}}{\mathrm{d}T}\left(\ln p/\mathrm{Pa} - \ln p^{\ominus}/\mathrm{Pa}\right)$$

$$= -\tfrac{3}{2}RT^2\frac{\mathrm{d}}{\mathrm{d}T}\left(\ln p/\mathrm{Pa}\right)$$

$$= -\tfrac{3}{2}RT^2\frac{\mathrm{d}}{\mathrm{d}T}\left(A + B/T + C\ln\left(T/\mathrm{K}\right)\right) = -\tfrac{3}{2}RT^2\times\left(\frac{-B}{T^2}+\frac{C}{T}\right)$$

$$= \boxed{\tfrac{3}{2}R\times\left(B - CT\right)} \quad \text{where} \quad B = -1.464\times10^4\ \mathrm{K} \quad \text{and} \quad C = -5.65$$

$$\mathrm{d}\left(\Delta_{\mathrm{f}} H^{\ominus}\right) = \Delta_{\mathrm{r}} C_{\mathrm{p}}^{\ominus}\,\mathrm{d}T\ \left[\text{from eqn 2B.6(a) applied to chemical reactions, 2C.7(a)}\right]$$

or $$\Delta_{\mathrm{r}} C_p^{\ominus} = \left(\frac{\partial \Delta_{\mathrm{f}} H^{\ominus}}{\partial T}\right)_p = -\tfrac{3}{2}CR = \boxed{70.5\ \mathrm{J\ K^{-1}\ mol^{-1}}}$$

6B.4 $\mathrm{CaCl_2\cdot NH_3(s)} \rightleftharpoons \mathrm{CaCl_2(s) + NH_3(g)}$ $\qquad K = \dfrac{p}{p^{\ominus}}$ and $\Delta_{\mathrm{r}} H^{\ominus} = +78\ \mathrm{kJ\ mol^{-1}}$

$$\Delta_{\mathrm{r}} G^{\ominus} = -RT\ln K = -RT\ \ln\frac{p}{p^{\ominus}}$$

$$= -(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(400\ \mathrm{K})\times\ln\left(\frac{1.71\ \mathrm{kPa}}{100.0\ \mathrm{kPa}}\right) \quad [p^{\ominus} = 1\ \mathrm{bar} = 100.0\ \mathrm{kPa}]$$

$$= +13.5\ \mathrm{kJ\ mol^{-1}}\ \text{at}\ 400\ \mathrm{K}$$

$$\frac{\Delta_{\mathrm{r}} G^{\ominus}(T_2)}{T_2} - \frac{\Delta_{\mathrm{r}} G^{\ominus}(T_1)}{T_1} = \Delta_{\mathrm{r}} H^{\ominus}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\ \left[\text{6B.4 and 6A.14}\right]$$

Therefore, taking $T_1 = 400\ \mathrm{K}$ and letting $T = T_2$ be any temperature in the range 350 K to 470 K,

$$\Delta_{\mathrm{r}} G^{\ominus}(T) = \left(\frac{T}{400\mathrm{K}}\right)\times\ (13.5\ \mathrm{kJ\ mol^{-1}})\ +\ (78\ \mathrm{kJ\ mol^{-1}})\ \times\ \left(1-\frac{T}{400\ \mathrm{K}}\right)$$

$$= (78\ \mathrm{kJ\ mol^{-1}}) + \left(\frac{(13.5-78)\ \mathrm{kJ\ mol^{-1}}}{400}\right)\times\left(\frac{T}{\mathrm{K}}\right)$$

That is, $\Delta_{\mathrm{r}} G^{\ominus}(T)/(\mathrm{kJ\ mol^{-1}}) = \boxed{78 - 0.161\times\left(T/\mathrm{K}\right)}$.

6B.6 The equilibrium we need to consider is $\mathrm{I_2(g)} \rightleftharpoons 2\ \mathrm{I(g)}$ (M_{I} = 126.90 g mol^{-1}). It is convenient to express the equilibrium constant in terms of α, the degree of dissociation of $\mathrm{I_2}$, which is the predominant species at low temperatures. Recognizing that the data $n_{\mathrm{I_2}}$ is related to the total iodine mass, m_{I}, by $n_{\mathrm{I_2}} = m_{\mathrm{I}}/M_{\mathrm{I_2}}$ we draw the following table.

	I	$\mathrm{I_2}$	Total
Equilibrium amounts	$2\alpha n_{\mathrm{I_2}}$	$(1-\alpha)n_{\mathrm{I_2}}$	$(1+\alpha)n_{\mathrm{I_2}}$
Mole fraction	$\dfrac{2\alpha}{1+\alpha}$	$\dfrac{1-\alpha}{1+\alpha}$	1
Partial pressure	$\dfrac{2\alpha p}{1+\alpha}$	$\left(\dfrac{1-\alpha}{1+\alpha}\right)p$	p

The equilibrium constant for the dissociation is

$$K = \frac{\left(p_{\rm I}/p^{\ominus}\right)^2}{p_{\rm I_2}/p^{\ominus}} = \frac{p_{\rm I}^2}{p_{\rm I_2}p^{\ominus}} = \frac{4\alpha^2\left(p/p^{\ominus}\right)}{1-\alpha^2}$$

We also know that

$$pV = n_{\rm total}RT = (1+\alpha)n_{\rm I_2}RT$$

Implying that $\alpha = \dfrac{pV}{n_{\rm I_2}RT} - 1$ where V = 342.68 cm^3. The provided data along with calculated values of α and $K(T)$ are summarized in the following table.

T / K	973	1073	1173
p / atm	0.06244	0.07500	0.09181
$10^4\ n_{\rm I_2}$ / mol	2.4709	2.4555	2.4366
α	0.08459	0.1887	0.3415
K	1.82×10^{-3}	1.12×10^{-2}	4.91×10^{-2}

Since $\Delta_{\rm r}H^{\ominus}$ is expected to be approximately a constant over this temperature range and since $\Delta_{\rm r}H^{\ominus} = -R\left(\dfrac{{\rm d}\ln K}{{\rm d}(1/T)}\right)$ [6B.2(b)], a plot of ln$K$ against 1/T should be linear with slope = $-\Delta_{\rm r}H^{\ominus}/R$. The linear regression fit to the plot is found to be ln$K$ = 13.027–(18809 K)/T with R^2 = 0.999969. Thus,

$$\Delta_{\rm r}H^{\ominus} = -(-18809\ {\rm K})R = \boxed{+156\ {\rm kJ\ mol^{-1}}}$$

6B.1 $H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta_{\rm f}H^{\ominus} = -285.83$ kJ mol^{-1} and $\Delta_{\rm f}S^{\ominus} = -163.343$ J K^{-1} mol^{-1} at 298.15 K

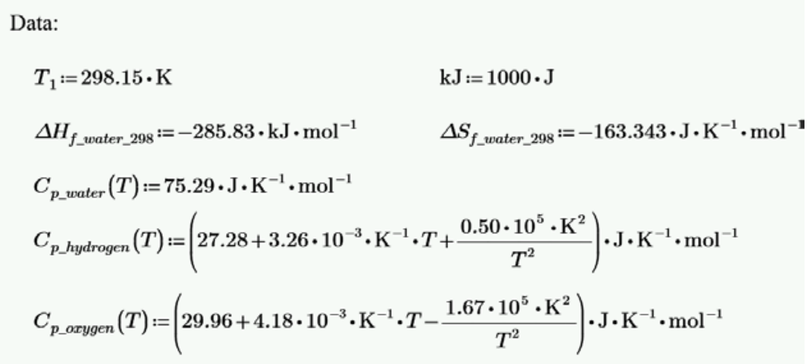
Let the temperatures of interest be T_1 = 298.15 K and T_2. $\Delta_{\rm f}G(T_2)$ at 1 bar can be calculated from the reaction thermodynamic properties at T_1 with the following relations.

$$\Delta_{\rm r}H(T_2) = \Delta_{\rm r}H(T_1) + \int_{T_1}^{T_2}\Delta_{\rm r}C_p(T)\,{\rm d}T\ \ [2{\rm C}.7({\rm a})\ {\rm and}\ ({\rm b});\ \Delta_{\rm r}C_p(T) = \sum_{\rm J}\nu_{\rm J}C_{p,{\rm J}}]$$

$$\Delta_{\rm r}S(T_2) = \Delta_{\rm r}S(T_1) + \int_{T_1}^{T_2}\frac{\Delta_{\rm r}C_p(T)}{T}{\rm d}T\ \ [3{\rm A}.19\ \text{applied to reaction equations}]$$

$$\Delta_{\rm r}G(T_2) = \Delta_{\rm r}H(T_2) - T_2\Delta_{\rm r}S(T_2)$$

The computation is most easily performed using the function capability and numeric integrations of either the scientific calculator or a computer software package. The following is a Mathcad Prime 2 worksheet for the calculation of $\Delta_{\rm f}G$ for 273.15 K ≤ T_2 ≤ 373.15 K at 1 bar.



Data:

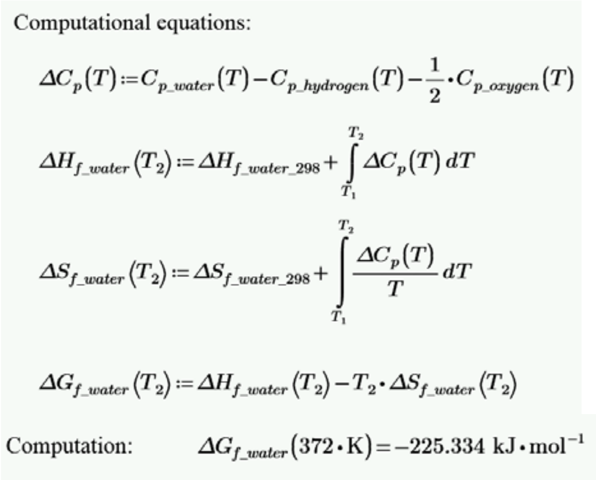
$T_1 := 298.15\cdot{\rm K}$ ${\rm kJ} := 1000\cdot{\rm J}$

$\Delta H_{f\_water\_298} := -285.83\cdot{\rm kJ}\cdot{\rm mol^{-1}}$ $\Delta S_{f\_water\_298} := -163.343\cdot{\rm J}\cdot{\rm K^{-1}}\cdot{\rm mol^{-1}}$

$C_{p\_water}(T) := 75.29\cdot{\rm J}\cdot{\rm K^{-1}}\cdot{\rm mol^{-1}}$

$C_{p\_hydrogen}(T) := \left(27.28 + 3.26\cdot10^{-3}\cdot{\rm K^{-1}}\cdot T + \dfrac{0.50\cdot10^5\cdot{\rm K^2}}{T^2}\right)\cdot{\rm J}\cdot{\rm K^{-1}}\cdot{\rm mol^{-1}}$

$C_{p\_oxygen}(T) := \left(29.96 + 4.18\cdot10^{-3}\cdot{\rm K^{-1}}\cdot T - \dfrac{1.67\cdot10^5\cdot{\rm K^2}}{T^2}\right)\cdot{\rm J}\cdot{\rm K^{-1}}\cdot{\rm mol^{-1}}$



Computational equations:

$$\Delta C_p(T) := C_{p\_water}(T) - C_{p\_hydrogen}(T) - \frac{1}{2}\cdot C_{p\_oxygen}(T)$$

$$\Delta H_{f\_water}(T_2) := \Delta H_{f\_water\_298} + \int_{T_1}^{T_2} \Delta C_p(T)\, dT$$

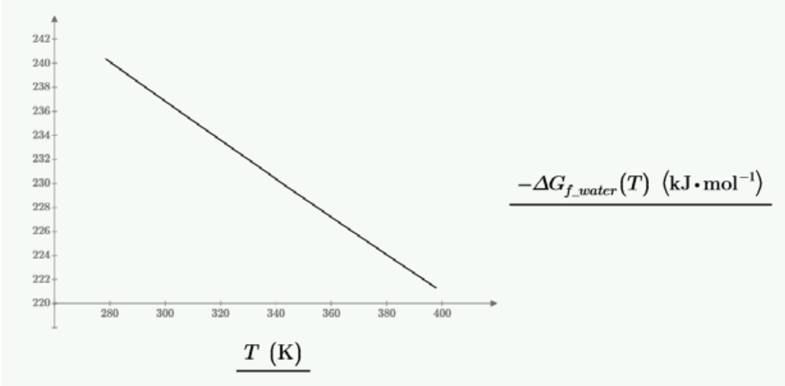
$$\Delta S_{f\_water}(T_2) := \Delta S_{f\_water\_298} + \int_{T_1}^{T_2} \frac{\Delta C_p(T)}{T}\, dT$$

$$\Delta G_{f\_water}(T_2) := \Delta H_{f\_water}(T_2) - T_2\cdot \Delta S_{f\_water}(T_2)$$

Computation: $\Delta G_{f\_water}(372\cdot \text{K}) = -225.334\ \text{kJ}\cdot\text{mol}^{-1}$

Thus, with numerical integrations we have found that $\Delta_f G^{\ominus} = \boxed{-225.334\ \text{kJ mol}^{-1}}$. The worksheet also makes it very easy to examine, even plot, changes in the reaction thermodynamic properties. The following worksheet plot shows the variation of the formation Gibb's energy with temperature. The plot shows a decrease with temperature in a near-linear manner. Can you explain why?

$T := 273\cdot\text{K}, 278\cdot\text{K} .. 398\cdot\text{K}$



6C Electrochemical cells

Answers to discussion questions

6C.2 A salt bridge connecting two half-cells is usually a U-tube filled with potassium chloride in agar jelly. It provides the mobile electrolyte for completing the circuit of an electrochemical cell. In its absence, the cell cannot generate an electrical current through the single wire that connects the two electrodes and the circuit is said to be "open". No electron can leave or enter either half-cell, because this act would cause the net electronic charge of the half-cell to be non-zero. The strong electrostatic force prevents this from happening and causes macroscopic objects to normally have a zero net electrical charge. However, a salt bridge provides an anion to the anodic half-cell for every electron that leaves while simultaneously providing a cation to the cathodic half-cell for every electron that enters. This is a "closed" electrical circuit in which the net charge of each half-cell remains zero but an electric current can be generated.

6C.4 When a current is being drawn from an electrochemical cell, the cell potential is altered by the formation of charge double layers at the surface of electrodes and by the formation of solution chemical potential gradients (concentration gradients). Resistive heating of the cell circuits may occur and junction potentials between dissimilar materials both external and external to the cell may change.

Solutions to exercises

6C.1(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.

$E^\ominus$

(i) R: $\text{Ag}_2\text{CrO}_4(\text{s}) + 2\ \text{e}^- \rightarrow 2\ \text{Ag(s)} + \text{CrO}_4^{2-}(\text{aq})$ $+0.45\ \text{V}$

L: $\text{Cl}_2(\text{g}) + 2\ \text{e}^- \rightarrow 2\ \text{Cl}^-(\text{aq})$ $+1.36\ \text{V}$

Overall(R − L): $\text{Ag}_2\text{CrO}_4(\text{s}) + 2\ \text{Cl}^-(\text{aq}) \rightarrow 2\ \text{Ag(s)} + \text{CrO}_4^{2-}(\text{aq}) + \text{Cl}_2(\text{g})$ $\boxed{-0.91\ \text{V}}$

(ii) R: $\text{Sn}^{4+}(\text{aq}) + 2\ \text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$ $+0.15\ \text{V}$

L: $2\ \text{Fe}^{3+}(\text{aq}) + 2\text{e}^- \rightarrow 2\ \text{Fe}^{2+}(\text{aq})$ $+0.77\ \text{V}$

Overall (R − L): $\text{Sn}^{4+}(\text{aq}) + 2\ \text{Fe}^{2+}(\text{aq}) \rightarrow \text{Sn}^{2+}(\text{aq}) + 2\ \text{Fe}^{3+}(\text{aq})$ $\boxed{-0.62\ \text{V}}$

(iii) R: $\text{MnO}_2(\text{s}) + 4\ \text{H}^+(\text{aq}) + 2\ \text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\ \text{H}_2\text{O(l)}$ $+1.23\ \text{V}$

L: $\text{Cu}^{2+}(\text{aq}) + 2\,\text{e}^- \rightarrow \text{Cu(s)}$ $+0.34\ \text{V}$

Overall (R − L): $\text{Cu(s)} + \text{MnO}_2(\text{s}) + 4\ \text{H}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(1)$ $\boxed{+0.89\ \text{V}}$

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}.

6C.2(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 number of electrons to ensure proper cancellation. We first identify the half-reactions, and then set up the corresponding cell.

$E^\ominus$

(i) R: $2\ \text{H}_2\text{O}(1) + 2\ \text{e}^- \rightarrow 2\ \text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$ $-0.83\ \text{V}$

L: $2\ \text{Na}^+(\text{aq}) + 2\ \text{e}^- \rightarrow 2\ \text{Na(s)}$ $-2.71\ \text{V}$

and the cell is

$\text{Na(s)}|\text{NaOH(aq)}|\text{H}_2(\text{g})|\text{Pt}$ $\boxed{+1.88\ \text{V}}$

(ii) R: $\text{I}_2(\text{s}) + 2\ \text{e}^- \rightarrow 2\ \text{I}^-(\text{aq})$ $+0.54\ \text{V}$

L: $2\ \text{H}^+(\text{aq}) + 2\ \text{e}^- \rightarrow \text{H}_2(\text{g})$ 0

and the cell is

$\text{Pt}|\text{H}_2(\text{g})|\text{H}^+(\text{aq}), \text{I}^-(\text{aq})|\text{I}_2(\text{s})|\text{Pt}$ $\boxed{+0.54\ \text{V}}$

(iii) R: $2\ \text{H}^+(\text{aq}) + 2\ \text{e}^- \rightarrow \text{H}_2(\text{g})$ 0

L: $2\ \text{H}_2\text{O}(1) + 2\ \text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\ \text{OH}^-(\text{aq})$ $-0.83\ \text{V}$

and the cell is

$\text{Pt}|\text{H}_2(\text{g})|\text{OH}^-(\text{aq})\|\text{H}^+(\text{aq})|\text{H}_2(\text{g})|\text{Pt}$ $\boxed{+0.83\ \text{V}}$

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.

6C.2(b) $\text{Pt}|\text{H}_2(\text{g}, p^{\ominus})\,|\,\text{HCl(aq,0.010 mol kg}^{-1})|\text{AgCl(s)}|\text{Ag}$

(i)	R:	$\text{AgCl(s)} + \text{e}^- \rightarrow \text{Ag(s)} + \text{Cl}^-\text{(aq)}$	$E^{\ominus} = +0.22\text{ V}$
	L:	$\text{HCl(aq)} + \text{e}^- \rightarrow \tfrac{1}{2}\,\text{H}_2\text{(g)} + \text{Cl}^-\text{(aq)}$	$E^{\ominus} = +0.00\text{ V}$
	2×(R – L):	$2\,\text{AgCl(s)} + \text{H}_2\text{(g)} \rightarrow 2\,\text{Ag(s)} + 2\,\text{HCl(aq)}$	$E^{\ominus}_{\text{cell}} = +0.22\text{ V}$ 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:

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{\nu F}\ln Q \text{ [6C.4]}$$

$$Q = \frac{\left(a_{\text{HCl(aq)}}\right)^2}{a_{\text{H}_2\text{(g)}}} = \frac{\left(a_{\text{H}^+\text{(aq)}}a_{\text{Cl}^-\text{(aq)}}\right)^2}{a_{\text{H}_2\text{(g)}}} = \frac{\left(\gamma_\pm^2\left(b_{\text{HCl}}/b^{\ominus}\right)^2\right)^2}{p/p^{\ominus}} = \gamma_\pm^4\left(b_{\text{HCl}}/b^{\ominus}\right)^4 \text{ (i.e., } p = p^{\ominus}\text{)}$$

Thus,

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{2F}\ln\left\{\gamma_\pm^4\left(b_{\text{HCl}}/b^{\ominus}\right)^4\right\} \quad\text{or}\quad \boxed{E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{2RT}{F}\ln\left\{\gamma_\pm\left(b_{\text{HCl}}/b^{\ominus}\right)\right\}}$$

(ii) $\Delta_{\text{r}}G^{\ominus} = -\nu F E^{\ominus}_{\text{cell}} = -2\times(9.6485\times10^4\text{ C mol}^{-1})\times(0.22\text{ V}) = \boxed{-42\text{ kJ mol}^{-1}}$

(iii) The ionic strength and mean activity coefficient are:

$$I = \tfrac{1}{2}\sum_{\text{i}} z_i^2\left(b_i/b^{\ominus}\right)\text{ [5F.9]} = \tfrac{1}{2}\left\{1(0.010) + 1(.010)\right\} = 0.010$$

$$\log\gamma_\pm = -\left|z_+z_-\right|AI^{1/2}\text{ [5F.8]} = -1\times(0.509)\times(0.010)^{1/2} = -0.0509$$

$$\gamma_\pm = 0.889$$

Therefore,

$$\begin{aligned}E_{\text{cell}} &= E^{\ominus}_{\text{cell}} - \frac{2RT}{F}\ln\left\{\gamma_\pm\left(b_{\text{HCl}}/b^{\ominus}\right)\right\}\\ &= 0.22\text{ V} - \frac{2\times\left(8.3145\text{ J mol}^{-1}\text{ K}^{-1}\right)\times\left(298.15\text{ K}\right)}{9.6485\times10^5\text{ C mol}^{-1}}\ln\left\{(0.889)\times(0.010)\right\} = 0.22\text{ V} + 0.24\text{ V}\\ &= \boxed{+0.46\text{ V}}\end{aligned}$$

Solutions to problems

6C.2 Cell: $\text{Hg}|\text{Hg}_2\text{Cl}_2\text{(s)}|\text{HCl(aq)}|\text{Q}\cdot\text{QH}_2|\text{Au}$ $\quad E_{\text{cell}} = +0.190\text{ V}$ and $\nu = 2$

The electrode half-reactions and their standard potentials are

	$E^{\ominus}$
$\text{R}: \text{ Q(aq)} + 2\,\text{H}^+\text{(aq)} + 2\,\text{e}^- \rightarrow \text{QH}_2\text{(aq)}$	0.6994 V
$\text{L}: \text{ Hg}_2\text{Cl}_2\text{(s)} + 2\,\text{e}^- \rightarrow 2\,\text{Hg(l)} + 2\,\text{Cl}^-\text{(aq)}$	0.2676 V
$\text{Overall (R – L)}: \text{ Q(aq)} + 2\,\text{H}^+\text{(aq)} + 2\,\text{Hg(l)} + 2\,\text{Cl}^-\text{(aq)} \rightarrow \text{QH}_2\text{(aq)} + \text{Hg}_2\text{Cl}_2\text{(s)}$	0.4318 V

The reaction quotient is directly related to the pH, a relation that is simplified by noting that for an HCl solution $b_{\text{H}^+} = b_{\text{Cl}^-}$ while for the $\text{Q}\cdot\text{QH}_2$ equimolecular complex of quinone $b_{\text{Q}} = b_{\text{QH}_2}$.

$$Q = \frac{a_{\text{QH}_2}}{a_{\text{Q}}a_{\text{H}^+}^2a_{\text{Cl}^-}^2}$$

The Debye−Hückel limiting law makes use of the mean activity coefficient for the compound M_pX_q defined by $a_J = \gamma_{\pm}b_J$. Thus, $a_{QH_2}/a_Q = 1$, $a_{H^+} = a_{Cl^-}$, and the reaction quotient becomes

$$Q = a_{H^+}^{-4}$$

The definition of pH provides the relation to the reaction quotient.

$$\text{pH} \equiv -\log\left(a_{H^+}\right) = -\frac{\ln\left(a_{H^+}\right)}{\ln(10)} = -\frac{\ln\left(Q^{-1/4}\right)}{\ln(10)} = \frac{\ln(Q)}{4\ln(10)} \quad \text{or} \quad \ln(Q) = 4\ln(10)\,\text{pH}$$

The Nernst equation [6C.4] at 25 °C is now used to relate cell potentials to the pH.

$$\begin{aligned} E_{\text{cell}} &= E^{\ominus}_{\text{cell}} - \frac{25.693\times10^{-3}\ \text{V}}{\nu}\ln Q \\ &= E^{\ominus}_{\text{cell}} - \frac{25.693\times10^{-3}\ \text{V}}{\nu}\left(4\ln(10)\ \text{pH}\right) \end{aligned}$$

$$\begin{aligned} \text{pH} &= \frac{\nu}{0.23664\ \text{V}}\left(E^{\ominus}_{\text{cell}} - E_{\text{cell}}\right) \\ &= \frac{2}{0.23664\ \text{V}}\times(0.4318-0.190)\ \text{V} \\ &= \boxed{2.04} \end{aligned}$$

6D Electrode potentials

Answers to discussion questions

6D.2 The pH of an aqueous solution can in principle be measured with any electrode having an emf that is sensitive to H^+(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 *I*6.2).

Solutions to exercises

6D.1(b) In each case the equilibrium constant is calculated with the expression $\ln K = \dfrac{\nu F E^{\ominus}_{\text{cell}}}{RT}$ [6C.5].

(i) $\text{Sn(s)} + \text{CuSO}_4\text{(aq)} \rightleftharpoons \text{Cu(s)} + \text{SnSO}_4\text{(aq)}$

$$\left.\begin{array}{ll} \text{R: } \text{Cu}^{2+} + 2\ \text{e}^- \rightarrow \text{Cu(s)} & +0.34\ \text{V} \\ \text{L: } \text{Sn}^{2+}\text{(aq)} + 2\ \text{e}^- \rightarrow \text{Sn(s)} & -0.14\ \text{V} \end{array}\right\} E^{\ominus}_{\text{cell}} = +0.48\ \text{V}$$

$$\ln K = \frac{\nu F E^{\ominus}_{\text{cell}}}{RT}\ [6\text{C}.5] = \frac{(2)\times(0.48\ \text{V})}{25.693\ \text{mV}} = 37.\overline{4}$$

$$K = \text{e}^{37.\overline{4}} = \boxed{1.7\times10^{16}}$$

(ii) $\mathrm{Cu(s)+Cu^{2+}(aq)} \rightleftharpoons \mathrm{2\ Cu^{+}(aq)}$

$$\left.\begin{array}{ll}\mathrm{R:\ Cu^{2+}+e^{-}\rightarrow Cu^{+}(aq)} & +0.16\ \mathrm{V} \\ \mathrm{L:\ Cu^{+}(aq)+e^{-}\rightarrow Cu(s)} & +0.52\ \mathrm{V}\end{array}\right\} E^{\ominus}_{\text{cell}} = -0.36\ \mathrm{V}$$

$$\ln K = \frac{\nu F E^{\ominus}_{\text{cell}}}{RT}\ \left[6\mathrm{C}.5\right] = \frac{(1)\times(-0.36\ \mathrm{V})}{25.693\ \mathrm{mV}} = -14.\bar{0}$$

$$K = \mathrm{e}^{-14.\bar{0}} = \boxed{8.3\times10^{-7}}$$

6D.2(b) Bi|Bi$_2$S$_3$(s)|Bi$_2$S$_3$(aq)|Bi

	$E^{\ominus}$	
R: $\mathrm{2\ Bi^{3+}(aq)+6\ e^{-}\rightarrow 2\ Bi(s)}$	+0.20 V	
L: $\mathrm{Bi_2S_3(s)+6\ e^{-}\rightarrow 2\ Bi(s)+3\ S^{2-}(aq)}$	−0.76 V	
Overall(R − L): $\mathrm{2\ Bi^{3+}(aq)+3\ S^{2-}(aq)\rightarrow Bi_2S_3(s)}$	+0.96 V	$\nu = 6$

(i) $$\ln K = \frac{\nu F E^{\ominus}_{\text{cell}}}{RT}\ [6\mathrm{C}.5] = \frac{6(0.96\,\mathrm{V})}{(25.693\times10^{-3}\ \mathrm{V})} = 22\bar{4}$$

$$K = \mathrm{e}^{22\bar{4}} = 1.9\times10^{97}$$

The solubility equilibrium is written as the reverse of the cell reaction. Therefore, the solubility product of Bi$_2$S$_3$(s) is $K_{\text{sp}} = K^{-1} = 1\ /\ 1.9\times10^{97} = \boxed{5.3\times10^{-98}}$.

(ii) The solubility product of Bi$_2$S$_3$(s) is very small. Consequently, the molar solubility, *s*, of Bi$_2$S$_3$(s) must also be very low and we can reasonably take the activity coefficients of the aqueous ions to equal 1.

$$K_{\text{sp}} = \left[\mathrm{Bi^{2+}}\right]^2\left[\mathrm{S^{2-}}\right]^3/\left(c^{\ominus}\right)^5 = (2s)^2(3s)^3/\left(c^{\ominus}\right)^5 = 108\left(s/c^{\ominus}\right)^5$$

$$s = \left(K_{\text{sp}}/108\right)^{1/5}c^{\ominus} = \left(5.3\times10^{-98}/108\right)^{1/5}\ \mathrm{mol\ dm^{-3}} = \boxed{1.4\times10^{-20}\ \mathrm{mol\ dm^{-3}}\ \text{or } 7.2\ \mathrm{ag\ dm^{-3}}}$$

Solutions to problems

6D.2 The method of the solution is first to determine $\Delta_{\mathrm{r}}G^{\ominus}, \Delta_{\mathrm{r}}H^{\ominus}$, and $\Delta_{\mathrm{r}}S^{\ominus}$ at 25 °C for the cell reaction

$$\tfrac{1}{2}\mathrm{H_2(g)+AgCl(s)\rightarrow Ag(s)+HCl(aq)} \qquad \nu = 1$$

and then, from the values of these quantities and the known values of $\Delta_{\mathrm{f}}G^{\ominus}$, $\Delta_{\mathrm{f}}H^{\ominus}$, and $S^{\ominus}$, for all the species other than $\mathrm{Cl^{-}(aq)}$, to calculate $\Delta_{\mathrm{f}}G^{\ominus}$, $\Delta_{\mathrm{f}}H^{\ominus}$, and $S^{\ominus}$ for $\mathrm{Cl^{-}(aq)}$.

Since $E^{\ominus}_{\text{cell}} = E^{\ominus}_{\mathrm{AgCl/Ag,Cl^{-}}} - E^{\ominus}_{\mathrm{H^{+}/H_2}} = E^{\ominus}_{\mathrm{AgCl/Ag,Cl^{-}}} - 0 = E^{\ominus}_{\mathrm{AgCl/Ag,Cl^{-}}}$, we have (R.G. Bates and V.E. Bowers, *J. Res. Nat. Bur. Stand.*, **53**, 283 (1954)):

$$E^{\ominus}_{\text{cell}}/\mathrm{V} = 0.236\,59 - 4.8564\times10^{-4}\,(\theta/{}^{\circ}\mathrm{C}) - 3.4205\times10^{-6}\,(\theta/{}^{\circ}\mathrm{C})^2 + 5.869\times10^{-9}\,(\theta/{}^{\circ}\mathrm{C})^3$$

and we proceed with the calculation of the electrochemical and thermodynamic reaction properties at 25 °C.

$$\begin{aligned} E^{\ominus}_{\text{cell}}/\mathrm{V} &= (0.23659)-(4.8564\times10^{-4})\times(25.00)-(3.4205\times10^{-6})\times(25.00)^2+(5.869\times10^{-9})\times(25.00)^3 \\ &= +0.22240\,\mathrm{V}\end{aligned}$$

$$\begin{aligned}\Delta_{\mathrm{r}}G^{\ominus} &= -\nu F E^{\ominus}_{\text{cell}} \\ &= -1\times(96.485\ \mathrm{kC\ mol^{-1}})\times(0.22240\ \mathrm{V}) = -21.46\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

$$\Delta_r S^{\ominus} = -\left(\frac{\partial \Delta_r G^{\ominus}}{\partial T}\right)_p = \nu F\left(\frac{\partial E^{\ominus}_{\text{cell}}}{\partial T}\right)_p \ [6\text{C}.6] = \nu F\left(\frac{\partial E^{\ominus}_{\text{cell}}}{\partial \theta}\right)_p \frac{{}^\circ\text{C}}{\text{K}} \quad \left[\mathrm{d}\theta/{}^\circ\text{C} = \mathrm{d}T/\text{K}\right]$$

$$= \nu F\left\{\left(-4.8564\times10^{-4}/{}^\circ\text{C}\right) - 2\times\left(3.4205\times10^{-6}\,\theta/({}^\circ\text{C})^2\right) + 3\times\left(5.869\times10^{-9}\,\theta^2/({}^\circ\text{C})^3\right)\right\}\frac{{}^\circ\text{C V}}{\text{K}}$$

$$= 1\times(96.485\text{ kC mol}^{-1})\times\left\{\begin{matrix}\left(-4.8564\times10^{-4}\right) - 2\times\left(3.4205\times10^{-6}\right)\times(25) \\ +3\times\left(5.869\times10^{-9}\right)\times(25)^2\end{matrix}\right\}\frac{\text{V}}{\text{K}}$$

$$= -62.30\text{ J K}^{-1}\text{ mol}^{-1}$$

$$\Delta_r H^{\ominus} = \Delta_r G^{\ominus} + T\Delta_r S^{\ominus}$$

$$= -(21.46\text{ kJ mol}^{-1}) + (298.15\text{ K})\times(-62.30\text{ J K}^{-1}\text{ mol}^{-1}) = -40.03\text{ kJ mol}^{-1}$$

The cell reaction Gibb's energy is related to formation Gibb's energies by

$$\Delta_r G^{\ominus} = \Delta_f G^{\ominus}\left(\text{H}^+\right) + \Delta_f G^{\ominus}\left(\text{Cl}^-\right) - \Delta_f G^{\ominus}\left(\text{AgCl}\right)$$

$$= \Delta_f G^{\ominus}\left(\text{C1}^-\right) - \Delta_f G^{\ominus}\left(\text{AgCl}\right) \quad \left[\Delta_f G^{\ominus}\left(\text{H}^+\right) = 0\right]$$

Hence, $\Delta_f G^{\ominus}\left(\text{Cl}^-\right) = \Delta_r G^{\ominus} + \Delta_f G^{\ominus}\left(\text{AgCl}\right)$

$$= \left(-21.46 - 109.79\right)\text{ kJ mol}^{-1}$$

$$= \boxed{-131.25\text{ kJ mol}^{-1}}$$

Similarly, $\Delta_f H^{\ominus}\left(\text{Cl}^-\right) = \Delta_r H^{\ominus} + \Delta_f H^{\ominus}\left(\text{AgCl}\right)$

$$= \left(-40.03 - 127.07\right)\text{ kJ mol}^{-1}$$

$$= \boxed{-167.10\text{ kJ mol}^{-1}}$$

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 $S^{\ominus}\left(\text{H}^+\right) = 0$. Then,

$$S^{\ominus}\left(\text{Cl}^-\right) = \Delta_r S^{\ominus} - S^{\ominus}\left(\text{Ag}\right) + \tfrac{1}{2}S^{\ominus}\left(\text{H}_2\right) + S^{\ominus}\left(\text{AgCl}\right)$$

$$= \left\{(-62.30) - (42.55) + \tfrac{1}{2}\times(130.68) + (96.2)\right\}\text{ J K}^{-1}\text{ mol}^{-1}$$

$$= \boxed{+56.7\text{ J K}^{-1}\text{ mol}^{-1}}$$

Integrated activities

6.3 (a) $I = \dfrac{1}{2}\left\{\left(\dfrac{b}{b^{\ominus}}\right)_+ z_+^2 + \left(\dfrac{b}{b^{\ominus}}\right)_- z_-^2\right\}[5\text{F}.9] = 4\left(\dfrac{b}{b^{\ominus}}\right)$

For CuSO$_4$, $I = (4)\times(1.0\times10^{-3}) = \boxed{4.0\times10^{-3}}$

For ZnSO$_4$, $I = (4)\times(3.0\times10^{-3}) = \boxed{1.2\times10^{-2}}$

(b) $\log\gamma_\pm = -|z_+z_-|AI^{1/2}$ [5F.8]

$$\log\gamma_\pm(\text{CuSO}_4) = -(4)\times(0.509)\times(4.0\times10^{-3})^{1/2} = -0.12\overline{88}$$

$$\gamma_\pm(\text{CuSO}_4) = \boxed{0.74}$$

$$\log\gamma_\pm(\text{ZnSO}_4) = -(4)\times(0.509)\times(1.2\times10^{-2})^{1/2} = -0.22\overline{30}$$

$$\gamma_\pm(\text{ZnSO}_4) = \boxed{0.60}$$

(c) The reaction in the Daniell cell is

$$\text{Cu}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + \text{Zn(s)} \rightarrow \text{Cu(s)} + \text{Zn}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$$

Hence, $Q=\dfrac{a(\mathrm{Zn}^{2+})a(\mathrm{SO}_4^{2-},\mathrm{R})}{a(\mathrm{Cu}^{2+})a(\mathrm{SO}_4^{2-},\mathrm{L})}$

$$=\frac{\gamma_+ b_+(\mathrm{Zn}^{2+})\gamma_- b_-(\mathrm{SO}_4^{2-},\mathrm{R})}{\gamma_+ b_+(\mathrm{Cu}^{2+})\gamma_- b_-(\mathrm{SO}_4^{2-},\mathrm{L})}\qquad\left[b\equiv\frac{b}{b^{\ominus}}\text{ here and below}\right]$$

where the designations R and L refer to the right and left sides of the equation for the cell reaction and all b are assumed to be unitless, that is, $b/b^{\ominus}$.

$$b_+(\mathrm{Zn}^{2+})=b_-(\mathrm{SO}_4^{2-},\mathrm{R})=b(\mathrm{ZnSO}_4)$$

$$b_+(\mathrm{Cu}^{2+})=b_-(\mathrm{SO}_4^{2-},\mathrm{L})=b(\mathrm{CuSO}_4)$$

Therefore,

$$Q=\frac{\gamma_\pm^2(\mathrm{ZnSO}_4)b^2(\mathrm{ZnSO}_4)}{\gamma_\pm^2(\mathrm{CuSO}_4)b^2(\mathrm{CuSO}_4)}=\frac{(0.60)^2\times(3.0\times10^{-3})^2}{(0.74)^2\times(1.0\times10^{-3})^2}=5.9\overline{2}=\boxed{5.9}$$

(d) $E^{\ominus}_{\mathrm{cell}}=-\dfrac{\Delta_\mathrm{r}G^{\ominus}}{\nu F}[6\mathrm{C}.3]=\dfrac{-(-212.7\times10^3\ \mathrm{J\ mol^{-1}})}{(2)\times(9.6485\times10^4\ \mathrm{C\ mol^{-1}})}=\boxed{+1.102\ \mathrm{V}}$

(e) $E_{\mathrm{cell}}=E^{\ominus}_{\mathrm{cell}}-\dfrac{25.693\times10^{-3}\ \mathrm{V}}{\nu}\ln Q=(1.102\ \mathrm{V})-\left(\dfrac{25.693\times10^{-3}\ \mathrm{V}}{2}\right)\ln(5.9\overline{2})$

$$=(1.102\ \mathrm{V})-(0.023\ \mathrm{V})=\boxed{+1.079\ \mathrm{V}}$$

6.4 $\mathrm{Pt|H_2\,(g,}p^{\ominus})\mathrm{|NaOH(aq,0.01000\ mol\ kg^{-1}),NaCl(aq,0.01125\ mol\ kg^{-1})|AgCl(s)|Ag(s)}$

$$\mathrm{H_2(g,}\ p^{\ominus})+2\ \mathrm{AgCl(s)}\rightarrow 2\ \mathrm{Ag(s)}+2\ \mathrm{Cl^-(aq)}+2\ \mathrm{H^+(aq)}$$

where $v = 2$ [Activities of solids equal 1 and $p_{\mathrm{H_2}}=p^{\ominus}$.]

$$E_{\mathrm{cell}}=E^{\ominus}_{\mathrm{cell}}-\frac{RT}{2F}\ln\left\{a_{\mathrm{H^+}}a_{\mathrm{Cl^-}}\right\}^2\quad[6\mathrm{C}.4\text{ and }6\mathrm{A}.12(\mathrm{b})]$$

$$=E^{\ominus}_{\mathrm{cell}}-\frac{RT}{F}\ln\left\{a_{\mathrm{H^+}}a_{\mathrm{Cl^-}}\right\}=E^{\ominus}-\frac{RT}{F}\ln\frac{K_\mathrm{w}a_{\mathrm{Cl^-}}}{a_{\mathrm{OH^-}}}=E^{\ominus}-\frac{RT}{F}\ln\frac{K_\mathrm{w}\gamma_\pm b_{\mathrm{Cl^-}}}{\gamma_\pm b_{\mathrm{OH^-}}}$$

$$=E^{\ominus}_{\mathrm{cell}}-\frac{RT}{F}\ln\frac{K_\mathrm{w}b_{\mathrm{Cl^-}}}{b_{\mathrm{OH^-}}}=E^{\ominus}-\frac{RT}{F}\ln K_\mathrm{w}-\frac{RT}{F}\ln\frac{b_{\mathrm{Cl^-}}}{b_{\mathrm{OH^-}}}$$

$$=E^{\ominus}_{\mathrm{cell}}+\ln10\frac{RT}{F}\times\mathrm{p}K_\mathrm{w}-\frac{RT}{F}\ln\frac{b_{\mathrm{Cl^-}}}{b_{\mathrm{OH^-}}}\quad\left(\mathrm{p}K_\mathrm{w}=-\log K_\mathrm{w}=\frac{-\ln K_\mathrm{w}}{\ln10}\right)$$

Hence, $\mathrm{p}K_\mathrm{w}=\dfrac{E_{\mathrm{cell}}-E^{\ominus}_{\mathrm{cell}}}{\ln10\ RT/F}+\dfrac{\ln\left(\dfrac{b_{\mathrm{Cl^-}}}{b_{\mathrm{OH^-}}}\right)}{\ln10}$

$$=\left(5039.75\ \mathrm{V^{-1}}\right)\times\left(\frac{E_{\mathrm{cell}}-E^{\ominus}_{\mathrm{cell}}}{T/\mathrm{K}}\right)+\frac{\ln\left(0.0100/0.01125\right)}{\ln10}$$

$$==\left(5039.75\ \mathrm{V^{-1}}\right)\times\left(\frac{E_{\mathrm{cell}}-E^{\ominus}_{\mathrm{cell}}}{T/\mathrm{K}}\right)-0.05115$$

Using information of the data tables, we find that

$$E^{\ominus}_{\mathrm{cell}}=E^{\ominus}_\mathrm{R}-E^{\ominus}_\mathrm{L}=E^{\ominus}(\mathrm{AgCl,\ Ag})-E^{\ominus}\left(\mathrm{H^+/H_2}\right)=+0.22\ \mathrm{V}-0=+0.22\ \mathrm{V}\ .$$

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 ed): $E^{\ominus}_{\text{cell}} = 0.22233\ \text{V}$. We then draw up the following table.

θ / °C	20.0	25.0	30.0
E_{cell} / V	1.04774	1.04864	1.04942
pK_{w}	$\boxed{14.14}$	$\boxed{13.92}$	$\boxed{13.70}$

Inspection of the table reveals that for each 5 K increase in temperature the value of pK_{w} decreases by 0.22 and, consequently, d(pK_{w})/dT = −0.22 / 5.0 K = −0.044 K^{-1}. Thus, at 25°C:

$$\frac{\text{d}\ln K_{\text{w}}}{\text{d}T} = \frac{\Delta_{\text{w}}H^{\ominus}}{RT^2}\quad [\text{6B.2(a)}]$$

$$\Delta_{\text{w}}H^{\ominus} = RT^2\frac{\text{d}\ln K_{\text{w}}}{\text{d}T} = \ln 10\times RT^2\frac{\text{d}\log K_{\text{w}}}{\text{d}T} = -\ln 10\times RT^2\frac{\text{d}\,\text{p}K_{\text{w}}}{\text{d}T}$$

$$= -\ln 10\times\left(8.3145\times10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1}\right)\times\left(298.15\ \text{K}\right)^2\times\left(-0.044\ \text{K}^{-1}\right)$$

$$= \boxed{+74.9\ \text{kJ mol}^{-1}}$$

$$\Delta_{\text{w}}G^{\ominus} = -RT\ln K_{\text{w}} = \ln 10\times RT\times\text{p}K_{\text{w}} = \boxed{+79.5\ \text{kJ mol}^{-1}}$$

$$\Delta_{\text{w}}S^{\ominus} = \frac{\Delta_{\text{w}}H^{\ominus}-\Delta_{\text{w}}G^{\ominus}}{T} = \boxed{-15.4\ \text{J K}^{-1}\ \text{mol}^{-1}}$$

6.5‡ Electrochemical Cell Equation: $\tfrac{1}{2}\text{H}_2(\text{g},1\ \text{bar}) + \text{AgCl(s)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{Ag(s)}$

with $a(\text{H}_2) = 1\ \text{bar} = p^{\ominus}$ and $a_{\text{Cl}^-} = \gamma_{\text{Cl}^-}b$.

Weak acid Equilibrium: $\text{BH}^+ \rightleftharpoons \text{B} + \text{H}^+$ with $b_{\text{BH}^+} = b_{\text{B}} = b$

$$K_{\text{a}} = a_{\text{B}}a_{\text{H}^+}/a_{\text{BH}^+} = \gamma_{\text{B}}ba_{\text{H}^+}/\left(\gamma_{\text{BH}^+}b\right) = \gamma_{\text{B}}a_{\text{H}^+}/\gamma_{\text{BH}^+}$$

Thus, $a_{\text{H}^+} = \gamma_{\text{BH}^+}K_{\text{a}}/\gamma_{\text{B}}$.

Ionic strength (neglect b_{H^+} because $b_{\text{H}^+} << b$): $I = \tfrac{1}{2}\{z^2_{\text{BH}^+}b_{\text{BH}^+} + z^2_{\text{Cl}^-}b_{\text{Cl}^-}\} = b$.

According to the Nernst equation [6C.4]

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{F}\ln\left(\frac{a_{\text{H}^+}a_{\text{Cl}^-}}{p(\text{H}_2)/p^{\ominus}}\right) = E^{\ominus}_{\text{cell}} - \frac{RT\ \ln(10)}{F}\log(a_{\text{H}^+}a_{\text{Cl}^-})$$

$$\frac{F}{RT\ln(10)}\left(E_{\text{cell}} - E^{\ominus}_{\text{cell}}\right) = -\log(a_{\text{H}^+}\gamma_{\text{Cl}^-}b) = -\log\left(\frac{K_{\text{a}}\gamma_{\text{BH}^+}\gamma_{\text{Cl}^-}b}{\gamma_{\text{B}}}\right)$$

$$= \text{p}K_{\text{a}} - \log(b) - 2\log(\gamma_{\pm})\quad\text{where}\quad \gamma^2_{\pm} \equiv \gamma_{\text{BH}^+}\gamma_{\text{Cl}^-}/\gamma_{\text{B}}$$

Substitution of the Davies equation,

$$\log\gamma_{\pm} = -\frac{A|z_+z_-|I^{1/2}}{1+BI^{1/2}} + CI\quad [\text{5F.11(b)}],$$

gives

$$\frac{F}{RT\ln(10)}\left(E_{\text{cell}} - E^{\ominus}_{\text{cell}}\right) = \text{p}K_{\text{a}} - \log(b) + \frac{2A\sqrt{b}}{1+B\sqrt{b}} - 2Cb\qquad\text{where}\quad A = 0.5091.$$

The expression to the left of the above equality is experimental data that is a function of b. The parameters pK_{a}, B, and C on the right side are systematically varied with a mathematical regression software package like Mathcad until the right side fits the left side in a least squares sense. The results are: $\boxed{\text{p}K_{\text{a}} = 6.736}$, $\boxed{B = 1.997}$, and $\boxed{C = -0.121}$.

The mean activity coefficient is calculated with the equation $\gamma_{\pm} = 10^{\left(\frac{-AI^{1/2}}{1+BI^{1/2}}+Cb\right)}$ for desired values of b and I. Figure I6.1 shows a $\gamma_{\pm}$ against I plot for $b = 0.04 \text{ mol kg}^{-1}$ and $0 \le I \le 0.1$.

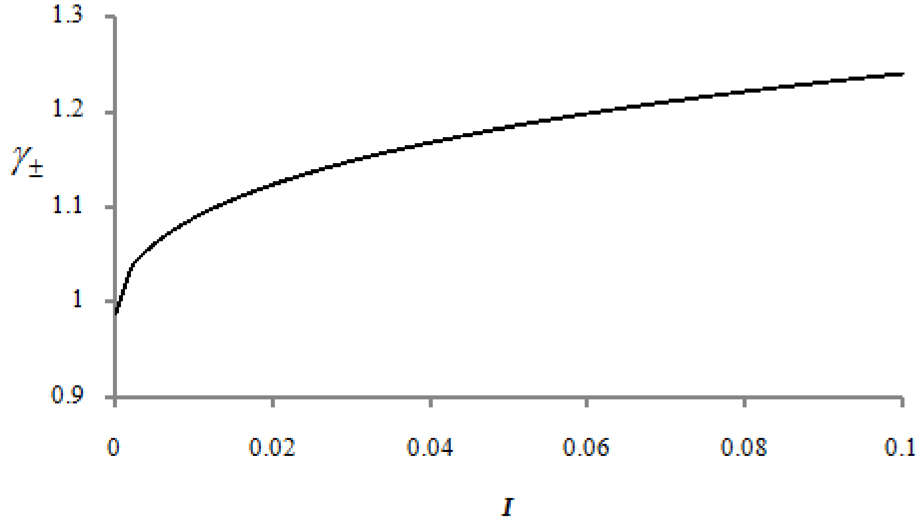


Figure I6.1

6.6 $\Delta_r G = \Delta_r G^{\ominus} + RT \ln Q$ [6A.10]

In Equation 6A.10 molar solution concentrations are used with 1 M standard states ($c^{\ominus} = 1 \text{ mol dm}^{-3}$). The standard state ($\ominus$) pH equals zero in contrast to the biological standard state ($\oplus$) of pH 7. For the ATP hydolysis

$$\text{ATP(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{ADP(aq)} + \text{P}_\text{i}^-\text{(aq)} + \text{H}_3\text{O}^+\text{(aq)}$$

we can calculate the standard state free energy given the biological standard free energy of about –31 kJ mol^{-1} (Impact On Biochemistry *I*6.1).

$$\Delta_r G^{\oplus} = \Delta_r G^{\ominus} + RT \ln Q^{\oplus} \quad [6A.10]$$

$$\Delta_r G^{\ominus} = \Delta_r G^{\oplus} - RT \ln Q^{\oplus}$$

$$= -31 \text{ kJ mol}^{-1} - \left(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}\right) \times (310 \text{ K}) \ln\left(10^{-7} \text{ M/1 M}\right)$$

$$= +11 \text{ kJ mol}^{-1}$$

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$_\text{i}^-$] = 1.0×10^{-3} M, is interesting.

$$\Delta_r G = \Delta_r G^{\ominus} + RT \ln Q = \Delta_r G^{\ominus} + RT \ln\left(\frac{[\text{ADP}] \times [\text{P}_\text{i}^-] \times [\text{H}^+]}{[\text{ATP}] \times (1 \text{ M})^2}\right)$$

$$= +11 \text{ kJ mol}^{-1} + \left(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}\right) \times (310 \text{ K}) \ln\left(10^{-3} \times 10^{-7}\right)$$

$$= -48 \text{ kJ mol}^{-1}$$

The concentration conditions in biological cells make the hydrolysis of ATP spontaneous and very exergonic. A maximum of 48 kJ of work is available to drive coupled chemical reactions when a mole of ATP is hydrolyzed.

6.7 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.

$CH_3CH_2OH \rightarrow CH_3CHO \rightarrow CH_3COOH \rightarrow CO_2 + H_2O$
ethanol ethanal ethanoic acid

The nitrate oxidant may receive electrons to yield any of the following products.

$NO_3^- \rightarrow NO_2^- \rightarrow N_2 \rightarrow NH_3$
nitrate nitrite dinitrogen ammonia

Oxidation of two ethanol molecules to carbon dioxide and water can transfer 8 electrons to nitrate during the formation of ammonia. The half-reactions and net reaction are:

$$2\,[CH_3CH_2OH(l) \rightarrow 2\,CO_2(g) + H_2O(l) + 4\,H^+(aq) + 4\,e^-]$$
$$NO_3^-(aq) + 9\,H^+(aq) + 8\,e^- \rightarrow NH_3(aq) + 3\,H_2O(l)$$

$$2\,CH_3CH_2OH(l) + H^+(aq) + NO_3^-(aq) \rightarrow 4\,CO_2(g) + 5\,H_2O(l) + NH_3(aq)$$

$\Delta_r G^\ominus = -2331.29\text{ kJ}$ 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.

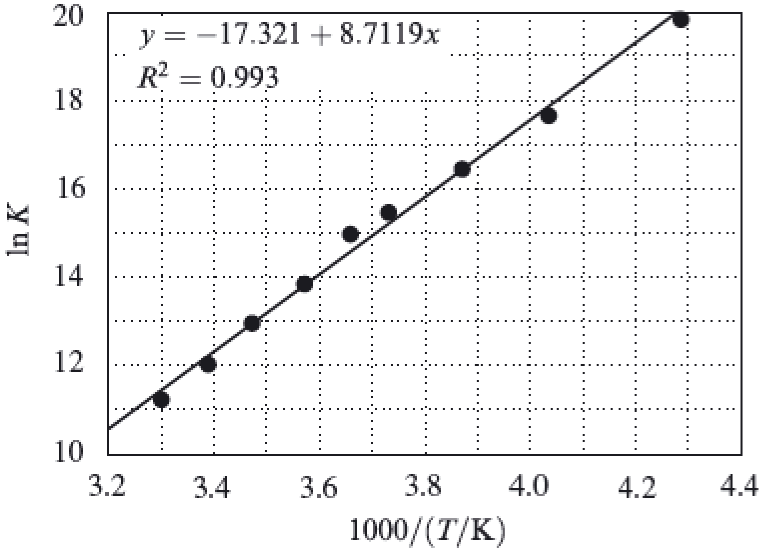
6.8‡ **(a)** The equilibrium constant is given by

$$K = \exp\left(\frac{-\Delta_r G^\ominus}{RT}\right) = \exp\left(\frac{-\Delta_r H^\ominus}{RT}\right)\exp\left(\frac{\Delta_r S^\ominus}{R}\right) \quad [6A.18]$$

so $\ln K = -\dfrac{-\Delta_r H^\ominus}{RT} + \dfrac{\Delta_r S^\ominus}{R}$.

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 $\Delta_r S^\ominus/R$ (Fig. I6.2).

Figure I6.2



So $\Delta_r H^\ominus = -R \times \text{slope} = -(8.3145\times10^{-3}\text{ kJ mol}^{-1}\text{ K}^{-1})\times(8.71\times10^{3}\text{ K})$

$= \boxed{-72.4\text{ kJ mol}^{-1}}$

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 $\Delta_f H^\ominus((ClO)_2) = \Delta_r H^\ominus + 2\,\Delta_f H^\ominus(ClO)$.

$\Delta_f H^\ominus((ClO)_2) = [-72.4 + 2(101.8)]\text{kJ mol}^{-1} = \boxed{+131.2\text{ kJ mol}^{-1}}$

$$S^{\ominus}\left((\mathrm{ClO})_2\right) = \left[-144 + 2(226.6)\right] \mathrm{J\ K^{-1}\ mol^{-1}} = \boxed{+309.2\ \mathrm{J\ K^{-1}\ mol^{-1}}}$$

7 Introduction to quantum theory

7A The origins of quantum mechanics

Answers to discussion questions

7A.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 relation $E = nh\nu = nhc/\lambda$ 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.

7A.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 of wave–particle duality include the quantization of available energies for small fundamental particles like electrons, atoms, and molecules. Another consequence is the impossibility of simultaneously specifying with unlimited precision the values of the complementary observables position and momentum. Likewise, the values of energy and the time of an event occurrence cannot be simultaneously measured with unlimited precision. Wave-particle duality causes the multiplied uncertainties of **complementary observables**, such as x and p_x or E and t, to be greater than, or equal to, $\hbar/2$ (i.e., the **Heisenberg uncertainty principle** of eqns 7C.13a and 7C.17). 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, often called postulates (text 7C.4), of quantum mechanics to interpret their behavior and observable properties. These tenets are elaborated upon throughout text Chapter 7 Sections A, B, and C. Here's a summary of these tenets:

Tenet I: 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, ...) in the system.

Tenet II, The **Born interpretation**: For a system described by the wavefunction $\psi(\boldsymbol{r})$, the probability of finding the particle in the volume $d\tau$ is proportional to $|\psi|^2 d\tau = \psi^*\psi d\tau$. The constant of proportionality, the **normalization constant**, is chosen so that the integral $\int_{\text{all space}} |\psi|^2 d\tau$ equals 1.

Tenet III: For each observable property Ω of a system there is a corresponding operator $\hat{\Omega}$ built from the following position and linear momentum operators.

$$\hat{x} = x\times \qquad \text{and} \qquad \hat{p}_x = \frac{\hbar}{\mathrm{i}}\frac{d}{dx} \quad [7C.3]$$

Tenet IV: 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.

Tenet V: 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 $|c_k|^2$.

Solutions to exercises

7A.1(b) $\Delta E = h\nu = h/T \quad [T = \text{period} = 1/\nu] \quad$ and $\quad \Delta E_{\mathrm{m}} = N_{\mathrm{A}}\Delta E$

(i) For T = 2.50 fs

$$\Delta E = \left(6.626\times10^{-34}\ \mathrm{J\ s}\right)/\left(2.50\times10^{-15}\ \mathrm{s}\right) = \boxed{2.65\times10^{-19}\ \mathrm{J}}$$

$$\Delta E_\mathrm{m} = \left(6.022\times10^{23}\ \mathrm{mol^{-1}}\right)\times\left(2.65\times10^{-19}\ \mathrm{J}\right) = \boxed{160\ \mathrm{kJ\ mol^{-1}}}$$

(ii) For $T = 2.21$ fs

$$\Delta E = \left(6.626\times10^{-34}\ \mathrm{J\ s}\right)/\left(2.21\times10^{-15}\ \mathrm{s}\right) = \boxed{3.00\times10^{-19}\ \mathrm{J}}$$

$$\Delta E_\mathrm{m} = \left(6.022\times10^{23}\ \mathrm{mol^{-1}}\right)\times\left(3.00\times10^{-19}\ \mathrm{J}\right) = \boxed{181\ \mathrm{kJ\ mol^{-1}}}$$

(iii) For $T = 1.0$ ms

$$\Delta E = \left(6.626\times10^{-34}\ \mathrm{J\ s}\right)/\left(1.0\times10^{-3}\ \mathrm{s}\right) = \boxed{6.6\times10^{-31}\ \mathrm{J}}$$

$$\Delta E_\mathrm{m} = \left(6.022\times10^{23}\ \mathrm{mol^{-1}}\right)\times\left(6.6\times10^{-31}\ \mathrm{J}\right) = \boxed{4.0\times10^{-10}\ \mathrm{kJ\ mol^{-1}}}$$

7A.2(b) $E = h\nu = \dfrac{hc}{\lambda}\ \ [\text{Example 7A.2}] = \dfrac{\left(6.626\times10^{-34}\ \mathrm{J\ s}\right)\times\left(2.998\times10^{8}\ \mathrm{m\ s^{-1}}\right)}{\lambda} = \dfrac{1.986\times10^{-25}\ \mathrm{J\ m}}{\lambda}$

$$E_\mathrm{m} = N_\mathrm{A}E = \frac{N_\mathrm{A}hc}{\lambda} = \frac{0.1196\ \mathrm{J\ m}}{\lambda}$$

We can therefore draw up the following table.

λ / m	E / J	E_m / (kJ mol^{-1})
(i) 200×10^{-9}	9.93×10^{-19}	598
(ii) 150×10^{-12}	1.32×10^{-15}	7.97×10^{5}
(iii) 1.00×10^{-2}	1.99×10^{-23}	0.012

7A.3(b) Upon 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: $E_\mathrm{k} = E_\mathrm{photon} = \tfrac{1}{2}m_\mathrm{He}v^2$. The values of E_photon are calculated in Exercise 7A.2(b) so the atom is accelerated to the speed

$$v = \sqrt{\frac{2E_\mathrm{photon}}{m_\mathrm{He}}} = \sqrt{\frac{2E_\mathrm{photon}}{4.0026\times u}}$$

$$= \sqrt{\frac{2E_\mathrm{photon}}{4.0026\times\left(1.66054\times10^{-27}\ \mathrm{kg}\right)}} = \left(1.7347\times10^{13}\ \mathrm{m\ s^{-1}}\right)\times\sqrt{E_\mathrm{photon}/\mathrm{J}}$$

We can therefore draw up the following table.

λ	E_photon / J	v / (km s^{-1})
(i) 200×10^{-9}	9.93×10^{-19}	17.3
(ii) 150×10^{-12}	1.32×10^{-15}	630
(iii) 1.00×10^{-2}	1.99×10^{-23}	0.0774

7A.4(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 $E_\mathrm{photon} = h\nu = hc/\lambda$ [C.3]. The total number of photons emitted in an interval Δt is then the total energy divided by the energy per photon.

$$N = \frac{P\Delta t}{E_\mathrm{photon}} = \frac{P\Delta t\lambda}{hc}$$

Assuming that de Broglie's relation 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

$$p = Np_{\text{photon}} = \frac{Nh}{\lambda}\ [7\text{A}.14] = \frac{P\Delta t\lambda}{hc}\times\frac{h}{\lambda} = \frac{P\Delta t}{c}$$

Since $p = (mv)_{\text{spacecraft}}$, the final speed of the spacecraft is

$$v = \frac{P\Delta t}{c\, m_{\text{spacecraft}}}$$

$$= \frac{(1.50\times10^{3}\ \text{W})\times(10\ \text{y})\times(3.1557\times10^{7}\ \text{s y}^{-1})}{(2.9979\times10^{8}\ \text{m s}^{-1})\times(10.0\ \text{kg})} = \boxed{158\ \text{m s}^{-1}}$$

7A.5(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 $E_{\text{photon}} = h\nu = hc/\lambda$ [C.3]. The total number of photons emitted in an interval Δt is then the total energy divided by the energy per photon.

$$N = \frac{P\Delta t}{E_{\text{photon}}} = \frac{P\Delta t\lambda}{hc}$$

$$= \frac{(1.00\ \text{s})\times(700\times10^{-9}\ \text{m})}{(6.626\times10^{-34}\ \text{J s})\times(2.998\times10^{8}\ \text{m s}^{-1})}P = (3.52\times10^{18})\times P/\text{W}$$

(i) When P = 0.10 W, $N = \boxed{3.52\times10^{17}}$.

(ii) When P = 1.0 W, $N = \boxed{3.52\times10^{18}}$.

7A.6(b) $E_{\text{k}} = h\nu - \Phi = \frac{hc}{\lambda} - \Phi$ [7A.13] and, since $E_{\text{k}} = \tfrac{1}{2}m_{\text{e}}v^{2}$, $v = \sqrt{2E_{\text{k}}/m_{\text{e}}}$

$$\Phi = 2.09\,\text{eV} = (2.09)\times(1.602\times10^{-19}\ \text{J}) = 3.35\times10^{-19}\ \text{J}$$

(i) For λ = 650 nm

$$E_{\text{k}} = \frac{(6.626\times10^{-34}\ \text{J s})\times(2.998\times10^{8}\ \text{m s}^{-1})}{650\times10^{-9}\ \text{m}} - 3.35\times10^{-19}\ \text{J} = 3.06\times10^{-19}\ \text{J} - 3.35\times10^{-19}\ \text{J}$$

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.

(ii) For λ = 195 nm

$$E_{\text{k}} = \frac{(6.626\times10^{-34}\ \text{J s})\times(2.998\times10^{8}\ \text{m s}^{-1})}{195\times10^{-9}\ \text{m}} - 3.35\times10^{-19}\ \text{J} = 1.02\times10^{-18}\ \text{J} - 3.35\times10^{-19}\ \text{J}$$

$$= \boxed{6.84\times10^{-19}\ \text{J}}$$

$$v = \sqrt{2\times(6.84\times10^{-19}\ \text{J})/(9.109\times10^{-31}\ \text{kg})} = \boxed{1.23\ \text{Mm s}^{-1}}$$

7A.7(b) $E_{\text{binding}} = E_{\text{photon}} - E_{\text{k}} = h\nu - \tfrac{1}{2}m_{\text{e}}v^{2} = \frac{hc}{\lambda} - \tfrac{1}{2}m_{\text{e}}v^{2}$

$$E_{\text{binding}} = \frac{hc}{\lambda} - \tfrac{1}{2}m_{\text{e}}v^{2}$$

$$= \frac{(6.626\times10^{-34}\ \text{J s})\times(2.998\times10^{8}\ \text{m s}^{-1})}{121\times10^{-12}\ \text{m}} - \tfrac{1}{2}(9.109\times10^{-31}\ \text{kg})\times(5.69\times10^{7}\ \text{m s}^{-1})^{2}$$

$$= (1.67\times10^{-16}\ \text{J})\times\left(\frac{1\ \text{eV}}{1.602\times10^{-19}\ \text{J}}\right) = \boxed{1.04\ \text{keV}}\ \text{without a relativistic mass correction}$$

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.

$$m = \frac{m_{\text{e}}}{\left(1-(v/c)^{2}\right)^{1/2}} = \frac{9.109\times10^{-31}\ \text{kg}}{\left(1-(5.69\times10^{7}\ \text{m s}^{-1}/2.998\times10^{8}\ \text{m s}^{-1})^{2}\right)^{1/2}} = 9.28\times10^{-31}\ \text{kg}$$

$$
\begin{aligned}
E_{\text{binding}} &= \frac{hc}{\lambda} - \tfrac{1}{2}mv^2 \\
&= \frac{(6.626\times10^{-34}\ \text{J s})\times(2.998\times10^{8}\ \text{m s}^{-1})}{121\times10^{-12}\ \text{m}} - \tfrac{1}{2}(9.28\times10^{-31}\ \text{kg})\times(5.69\times10^{7}\ \text{m s}^{-1})^2 \\
&= (1.39\times10^{-16}\ \text{J})\times\left(\frac{1\ \text{eV}}{1.602\times10^{-19}\ \text{J}}\right) = \boxed{0.870\ \text{keV}}\ \text{with the relativistic mass correction}
\end{aligned}
$$

7A.8(b) The de Broglie relation is $\lambda = \dfrac{h}{p}\ [7\text{A}.14] = \dfrac{h}{mv}$.

Hence, $v = \dfrac{h}{m_{\text{p}}\lambda} = \dfrac{6.626\times10^{-34}\ \text{J s}}{(1.673\times10^{-27}\ \text{kg})\times(100\times10^{-12}\ \text{m})} = \boxed{3.96\times10^{3}\ \text{m s}^{-1}}$

The kinetic energy acquired by a proton upon acceleration through a voltage of $\mathcal{E}$ equals $e\mathcal{E}$.

$$E_{\text{k}} = \frac{m_{\text{p}}v^2}{2} = e\mathcal{E}$$

Solving for the potential difference gives

$$
\begin{aligned}
\mathcal{E} &= \frac{m_{\text{p}}v^2}{2e} \\
&= \frac{(1.673\times10^{-27}\ \text{kg})\times(3.96\times10^{3}\ \text{m s}^{-1})^2}{2\times(1.602\times10^{-19}\ \text{C})} \\
&= \boxed{8.19\times10^{-2}\ \text{V}}
\end{aligned}
$$

7A.9(b) The de Broglie relation is $\lambda = \dfrac{h}{p}\ [7\text{A}.14] = \dfrac{h}{mv}$.

Hence, $v = \dfrac{h}{m_{\text{p}}\lambda} = \dfrac{6.626\times10^{-34}\ \text{J s}}{(1.673\times10^{-27}\ \text{kg})\times(3.0\times10^{-2}\ \text{m})} = \boxed{1.3\times10^{-5}\ \text{m s}^{-1}}$, which is extremely slow!

7A.10(b) The momentum of a photon is

$$p = \frac{h}{\lambda}\ [7\text{A}.14] = \frac{6.626\times10^{-34}\ \text{J s}}{350\times10^{-9}\ \text{m}} = \boxed{1.89\times10^{-27}\ \text{kg m s}^{-1}}$$

The momentum of a particle is $p = mv$ so the speed of a hydrogen molecule that has the above momentum is

$$v = \frac{p}{m_{\text{H}_2}} = \frac{p}{M_{\text{H}_2}/N_{\text{A}}} = \frac{1.89\times10^{-27}\ \text{kg m s}^{-1}}{(2.016\times10^{-3}\ \text{kg mol}^{-1}/6.022\times10^{23}\ \text{mol}^{-1})} = \boxed{0.565\ \text{m s}^{-1}}$$

7A.11(b) The de Broglie wavelength is $\lambda = \dfrac{h}{p}$ [7A.14]. The kinetic energy acquired by an electron upon 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

$\lambda = \dfrac{h}{(2me\mathcal{E})^{1/2}}$.

(i) $$\lambda = \frac{6.626\times10^{-34}\ \text{J s}}{\{2\times(9.109\times10^{-31}\ \text{kg})\times(1.602\times10^{-19}\ \text{C})\times(100\ \text{V})\}^{1/2}} = \boxed{123\ \text{pm}}$$

(ii) $$\lambda = \frac{6.626\times10^{-34}\ \text{J s}}{\{2\times(9.109\times10^{-31}\ \text{kg})\times(1.602\times10^{-19}\ \text{C})\times(1.0\times10^{3}\ \text{V})\}^{1/2}} = \boxed{39\ \text{pm}}$$

(iii) $$\lambda = \frac{6.626\times10^{-34}\ \text{J s}}{\{2\times(9.109\times10^{-31}\ \text{kg})\times(1.602\times10^{-19}\ \text{C})\times(100\times10^{3}\ \text{V})\}^{1/2}} = \boxed{3.88\ \text{pm}}$$

Solutions to problems

7A.2 As λ increases, $hc/\lambda kT$ decreases, and at very long wavelength $hc/\lambda kT \ll 1$. Hence we can expand the exponential in a power series. Let $x = hc/\lambda kT$, then $e^x = 1 + x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \cdots$ and the Planck distribution becomes

$$\rho = \frac{8\pi hc}{\lambda^5\left(1 + x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \cdots - 1\right)} = \frac{8\pi hc}{\lambda^5\left(x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \cdots\right)}$$

When x is much, much smaller than one, second and higher order terns in x become negligibly small compared to x. Consequently,

$$\lim_{\lambda\to\infty}\rho = \frac{8\pi hc}{\lambda^5 x} = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{hc/\lambda kT}\right) = \boxed{\frac{8\pi kT}{\lambda^4}}$$

This is the Rayleigh–Jeans law [7A.4].

7A.4 Since $\lambda_{\max}T \cong \tfrac{1}{5}hc/k$ by Wien's law, we find the mean of the $\lambda_{\max}T$ values and obtain h from the equation $h = \frac{5k}{c}\left(\lambda_{\max}T\right)_{\text{mean}}$. 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 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,

$$h = \frac{(5)\times(1.38066\times10^{-23}\ \text{J K}^{-1})\times(2.84\times10^{-3}\ \text{m K})}{2.99792\times10^{8}\ \text{m s}^{-1}} = \boxed{6.54\times10^{-34}\ \text{J s}}$$

Comment. Planck's estimate of the constant h in his first paper of 1900 on black body radiation was 6.55×10^{-27} erg sec$(1\,\text{erg} = 10^{-7}\ \text{J})$ 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.

7A.6 The total energy density of black-body radiation is

$$\mathcal{E} = \int_0^\infty \rho(\lambda)\,\mathrm{d}\lambda = 8\pi hc\int_0^\infty \frac{\mathrm{d}\lambda}{\lambda^5\left(e^{hc/\lambda kT} - 1\right)} \qquad [7\text{A}.6]$$

Let $x = \frac{hc}{\lambda kT}$. Then, $\mathrm{d}x = -\frac{hc}{\lambda^2 kT}\mathrm{d}\lambda$ or $\mathrm{d}\lambda = -\frac{\lambda^2 kT}{hc}\mathrm{d}x$.

$$\mathcal{E} = 8\pi kT\int_0^\infty \frac{\lambda^2\mathrm{d}x}{\lambda^5\left(e^x - 1\right)} = 8\pi kT\int_0^\infty \frac{\mathrm{d}x}{\lambda^3\left(e^x - 1\right)} = 8\pi kT\left(\frac{kT}{hc}\right)^3\int_0^\infty \frac{x^3\mathrm{d}x}{\left(e^x - 1\right)} = 8\pi kT\left(\frac{kT}{hc}\right)^3\left(\frac{\pi^4}{15}\right)$$

$$= \left(\frac{8\pi^5 k^4}{15h^3c^3}\right)T^4 = \boxed{\left(\frac{4}{c}\right)\sigma T^4} \quad \text{where } \sigma = \frac{2\pi^5k^4}{15h^3c^2} \text{ is the Stefan-Boltzmann constant}$$

This is the Stefan-Boltzmann law that specifies that the total energy-density of black-body radiation is proportional to T^4.

7A.8[‡] The wavelength $\lambda_{\max}$ at which the spectral distribution of the sun is a maximum is nicely estimated with Wien's law (see Problem 7A.7)

$$\lambda_{\max} = \frac{hc}{5kT}\ [\text{Wien's law}] = \frac{\left(6.626\times10^{-34}\ \text{J s}\right)\times\left(2.998\times10^{8}\ \text{m s}^{-1}\right)}{5\times\left(1.381\times10^{-23}\ \text{J K}^{-1}\right)\times\left(5800\ \text{K}\right)}$$

$$= 4.96\times10^{-7}\ \text{m} = \boxed{49\overline{6}\ \text{nm, blue-green}}$$

7B Dynamics of microscopic systems

Answers to discussion questions

7B.2 A central principle of quantum mechanics is that the wavefunction contains all the dynamical information about the system it describes. The normalized wavefunction $\psi(\boldsymbol{r})$ itself is called the **probability amplitude**. It contains information about the location of a particle. $|\psi(\boldsymbol{r})|^2$ is the **probability density** at the point $\boldsymbol{r}$, and to obtain the **probability** of finding a particle in an infinitesimal volume $\mathrm{d}\tau = \mathrm{d}x\mathrm{d}y\mathrm{d}z$ at $\boldsymbol{r}$ it must be multiplied by $\mathrm{d}\tau$. The probability of finding a particle in a region is found by integration of the probability density over the region:

$$P = \int_{\text{region}} \left|\psi(\boldsymbol{r})\right|^2 \mathrm{d}\tau$$

7B.4 For the wavefunction that is normalized to 1 the integral over the whole of space of the probability density, $|\psi(\boldsymbol{r})|^2$, equals 1: $\int_{\text{all space}} \left|\psi(\boldsymbol{r})\right|^2 \mathrm{d}\tau = 1$. The normalized wavefunction has the advantages of simplify expressions for measurable quantities. First, the probability of finding a particle in a region is found by integration of the probability density over the region:

$$P = \int_{\text{region}} \left|\psi(\boldsymbol{r})\right|^2 \mathrm{d}\tau$$

For an unnormalized wavefunction this probability is expressed as

$$P = \int_{\text{region}} \left|\psi(\boldsymbol{r})\right|^2 \mathrm{d}\tau \Big/ \int_{\text{all space}} \left|\psi(\boldsymbol{r})\right|^2 \mathrm{d}\tau$$

Similarly, the expectation value of the dynamical property Ω is given by the simplified integration:

$$\langle \Omega \rangle = \int \psi^* \hat{\Omega} \psi \mathrm{d}\tau \quad [7\text{C}.11]$$

Solutions to exercises

7B.1(b) The time-dependent, wavefunction in two-dimensional space is a function of x, y, and time t so we write $\psi(x,y,t)$ or $\psi(\boldsymbol{r},t)$. The infinitesimal space element is $\mathrm{d}\tau = \mathrm{d}x\mathrm{d}y$ with each variable ranging from $-\infty$ to $+\infty$. For systems with symmetry in the xy plane it is best to work in the polar coordinates r and ϕ where $r^2 = x^2 + y^2$ and $x = r\cos\phi$. These variables have the ranges $0 \le r \le \infty$ and $0 \le \phi \le 2\pi$ with the infinitesimal space element $\mathrm{d}\tau = r\,\mathrm{d}r\,\mathrm{d}\phi$.

It is reasonable to expect that in some special cases the probability densities in each of the two independent directions and time should be mutually independent. Subsequently, the wavefunction in such a case must be the product of independent wavefunctions: $\psi(\boldsymbol{r},t) \propto X(x)\times Y(y) \times T(t)$.

7B.2(b) An isolated, freely moving helium atom is expected to have a translational, time-dependent wavefunction that is a function of the center-of-mass coordinates x_{cm}, y_{cm}, and z_{cm} and time t also. So we write $\psi_{\text{cm}}(x_{\text{cm}},y_{\text{cm}},z_{\text{cm}},t)$ or $\psi_{\text{cm}}(\boldsymbol{r}_{\mathbf{cm}},t)$. The infinitesimal space element for the center-of-mass variables is $\mathrm{d}\tau_{\text{cm}} = \mathrm{d}x_{\text{cm}}\mathrm{d}y_{\text{cm}}\mathrm{d}z_{\text{cm}}$ with each variable ranging from $-\infty$ to $+\infty$.

The helium atom also has variables for the coordinates of two electrons with respect to the center-of-mass of the atom. They are the coordinates x_1, y_1, and z_1 of electron "number 1" and coordinates x_2, y_2, and z_2 of the electron "number 2". The electronic wavefunction can be written as $\psi_{\text{el}}(\boldsymbol{r}_1,\boldsymbol{r}_2,t)$. The infinitesimal space element is $\mathrm{d}\tau = \mathrm{d}x_1\mathrm{d}y_1\mathrm{d}z_1\mathrm{d}x_2\mathrm{d}y_2\mathrm{d}z_2$ with each variable ranging from $-\infty$ to $+\infty$.

In general we expect that the total wavefunction is the product $\psi_{\text{cm}}(\boldsymbol{r}_{\mathbf{cm}},t) \times \psi_{\text{el}}(\boldsymbol{r}_1,\boldsymbol{r}_2,t)$. Furthermore, we expect that there are special cases for which the translational wavefunction exhibits the separation of variables: $\psi_{\text{cm}}(\boldsymbol{r}_{\mathbf{cm}},t) \propto X_{\text{cm}}(x_{\text{cm}}) \times Y(y_{\text{cm}}) \times Z_{\text{cm}}(z_{\text{cm}}) \times T(t)$. The electronic wavefunction does not exhibit the separation of variables in either the Cartesian or spherical polar coordinate systems because the electrostatic potential between the two electrons depends upon the distance between them.

7B.3(b) The normalized wavefunction is $\psi(x) = N\sin(2\pi x/L)$ where N is the normalization constant.

$$\int_0^{2\pi}\psi^*\psi\ \mathrm{d}\varphi=1\ [\text{7B.4c}]$$

$$N^2\int_0^L \sin^2(2\pi x/L)\ \mathrm{d}x = N^2\left\{\frac{x}{2}-\frac{\sin(4\pi x/L)}{8\pi/L}\right\}_{x=0}^{x=L}=\frac{N^2L}{2}=1$$

$$\boxed{N=\left(\frac{2}{L}\right)^{1/2}}$$

7B.4(b) The normalized wavefunction is $\psi(x) = (2/L)^{½}\sin(2\pi x/L)$ 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

$$|\psi(L/2)|^2\mathrm{d}x = (2/L)\sin^2(2\pi L/2L)\,\mathrm{d}x = (2/L)\sin^2(\pi)\,\mathrm{d}x = (2/L)\times 0\ \mathrm{d}x = 0$$

The probability of finding the electron in an infinitesimal volume element at the center of the carbon nanotube equals $\boxed{\text{zero}}$.

7B.5(b) The normalized wavefunction is $\psi=\left(\frac{2}{L}\right)^{½}\sin(2\pi x/L)$.

$$\text{Probability that } L/4\le x\le L/2=\int_{L/4}^{L/2}\psi^*\psi\ \mathrm{d}x$$

$$=\left(\frac{2}{L}\right)\int_{L/4}^{L/2}\sin^2(2\pi x/L)\ \mathrm{d}x=\left(\frac{2}{L}\right)\left\{\frac{x}{2}-\frac{\sin(4\pi x/L)}{8\pi/L}\right\}\Bigg|_{x=L/4}^{x=L/2}$$

$$=\left(\frac{2}{L}\right)\left[\left\{\frac{L}{4}-\frac{\sin(4\pi L/2L)}{8\pi/L}\right\}-\left\{\frac{L}{8}-\frac{\sin(4\pi L/4L)}{8\pi/L}\right\}\right]$$

$$=\left\{\frac{1}{2}-\frac{\sin(2\pi)}{4\pi}\right\}-\left\{\frac{1}{4}-\frac{\sin(\pi)}{4\pi}\right\}=\left\{\frac{1}{2}-0\right\}-\left\{\frac{1}{4}-0\right\}$$

$$=\boxed{\frac{1}{4}}$$

Solutions to problems

7B.2 In each case the normalization constant $N^{-2}=\int|\psi|^2\mathrm{d}\tau$ 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

$$N^{-2}=\int|\psi|^2\mathrm{d}\tau=\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}|\psi|^2\,r^2\sin\theta\ \mathrm{d}r\ \mathrm{d}\theta\ \mathrm{d}\phi\qquad\left[\text{Note that } \mathrm{d}\tau=r^2\sin\theta\ \mathrm{d}r\ \mathrm{d}\theta\ \mathrm{d}\phi.\right]$$

$$=\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}r^2\times\left(R(r)\times\Theta(\theta)\times\Phi(\phi)\right)^2\sin\theta\ \mathrm{d}r\ \mathrm{d}\theta\ \mathrm{d}\phi$$

$$=\int_{r=0}^{\infty}r^2\times R(r)^2\ \mathrm{d}r\times\int_{\theta=0}^{\pi}\sin(\theta)\times\Theta(\theta)^2\ \mathrm{d}\theta\times\int_{\phi=0}^{2\pi}\Phi(\phi)^2\ \mathrm{d}\phi$$

In the special case (i) for which $\Theta(\theta)=1$ and $\Phi(\phi)=1$:

$$\int_{\theta=0}^{\pi}\sin(\theta)\times\Theta(\theta)^2\ \mathrm{d}\theta\times\int_{\phi=0}^{2\pi}\Phi(\phi)^2\ \mathrm{d}\phi=\int_{\theta=0}^{\pi}\sin(\theta)\mathrm{d}\theta\times\int_{\phi=0}^{2\pi}\mathrm{d}\phi$$

$$=\left[-\cos\theta\right]_{\theta=0}^{\pi}\times\left[\phi\right]_{\phi=0}^{2\pi}$$

$$=4\pi$$

and the 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 $\psi^2=\left(2-\dfrac{r}{a_0}\right)^2\mathrm{e}^{-2r/a_0}$.

$$N^{-2}=4\pi\int_{r=0}^{\infty}r^2\times R(r)^2\,\mathrm{d}r$$
$$=4\pi\int_{r=0}^{\infty}r^2\times\left\{\left(2-\frac{r}{a_0}\right)\mathrm{e}^{-r/a_0}\right\}^2\mathrm{d}r$$
$$=4\pi a_0^3\int_{\chi=0}^{\infty}\chi^2\times\left\{(2-\chi)\mathrm{e}^{-\chi}\right\}^2\mathrm{d}\chi\quad\text{where}\quad\chi=r/a_0$$
$$=4\pi a_0^3\int_{\chi=0}^{\infty}\left\{4\chi^2-4\chi^3+\chi^4\right\}\mathrm{e}^{-2\chi}\mathrm{d}\chi\quad\left[\text{Use the standard integral }\int_0^{\infty}\chi^n\mathrm{e}^{-a\chi}\mathrm{d}\chi=n!/a^{n+1}\right]$$
$$=4\pi a_0^3\left\{4\times 2!/2^{2+1}-4\times 3!/2^{3+1}+4!/2^{4+1}\right\}$$
$$=\pi a_0^3$$

Hence, $\boxed{N=\left(\pi a_0^3\right)^{-1/2}}$ 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 $\psi=r\sin\theta\cos\phi\,\mathrm{e}^{-r/2a_0}$ and $\psi^2=r^2\sin^2\theta\cos^2\phi\,\mathrm{e}^{-r/a_0}$.

$$N^{-2}=\tfrac{4}{3}\pi\int_{r=0}^{\infty}r^2\times R(r)^2\,\mathrm{d}r$$
$$=\tfrac{4}{3}\pi\int_{r=0}^{\infty}r^2\times\left\{r\,\mathrm{e}^{-r/2a_0}\right\}^2\mathrm{d}r$$
$$=\tfrac{4}{3}\pi a_0^5\int_{\chi=0}^{\infty}\chi^4\mathrm{e}^{-\chi}\mathrm{d}\chi\quad\text{where}\quad\chi=r/a_0$$
$$=\left(\tfrac{4}{3}\pi a_0^5\right)\times(4!)\quad\left[\text{Use the standard integral }\int_0^{\infty}\chi^n\mathrm{e}^{-a\chi}\mathrm{d}\chi=n!/a^{n+1}\right]$$
$$=32\pi a_0^5$$

Hence, $\boxed{N=\left(32\pi a_0^5\right)^{-1/2}}$ 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.

$$\int\psi_1\psi_2\mathrm{d}\tau=\int\left\{\left(2-\frac{r}{a_o}\right)\mathrm{e}^{-\frac{r}{a_o}}\right\}\left\{r\sin\theta\cos\phi\,\mathrm{e}^{-\frac{r}{2a_o}}\right\}\mathrm{d}\tau$$
$$=\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\left\{\left(2-\frac{r}{a_o}\right)\mathrm{e}^{-\frac{r}{a_o}}\right\}\left\{r\sin\theta\cos\phi\,\mathrm{e}^{-\frac{r}{2a_o}}\right\}r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi$$
$$=\int_{r=0}^{\infty}\left\{\left(2r^3-\frac{r^4}{a_o}\right)\mathrm{e}^{-\frac{3r}{2a_o}}\right\}\mathrm{d}r\times\int_{\theta=0}^{\pi}\sin^2\theta\,\mathrm{d}\theta\times\int_{\phi=0}^{2\pi}\cos\phi\,\mathrm{d}\phi$$

The integral on the far right equals zero:

$$\int_{\phi=0}^{2\pi}\cos\phi\,\mathrm{d}\phi=\sin\phi\,\Big|_0^{2\pi}=\sin(2\pi)-\sin(0)=0-0=0$$

Hence, $\int\psi_1\psi_2\mathrm{d}\tau=0$ and we conclude that the wavefunctions are orthogonal.

7B.4 The normalized wavefunction is $\psi=\left(\dfrac{2}{L}\right)^{1/2}\sin\left(\dfrac{\pi x}{L}\right)$ and the probability that the particle will be found between a and b is

$$P(a,b)=\int_a^b \psi^2\mathrm{d}x$$

$$=\frac{2}{L}\int_a^b \sin^2\frac{\pi x}{L}\mathrm{d}x=\frac{2}{L}\left(\frac{x}{2}-\frac{L}{4\pi}\sin\frac{2\pi x}{L}\right)\Bigg|_a^b \quad \text{[standard integral]}$$

$$=\left(\frac{x}{L}-\frac{1}{2\pi}\sin\frac{2\pi x}{L}\right)\Bigg|_a^b$$

$$=\frac{b-a}{L}-\frac{1}{2\pi}\left(\sin\frac{2\pi b}{L}-\sin\frac{2\pi a}{L}\right)$$

Calculations with the above expression may be compared to the small-range approximation that uses the mid-range value $m = (a + b)/2$:

$$P(a,b)\simeq|\psi(m)|^2\times(b-a)=\frac{2}{L}\times\left(\sin\left(\frac{\pi\times m}{L}\right)\right)^2\times(b-a)$$

$$L=10.0\ \text{nm}$$

(a) $P(4.95,5.05)=\dfrac{0.10}{10.0}-\dfrac{1}{2\pi}\left(\sin\dfrac{(2\pi)\times(5.05)}{10.0}-\sin\dfrac{(2\pi)\times(4.95)}{10.0}\right)=\boxed{0.020}$

Small range approximation: $\dfrac{2}{10}\times\left(\sin\left(\dfrac{\pi\times5.00}{10}\right)\right)^2\times(5.05-4.95)=0.020$

(b) $P(1.95,2.05)=\dfrac{0.10}{10.0}-\dfrac{1}{2\pi}\left(\sin\dfrac{(2\pi)\times(2.05)}{10.0}-\sin\dfrac{(2\pi)\times(1.95)}{10.0}\right)=\boxed{6.91\times10^{-3}}$

Small range approximation: $\dfrac{2}{10}\times\left(\sin\left(\dfrac{\pi\times2.00}{10}\right)\right)^2\times(2.05-2.95)=6.91\times10^{-3}$

(c) $P(9.90,10.0)=\dfrac{0.10}{10.0}-\dfrac{1}{2\pi}\left(\sin\dfrac{(2\pi)\times(10.0)}{10.0}-\sin\dfrac{(2\pi)\times(9.90)}{10.0}\right)=\boxed{6.58\times10^{-6}}$

Small range approximation: $\dfrac{2}{10}\times\left(\sin\left(\dfrac{\pi\times9.95}{10}\right)\right)^2\times(10.00-9.90)=4.93\times10^{-6}$

(d) $P(5.0,10.0)=\boxed{0.5}$ [because the wavefunction is symmetrical around $x = L/2$]

(e) $P\left(\dfrac{1}{3}L,\dfrac{2}{3}L\right)=\dfrac{1}{3}-\dfrac{1}{2\pi}\left(\sin\dfrac{4\pi}{3}-\sin\dfrac{2\pi}{3}\right)=\boxed{0.609}$

Small range approximation: $\dfrac{2}{10}\times\left(\sin\left(\dfrac{\pi}{2}\right)\right)^2\times\left(\dfrac{2}{3}-\dfrac{1}{3}\right)\times10=0.6667$

7B.6 $\psi(x)=N\ \mathrm{e}^{-x^2/2a^2}$

(a) $\int_{-\infty}^{\infty}|\psi(x)|\mathrm{d}x=1$ [normalization condition]

$$N^2\int_{-\infty}^{\infty}\mathrm{e}^{-x^2/a^2}\mathrm{d}x=1$$

$$N^2=\frac{1}{\int_{-\infty}^{\infty}\mathrm{e}^{-x^2/a^2}\mathrm{d}x}=\frac{1}{a\pi^{1/2}} \quad \text{[standard integral]}$$

$$\boxed{N=\left(\frac{1}{a\pi^{1/2}}\right)^{1/2}}$$

(b) The probability $P(-a,a)$ that the position is such that $-a\le x\le a$ is

$$P(-a,a)=\int_{-a}^{a}|\psi(x)|\mathrm{d}x=N^2\int_{-a}^{a}\mathrm{e}^{-x^2/a^2}\mathrm{d}x$$

$$=\frac{1}{a\pi^{1/2}}\int_{-a}^{a}\mathrm{e}^{-x^2/a^2}\mathrm{d}x=\mathrm{erf}\,(1)=\boxed{0.843}$$

7C The principles of quantum theory

Answers to discussion questions

7C.2 For each observable property Ω of a system there is a corresponding operator $\hat{\Omega}$ built from the following position and linear momentum operators:

$$\hat{x} = x\times \quad \text{and} \quad \hat{p}_x = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x} \qquad [7\text{C}.3]$$

If the system wavefunction ψ is an eigenfunction of $\hat{\Omega}$, the outcome of a measurement of Ω will be the eigenvalue ω. Because the value of an observable is a real quantity, the operator of an observable must be a hermitian operator. That is:

$$\int f^*\hat{\Omega}g\,\mathrm{d}\tau = \left(\int g^*\hat{\Omega}f\,\mathrm{d}\tau\right)^* \qquad [7\text{C}.7]$$

When the system wavefunction ψ is not an eigenfunction of $\hat{\Omega}$, we can only find the average or expectation value of the dynamical property by performing the integration shown in eqn 7C.11: $\langle\Omega\rangle = \int \psi^*\hat{\Omega}\psi\,\mathrm{d}\tau$.

7C.4 A wavepacket is a sharply localized wavefunction formed by the superposition of an infinite number of wavefunctions each of which has a different linear momentum. Being extremely localized, the modulus square of the wavefunction is non-zero at the precise location of the particle and zero elsewhere. However, each of the infinite momentum values has a non-zero probability of being observed so a momentum measurement is unpredictable. This is the conceptualization of the Heisenberg uncertainty principle which indicates that, when there is no uncertainty in knowledge of the particle position, there is an infinite uncertainty in knowledge of the particle momentum. Quantitatively, the product of the uncertainty in position and the uncertainty in momentum must always be greater or equal to $\hbar/2$ (eqn. 7C.13a).

Solutions to exercises

7C.1(b) The Coulomb potential energy between point charge Q_1 and point charge Q_2 at a distance r in a vacuum is

$$V = \frac{Q_1Q_2}{4\pi\varepsilon_0 r}$$

With one charge at the coordinate origin and the other at the position (x,y,z), the distance is given by the expression

$$r = \left(x^2 + y^2 + z^2\right)^{1/2}$$

To construct the potential energy operator, $\hat{V}$, we replace the position x in the classical expression with the position operator identity $\hat{x} = x\times$. Likewise, y is replaced with $\hat{y} = y\times$ and z is replaced with $\hat{z} = z\times$. We find that the potential energy operator is identical to the classical Coulomb potential.

$$\hat{V} = \frac{Q_1Q_2}{4\pi\varepsilon_0 r} = \frac{Q_1Q_2}{4\pi\varepsilon_0\left(x^2 + y^2 + z^2\right)^{1/2}}$$

7C.2(b) $\int_0^{2\pi}\psi_i^*\hat{l}_z\psi_j\mathrm{d}\phi = \frac{\hbar}{\mathrm{i}}\int_0^{2\pi}\psi_i^*\frac{\mathrm{d}\psi_j}{\mathrm{d}\phi}\mathrm{d}\phi$

Application of 'integration by parts' yields

$$\int_0^{2\pi}\psi_i^*\hat{l}_z\psi_j\mathrm{d}\phi = \frac{\hbar}{\mathrm{i}}\psi_i^*\psi_j\Big|_0^{2\pi} - \frac{\hbar}{\mathrm{i}}\int_0^{2\pi}\psi_j\frac{\mathrm{d}\psi_i^*}{\mathrm{d}\phi}\mathrm{d}\phi$$

The first term to the right vanishes because the wavefunction must repeat itself every 2π radian (i.e., $\psi_i(0) = \psi_i(2\pi)$).

$$\int_0^{2\pi}\psi_i^{*}\hat{l}_z\psi_j\mathrm{d}\phi = -\frac{\hbar}{\mathrm{i}}\int_0^{2\pi}\psi_j\frac{\mathrm{d}\psi_i^{*}}{\mathrm{d}\phi}\mathrm{d}\phi = \left\{\frac{\hbar}{\mathrm{i}}\int_0^{2\pi}\psi_j^{*}\frac{\mathrm{d}\psi_i}{\mathrm{d}\phi}\mathrm{d}\phi\right\}^{*}$$

$$= \left\{\int_0^{2\pi}\psi_j^{*}\hat{l}_z\psi_i\mathrm{d}\phi\right\}^{*}$$

This is the condition of eqn 7C.7 so $\hat{l}_z$ is an hermitian operator.

7C.3(b) ψ_i and ψ_j are orthogonal if $\int\psi_i^{*}\psi_j\ \mathrm{d}\tau = 0$ [7C.8]. Where $n \neq m$ and both n and m are integers,

$$\int_0^L \cos(n\pi x/L)\times\cos(m\pi x/L)\ \mathrm{d}x = \left[\frac{\sin(\pi(n-m)x/L)}{2\pi(n-m)/L}+\frac{\sin(\pi(n+m)x/L)}{2\pi(n+m)/L}\right]_{x=0}^{x=L}$$

$$= \frac{\sin(\pi(n-m))}{2\pi(n-m)/L}+\frac{\sin(\pi(n+m))}{2\pi(n+m)/L}-\left\{\frac{\sin(0)}{2\pi(n-m)/L}+\frac{\sin(0)}{2\pi(n+m)/L}\right\}$$

$= 0$ because the sine of an integer multiple of π equals zero.

Thus, the functions $\cos(n\pi x/L)$ and $\cos(m\pi x/L)$ are orthogonal in the region $0 \le x \le L$.
Alternatively, successively integrate by parts.

$$\int_0^L \cos(n\pi x/L)\times\cos(m\pi x/L)\ \mathrm{d}x$$

$$= \left[\cos(n\pi x/L)\times\left(\frac{\sin(m\pi x/L)}{m\pi/L}\right)\right]_{x=0}^{x=L} - \int_0^L (n\pi/L)(-\sin(n\pi x/L))\times\left(\frac{\sin(m\pi x/L)}{m\pi/L}\right)\mathrm{d}x \text{ [integration by parts]}$$

$$= \left(\frac{n}{m}\right)\int_0^L \sin(n\pi x/L)\times\sin(m\pi x/L)\ \mathrm{d}x \text{ [use } \sin(m\pi)=0 \text{ for multiples of } \pi]$$

$$= \left(\frac{n}{m}\right)\times\left\{\left[\sin(n\pi x/L)\times\left(\frac{-\cos(m\pi x/L)}{m\pi/L}\right)\right]_{x=0}^{x=L} - \int_0^L (n\pi/L)(\cos(n\pi x/L))\times\left(\frac{-\cos(m\pi x/L)}{m\pi/L}\right)\mathrm{d}x\right\} \text{ [integration by parts]}$$

$$= \left(\frac{n}{m}\right)^2\times\left\{\int_0^L \cos(n\pi x/L)\times\cos(m\pi x/L)\ \mathrm{d}x\right\} \text{ [use } \sin(n\pi)=0 \text{ for multiples of } \pi]$$

Thus, $\left(1-\left(\frac{n}{m}\right)^2\right)\times\left\{\int_0^L \cos(n\pi x/L)\times\cos(m\pi x/L)\ \mathrm{d}x\right\} = 0$

and we conclude that the integral necessarily equals zero when $n \neq m$.

7C.4(b) ψ_i and ψ_j are orthogonal if $\int\psi_i^{*}\psi_j\ \mathrm{d}\tau = 0$ [7C.8].

$$\int_0^{2\pi}\left(\mathrm{e}^{\mathrm{i}\phi}\right)^{*}\times\mathrm{e}^{-\mathrm{i}\phi}\mathrm{d}\phi = \int_0^{2\pi}\mathrm{e}^{-\mathrm{i}\phi}\times\mathrm{e}^{-\mathrm{i}\phi}\mathrm{d}\phi = \int_0^{2\pi}\mathrm{e}^{-2\mathrm{i}\phi}\mathrm{d}\varphi = -\frac{1}{2\mathrm{i}}\ \mathrm{e}^{-2\mathrm{i}\phi}\Big|_{\phi=0}^{\phi=2\pi}$$

$$= -\frac{1}{2\mathrm{i}}\left(\mathrm{e}^{-4\pi\mathrm{i}}-\mathrm{e}^{0}\right) = -\frac{1}{2\mathrm{i}}\left(\mathrm{e}^{-4\pi\mathrm{i}}-1\right)$$

$$= -\frac{1}{2\mathrm{i}}\{\cos(-4\pi)-\mathrm{i}\sin(-2\pi)-1\} = -\frac{1}{2\mathrm{i}}\{1-0-1\} = 0$$

(The Euler identity $\mathrm{e}^{ai} = \cos(a) - i\sin(a)$ has been used in the math manipulations.)

Thus, the functions $\mathrm{e}^{\mathrm{i}\phi}$ and $\mathrm{e}^{-\mathrm{i}\phi}$ are orthogonal in the region $0 \le \phi \le 2\pi$

7C.5(b) The normalized form of this wavefunction and derivatives are:

$$\psi(x) = \left(\frac{2}{L}\right)^{1/2}\sin(\pi x/L)$$

$$\frac{\mathrm{d}\psi}{\mathrm{d}x} = \left(\frac{2}{L}\right)^{1/2}\left(\frac{\pi}{L}\right)\cos(\pi x/L)$$

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\left(\frac{2}{L}\right)^{1/2}\left(\frac{\pi}{L}\right)^2\sin(\pi x/L) = -\left(\frac{\pi}{L}\right)^2\psi$$

The expectation value of the electron kinetic energy is:

$$\langle E_{\mathrm{k}}\rangle = \int_0^L \psi^* \hat{E}_{\mathrm{k}}\,\psi\ \mathrm{d}x\ [7.2] = \int_0^L \psi^*\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\right)\psi\ \mathrm{d}x = \left(-\frac{\hbar^2}{2m}\right)\int_0^L \psi^*\left(\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}\right)\ \mathrm{d}x$$

$$= -\left(-\frac{\hbar^2}{2m}\right)\left(\frac{\pi}{L}\right)^2 \int_0^L \psi^*\psi\ \ \mathrm{d}x = \left(\frac{\hbar^2}{2m}\right)\left(\frac{\pi}{L}\right)^2 = \boxed{\frac{h^2}{8mL^2}}$$

7C.6(b) The normalization constant for this wavefunction is:

$$N = \frac{1}{\left(\int_0^{2\pi} \mathrm{e}^{-\mathrm{i}\phi}\times \mathrm{e}^{\mathrm{i}\phi}\ \mathrm{d}x\right)^{1/2}}\ \ [7\mathrm{B}.3] = \frac{1}{\left(\int_0^{2\pi} 1\,\mathrm{d}x\right)^{1/2}} = \frac{1}{(2\pi)^{1/2}}$$

Working with the normalized wavefunction and using the symbol J_z to represent angular momentum about the axis that is perpendicular to the plane of rotation, we find:

$$\psi(\phi) = \left(\frac{1}{2\pi}\right)^{1/2}\ \mathrm{e}^{\mathrm{i}\phi}$$

$$\langle J_z\rangle = \int_0^{2\pi} \psi^* \hat{J}_z\ \psi\ \mathrm{d}\phi\ [7\mathrm{C}.11] = \left(\frac{1}{2\pi}\right)\int_0^{2\pi} \mathrm{e}^{-\mathrm{i}\phi}\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}\varphi}\right)\mathrm{e}^{\mathrm{i}\phi}\ \mathrm{d}\phi$$

$$= \left(\frac{1}{2\pi}\right)\times\left(\frac{\hbar}{\mathrm{i}}\right)\int_0^{2\pi} \mathrm{e}^{-\mathrm{i}\phi}\left(\frac{\mathrm{d}\mathrm{e}^{\mathrm{i}\phi}}{\mathrm{d}\phi}\right)\mathrm{d}\phi = \left(\frac{1}{2\pi}\right)\times\left(\frac{\hbar}{\mathrm{i}}\right)\times\mathrm{i}\times\int_0^{2\pi} \mathrm{e}^{-\mathrm{i}\phi}\mathrm{e}^{\mathrm{i}\phi}\ \mathrm{d}\varphi = \left(\frac{\hbar}{2\pi}\right)\times\int_0^{2\pi} 1\,\mathrm{d}\phi$$

$$= \left(\frac{\hbar}{2\pi}\right)\times 2\pi = \boxed{\hbar}$$

7C.7(b) The minimum uncertainty in position is 100 pm. Therefore, since $\Delta x\Delta p \geq \tfrac{1}{2}\hbar$,

$$\Delta p \geq \frac{\hbar}{2\Delta x} = \frac{1.0546\times 10^{-34}\,\mathrm{J\,s}}{2(100\times 10^{-12}\,\mathrm{m})} = 5.3\times 10^{-25}\ \mathrm{kg\,m\,s^{-1}}$$

$$\Delta v = \frac{\Delta p}{m} = \frac{5.3\times 10^{-25}\,\mathrm{kg\,m\,s^{-1}}}{9.11\times 10^{-31}\,\mathrm{kg}} = \boxed{5.8\times 10^5\ \mathrm{m\ s^{-1}}}$$

7C.8(b) The desired uncertainty in the electron momentum is

$$\Delta p = 1.00\times 10^{-5}\ p = 1.00\times 10^{-5}\ m_{\mathrm{e}}v$$

$$= \left(1.00\times 10^{-5}\right)\times\left(9.109\times 10^{-31}\ \mathrm{kg}\right)\times\left(995\times 10^3\ \mathrm{m\ s^{-1}}\right) = 9.06\times 10^{-30}\ \mathrm{kg\ m\ s^{-1}}$$

Thus, the minimum uncertainty in position must be

$$\Delta x = \frac{\hbar}{2\Delta p}\ \ [7\mathrm{C}.13\mathrm{a}] = \frac{1.055\times 10^{-34}\ \mathrm{J\ s}}{2\times\left(9.06\times 10^{-30}\ \mathrm{kg\ m\ s^{-1}}\right)} = \boxed{5.82\ \mu\mathrm{m}}$$

7C.9(b) The quantity $\left[\hat{\Omega}_1,\hat{\Omega}_2\right] = \hat{\Omega}_1\hat{\Omega}_2 - \hat{\Omega}_2\hat{\Omega}_1$ [7C.15] 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 $\left[\hat{\Omega}_1,\hat{\Omega}_2\right]\psi(x) = \hat{\Omega}_1\hat{\Omega}_2\psi(x) - \hat{\Omega}_2\hat{\Omega}_1\psi(x)$.

$$\left[a,a^\dagger\right]\psi(x) = \left[\frac{\hat{x}+\mathrm{i}\hat{p}}{2^{1/2}},\frac{\hat{x}-\mathrm{i}\hat{p}}{2^{1/2}}\right]\psi(x) = \tfrac{1}{2}\left[\hat{x}+\mathrm{i}\hat{p},\hat{x}-\mathrm{i}\hat{p}\right]\psi(x) \quad \text{where} \quad \hat{p} = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x} \quad \text{and} \quad \hat{x} = x\times$$

$$= \tfrac{1}{2}\left[\hat{x}+\mathrm{i}\hat{p},\hat{x}-\mathrm{i}\hat{p}\right]\psi(x) = \tfrac{1}{2}\left\{\left(\hat{x}+\mathrm{i}\hat{p}\right)\left(\hat{x}-\mathrm{i}\hat{p}\right) - \left(\hat{x}-\mathrm{i}\hat{p}\right)\left(\hat{x}+\mathrm{i}\hat{p}\right)\right\}\psi(x)$$

$$= \tfrac{1}{2}\left\{\left(\hat{x}^2 + \mathrm{i}\hat{p}\hat{x} - \hat{x}\mathrm{i}\hat{p} - \mathrm{i}^2\hat{p}^2\right) - \left(\hat{x}^2 - \mathrm{i}\hat{p}\hat{x} + \hat{x}\mathrm{i}\hat{p} - \mathrm{i}^2\hat{p}^2\right)\right\}\psi(x)$$

$$= \left(\mathrm{i}\hat{p}\hat{x} - \hat{x}\mathrm{i}\hat{p}\right)\psi(x) = \hbar\left(\frac{\mathrm{d}}{\mathrm{d}x}x - x\frac{\mathrm{d}}{\mathrm{d}x}\right)\psi(x) = \hbar\left(\frac{\mathrm{d}}{\mathrm{d}x}x\psi(x) - x\frac{\mathrm{d}}{\mathrm{d}x}\psi(x)\right)$$

$$= \hbar\left(\psi(x) + x\frac{\mathrm{d}}{\mathrm{d}x}\psi(x) - x\frac{\mathrm{d}}{\mathrm{d}x}\psi(x)\right) = \hbar\psi(x)$$

Thus, $\left[a,a^\dagger\right] = \boxed{\hbar}$.

Solutions to problems

7C.2 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

$$\hat{x} = x\times \qquad \text{and} \qquad \hat{p}_x = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x} \quad [7\text{C}.3]$$

The operator for p_x^2 is

$$\hat{p}_x^{\,2} = \hat{p}_x\hat{p}_x = \left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right)\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right)$$

$$= -\hbar^2\frac{\mathrm{d}^2}{\mathrm{d}x^2} \qquad \text{for one-dimensional systems}$$

$$= -\hbar^2\left(\frac{\partial^2}{\partial x^2}\right)_{y,z} \qquad \text{for three-dimensional systems}$$

(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

$$\hat{E}_\mathrm{k} = \frac{1}{2m}\left(\hat{p}_x^{\,2} + \hat{p}_y^{\,2} + \hat{p}_z^{\,2}\right) = -\frac{\hbar^2}{2m}\left(\left(\frac{\partial^2}{\partial x^2}\right)_{y,z} + \left(\frac{\partial^2}{\partial y^2}\right)_{x,z} + \left(\frac{\partial^2}{\partial z^2}\right)_{x,y}\right)$$

$$= \boxed{-\frac{\hbar^2}{2m}\nabla^2} \text{ where } \nabla^2 = \left(\frac{\partial^2}{\partial x^2}\right)_{y,z} + \left(\frac{\partial^2}{\partial y^2}\right)_{x,z} + \left(\frac{\partial^2}{\partial z^2}\right)_{x,y} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

(b) The inverse separation, $1/x$

$$\hat{\frac{1}{x}} = \boxed{\frac{1}{x}\times}$$

The inverse separation in three dimensions is determined by the vector magnitude of the position vector $\vec{r} = x\vec{\mathbf{i}} + y\vec{\mathbf{j}} + z\vec{\mathbf{k}}$:

$$\hat{\frac{1}{r}} = \boxed{\frac{1}{\left\{x^2 + y^2 + z^2\right\}^{1/2}}}$$

(c) The electric dipole moment for J point charges Q_J at the positions x_J is $\boxed{\sum_\mathrm{J} Q_\mathrm{J} x_\mathrm{J}}$. Similarly, 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

$$\mu = \left\{\mu_x^{\,2} + \mu_y^{\,2} + \mu_z^{\,2}\right\}^{1/2} = \left\{\left(\sum_\mathrm{J} Q_\mathrm{J} x_\mathrm{J}\right)^2 + \left(\sum_\mathrm{J} Q_\mathrm{J} y_\mathrm{J}\right)^2 + \left(\sum_\mathrm{J} Q_\mathrm{J} z_\mathrm{J}\right)^2\right\}^{1/2}$$

(d) The root mean square deviation of position in one dimension is

$$\Delta x = \boxed{\left\{\left\langle x^2\right\rangle - \left\langle x\right\rangle^2\right\}^{1/2}} \quad [7\text{C}.13\text{b}]$$

The root mean square deviation of momentum in one dimension is

$$\Delta p_x = \left\{\left\langle\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right)^2\right\rangle - \left\langle\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right\rangle^2\right\}^{1/2} \quad [7\text{C}.13\text{b}]$$

$$= \boxed{\frac{\hbar}{\mathrm{i}}\left\{\left\langle\frac{\mathrm{d}^2}{\mathrm{d}x^2}\right\rangle - \left\langle\frac{\mathrm{d}}{\mathrm{d}x}\right\rangle^2\right\}^{1/2}}$$

7C.4 Operate on each function *f* with $\hat{i}$ (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 $\hat{i}$ and the constant is the eigenvalue [7C.2a, b, and c].

(a) $f = x^3 - kx$

$$\hat{i}(x^3 - kx) = -x^3 + kx = -f$$

$\boxed{\text{Yes}}$, *f* is an eigenfunction with eigenvalue $\boxed{-1}$.

(b) $f = \cos kx$

$$\hat{i}\cos kx = \cos(-kx) = \cos kx = f$$

$\boxed{\text{Yes}}$, *f* is an eigenfunction with eigenvalue $\boxed{+1}$.

(c) $f = x^2 + 3x - 1$

$$\hat{i}(x^2 + 3x - 1) = x^2 - 3x - 1 \neq \text{constant} \times f$$

$\boxed{\text{No}}$, *f* is not an eigenfunction of $\hat{i}$.

7C.6 Suppose that $\hat{\Omega}$ is a hermitian operator. Then, by definition of a hermitian operator:

$$\int f^*\hat{\Omega}^2 g\,\mathrm{d}\tau = \left(\int g^*\hat{\Omega}^2 f\,\mathrm{d}\tau\right)^* \qquad [7\text{C}.7]$$

We show that $\hat{\Omega}^2$ is hermitian as follows.

$$\begin{aligned}\int f^*\hat{\Omega}^2 g\,\mathrm{d}\tau &= \int f^*\hat{\Omega}\left(\hat{\Omega}g\right)\mathrm{d}\tau \\ &= \left(\int\left(\hat{\Omega}g\right)^*\hat{\Omega}f\,\mathrm{d}\tau\right)^* \quad [\hat{\Omega}\text{ is hermitian.}] \\ &= \int\left(\hat{\Omega}f\right)^*\hat{\Omega}g\,\mathrm{d}\tau \\ &= \left(\int g^*\hat{\Omega}\left(\hat{\Omega}f\right)\mathrm{d}\tau\right)^* \quad [\hat{\Omega}\text{ is hermitian.}]\end{aligned}$$

$$\int f^*\hat{\Omega}^2 g\,\mathrm{d}\tau = \left(\int g^*\hat{\Omega}^2 f\,\mathrm{d}\tau\right)^*$$

The last expression satisfies the definition of a hermitian operator so we conclude that $\hat{\Omega}^2$ is hermitian.

7C.8 $\psi(\phi) = \left(\dfrac{1}{2\pi}\right)^{1/2}\mathrm{e}^{-\mathrm{i}m\phi}$ where $m = 0, \pm 1, \pm 2, \pm 3, \ldots$

The average position (angle) is given by:

$$\langle\phi\rangle = \int\psi^*\phi\psi\,\mathrm{d}\tau = \int_0^{2\pi}\left\{\left(\frac{1}{2\pi}\right)^{1/2}\mathrm{e}^{-\mathrm{i}m\phi}\right\}^*\phi\left\{\left(\frac{1}{2\pi}\right)^{1/2}\mathrm{e}^{-\mathrm{i}m\phi}\right\}\mathrm{d}\phi$$

$$= \left(\frac{1}{2\pi}\right)\int_0^{2\pi}\mathrm{e}^{\mathrm{i}m\phi}\,\phi\,\mathrm{e}^{-\mathrm{i}m\phi}\,\mathrm{d}\phi = \left(\frac{1}{2\pi}\right)\int_0^{2\pi}\phi\,\mathrm{d}\phi = \left(\frac{1}{2\pi}\right)\left(\frac{\phi^2}{2}\right)\Bigg|_0^{2\pi}$$

$$= \boxed{\pi}.$$

Note: This result applies to all values of the quantum number *m*, for it drops out of the calculation.

7C.10 The wavefunction $\psi = (\cos\chi)\mathrm{e}^{+\mathrm{i}kx} + (\sin\chi)\mathrm{e}^{-\mathrm{i}kx} = c_1\mathrm{e}^{+\mathrm{i}kx} + c_2\,\mathrm{e}^{-\mathrm{i}kx}$ is a superposition of the functions $\mathrm{e}^{+\mathrm{i}kx}$ and $\mathrm{e}^{-\mathrm{i}kx}$. We first demonstrate that the functions $\mathrm{e}^{+\mathrm{i}kx}$ and $\mathrm{e}^{-\mathrm{i}kx}$ are eigenfunctions of the linear momentum operator, $\hat{p}_x = \dfrac{\hbar}{\mathrm{i}}\dfrac{\mathrm{d}}{\mathrm{d}x}$ [7C.3], that have the eigenvalues $+k\hbar$ and $-k\hbar$, respectively.

$$\hat{p}_x \mathrm{e}^{+\mathrm{i}kx} = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\mathrm{e}^{+\mathrm{i}kx} = \left(\frac{\hbar}{\mathrm{i}}\right)\times(\mathrm{i}k)\mathrm{e}^{+\mathrm{i}kx} = +k\hbar\mathrm{e}^{+\mathrm{i}kx}$$

$$\hat{p}_x \mathrm{e}^{-\mathrm{i}kx} = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\mathrm{e}^{-\mathrm{i}kx} = \left(\frac{\hbar}{\mathrm{i}}\right)\times(-\mathrm{i}k)\mathrm{e}^{-\mathrm{i}kx} = -k\hbar\mathrm{e}^{-\mathrm{i}kx}$$

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 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 (see text Section 7C.2).

(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 $\boxed{\psi = 0.95\,\mathrm{e}^{\mathrm{i}kx} \pm 0.32\,\mathrm{e}^{-\mathrm{i}kx}}$.

(d) $\psi = (\cos\chi)\mathrm{e}^{+\mathrm{i}kx} + (\sin\chi)\mathrm{e}^{-\mathrm{i}kx} = c_1\mathrm{e}^{+\mathrm{i}kx} + c_2\,\mathrm{e}^{-\mathrm{i}kx}$

The expectation value for kinetic energy depends upon the curvature of the wavefunction so we begin by finding the expression for $\mathrm{d}^2\psi/\mathrm{d}x^2$.

$$\frac{\mathrm{d}\psi}{\mathrm{d}x} = \mathrm{i}kc_1\mathrm{e}^{+\mathrm{i}kx} - \mathrm{i}kc_2\mathrm{e}^{-\mathrm{i}kx}$$

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -k^2c_1\mathrm{e}^{+\mathrm{i}kx} - k^2c_2\mathrm{e}^{-\mathrm{i}kx} = -k^2\psi$$

Thus, ψ is an eigenfunction of the $\mathrm{d}^2\psi/\mathrm{d}x^2$ operator and it must also be an eigenfunction of the kinetic energy operator.

$$\hat{E}_\mathrm{k}\psi = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi \text{ [7C.5]} = \frac{(\hbar k)^2}{2m}\psi$$

The kinetic energy of the particle is the eigenvalue $\boxed{\dfrac{(\hbar k)^2}{2m}}$.

7C.12 The ground-state wavefunction of a hydrogen atom is $\psi = (1/\pi a_0^3)^{1/2}\mathrm{e}^{-r/a_0}$. Calculate (a) the mean potential energy and (b) the mean kinetic energy of an electron in the ground state of a hydrogenic atom.

The normalized wavefunction is $\psi = \left(\dfrac{1}{\pi a_0^{\,3}}\right)^{1/2}\mathrm{e}^{-r/a_0}$.

(a) $\langle V\rangle = \int\psi^*\hat{V}\psi\,\mathrm{d}\tau \quad \left[\hat{V} = -\dfrac{e^2}{4\pi\varepsilon_0 r}\right]$

$$= \int\psi^*\left(\frac{-e^2}{4\pi\varepsilon_0}\cdot\frac{1}{r}\right)\psi\,\mathrm{d}\tau = \frac{1}{\pi a_0^{\,3}}\left(\frac{-e^2}{4\pi\varepsilon_0}\right)\int_0^\infty r\mathrm{e}^{-2r/a_0}\mathrm{d}r\times 4\pi$$

$$= \frac{1}{\pi a_0^{\,3}}\left(\frac{-e^2}{4\pi\varepsilon_0}\right)\times\left(\frac{a_0}{2}\right)^2\times 4\pi = \boxed{\frac{-e^2}{4\pi\varepsilon_0 a_0}}$$

(b) In one-dimension: $\hat{E}_\mathrm{k} = \dfrac{\hat{p}_x^{\,2}}{2m} = \dfrac{1}{2m}\left(\dfrac{\hbar}{\mathrm{i}}\dfrac{\mathrm{d}}{\mathrm{d}x}\right)\left(\dfrac{\hbar}{\mathrm{i}}\dfrac{\mathrm{d}}{\mathrm{d}x}\right) = \boxed{-\dfrac{\hbar^2}{2m}\dfrac{\mathrm{d}^2}{\mathrm{d}x^2}}$ [7C.5]. For three-dimensional systems such as the hydrogen atom the kinetic energy operator is

$$\hat{E}_\mathrm{k} = \frac{\hat{p}_x^{\,2}}{2m} + \frac{\hat{p}_y^{\,2}}{2m} + \frac{\hat{p}_z^{\,2}}{2m} = -\frac{\hbar^2}{2m}\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right\} = \boxed{-\frac{\hbar^2}{2m}\nabla^2}$$

where $\dfrac{\partial^2}{\partial x^2} = \left(\dfrac{\partial^2}{\partial x^2}\right)_{y,z}$, $\dfrac{\partial^2}{\partial y^2} = \left(\dfrac{\partial^2}{\partial y^2}\right)_{x,z}$, $\dfrac{\partial^2}{\partial z^2} = \left(\dfrac{\partial^2}{\partial z^2}\right)_{x,y}$, and $\nabla^2 = \dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}$

The ∇^2 operator, called the laplacian operator or the del-squared operator, is advantageously written in spherical coordinates because the wavefunction has its simplest form in spherical coordinates. Mathematical handbooks report that

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2$$

where the Λ^2 operator, called the legendrian operator, is an operator of angle variables only.

$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$$

Since our wavefunction has no angular dependence, $\Lambda^2\psi = 0$ and the laplacian simplifies to

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}$$

$$\nabla^2\psi = \left\{\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right\}\left(\left(\frac{1}{\pi a_0{}^3}\right)^{1/2} \mathrm{e}^{-r/a_0}\right) = \left(\frac{1}{\pi a_0{}^3}\right)^{1/2}\left\{\frac{1}{a_0{}^2} - \frac{2}{r a_0}\right\}\mathrm{e}^{-r/a_0}$$

$$\left\langle \hat{E}_\mathrm{k}\right\rangle = -\frac{\hbar^2}{2m_\mathrm{e}}\int \psi^*\nabla^2\psi\,\mathrm{d}\tau = -\frac{\hbar^2}{2m_\mathrm{e}}\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\psi^*\nabla^2\psi\, r^2\sin\theta\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi$$

$$= -\frac{\hbar^2}{2m_\mathrm{e}}\int_{r=0}^{\infty} r^2\psi^*\nabla^2\psi\,\mathrm{d}r\int_{\theta=0}^{\pi}\sin\theta\,\mathrm{d}\theta\int_{\varphi=0}^{2\pi}\mathrm{d}\phi = -\frac{\hbar^2}{2m_\mathrm{e}}\int_{r=0}^{\infty} r^2\psi^*\nabla^2\psi\,\mathrm{d}r \times 4\pi$$

$$= -\frac{4\pi\hbar^2}{2m_\mathrm{e}}\left(\frac{1}{\pi a_0{}^3}\right)\int_{r=0}^{\infty}\left\{\frac{r^2}{a_0{}^2} - \frac{2r}{a_0}\right\}\mathrm{e}^{-2r/a_0}\,\mathrm{d}r = -\frac{4\pi\hbar^2}{2m_\mathrm{e}}\left(\frac{1}{\pi a_0{}^3}\right)\times a_0\left(\frac{1}{4} - \frac{1}{2}\right)$$

$$= \boxed{\frac{\hbar^2}{2m_\mathrm{e}a_0{}^2}} \qquad \left[\text{Note that } \int_0^\infty x^n\,\mathrm{e}^{-ax}\,\mathrm{d}x = \frac{n!}{a^{n+1}}\right]$$

7C.14 The uncertainty principle states that $\Delta p\Delta q \geq \tfrac{1}{2}\hbar$ where Δq and Δp are root-mean-square deviations $\Delta q = (\langle x^2\rangle - \langle x\rangle^2)^{1/2}$ and $\Delta p = (\langle p^2\rangle - \langle p\rangle^2)^{1/2}$. To verify whether the relationship holds for the particle in a state whose normalized wavefunction is $\psi = (2a/\pi)^{1/4}\mathrm{e}^{-ax^2}$, we need the quantum-mechanical averages $\langle x\rangle, \langle x^2\rangle, \langle p\rangle$, and $\langle p^2\rangle$.

$$\langle x\rangle = \int\psi^* x\psi\,\mathrm{d}\tau = \left(\frac{2a}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} x\mathrm{e}^{-2ax^2}\mathrm{d}x$$

$= 0$ [an odd integrand centered around $x = 0$]

$$\langle x^2\rangle = \int\psi^* x^2\,\psi\,\mathrm{d}\tau = \left(\frac{2a}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} x^2\mathrm{e}^{-2ax^2}\mathrm{d}x = \left(\frac{2a}{\pi}\right)^{1/2}\times\left(\frac{1}{8a}\right)\times\left(\frac{2\pi}{a}\right)^{1/2}$$

$$= \frac{1}{4a}$$

$$\langle p\rangle = \frac{\hbar}{\mathrm{i}}\int_{-\infty}^{\infty}\psi\frac{\mathrm{d}}{\mathrm{d}x}\psi\,\mathrm{d}x = \frac{\hbar}{\mathrm{i}}\int_{-\infty}^{\infty}(-2ax)\psi^2\,\mathrm{d}x = -\frac{2a\hbar}{\mathrm{i}}\int_{-\infty}^{\infty} x\psi^2\,\mathrm{d}x$$

$= 0$ [an odd integrand centered around $x = 0$]

$$\langle p^2\rangle = -\hbar^2\int_{-\infty}^{\infty}\psi\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi\,\mathrm{d}x = 2a\hbar^2\int_{-\infty}^{\infty}\left(\psi^2 - 2ax^2\psi^2\right)\mathrm{d}x = 2a\hbar^2\times\left(1 - 2a\times\left(\frac{2a}{\pi}\right)^{1/2}\times\left(\frac{1}{8a}\right)\times\left(\frac{2\pi}{a}\right)^{1/2}\right)$$

$$= a\hbar^2$$

Thus, $\Delta q\Delta p = \left(\langle x^2\rangle - \langle x\rangle^2\right)^{1/2}\times\left(\langle p^2\rangle - \langle p\rangle^2\right)^{1/2}$

$$= \left(\frac{1}{4a} - 0\right)^{1/2}\times\left(a\hbar^2 - 0\right)^{1/2}$$

$$= \boxed{\hbar/2}$$

This value of $\Delta q\Delta p$ is the minimum product consistent with the uncertainty principle.

7C.16 $\hat{x} = x\times$ and $\hat{p}_x = \dfrac{\hbar}{\mathrm{i}}\dfrac{\mathrm{d}}{\mathrm{d}x}$ [7C.3] and $\hat{H} = \dfrac{p_x^2}{2m} + V$ [7C.1b]

Frequent use is made of the rule for differentiation of a product: $\dfrac{\mathrm{d}}{\mathrm{d}x}fg = \left(\dfrac{\mathrm{df}}{\mathrm{d}x}\right)g + f\left(\dfrac{\mathrm{d}}{\mathrm{d}x}g\right)$.

(a) (i) V is a constant.

$$\left[\hat{H},\hat{p}_x\right]\psi = \left[\frac{\hat{p}_x{}^2}{2m}+V,\hat{p}_x\right]\psi = \left(\frac{\hat{p}_x{}^3}{2m}+V\,\hat{p}_x-\left\{\frac{\hat{p}_x{}^3}{2m}+\hat{p}_xV\right\}\right)\psi = \left(V\,\hat{p}_x-\hat{p}_xV\right)\psi$$

$$= 0\times\psi \quad \text{[because a constant commutes with } \hat{p}_x\text{]}$$

Thus, $\left[\hat{H},\hat{p}_x\right]=\boxed{0}$

(ii) $V(x) = \frac{1}{2}kx^2$

$$\left[\hat{H},\hat{p}_x\right]\psi = \left[\frac{\hat{p}_x{}^2}{2m}+\tfrac{1}{2}kx^2,\hat{p}_x\right]\psi = \left(\frac{\hat{p}_x{}^3}{2m}+\tfrac{1}{2}kx^2\,\hat{p}_x-\left\{\frac{\hat{p}_x{}^3}{2m}+\hat{p}_x\left(\tfrac{1}{2}kx^2\right)\right\}\right)\psi$$

$$= \tfrac{1}{2}kx^2\,\hat{p}_x\psi-\left(\frac{\hbar}{\mathrm{i}}\right)\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)\left(\tfrac{1}{2}kx^2\psi\right) = \tfrac{1}{2}kx^2\,\hat{p}_x\psi-\left(\frac{\hbar}{\mathrm{i}}\right)\left\{kx\psi+\left(\tfrac{1}{2}kx^2\right)\left(\frac{\mathrm{d}}{\mathrm{d}x}\psi\right)\right\}$$

$$= \tfrac{1}{2}kx^2\,\hat{p}_x\psi-\left(\frac{\hbar}{\mathrm{i}}\right)kx\psi-\left(\tfrac{1}{2}kx^2\right)\left(\frac{\hbar}{\mathrm{i}}\right)\left(\frac{\mathrm{d}}{\mathrm{d}x}\psi\right) = -\left(\frac{\hbar}{\mathrm{i}}\right)kx\psi = \mathrm{i}\hbar kx\psi$$

Thus, $\left[\hat{H},\hat{p}_x\right]=\boxed{\mathrm{i}\hbar kx}$

(b) (i) V is a constant.

$$\left[\hat{H},\hat{x}\right]\psi = \left[\frac{\hat{p}_x{}^2}{2m}+V,x\right]\psi = \left(\frac{\hat{p}_x{}^2}{2m}x+Vx-\left\{x\frac{\hat{p}_x{}^2}{2m}+xV\right\}\right)\psi$$

$$= \frac{1}{2m}\left(\hat{p}_x{}^2x-x\hat{p}_x{}^2\right)\psi \quad [x \text{ and } V \text{ commute when } V \text{ is constant.}]$$

$$= \frac{1}{2m}\left(\hat{p}_x{}^2\left(x\psi\right)-x\hat{p}_x{}^2\psi\right) = \frac{1}{2m}\left(-\hbar^2\frac{\mathrm{d}}{\mathrm{d}x}\frac{\mathrm{d}}{\mathrm{d}x}\left(x\psi\right)-x\hat{p}_x{}^2\psi\right)$$

$$= \frac{1}{2m}\left(-\hbar^2\frac{\mathrm{d}}{\mathrm{d}x}\left(\psi+x\frac{\mathrm{d}}{\mathrm{d}x}\psi\right)-x\hat{p}_x{}^2\psi\right) = \frac{1}{2m}\left(-\hbar^2\left(\frac{\mathrm{d}}{\mathrm{d}x}\psi+\frac{\mathrm{d}}{\mathrm{d}x}\psi+x\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi\right)-x\hat{p}_x{}^2\psi\right)$$

$$= -\frac{\hbar^2}{m}\frac{\mathrm{d}}{\mathrm{d}x}\psi = -\frac{\mathrm{i}\hbar}{m}\hat{p}_x\psi$$

Thus, $\left[\hat{H},\hat{x}\right]=\boxed{-\dfrac{\mathrm{i}\hbar}{m}\hat{p}_x}$

(ii) $V(x) = \frac{1}{2}kx^2$

$$\left[\hat{H},\hat{x}\right]\psi = \left[\frac{\hat{p}_x{}^2}{2m}+\tfrac{1}{2}kx^2,x\right]\psi = \left(\frac{\hat{p}_x{}^2x}{2m}+\tfrac{1}{2}kx^3-\left\{\frac{x\hat{p}_x{}^2}{2m}+\tfrac{1}{2}kx^3\right\}\right)\psi$$

$$= \frac{1}{2m}\left(\hat{p}_x{}^2\left(x\psi\right)-x\hat{p}_x{}^2\psi\right) = \frac{1}{2m}\left(\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right)\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right)\left(x\psi\right)-x\hat{p}_x{}^2\psi\right)$$

$$= \frac{1}{2m}\left(-\hbar^2\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)\left(\psi+x\frac{\mathrm{d}}{\mathrm{d}x}\psi\right)-x\hat{p}_x{}^2\psi\right) = \frac{1}{2m}\left(-\hbar^2\left(\frac{\mathrm{d}}{\mathrm{d}x}\psi+\frac{\mathrm{d}}{\mathrm{d}x}\left(x\frac{\mathrm{d}}{\mathrm{d}x}\psi\right)\right)-x\hat{p}_x{}^2\psi\right)$$

$$= \frac{1}{2m}\left(-\hbar^2\left(\frac{\mathrm{d}}{\mathrm{d}x}\psi+\frac{\mathrm{d}}{\mathrm{d}x}\psi+x\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi\right)-x\hat{p}_x{}^2\psi\right)$$

$$= -\frac{\hbar^2}{m}\frac{\mathrm{d}}{\mathrm{d}x}\psi = -\frac{\hbar^2}{m}\left(\frac{\mathrm{i}}{\hbar}\right)\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right)\psi = -\frac{\mathrm{i}\hbar}{m}\hat{p}_x\psi$$

Thus, $\left[\hat{H},\hat{x}\right]=\boxed{-\dfrac{\mathrm{i}\hbar}{m}\hat{p}_x}$

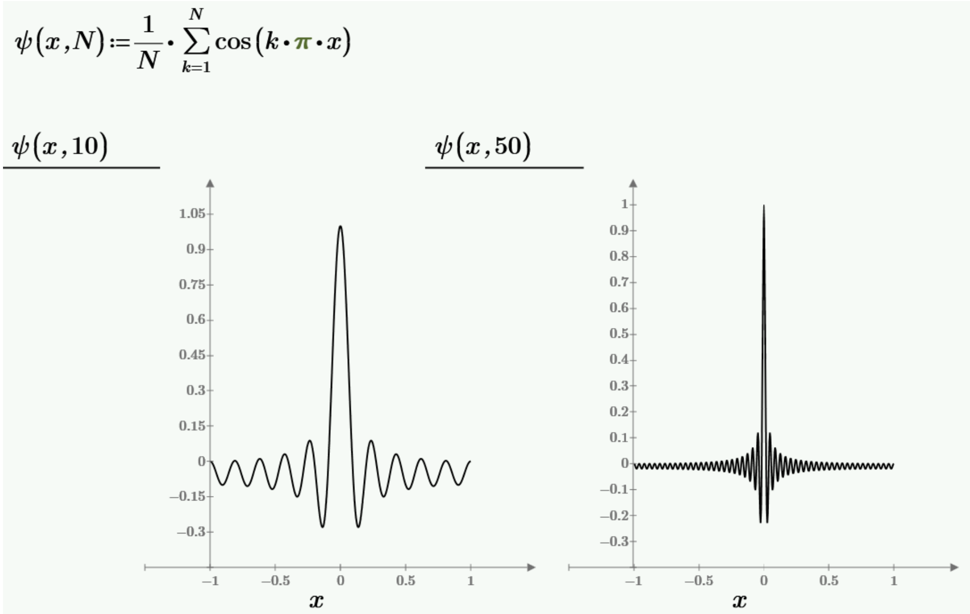
Integrated activities

7.2$^{\mathbf{LG}}$ Suppose that the wavefunction of an electron in a carbon nanotube is a linear combination of cos(*nx*) functions. (a) Use mathematical software, a spreadsheet, or the *Living graphs* (labelled $^{\mathrm{LG}}$) on the web site of this book to construct superpositions of cosine functions as

$$\psi(x) = \frac{1}{N}\sum_{k=1}^{N}\cos(k\pi x)$$

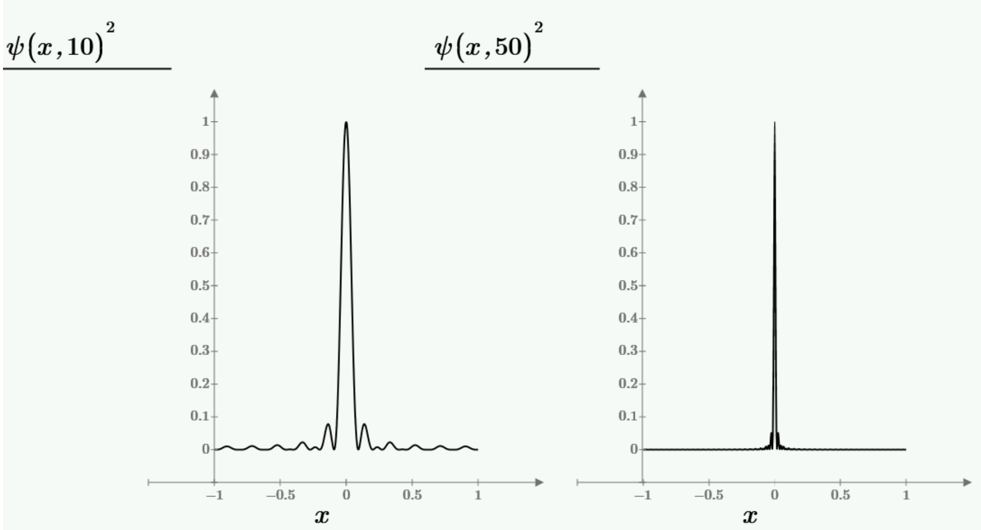
where the constant 1/*N* is introduced to keep the superpositions with the same overall magnitude. Set $x = 0$ at the centre of the screen and build the superposition there. (b) Explore how the probability density $\psi^2(x)$ changes with the value of *N*. (c) Evaluate the root mean square location of the packet, $\langle x^2\rangle^{1/2}$. (d) Determine the probability that a given momentum will be observed.

(a) The following Mathcad Prime 2 worksheet shows the effect of increasing the number *N* of superpositioned cosine functions. We see that as *N* increases the symmetrical peak at $x = 0$ narrows and sharpens.

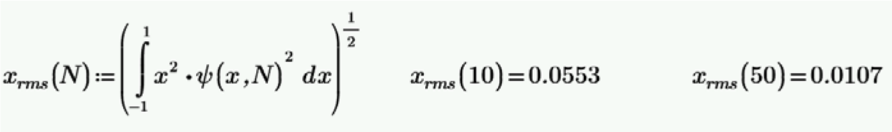


$$\psi(x,N) := \frac{1}{N}\cdot\sum_{k=1}^{N}\cos(k\cdot\pi\cdot x)$$

(b) Once again the probability density narrows and sharpens as the superposition is extended.



(c) The root mean square location of the packet, $\langle x^2\rangle^{1/2}$, approaches zero as the superposition is extended (i.e., the wavefunction narrows).



$$x_{rms}(N) := \left(\int_{-1}^{1} x^2 \cdot \psi(x,N)^2 \, dx\right)^{\frac{1}{2}} \qquad x_{rms}(10) = 0.0553 \qquad x_{rms}(50) = 0.0107$$

(d) This wavefunction is the superposition of N wavefunctions $\psi_{k=1,..N}$ each of which has the form $N^{-1}\cos(k\pi x)$ and the probability of any one of these equals N^{-2}. Momentum is more easily discussed by substitution using the identity

$$\cos(k\pi x) = ½\left(\mathrm{e}^{\mathrm{i}k\pi x} + \mathrm{e}^{-\mathrm{i}k\pi x}\right)$$

Then, $\psi_{k=1,..N}$ is the superposition of $½\mathrm{e}^{ik\pi x}$ and $½\mathrm{e}^{-ik\pi x}$. The magnitudes of their respective momentums are identically $kh/2$ but the former has momentum in the positive direction while the latter moves in the negative direction.

$$\hat{p}_x \times \left(½\mathrm{e}^{\mathrm{i}k\pi x}\right) = \left(\frac{\hbar}{\mathrm{i}}\right)\frac{\mathrm{d}}{\mathrm{d}x}\left(½\mathrm{e}^{\mathrm{i}k\pi x}\right) = \frac{kh}{2}\left(½\mathrm{e}^{\mathrm{i}k\pi x}\right) \quad \text{[Momentum eigenvalue equals } kh/2.\text{]}$$

$$\hat{p}_x \times \left(½\mathrm{e}^{-\mathrm{i}k\pi x}\right) = \left(\frac{\hbar}{\mathrm{i}}\right)\frac{\mathrm{d}}{\mathrm{d}x}\left(½\mathrm{e}^{-\mathrm{i}k\pi x}\right) = -\frac{kh}{2}\left(½\mathrm{e}^{-\mathrm{i}k\pi x}\right) \quad \text{[Momentum eigenvalue equals } -kh/2.\text{]}$$

We conclude that the probability of observing a momentum of $|kh/2|$ is $\boxed{N^{-2}}$. Also, when the momentum of magnitude $|kh/2|$ is observed in a long series of measurements, half of the observations with be in the positive direction and half will be in the negative direction.

8 The quantum theory of motion

8A Translation

Answers to discussion question

8A.2 Because translational motion in two or three dimensions can be separated into independent one-dimensional motions, many features of the one-dimensional solutions carry over. For example, quantization occurs in each dimension just as in the one-dimensional case; the energy associated with motion in each dimension has the same form as in the one-dimensional case; one-dimensional wavefunctions are factors in the multi-dimensional wavefunction. The concept of degeneracy—of more than one distinct wavefunction having the same energy—does not arise for a particle in a one-dimensional box, but it can arise in the multi-dimensional case (depending on the proportions of the box). For example, in a square two-dimensional box, the state with $n_1 = 1$ and $n_2 = 2$ has the same energy as the state $n_1 = 2$ and $n_2 = 1$.

Solutions to exercises

8A.1(b) If the wavefunction is an eigenfunction of an operator, the corresponding eigenvalue is the value of corresponding observable [Topic 7C.1(b)]. Applying the linear momentum operator $\hat{p} = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}$ [7C.3] to the wavefunction yields

$$\hat{p}\psi = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\psi = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\mathrm{e}^{\mathrm{i}kx} = \hbar k\mathrm{e}^{\mathrm{i}kx}$$

so the wavefunction is an eigenfunction of the linear momentum; thus, the value of the linear momentum is the eigenvalue

$$-\hbar k = -1.0546\times10^{-34}\ \mathrm{J\ s}\times5\times(10^{-9}\ \mathrm{m})^{-1} = \boxed{-5\times10^{-25}\ \mathrm{kg\ m\ s^{-1}}}$$

Similarly, applying the kinetic energy operator $\hat{E}_{\mathrm{k}} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$ [7C.5] to the wavefunction yields

$$\hat{E}_{\mathrm{k}}\psi = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\mathrm{e}^{-\mathrm{i}kx} = \frac{\hbar^2k^2}{2m}\mathrm{e}^{-\mathrm{i}kx}$$

so the wavefunction is an eigenfunction of this operator as well; thus, its value is the eigenvalue

$$\frac{\hbar^2k^2}{2m} = \frac{\{1.0546\times10^{-34}\ \mathrm{J\ s}\times5\times(10^{-9}\ \mathrm{m})^{-1}\}^2}{2\times1.67\times10^{-27}\ \mathrm{kg}} = \boxed{8\times10^{-23}\ \mathrm{J}}$$

8A.2(b) The wavefunction for the particle is [8A.2 with $B = 0$ because the particle is moving toward positive x

$$\psi_k = \boxed{A\mathrm{e}^{\mathrm{i}kx}}$$

The index k is given by the relationship

$$E_k = \frac{\hbar^2k^2}{2m}$$

But the kinetic energy of a 1.0 g particle travelling at 10 m s^{-1} is

$$E_k = \tfrac{1}{2}mv^2$$

Equating these two expressions and solving for k yields

$$\frac{\hbar^2k^2}{2m} = \tfrac{1}{2}mv^2$$

$$k = \frac{mv}{\hbar} = \frac{1.0\times10^{-3}\ \mathrm{kg}\times10\ \mathrm{m\ s^{-1}}}{1.0546\times10^{-34}\ \mathrm{J\ s}} = \boxed{9.5\times10^{31}\ \mathrm{m^{-1}}}$$

8A.3(b) $E = \dfrac{n^2h^2}{8m_\mathrm{e}L^2}$ [8A.6b]

$$\frac{h^2}{8m_\mathrm{e}L^2} = \frac{(6.626\times10^{-34}\ \mathrm{J\,s})^2}{8(9.109\times10^{-31}\ \mathrm{kg})\times(1.50\times10^{-9}\ \mathrm{m})^2} = 2.68\times10^{-20}\ \mathrm{J}$$

The conversion factors required are

1 eV = 1.602×10^{-19} J; 1 cm^{-1} = 1.986×10^{-23} J; 1 eV = 96.485 kJ mol^{-1}

(i) $$E_3 - E_1 = (9-1)\frac{h^2}{8m_\mathrm{e}L^2} = 8(2.68\times10^{-20}\ \mathrm{J})$$

$$= \boxed{2.14\times10^{-19}\ \mathrm{J}} = \boxed{1.34\,\mathrm{eV}} = \boxed{1.08\times10^{4}\ \mathrm{cm}^{-1}} = \boxed{129\,\mathrm{kJ\,mol}^{-1}}$$

(ii) $$E_7 - E_6 = (49-36)\frac{h^2}{8m_\mathrm{e}L^2} = 13(2.68\times10^{-20}\ \mathrm{J})$$

$$= \boxed{3.48\times10^{-19}\mathrm{J}} = \boxed{2.17\ \mathrm{eV}} = \boxed{1.75\times10^{4}\ \mathrm{cm}^{-1}} = \boxed{210\,\mathrm{kJ\,mol}^{-1}}$$

8A.4(b) The wavefunctions are [8A.6a]

$$\psi_n = \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)$$

The required probability is

$$P = \int \psi^*\psi\,\mathrm{d}x = \frac{2}{L}\int \sin^2\left(\frac{n\pi x}{L}\right)\mathrm{d}x \approx \frac{2\Delta x}{L}\sin^2\left(\frac{n\pi x}{L}\right)$$

where $\Delta x = 0.02L$ and the function is evaluated at x = 0.66 L.

(i) For n = 1 $$P = \frac{2(0.02L)}{L}\sin^2(0.66\pi) = \boxed{0.03\bar{1}}$$

(ii) For n = 2 $$P = \frac{2(0.02L)}{L}\sin^2[2(0.66\pi)] = \boxed{0.02\bar{9}}$$

8A.5(b) The expectation value is

$$\langle p\rangle = \int \psi^*\hat{p}\psi\,\mathrm{d}x$$

but first we need $\hat{p}\psi$ [7C.3, 8A.6a]

$$\hat{p}\psi = -\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right) = -\mathrm{i}\hbar\left(\frac{2}{L}\right)^{1/2}\frac{n\pi}{L}\cos\left(\frac{n\pi x}{L}\right)$$

so $$\langle p\rangle = \frac{-2\mathrm{i}\hbar n\pi}{L^2}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)\mathrm{d}x = \boxed{0}$$ for all n.

and $$\langle p^2\rangle = 2m\langle H\rangle = 2mE_n = \frac{h^2n^2}{4L^2}$$ for all n.

So for n = 2

$$\langle p^2\rangle = \boxed{\frac{h^2}{L^2}}$$

8A.6(b) The wavefunction is

$$\psi_n = \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right) \quad [8A.6a]$$

Hence $$\langle x\rangle = \int \psi^* x\psi\,\mathrm{d}x = \frac{2}{L}\int_0^L x\sin^2\left(\frac{n\pi x}{L}\right)\mathrm{d}x$$

Use integral T.11 from the Resource Section

$$\int x\sin^2 ax\,\mathrm{d}x = \frac{x^2}{4} - \frac{x\sin 2ax}{4a} - \frac{\cos 2ax}{8a^2}$$

so $$\langle x\rangle=\frac{2}{L}\left[\frac{x^2}{4}-\frac{Lx}{4n\pi}\sin\left(\frac{2n\pi x}{L}\right)-\frac{L^2}{8(n\pi)^2}\cos\left(\frac{2n\pi x}{L}\right)\right]\Bigg|_0^L=\boxed{\frac{L}{2}}\text{ for all }n.$$

$$\langle x^2\rangle=\frac{2}{L}\int_0^L x^2\sin^2\left(\frac{n\pi x}{L}\right)\mathrm{d}x$$

Use integral T.12 from the Resource Section

$$\int x^2\sin^2 ax\,\mathrm{d}x=\frac{x^3}{6}-\left(\frac{x^2}{4a}-\frac{1}{8a^3}\right)\sin 2ax-\frac{x\cos 2ax}{4a^2}$$

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 $n = 2$, $$\langle x^2\rangle=\boxed{L^2\left(\frac{1}{3}-\frac{1}{8\pi^2}\right)}$$

8A.7(b) The zero-point energy is the ground-state energy, that is, with $n_x = n_y = n_z = 1$:

$$E=\frac{(n_1^2+n_2^2+n_3^2)h^2}{8mL^2}\ [\text{8A.16b with equal lengths}]=\frac{3h^2}{8mL^2}$$

Set this equal to the rest energy mc^2 and solve for L:

$$mc^2=\frac{3h^2}{8mL^2}\qquad\text{so}\qquad L=\boxed{\left(\frac{3}{8}\right)^{1/2}\frac{h}{mc}=\left(\frac{3}{8}\right)^{1/2}\lambda_{\mathrm{C}}}$$

where λ_{C} is the Compton wavelength of a particle of mass m.

8A.8(b) $$\psi_5=\left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{5\pi x}{L}\right)\ [\text{8A.6a}]$$

$$P(x)\propto\psi_5^2\propto\sin^2\left(\frac{5\pi x}{L}\right)$$

Maxima and minima in $P(x)$ correspond to $\dfrac{\mathrm{d}\,P(x)}{\mathrm{d}x}=0$

$$\frac{\mathrm{d}}{\mathrm{d}x}P(x)\propto\frac{\mathrm{d}\psi^2}{\mathrm{d}x}\propto\sin\left(\frac{5\pi x}{L}\right)\cos\left(\frac{5\pi x}{L}\right)\propto\sin\left(\frac{10\pi x}{L}\right)\quad[2\sin\alpha\cos\alpha=\sin 2\alpha]$$

Now $\sin\theta = 0$ when $\theta = 0, \pi, 2\pi$, etc. (*i.e.*, when $\theta = n'\pi$ where n' is an integer).

Thus $\dfrac{10\pi x}{L}=n'\pi$ for $n'\le 10$ so $x=\dfrac{n'L}{10}$

$x = 0$ 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 $\dfrac{\mathrm{d}\psi}{\mathrm{d}x}=0$.

8A.9(b) In the original cubic box [8A.16b]

$$E_1=(n_1^2+n_2^2+n_3^2)\times\left(\frac{h^2}{8mL^2}\right)=\frac{K}{L^2},\quad K=(n_1^2+n_2^2+n_3^2)\times\left(\frac{h^2}{8m}\right)$$

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

$$\frac{\Delta E}{E} = \frac{1}{(0.9)^2} - 1 = 0.235 = \boxed{23.5\%}$$

8A.10(b) $E = \tfrac{3}{2}kT$ is the average translational energy of a gaseous molecule (see Topic 15C.2(a)).

(i) $$E = \tfrac{3}{2}kT = \frac{(n_1^2 + n_2^2 + n_3^2)h^2}{8mL^2}\ [8\text{A}.16\text{b}] = \frac{n^2h^2}{8mL^2}$$

so $$n = \frac{(12kTm)^{1/2}L}{h}$$

Before we evaluate this expression, we need the mass of a nitrogen molecule:

$$m = \frac{2 \times 14.01 \times 10^{-3}\ \text{kg mol}^{-1}}{6.022 \times 10^{23}\ \text{mol}^{-1}} = 4.653 \times 10^{-26}\ \text{kg}$$

Now $$n = \frac{(12 \times 1.381 \times 10^{-23}\ \text{J K}^{-1} \times 300\ \text{K} \times 4.653 \times 10^{-26}\ \text{kg})^{1/2} \times 1.00\ \text{m}}{6.626 \times 10^{-34}\ \text{J s}} = \boxed{7.26 \times 10^{10}}$$

(ii) 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

$$\Delta E = \frac{(2 \times 7.26 \times 10^{10} + 1) \times (6.626 \times 10^{-34}\ \text{J s})^2}{8 \times 4.653 \times 10^{-26}\ \text{kg} \times (1.00\ \text{m})^2} = \boxed{1.71 \times 10^{-31}\ \text{J}}$$

(iii) The de Broglie wavelength is obtained from

$$\lambda = \frac{h}{p} = \frac{h}{mv}\ [7\text{A}.14]$$

The velocity is obtained from

$$E_{\text{K}} = \tfrac{1}{2}mv^2 = \tfrac{3}{2}kT = \tfrac{3}{2}(1.381 \times 10^{-23}\ \text{J K}^{-1}) \times (300\ \text{K}) = 6.21 \times 10^{-21}\ \text{J}$$

So $$v = \left(\frac{2E_{\text{K}}}{m}\right)^{1/2} = \left(\frac{2 \times 6.21 \times 10^{-21}\ \text{J}}{4.653 \times 10^{-26}\ \text{kg}}\right)^{1/2} = 517\ \text{m s}^{-1}$$

and $$\lambda = \frac{6.626 \times 10^{-34}\ \text{J s}}{(4.653 \times 10^{-26}\ \text{kg}) \times (517\ \text{m s}^{-1})} = 2.76 \times 10^{-11}\ \text{m} = \boxed{27.6\ \text{pm}}$$

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,

$$\frac{\Delta E}{E} <<< 1.$$

8A.11(b) The energy levels are given by [8A.15b]

$$E_{n_1,n_2} = \left(\frac{n_1^{\,2}}{L_1^{\,2}} + \frac{n_2^{\,2}}{L_2^{\,2}}\right)\frac{h^2}{8m} = \left(\frac{n_1^{\,2}}{1} + \frac{n_2^{\,2}}{4}\right)\frac{h^2}{8mL^2}$$

$$E_{2,8} = \left(\frac{2^2}{1} + \frac{8^2}{4}\right)\frac{h^2}{8mL^2} = \frac{20h^2}{8mL^2} = \frac{5h^2}{2mL^2}$$

We are looking for another state that has the same energy. By inspection we note that the first term in parentheses in $E_{4,4}$ works out to be 4 and the second 16; we can arrange for those values to be reversed:

$$E_{1,4} = \left(\frac{4^2}{1} + \frac{4^2}{4}\right)\frac{h^2}{8mL^2} = \frac{5h^2}{2mL^2}$$

So in this box, the state $\boxed{n_1=4,\ n_2=4}$ is degenerate to the state $n_1=2$, $n_2=8$. The question notes that degeneracy frequently accompanies symmetry, and suggests that one might be surprised to find degeneracy in a box with unequal lengths. Symmetry is a matter of degree. This box is less symmetric than a square box, but it is more symmetric than boxes whose sides have a non-integer or irrational ratio. Every state of a square box except those with $n_1=n_2$ is degenerate (with the state that has n_1 and n_2 reversed). Only a few states in this box are degenerate. In this system, a state (n_1, n_2) is degenerate with a state ($n_2/2$, $2n_1$) as long as the latter state (a) exists (*i.e.*, $n_2/2$ must be an integer) and (b) is distinct from (n_1, n_2). A box with incommensurable sides, say, L and $2^{1/2}L$, would have no degenerate levels.

8A.12(b) The energy levels are [8A.16b]

$$E_{n_1,n_2,n_3} = \frac{(n_1^{\;2}+n_2^{\;2}+n_3^{\;2})h^2}{8m_\mathrm{e}L^2}$$

$$E_{1,1,1} = \frac{3h^2}{8mL^2}, \qquad \frac{14}{3}E_{1,1,1} = \frac{14h^2}{8mL^2}$$

Hence, we require the values of n_1, n_2 and n_3 that make

$$n_1^2+n_2^2+n_3^2 = 14 = 3^2+2^2+1^2$$

The degeneracy, then, is $\boxed{6}$, corresponding to (n_1, n_2, n_3) = (1, 2, 3), (1, 3, 2), (2, 1, 3), (2, 3, 1), (3, 1, 2), or (3, 2, 1).

8A.13(b) The transmission probability [8A.23a] depends on the energy of the tunneling particle relative to the barrier height ($\varepsilon = E/V$ = 1.5 eV/(2.0 eV) = 0.75), on the width of the barrier (L = 100 pm), and on the decay parameter of the wavefunction inside the barrier (κ), where [8A.20]

$$\kappa = \frac{\{2m(V-E)\}^{1/2}}{\hbar} = \frac{\{2\times 1.67\times 10^{-27}\ \mathrm{kg}\times(2.0-1.5)\ \mathrm{eV}\times 1.602\times 10^{-19}\ \mathrm{J\ eV^{-1}}\}^{1/2}}{1.0546\times 10^{-34}\ \mathrm{J\ s}}$$
$$= 1.\overline{6}\times 10^{11}\ \mathrm{m^{-1}}$$

so $\kappa L = 1.\overline{6}\times 10^{11}\ \mathrm{m^{-1}}\times 100\times 10^{-12}\ \mathrm{m} = 1\overline{6}$. Using eqn. 10.6 for the transmission probability yields

$$T = \left\{1+\frac{(\mathrm{e}^{\kappa L}-\mathrm{e}^{-\kappa L})^2}{16\varepsilon(1-\varepsilon)}\right\}^{-1} = \left\{1+\frac{(\mathrm{e}^{1\overline{6}}-\mathrm{e}^{-1\overline{6}})^2}{16\times 0.75\times(1-0.75)}\right\}^{-1} = \boxed{1.\overline{0}\times 10^{-13}}$$

Comment. In fact, the simplified eqn. 8A.23b gives the same result:

$$T = 16\varepsilon(1-\varepsilon)\mathrm{e}^{-2\kappa L} = 16\times 0.75\times(1-0.25)\times \mathrm{e}^{-2\times 1\overline{6}} = \boxed{1.\overline{0}\times 10^{-13}}$$

Eqn. 8A.23b is valid if $\kappa L >> 1$; however, κL need not be huge to make the positive exponential term in eqn. 10.6 dominant, reducing the expression to eqn. 8A.23b.

Solutions to problems

8A.2 **(a)** The energy levels are given by:

$$E_n = \frac{h^2n^2}{8mL^2}\ \text{[8A.6b]}$$

and we are looking for the energy difference between n = 6 and n = 7:

$$\Delta E = \frac{h^2(7^2-6^2)}{8mL^2}$$

Since there are 12 atoms on the conjugated backbone, the length of the box is 11 times the bond length:

$$L = 11(140\times 10^{-12}\ \mathrm{m}) = 1.54\times 10^{-9}\ \mathrm{m},$$

so $$\Delta E = \frac{(6.626\times 10^{-34}\ \mathrm{J\,s})^2(49-36)}{8(9.11\times 10^{-31}\ \mathrm{kg})(1.54\times 10^{-9}\ \mathrm{m})^2} = \boxed{3.30\times 10^{-19}\ \mathrm{J}}$$

(b) The relationship between energy and frequency is:

$$\Delta E = h\nu \qquad \text{so} \qquad \nu = \frac{\Delta E}{h} = \frac{3.30\times 10^{-19}\ \mathrm{J}}{6.626\times 10^{-34}\ \mathrm{J\,s}} = \boxed{4.95\times 10^{14}\ \mathrm{s^{-1}}}.$$

(c) Look at the terms in the energy expression that change with the number of conjugated atoms, N. The energy (and frequency) are inversely proportional to L^2 and directly proportional to $(n+1)^2 - n^2 = 2n + 1$, where n is the quantum number of the highest occupied state. Since n is proportional to N (equal to $N/2$) and L is approximately proportional to N (strictly to $N-1$), the energy and frequency are approximately proportional to N^{-1}. So *the absorption spectrum of a linear polyene shifts to lower frequency as the number of conjugated atoms increases*.

8A.4 **(a)** In the box, the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi = E\psi$$

Assume that the solution is a product of three functions of a single variable; that is, let

$$\psi(x,y,z) = X(x)Y(y)Z(z)\ .$$

Substituting into the Schrödinger equation gives

$$-\frac{\hbar^2}{2m}\left(YZ\frac{\partial^2 X}{\partial x^2}+XZ\frac{\partial^2 Y}{\partial y^2}+XY\frac{\partial^2 Z}{\partial z^2}\right) = EXYZ$$

Divide both sides by XYZ:

$$-\frac{\hbar^2}{2m}\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}\right) = E$$

For the purposes of illustration, isolate the terms that depend on x on the left side of the equation:

$$-\frac{\hbar^2}{2m}\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2}\right) = E+\frac{\hbar^2}{2m}\left(\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}\right)$$

Note that the left side depends only on one variable, x, while the right side depends on two different and independent variables, y and z. The only way that the two sides can be equal to each other for all x, y, and z is if they are both equal to a constant. Call that constant E_x, and we have, from the left side of the equation:

$$-\frac{\hbar^2}{2m}\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2}\right) = E_x \qquad \text{so} \qquad -\frac{\hbar^2}{2m}\frac{\partial^2 X}{\partial x^2} = E_x X\ .$$

Note that this is just the Schrödinger equation for a particle in a one-dimensional box. Note also that we could just as easily have isolated y terms or z terms, leading to similar equations.

$$-\frac{\hbar^2}{2m}\frac{\partial^2 Y}{\partial y^2} = E_y Y \ \text{ and } \qquad -\frac{\hbar^2}{2m}\frac{\partial^2 Z}{\partial z^2} = E_z Z$$

The assumption that the wavefunction can be written as a product of single-variable functions is a valid one, for we can find ordinary differential equations for the assumed factors. That is what it means for a partial differential equation to be separable.

(b) Since X, Y, and Z are particle-in-a-box wavefunctions of independent variables x, y, and z respectively, each of them has its own quantum number. The three-dimensional wavefunction is a product of the three, and therefore depends on all three quantum numbers:

$$\psi(x,y,z) = X(x)Y(y)Z(z) = \left(\frac{2}{L_1}\right)^{1/2}\sin\frac{n_x\pi x}{L_1}\times\left(\frac{2}{L_2}\right)^{1/2}\sin\frac{n_y\pi y}{L_2}\times\left(\frac{2}{L_3}\right)^{1/2}\sin\frac{n_z\pi z}{L_3}$$

Each constant of separation (E_x, E_y, and E_z) depends on its own quantum number. The three constants of separation add up to the total energy, which therefore depends on all three quantum numbers:

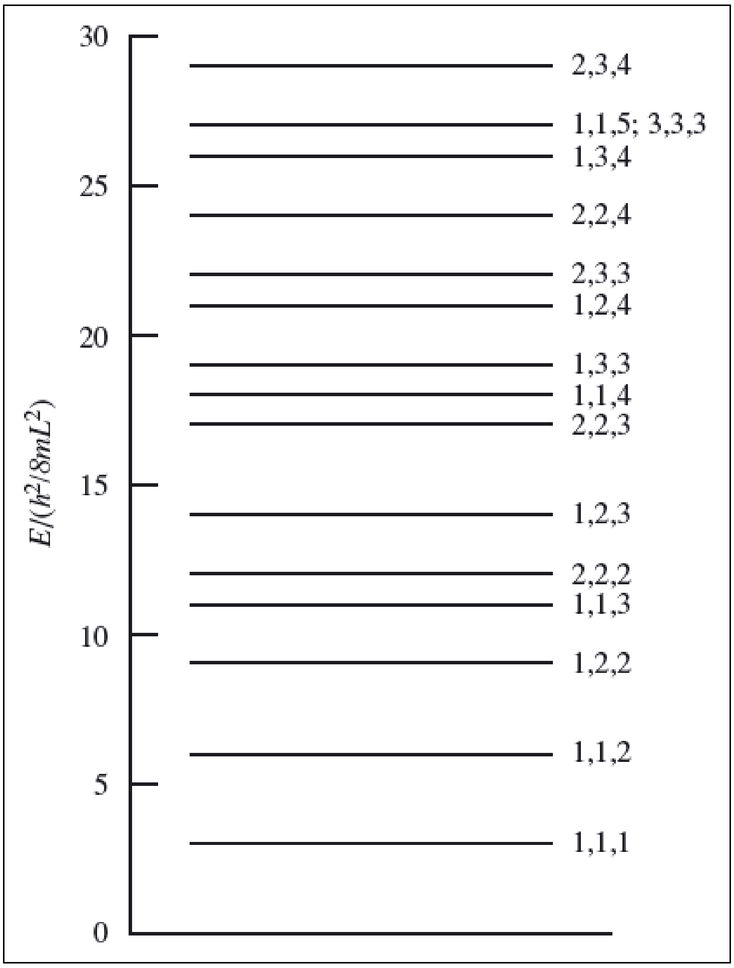
$$E = E_x + E_y + E_z = \frac{h^2}{8m}\left(\frac{n_x^{\,2}}{L_1^2}+\frac{n_y^{\,2}}{L_2^2}+\frac{n_z^{\,2}}{L_3^2}\right)$$

(c) For a cubic box, $L_1 = L_2 = L_3 = L$, so

$$E = \frac{h^2(n_x^{\,2}+n_y^{\,2}+n_z^{\,2})}{8mL^2}$$

The energy levels are shown in Figure 8A.1.

Figure 8A.1



(d) Compare this energy-level diagram to Figure 8A.2 of the textbook. The energy levels here are much more closely spaced. In a one-dimensional box, the 15th energy level is not reached until $\dfrac{E}{h^2/8mL^2}=225$, and the previous level is 29 units below that. In the three-dimensional box, the first 15 energy levels fit within the range of 29 units. The energy levels in a one-dimensional box are sparse compared to those in a three-dimensional box.

8A.6 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 8A.18 and 8A.21. Eqns 8A.22a and 8A.22b list four equations for the five unknown coefficients of the full wavefunction:

(a) $A+B=C+D$

(b) $C\mathrm{e}^{\kappa L}+D\mathrm{e}^{-\kappa L}=A'\mathrm{e}^{\mathrm{i}kL}$

(c) $\mathrm{i}kA-\mathrm{i}kB=\kappa C-\kappa D$

(d) $\kappa C\mathrm{e}^{\kappa L}-\kappa D\mathrm{e}^{-\kappa L}=\mathrm{i}kA'\mathrm{e}^{\mathrm{i}kL}$

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:

$$B=C+D-A=A-\frac{\kappa C}{\mathrm{i}k}+\frac{\kappa D}{\mathrm{i}k}.$$

Solve this equation for C:

$$C=\frac{2A+D\left(\dfrac{\kappa}{\mathrm{i}k}-1\right)}{\dfrac{\kappa}{\mathrm{i}k}+1}=\frac{2A\mathrm{i}k+D(\kappa-\mathrm{i}k)}{\kappa+\mathrm{i}k}.$$

Now note that the desired A' appears only in (b) and (d). Solve these for A' and set them equal:

$$A' = \mathrm{e}^{-\mathrm{i}kL}(C\mathrm{e}^{\kappa L} + D\mathrm{e}^{-\kappa L}) = \frac{\kappa \mathrm{e}^{-\mathrm{i}kL}}{\mathrm{i}k}(C\mathrm{e}^{\kappa L} - D\mathrm{e}^{-\kappa L})\ .$$

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:

$$\frac{(\kappa+\mathrm{i}k)^2\mathrm{e}^{-2\kappa L} - (\kappa-\mathrm{i}k)^2}{(\kappa-\mathrm{i}k)(\kappa+\mathrm{i}k)}D = \frac{2A\mathrm{i}k}{\kappa+\mathrm{i}k},$$

so $$D = \frac{2A\mathrm{i}k(\kappa-\mathrm{i}k)}{(\kappa+\mathrm{i}k)^2\mathrm{e}^{-2\kappa L} - (\kappa-\mathrm{i}k)^2}\ .$$

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:

$$A' = \mathrm{e}^{-\mathrm{i}kL}(C\mathrm{e}^{\kappa L} + D\mathrm{e}^{-\kappa L}) = \frac{2A\mathrm{i}k\mathrm{e}^{-\mathrm{i}kL}}{(\kappa+\mathrm{i}k)^2\mathrm{e}^{-2\kappa L} - (\kappa-\mathrm{i}k)^2}[(\kappa+\mathrm{i}k)\mathrm{e}^{-\kappa L} + (\kappa-\mathrm{i}k)\mathrm{e}^{-\kappa L}],$$

so $$\frac{A'}{A} = \frac{4\mathrm{i}k\kappa \mathrm{e}^{-\kappa L}\mathrm{e}^{-\mathrm{i}kL}}{(\kappa+\mathrm{i}k)^2\mathrm{e}^{-2\kappa L} - (\kappa-\mathrm{i}k)^2} = \frac{4\mathrm{i}k\kappa\mathrm{e}^{-\mathrm{i}kL}}{(\kappa+\mathrm{i}k)^2\mathrm{e}^{-\kappa L} - (\kappa-\mathrm{i}k)^2\mathrm{e}^{\kappa L}}.$$

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:

$$\begin{aligned}&(\kappa+\mathrm{i}k)^2(\kappa-\mathrm{i}k)^2\mathrm{e}^{-2\kappa L} - (\kappa-\mathrm{i}k)^4 - (\kappa+\mathrm{i}k)^4 + (\kappa-\mathrm{i}k)^2(\kappa+\mathrm{i}k)^2\mathrm{e}^{2\kappa L}\\ &\quad = (\kappa^2+k^2)^2(\mathrm{e}^{2\kappa L} + \mathrm{e}^{-2\kappa L}) - (\kappa^2 - 2\mathrm{i}\kappa k - k^2)^2 - (\kappa^2 + 2\mathrm{i}\kappa k - k^2)^2\\ &\quad = (\kappa^4 + 2\kappa^2k^2 + k^4)(\mathrm{e}^{2\kappa L} + \mathrm{e}^{-2\kappa L}) - (2\kappa^4 - 12\kappa^2k^2 + 2k^4).\end{aligned}$$

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 8.18 and 8.20 define k and κ. The factors involving 2, $\hbar$, and the mass cancel leaving $\kappa \propto (V-E)^{1/2}$ and $k \propto E^{1/2}$, 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:

$$T = \boxed{\left(\frac{(\mathrm{e}^{\kappa L} - \mathrm{e}^{-\kappa L})^2}{16\varepsilon(1-\varepsilon)} + 1\right)^{-1}}$$

If $\kappa L >> 1$, then the negative exponential is negligible compared to the positive, and the 1 inside the parentheses is negligible compared to the exponential:

$$T \approx \left(\frac{\mathrm{e}^{2\kappa L}}{16\varepsilon(1-\varepsilon)}\right)^{-1} = \frac{16\varepsilon(1-\varepsilon)}{\mathrm{e}^{2\kappa L}} = \boxed{16\varepsilon(1-\varepsilon)\mathrm{e}^{-2\kappa L}}$$

8A.8 We assume that the barrier begins at $x = 0$ and extends in the positive x direction.

(a) $$P = \int_{\text{barrier}} \psi^2 \,\mathrm{d}\tau = \int_0^\infty N^2 \mathrm{e}^{-2\kappa x}\,\mathrm{d}x = \boxed{\frac{N^2}{2\kappa}}$$

(b) $$\langle x \rangle = \int_0^\infty x\psi^2 \mathrm{d}x = N^2 \int_0^\infty x\mathrm{e}^{-2\kappa x}\mathrm{d}x = \frac{N^2}{(2\kappa)^2} = \boxed{\frac{N^2}{4\kappa^2}}$$

Question. Is N a normalization constant?

8B Vibrational motion

Answers to discussion question

8B.2 The correspondence principle (mentioned in Topic 8A.2(b)) 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 tunneling 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 8B.7 of the main text, particularly for $v = 18$, 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.

Solutions to exercises

8B.1(b) $$E = \left(v + \frac{1}{2}\right)\hbar\omega, \quad \omega = \left(\frac{k_\mathrm{f}}{m}\right)^{1/2} \quad [8B.4]$$

The zero-point energy corresponds to $v = 0$; hence

$$E_0 = \tfrac{1}{2}\hbar\omega = \tfrac{1}{2}\hbar\left(\frac{k_\mathrm{f}}{m}\right)^{1/2} = \tfrac{1}{2}(1.0546\times10^{-34}\ \mathrm{J\,s}) \times \left(\frac{285\ \mathrm{N\,m^{-1}}}{5.16\times10^{-26}\ \mathrm{kg}}\right)^{1/2}$$
$$= \boxed{3.92\times10^{-21}\ \mathrm{J}}$$

8B.2(b) The difference in adjacent energy levels is

$$\Delta E = E_{v+1} - E_v = \hbar\omega\ [8B.5] = \hbar\left(\frac{k_\mathrm{f}}{m}\right)^{1/2} \quad [8B.4]$$

so $$k_{\mathrm{f}} = \frac{m(\Delta E)^2}{\hbar^2} = \frac{(2.88\times10^{-25}\ \mathrm{kg})\times(3.17\times10^{-21}\ \mathrm{J})^2}{(1.0546\times10^{-34}\ \mathrm{J\,s})^2} = 260\ \mathrm{kg\ s^{-2}} = \boxed{260\ \mathrm{N\,m^{-1}}}$$

8B.3(b) The requirement for a transition to occur is that ΔE(system) = E(photon) ,

so $$\Delta E(\text{system}) = \hbar\omega\ [8\text{B}.5] = E(\text{photon}) = h\nu = \frac{hc}{\lambda}$$

Therefore, $$\frac{hc}{\lambda} = \frac{h\omega}{2\pi} = \left(\frac{h}{2\pi}\right)\times\left(\frac{k_{\mathrm{f}}}{m}\right)^{1/2}\ [8\text{B}.4]$$

$$\lambda = 2\pi c\left(\frac{m}{k_{\mathrm{f}}}\right)^{1/2} = (2\pi)\times(2.998\times10^{8}\ \mathrm{m\ s^{-1}})\times\left(\frac{15.9949\times1.6605\times10^{-27}\ \mathrm{kg}}{544\ \mathrm{N\ m^{-1}}}\right)^{1/2}$$

$$= 1.32\times10^{-5}\mathrm{m} = \boxed{13.2\ \mu\mathrm{m}}$$

8B.4(b) The frequency of a harmonic oscillator is [8B.4]

$$\omega = \left(\frac{k_{\mathrm{f}}}{m}\right)^{1/2}.$$

^{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:

$$\omega_{\mathrm{T}} = \omega_{\mathrm{H}}\left(\frac{m_{\mathrm{H}}}{m_{\mathrm{T}}}\right)^{1/2}$$

But the appropriate mass is not the mass of the molecule but its “effective mass” [8B.7]

$$\mu = \frac{m_1 m_2}{m_1+m_2} = \frac{m}{2}\ [m_1 = m_2 = m]$$

For H_2: $$\mu = \frac{m}{2} = \frac{1.0078\times(1.6605\times10^{-27}\ \mathrm{kg})}{2} = \boxed{8.3673\times10^{-28}\ \mathrm{kg}}$$

For T_2: $$\mu = \frac{m}{2} = \frac{3.0160\times(1.6605\times10^{-27}\ \mathrm{kg})}{2} = \boxed{2.5040\times10^{-27}\ \mathrm{kg}}$$

$$\omega_{\mathrm{T}} = 131.9\ \mathrm{THz}\times\left(\frac{8.3673\times10^{-28}\ \mathrm{kg}}{2.5040\times10^{-27}\ \mathrm{kg}}\right)^{1/2} = \boxed{76.2\ \mathrm{THz}}$$

8B.5(b) $\Delta E = \hbar\omega = h\nu$

(i) $$\Delta E = h\nu\ [8\text{B}.5] = (6.626\times10^{-34}\ \mathrm{J\,Hz^{-1}})\times(33\times10^{3}\ \mathrm{Hz}) = \boxed{2.2\times10^{-29}\ \mathrm{J}}$$

(ii) For a two-particle oscillator μ, replaces m in the expression for ω.

$$\Delta E = \hbar\omega = \hbar\left(\frac{k_{\mathrm{f}}}{\mu}\right)^{1/2}\ [8\text{B}.4] = \hbar\left(\frac{2k}{m}\right)^{1/2}$$

The last equality uses eqn 8B.7 for two equal masses, as in Exercise 8B.4(b).

$$\Delta E = (1.055\times10^{-34}\ \mathrm{J\,s})\times\left(\frac{(2)\times(1177\ \mathrm{N\,m^{-1}})}{(16.00)\times(1.6605\times10^{-27}\ \mathrm{kg})}\right)^{1/2} = \boxed{3.14\times10^{-20}\ \mathrm{J}}$$

8B.6(b) The zero-point energy is

$$E_0 = \frac{1}{2}\hbar\omega\ [8\text{B}.6] = \frac{\hbar}{2}\left(\frac{k}{\mu}\right)^{1/2}\ [8\text{B}.4]$$

μ = 14.0031× (1.6605×10^{-27} kg)/2 = 1.1626×10^{-26} kg
where we have used eqn 8B.7 for two equal masses, as in Exercise 8B.4(b).

$$E_0 = \frac{1.0546\times10^{-34}\ \mathrm{J\,s}}{2}\times\left(\frac{2293.8\ \mathrm{N\,m^{-1}}}{1.1626\times10^{-26}\ \mathrm{kg}}\right)^{1/2} = \boxed{2.3422\times10^{-20}\ \mathrm{J}}$$

8B.7(b) The harmonic oscillator wavefunctions have the form [8B.8]

$$\psi_v(x) = N_v H_v(y)\exp\left(-\tfrac{1}{2}y^2\right) \quad \text{with} \quad y = \frac{x}{\alpha} \quad \text{and} \quad \alpha = \left(\frac{\hbar^2}{mk_\mathrm{f}}\right)^{1/4}$$

The exponential function approaches zero only as x approaches ±∞, so the nodes of the wavefunction are the nodes of the Hermite polynomials.

$H_5(y) = 32y^5 - 160y^3 + 120y = 0$ [Table 8B.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 $$z = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{20 \pm \sqrt{20^2 - 4\times 4\times 15}}{2\times 4} = \frac{5 \pm \sqrt{10}}{2}$$

Evaluating the result numerically yields $z = 0.92$ or 4.08, so $y = \pm 0.96$ or ± 2.02. Therefore $x = \boxed{0, \pm 0.96\alpha, \text{ or } \pm 2.02\alpha}$.

Comment. Numerical values could also be obtained graphically by plotting $H_5(y)$.

8B.8(b) The most probable displacements are the values of x that maximize ψ^2. As noted in Exercise 8A.8(b), maxima in ψ^2 correspond to maxima *and* minima in ψ itself, so one can solve this exercise by finding all points where $\dfrac{\mathrm{d}\psi}{\mathrm{d}x} = 0$. From eqn 8B.8 and Table 8B.1, the wavefunction is

$$\psi_3(x) = N_3 H_3(y)\exp\left(-\tfrac{1}{2}y^2\right) \quad \text{with} \quad y = \frac{x}{\alpha},\ \alpha = \left(\frac{\hbar^2}{mk_\mathrm{f}}\right)^{1/4},\ \text{and } H_3(y) = 8y^3 - 12y\,.$$

$$\frac{\mathrm{d}\psi_3}{\mathrm{d}x} = \frac{\mathrm{d}y}{\mathrm{d}x}\frac{\mathrm{d}\psi_3}{\mathrm{d}y} = \frac{N_3}{\alpha}\left\{(24y^2 - 12)\exp\left(-\tfrac{1}{2}y^2\right) - (8y^3 - 12y)y\exp\left(-\tfrac{1}{2}y^2\right)\right\} = 0$$

Dividing through by constants and the exponential functions yields

$-8y^4 + 36\,y^2 - 12 = 0$.

Letting $z = y^2$ (and dividing through by –4) yields the quadratic equation

$2z^2 - 9z + 3 = 0$

so $$z = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{9 \pm \sqrt{9^2 - 2\times 3\times 4}}{2\times 2} = \frac{9 \pm \sqrt{57}}{4}$$

Evaluating the result numerically yields $z = 4.14$ or 0.363, so $y = \pm 2.03$ or ± 0.602. Therefore $x = \boxed{0, \pm 2.03\alpha, \text{ or } \pm 0.602\alpha}$.

8B.9(b) Example 8B.4 analyzes the classical turning points of the harmonic oscillator. In terms of the dimensionless variable y, the turning points are $y_\mathrm{tp} = \pm(2v+1)^{1/2}$. The probability of extension beyond the classical turning point is

$$P = \int_{x_\mathrm{tp}}^{\infty} \psi_v{}^2 \mathrm{d}x = \alpha N_v{}^2 \int_{y_\mathrm{tp}}^{\infty} \{H_v(y)\}^2 \mathrm{e}^{-y^2}\mathrm{d}y$$

For $v = 2$, $H_2(y) = 4y^2 - 2$ and $N_2 = \left(\dfrac{1}{8\alpha\pi^{1/2}}\right)^{1/2}$

$$P = 4\alpha N_2{}^2 \int_{5^{1/2}}^{\infty} (2y^2 - 1)^2 \mathrm{e}^{-y^2}\mathrm{d}y = 4\alpha N_2{}^2 \int_{5^{1/2}}^{\infty} (4y^4 - 4y^2 + 1)\mathrm{e}^{-y^2}\mathrm{d}y$$

Use integration by parts for $\int y^2 \mathrm{e}^{-y^2}\mathrm{d}y$:

$$\int u\mathrm{d}v = uv - \int v\mathrm{d}u$$

where $u = y, \quad \mathrm{d}v = y\mathrm{e}^{-y^2}\mathrm{d}y$

so $\mathrm{d}u = \mathrm{d}y, \quad v = -\tfrac{1}{2}\mathrm{e}^{-y^2}$

and $$\int y^2\mathrm{e}^{-y^2}\mathrm{d}y = -\tfrac{1}{2}y\mathrm{e}^{-y^2} + \tfrac{1}{2}\int \mathrm{e}^{-y^2}\mathrm{d}y$$

Use integration by parts for $\int y^4 \mathrm{e}^{-y^2}\mathrm{d}y$ as well:

$$\int u\mathrm{d}v = uv - \int v\mathrm{d}u$$

where $u = y^3, \quad \mathrm{d}v = y\mathrm{e}^{-y^2}\mathrm{d}y$

so $\mathrm{d}u = 3y^2\mathrm{d}y, \quad v = -\tfrac{1}{2}\mathrm{e}^{-y^2}$

and $\int y^4\mathrm{e}^{-y^2}\mathrm{d}y = -\tfrac{1}{2}y^3\mathrm{e}^{-y^2} + \tfrac{3}{2}\int y^2\mathrm{e}^{-y^2}\mathrm{d}y = -\tfrac{1}{2}y^3\mathrm{e}^{-y^2} - \tfrac{3}{4}y\mathrm{e}^{-y^2} + \tfrac{3}{4}\int \mathrm{e}^{-y^2}\mathrm{d}y$

The remaining integral can be expressed in terms of the error function.

$$\mathrm{erf}\, z = 1 - \frac{2}{\pi^{1/2}}\int_z^\infty \mathrm{e}^{-y^2}\mathrm{d}y$$

so $\int_{5^{1/2}}^\infty \mathrm{e}^{-y^2}\mathrm{d}y = \dfrac{\pi^{1/2}(1-\mathrm{erf}\,5^{1/2})}{2}$

Putting all the pieces together yields

$$P = 4\alpha N_2{}^2\left(\left(-2y^3\mathrm{e}^{-y^2} - y\mathrm{e}^{-y^2}\right)\Big|_{5^{1/2}}^{\infty} + \pi^{1/2}(1-\mathrm{erf}\,5^{1/2})\right)$$

$$P = \frac{1}{2\pi^{1/2}}\left(2\times 5^{3/2}\mathrm{e}^{-5} + 5^{1/2}\mathrm{e}^{-5} + \pi^{1/2}(1-\mathrm{erf}\,5^{1/2})\right)$$

Finally, using erf $5^{1/2}$ = 0.9984, $P = \boxed{0.048}$

Comment. This is the probability of an extension greater than the positive classical turning point. There is an equal probability of a compression smaller than the negative classical turning point, so the total probability of finding the oscillator in a classically forbidden region is $\boxed{0.095}$.

Comment. Note that molecular parameters such as *m* and *k* do not enter into the calculation.

Solutions to problems

8B.2 In effect, we are looking for the vibrational frequency of an O atom bound, with a force constant equal to that of free CO, to an infinitely massive and immobile protein complex. The angular frequency is [8B.4]

$$\omega = \left(\frac{k_\mathrm{f}}{m}\right)^{1/2}$$

where *m* is the mass of the O atom

$m = 16.0 \times (1.66\times 10^{-27}\ \mathrm{kg}) = 2.66\times 10^{-26}\ \mathrm{kg}$,

and k_f is the same force constant as in Problem 8B.1. In that problem (unlike this one), the mass appropriate for the vibration of the free CO molecule was the effective mass.

$$k_\mathrm{f} = \omega^2\mu = 4\pi^2c^2\tilde{\nu}^2\mu = \frac{4\pi^2c^2\tilde{\nu}^2 m_1m_2}{m_1+m_2} = 1902\ \mathrm{N\,m^{-1}}$$

Hence the frequency for haem-bound CO would be

$$\omega = \left(\frac{1902\,\mathrm{N\,m^{-1}}}{2.66\times 10^{-26}\,\mathrm{kg}}\right)^{1/2} = \boxed{2.68\times 10^{14}\,\mathrm{s^{-1}}}$$

8B.4 The Schrödinger equation is $-\dfrac{\hbar^2}{2m}\dfrac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \tfrac{1}{2}kx^2\psi = E\psi$

We try $\psi = \mathrm{e}^{-gx^2}$, so $\dfrac{\mathrm{d}\psi}{\mathrm{d}x} = -2gx\mathrm{e}^{-gx^2}$

and $\dfrac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -2g\mathrm{e}^{-gx^2} + 4g^2x^2\mathrm{e}^{-gx^2} = -2g\psi + 4g^2x^2\psi$

Inserting into the Schrödinger equation yields

$$\left(\frac{\hbar^2 g}{m}\right)\psi - \left(\frac{2\hbar^2g^2}{m}\right)x^2\psi + \tfrac{1}{2}kx^2\psi = E\psi$$

$$\left(\frac{\hbar^2 g}{m} - E\right)\psi + \left(\tfrac{1}{2}k - \frac{2\hbar^2 g^2}{m}\right)x^2\psi = 0$$

This equation is satisfied if

$$E = \frac{\hbar^2 g}{m} \quad \text{and} \quad 2\hbar^2 g^2 = \tfrac{1}{2}mk, \quad \text{or} \quad \boxed{g = \tfrac{1}{2}\left(\frac{mk}{\hbar^2}\right)^{1/2}}$$

Therefore,

$$E = \tfrac{1}{2}\hbar\left(\frac{k}{m}\right)^{1/2} = \tfrac{1}{2}\hbar\omega \quad \text{if } \omega = \left(\frac{k}{m}\right)^{1/2}$$

8B.6 $$\langle x^n\rangle = \alpha^n\langle y^n\rangle = \alpha^n\int_{-\infty}^{+\infty}\psi y^n\psi\,\mathrm{d}x = \alpha^{n+1}\int_{-\infty}^{+\infty}\psi^2 y^n\,\mathrm{d}y \quad [x = \alpha y]$$

$$\langle x^3\rangle \propto \int_{-\infty}^{+\infty}\psi^2 y^3\,\mathrm{d}y = \boxed{0} \text{ by symmetry} \quad [y^3 \text{ is an odd function of } y]$$

$$\langle x^4\rangle = \alpha^5\int_{-\infty}^{+\infty}\psi y^4\psi\,\mathrm{d}y$$

$$y^4\psi = y^4 N H_v \mathrm{e}^{-y^2/2}$$

$$y^4 H_v = y^3\left(\tfrac{1}{2}H_{v+1} + vH_{v-1}\right) = y^2\left[\tfrac{1}{2}\left(\tfrac{1}{2}H_{v+2} + (v+1)H_v\right) + v\left(\tfrac{1}{2}H_v + (v-1)H_{v-2}\right)\right]$$

$$= y^2\left[\tfrac{1}{4}H_{v+2} + \left(v+\tfrac{1}{2}\right)H_v + v(v-1)H_{v-2}\right]$$

$$= y\left[\tfrac{1}{4}\left(\tfrac{1}{2}H_{v+3} + (v+2)H_{v+1}\right) + \left(v+\tfrac{1}{2}\right)\times\left(\tfrac{1}{2}H_{v+1} + vH_{v-1}\right)\right.$$

$$\left. + v(v-1)\times\left(\tfrac{1}{2}H_{v-1} + (v-2)H_{v-3}\right)\right]$$

$$= y\left(\tfrac{1}{8}H_{v+3} + \tfrac{3}{4}(v+1)H_{v+1} + \tfrac{3}{2}v^2H_{v-1} + v(v-1)\times(v-2)H_{v-3}\right)$$

Only yH_{v+1} and yH_{v-1} lead to H_v and contribute to the expectation value (since H_v is orthogonal to all except H_v) [Table 8B.1]; hence

$$y^4H_v = \tfrac{3}{4}y\{(v+1)H_{v+1} + 2v^2H_{v-1}\} + \ \ldots$$

$$= \tfrac{3}{4}\left[(v+1)\left(\tfrac{1}{2}H_{v+2} + (v+1)H_v\right) + 2v^2\left(\tfrac{1}{2}H_v + (v-1)H_{v-2}\right)\right] + \ \ldots$$

$$= \tfrac{3}{4}\{(v+1)^2H_v + v^2H_v\} + \ \ldots$$

$$= \tfrac{3}{4}(2v^2 + 2v + 1)H_v + \ \ldots$$

Therefore

$$\int_{-\infty}^{+\infty}\psi y^4\psi\,\mathrm{d}y = \tfrac{3}{4}(2v^2+2v+1)N^2\int_{-\infty}^{+\infty}H_v^2\mathrm{e}^{-y^2}\,\mathrm{d}y = \frac{3}{4\alpha}(2v^2+2v+1)$$

and so

$$\langle x^4\rangle = (\alpha^5)\times\left(\frac{3}{4\alpha}\right)\times(2v^2+2v+1) = \boxed{\frac{3}{4}(2v^2+2v+1)\alpha^4}$$

8B.8 Call the integral I:

$$I = \int\psi_{v'}x\psi_v\,\mathrm{d}x = \alpha^2\int\psi_{v'}y\psi_v\,\mathrm{d}y \quad [x = \alpha y]$$

$$y\psi_v = N_v\left(\frac{H_{v+1}}{2} + vH_{v-1}\right)\mathrm{e}^{-y^2/2} \quad \text{[Table 8B.1]}$$

Hence $$I = \alpha^2N_vN_{v'}\int\left(\frac{1}{2}H_{v'}H_{v+1} + vH_{v'}H_{v-1}\right)\mathrm{e}^{-y^2}\mathrm{d}y = 0 \quad \text{unless } v' = v\pm1 \text{ [Table 8B.1]}$$

For $v' = v + 1$

$$I = \frac{\alpha^2N_vN_{v+1}}{2}\int H_{v+1}^2\mathrm{e}^{-y^2}\,\mathrm{d}y = \frac{\alpha^2N_vN_{v+1}}{2}\pi^{1/2}2^{v+1}(v+1)! = \boxed{\alpha\left(\frac{v+1}{2}\right)^{1/2}}$$

For $v' = v - 1$

$$I = v\alpha^2 N_v N_{v-1}\int H_{v-1}^2 \mathrm{e}^{-y^2}\,\mathrm{d}y = v\alpha^2 N_v N_{v-1}\pi^{1/2}2^{v-1}(v-1)! = \boxed{\alpha\left(\frac{v}{2}\right)^{1/2}}$$

No other values of v' result in a nonzero value for I; hence, no other transitions are allowed.

8B.10 To address this time-dependent problem, we need a time-dependent wavefunction, made up from solutions of the time-dependent Schrödinger equation

$$\hat{H}\Psi(x,t) = \mathrm{i}\hbar\frac{\partial\Psi(x,t)}{\partial t}\ \text{[Table 7B.1]}$$

If $\psi(x)$ is an eigenfunction of the energy operator with energy eigenvalue E, then

$$\Psi(x,t) = \psi(x)\mathrm{e}^{-\mathrm{i}Et/\hbar}$$

is a solution of the time-dependent Schrödinger equation (provided the energy operator is not itself time dependent). To verify this, evaluate both sides of the time-dependent Schrödinger equation. On the left we have

$$\hat{H}\Psi(x,t) = \hat{H}\psi(x)\mathrm{e}^{-\mathrm{i}Et/\hbar} = E\psi(x)\mathrm{e}^{-\mathrm{i}Et/\hbar} = E\Psi(x,t)$$

On the right we have

$$\mathrm{i}\hbar\frac{\partial\Psi(x,t)}{\partial t} = \mathrm{i}\hbar\psi(x)\frac{\partial}{\partial t}\mathrm{e}^{-\mathrm{i}Et/\hbar} = -\mathrm{i}^2E\psi(x)\mathrm{e}^{-\mathrm{i}Et/\hbar} = E\Psi(x,t),$$

the same as on the left. Our wavepacket is an arbitrary superposition of time-evolving harmonic oscillator states (as in Problem 8B.9),

$$\Psi(x,t) = \sum_{v=0} c_v\psi_v(x)\mathrm{e}^{-\mathrm{i}E_vt/\hbar}$$

where $\psi_v(x)$ are time-independent harmonic-oscillator wavefunctions and

$$E_v = (v+\tfrac{1}{2})\hbar\omega\ \text{[8B.4]}$$

Hence, the wavepacket is

$$\Psi(x,t) = \mathrm{e}^{-\mathrm{i}\omega t/2}\sum_{v=0} c_v\psi_v(x)\mathrm{e}^{-\mathrm{i}v\omega t}$$

The angular frequency ω is related to the period T by $T = 2\pi/\omega$, so we can evaluate the wavepacket at any whole number of periods after t, that is at a time $t+nT$, where n is any integer. (n is not a quantum number.) Note that

$$t + nT = t + 2\pi n\,/\,\omega,$$

so
$$\Psi(x,t+nT) = \mathrm{e}^{-\mathrm{i}\omega t/2}\mathrm{e}^{-\mathrm{i}\omega nT/2}\sum_{v=0} c_v\psi_v(x)\mathrm{e}^{-\mathrm{i}v\omega t}\mathrm{e}^{-\mathrm{i}v\omega nT} = \mathrm{e}^{-\mathrm{i}\omega t/2}\mathrm{e}^{-\mathrm{i}\pi n}\sum_{v=0} c_v\psi_v(x)\mathrm{e}^{-\mathrm{i}v\omega t}\mathrm{e}^{-2\pi\mathrm{i}vn}$$

Since the exponential of (2πi × any integer) = 1, we note that the last factor inside the sum is 1 for every state. Also, since $\mathrm{e}^{-\mathrm{i}n\pi} = (-1)^n$, we have

$$\Psi(x,t+nT) = (-1)^n\Psi(x,t) \quad .$$

At any whole number of periods after time t, the wavefunction is either the same as at time t or –1 times its value at time t. Either way, $|\Psi|^2$ returns to its original value each period, so the wavepacket returns to the same spatial distribution each period.

8B.12
$$V = -\frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{r}\,[\text{9A.4 with } Z=1] = \alpha x^b \quad \text{with } b=-1 \quad [x\to r]$$

Since $2\langle E_{\mathrm{K}}\rangle = b\langle V\rangle = -\langle V\rangle$ [virial theorem, 8B.14]

Therefore, $\langle E_{\mathrm{K}}\rangle = \boxed{-\frac{1}{2}\langle V\rangle}$

8C Rotational motion

Answers to discussion question

8C.2 Rotational motion on a ring and on a sphere share features such as the form of the energy (square of the angular momentum over twice the moment of inertia) and the lack of zero-point energy because the ground state does not restrict the angular position of the particle. Degeneracy is possible in both cases. In the case of the ring, the axis of rotation is specified, but not in the case of the sphere. This distinction gives rise to the fact that angular momenta about different perpendicular axes **cannot** be simultaneously specified: $\hat{l}_x$, $\hat{l}_y$, and $\hat{l}_z$ are complementary in the sense described in Topic 7C.3.

Solutions to exercises

8C.1(b) The magnitude of angular momentum is [8C.21a]

$$\langle l^2\rangle^{1/2} = \{l(l+1)\}^{1/2}\hbar = (2\times 3)^{1/2}\hbar = \boxed{6^{1/2}\hbar}$$

Possible projections on to an arbitrary axis are [8C.21b]

$$\langle l_z\rangle = m_l\hbar$$

where m_l =0 or ±1 or ±2. So possible projections include $\boxed{0, \pm\hbar, \pm 2\hbar}$.

8C.2(b) Orthogonality requires that [7C.8]

$$\int \psi_m^*\psi_n \,\mathrm{d}\tau = 0 \text{ if } m \neq n.$$

Performing the integration on the wavefunction [8C.11]

$$\int \psi_{m_l}^*\psi_{n_l}\mathrm{d}\tau = \int_0^{2\pi} N\mathrm{e}^{-\mathrm{i}m_l\phi}N\mathrm{e}^{\mathrm{i}n_l\phi}\mathrm{d}\phi = N^2\int_0^{2\pi}\mathrm{e}^{\mathrm{i}(n_l-m_l)\phi}\mathrm{d}\phi$$

If $m_l \neq n_l$, then

$$\int \psi_{m_l}^*\psi_{m_l}\,\mathrm{d}\tau = \frac{N^2}{\mathrm{i}(n_l-m_l)}\mathrm{e}^{\mathrm{i}(n_l-m_l)\phi}\Bigg|_0^{2\pi} = \frac{N^2}{\mathrm{i}(n_l-m_l)}(1-1) = 0$$

Therefore, they are orthogonal.

8C.3(b) The energy levels of a particle on a ring are given by [8C.6b]

$$E = \frac{m_l^2\mathrm{h}^2}{2I} = \frac{m_l^2\mathrm{h}^2}{2mr^2}, \qquad m_l = 0, \pm1, \pm2, ...$$

We set this quantity equal to the classical energy and solve for $|m_l|$:

$$E = \frac{m_l^2\mathrm{h}^2}{2mr^2} = \frac{kT}{2} \quad \text{so}$$

$$|m_l| = \frac{r(kTm)^{1/2}}{\mathrm{h}}$$

$$= \frac{(100\times10^{-12}\ \mathrm{m})\times\{(1.381\times10^{-23}\ \mathrm{J\,K^{-1}})\times(298\ \mathrm{K})\times(1.6726\times10^{-27}\ \mathrm{kg})\}^{1/2}}{1.0546\times10^{-34}\ \mathrm{J\,s}}$$

$$= \boxed{2.49}$$

Of course, m_l must be an integer, so m_l = ±2 is the closest energy level.

Comment. The correspondence principle (Topic 8A.2(b)) 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 8A.9(b), but it is much more classical than that of part (b) in Exercise 8B.5(b).

8C.4(b) The energy levels are [8C.20]

$$E = \frac{l(l+1)\mathrm{h}^2}{2I}, \quad l = 0, 1, 2, ...$$

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:

$$\Delta E = E_1 = \frac{1\times2\times(1.0546\times10^{-34}\ \mathrm{J\,s})^2}{2\times(3.07\times10^{-45}\ \mathrm{kg\,m^2})} = \boxed{3.62\times10^{-24}\ \mathrm{J}}$$

8C.5(b) The energy levels are [8C.20]

$$E = \frac{l(l+1)\hbar^2}{2I}, \quad l = 0, 1, 2, \ldots$$

So the excitation energy is

$$\Delta E = E_2 - E_1 = \frac{(3 \times 4 - 2 \times 3) \times (1.0546 \times 10^{-34}\ \text{J s})^2}{2 \times (3.07 \times 10^{-45}\ \text{kg m}^2)} = \boxed{1.09 \times 10^{-23}\ \text{J}}$$

8C.6(b) The energy levels are [8C.20]

$$E = \frac{l(l+1)\hbar^2}{2I}, \quad l = 0, 1, 2, \ldots$$

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 [8C.21a]

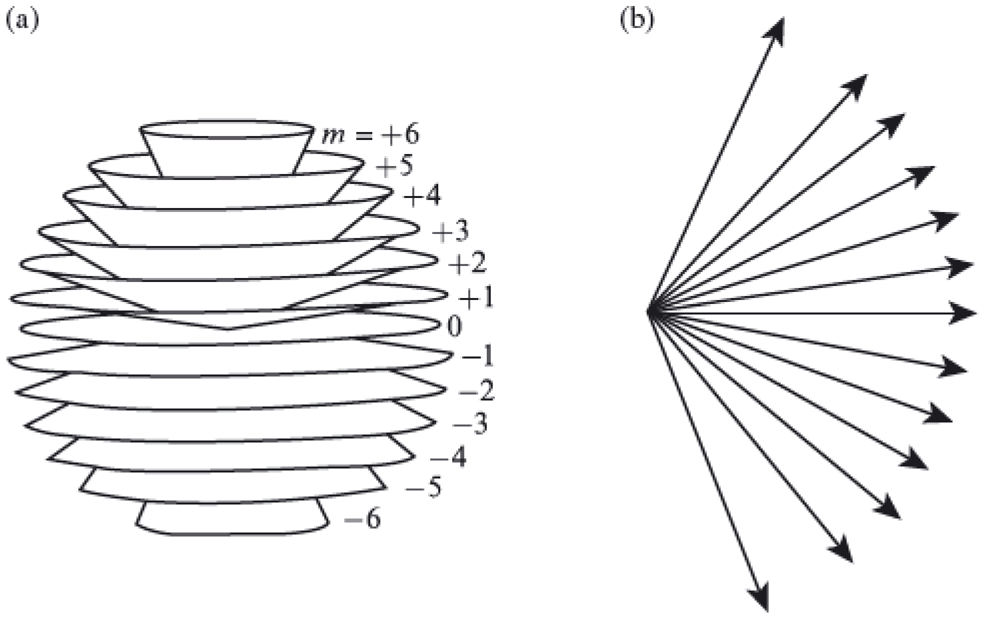
$$\{l(l+1)\}^{1/2}\hbar = \boxed{2^{1/2}\hbar} = 2^{1/2} \times (1.0546{\times}10^{-34}\ \text{J s}) = \boxed{1.49{\times}10^{-34}\ \text{J s}}.$$

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.

8C.7(b) The cones are constructed as described in Topic 8C.2(e) and Figure 8C.11b 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 8C.1(a).

The vectors follow, in units of $\hbar$. From the highest-pointing to the lowest-pointing vectors (Figure 8C.1(b)), the values of m_l are 6, 5, 4, 3, 2, 1, 0, –1, –2, –3, –4, –5, and –6.

Figure 8C.1



8C.8(b) The rotational energy depends only on the quantum number l [8C.20], but there are distinct states for every allowed value of m_l, which can range from $-l$ to l in integer steps. For $l = 4$, possible values of $m_l = -4, -3, -2, -1, 0, 1, 2, 3, 4$. There are 9 such values, so the degeneracy is $\boxed{9}$.

Solutions to problems

8C.2 Mathematical software can animate the real part or the imaginary part of $\Psi(\phi,t)$, or you may wish to have it display $|\Psi(\phi,t)|^2$. 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, but only circulates. 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 ($2\pi\mathrm{i}$ × an integer):

$$T = \frac{4\pi I}{\hbar}$$

making the exponent $\frac{\mathrm{i}E_{m_l}t}{\hbar}$ equal to $2\pi\mathrm{i}m_l^2$ when $t = T$ and at intervals of T thereafter. An example of this approach using Mathcad is illustrated below:

Wavepacket on a Ring as a MathCad Document. Let $\tau = \frac{h \cdot t}{4 \cdot \pi \cdot I}$

and let each function in the superposition of m+1 functions contribute with equal probability (i.e., 1/m+1). The normalized angular momentum functions are:

$$\psi(m,\phi) := \left(\frac{1}{2\cdot\pi}\right)^{\frac{1}{2}} \cdot e^{i\cdot m\cdot\phi}$$ [8.38b] where m is an integer.

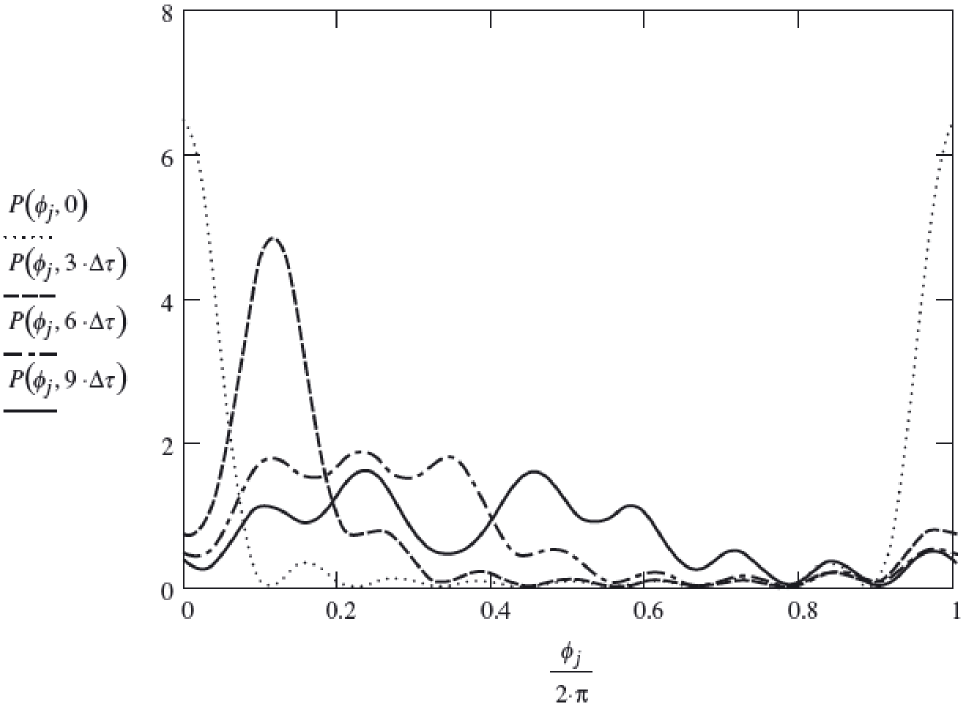
The normalized superposition is

$$\Psi(m_{max},\phi,\tau) := \left(\frac{1}{m+1}\right)^{\frac{1}{2}} \cdot \sum_{m=0}^{m_{max}} \psi(m,\phi)\cdot e^{-i\cdot m^2\cdot\tau}$$

$N := 500 \quad j := 0..N \quad \phi_j := \frac{2\cdot\pi\cdot j}{N} \quad m_{max} := 8 \quad \Delta\tau := .03$

The probability density of the superposition is $P(\phi,\tau) := \Psi(m_{max},\phi,\tau)\cdot\overline{\Psi}(m_{max},\phi,\tau)$

Figure 8C.2



The plots (Figure 8C.2) show that as the initially localized wave propagates around the ring it spreads with time and the uncertainty in knowing particle position increases. The effect of increasing or decreasing the energies accessible to the particle may be explored by increasing or decreasing the value of m_{max} in the MathCad document.

8C.4 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 [8C.6b]

$$E=\frac{m_l^2\hbar^2}{2I}$$

where the moment of inertia is the mass of the particle times the radius of the circular ring

$$I = ma^2.$$

The eigenfunctions are [8C.6a]

$$\psi=\frac{\mathrm{e}^{\mathrm{i}m_l\Phi}}{(2\pi)^{1/2}}$$

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:

$$\frac{Y}{X}=\tan\Phi \quad \text{so} \quad \Phi=\tan^{-1}\frac{Y}{X}=\tan^{-1}\frac{ay}{bx}$$

8C.6 The Schrödinger equation is [8C.16]

$$-\frac{\hbar^2}{2m}\nabla^2\psi=E\psi$$

Since r = constant, the first term is eliminated and the Schrödinger equation may be rewritten

$$-\frac{\hbar^2}{2mr^2}\Lambda^2\psi=E\psi \ \text{ or } \ -\frac{\hbar^2}{2I}\Lambda^2\psi=E\psi\ [I=mr^2] \ \text{ or } \ \Lambda^2\psi=-\frac{2IE\psi}{\hbar^2} \quad [8C.18]$$

where $$\Lambda^2=\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$$

Now use the specified $\psi=Y_{l,m_l}$ from Table 8C.1, and see if they satisfy this equation.

(a) Because $Y_{0,0}$ is a constant, all derivatives with respect to angles are zero, so $\Lambda^2Y_{0,0}=\boxed{0}$, implying that $E=\boxed{0}$ and angular momentum = $\boxed{0}$ [from $\{l(l+1)\}^{1/2}\hbar$]

(b) $$\Lambda^2Y_{2,-1}=\frac{1}{\sin^2\theta}\frac{\partial^2Y_{2,-1}}{\partial\phi^2}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y_{2,-1}}{\partial\theta} \quad \text{where} \quad Y_{2,-1}=N\cos\theta\sin\theta\,\mathrm{e}^{-\mathrm{i}\phi}$$

$$\frac{\partial Y_{2,-1}}{\partial\theta}=N\mathrm{e}^{-\mathrm{i}\phi}(\cos^2\theta-\sin^2\theta)$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y_{2,-1}}{\partial\theta} = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta N\mathrm{e}^{-\mathrm{i}\phi}(\cos^2\theta-\sin^2\theta)$$

$$= \frac{N\mathrm{e}^{-\mathrm{i}\phi}}{\sin\theta}\Big(\sin\theta(-4\cos\theta\sin\theta)+\cos\theta(\cos^2\theta-\sin^2\theta)\Big)$$

$$= N\mathrm{e}^{-\mathrm{i}\phi}\left(-6\cos\theta\sin\theta+\frac{\cos\theta}{\sin\theta}\right) \quad [\cos^3\theta=\cos\theta(1-\sin^2\theta)]$$

$$\frac{1}{\sin^2\theta}\frac{\partial^2 Y_{2,-1}}{\partial\phi^2} = \frac{-N\cos\theta\sin\theta\,\mathrm{e}^{-\mathrm{i}\phi}}{\sin^2\theta} = \frac{-N\cos\theta\,\mathrm{e}^{-\mathrm{i}\phi}}{\sin\theta}$$

so $\quad \Lambda^2 Y_{2,-1} = N\mathrm{e}^{-\mathrm{i}\phi}(-6\cos\theta\sin\theta) = -6Y_{2,-1} = -2(2+1)Y_{2,-1}$ [i.e., $l = 2$]

and hence

$$-6Y_{2,-1} = -\frac{2IE}{\hbar^2}Y_{2,-1}, \text{ implying that } \boxed{E=\frac{3\hbar^2}{I}}$$

and the angular momentum is $\{2(2+1)\}^{1/2}\hbar = \boxed{6^{1/2}\hbar}$.

(c) $\quad \Lambda^2 Y_{3,3} = \frac{1}{\sin^2\theta}\frac{\partial^2 Y_{3,3}}{\partial\phi^2}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y_{3,3}}{\partial\theta} \quad$ where $\quad Y_{3,3} = N\sin^3\theta\,\mathrm{e}^{3\mathrm{i}\phi}$

$$\frac{\partial Y_{3,3}}{\partial\theta} = 3N\sin^2\theta\cos\theta\,\mathrm{e}^{3\mathrm{i}\phi}$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y_{3,3}}{\partial\theta} = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}3N\sin^3\theta\cos\theta\,\mathrm{e}^{3\mathrm{i}\phi}$$

$$= \frac{3N\mathrm{e}^{3\mathrm{i}\phi}}{\sin\theta}(3\sin^2\theta\cos^2\theta-\sin^4\theta) = 3N\mathrm{e}^{3\mathrm{i}\phi}\sin\theta(3\cos^2\theta-\sin^2\theta)$$

$$= 3N\mathrm{e}^{3\mathrm{i}\phi}\sin\theta(3-4\sin^2\theta) \quad [\cos^3\theta=\cos\theta(1-\sin^2\theta)]$$

$$\frac{1}{\sin^2\theta}\frac{\partial^2 Y_{3,3}}{\partial\phi^2} = \frac{-9N\sin^3\theta\,\mathrm{e}^{3\mathrm{i}\phi}}{\sin^2\theta} = -9N\sin\theta\,\mathrm{e}^{3\mathrm{i}\phi}$$

so $\quad \Lambda^2 Y_{3,3} = -12N\sin^3\theta\,\mathrm{e}^{3\mathrm{i}\phi} = -12Y_{3,3} = -3(3+1)Y_{3,3}$ [i.e., $l = 3$]

and hence

$$-12Y_{3,3} = -\frac{2IE}{\hbar^2}Y_{3,3}, \text{ implying that } \boxed{E=\frac{6\hbar^2}{I}}$$

and the angular momentum is $\{3(3+1)\}^{1/2}\hbar = \boxed{12^{1/2}\hbar}$.

8C.8 $\quad \nabla^2 = \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$ [8C.15b]

$$\frac{\partial^2}{\partial x^2}f = -a^2\cos ax\cos by\cos cz = -a^2 f$$

Similarly, $\quad \frac{\partial^2}{\partial y^2}f = -b^2 f \qquad \frac{\partial^2}{\partial y^2}f = -c^2 f$

so f is an eigenfunction with eigenvalue $\boxed{-(a^2+b^2+c^2)}$.

8C.10 Upon 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 $\quad \frac{\partial}{\partial\phi} = \frac{\partial x}{\partial\phi}\frac{\partial}{\partial x}+\frac{\partial y}{\partial\phi}\frac{\partial}{\partial y}+\frac{\partial z}{\partial\phi}\frac{\partial}{\partial z}$ [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, $\dfrac{\partial}{\partial \phi} = -y\dfrac{\partial}{\partial x} + x\dfrac{\partial}{\partial y}$

Upon substitution,

$$\ddot{p}_z = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial \phi} = -\mathrm{i}\hbar\frac{\partial}{\partial \phi}$$

8C.12 **(a)** Within the sphere, the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2\right)\psi = E\psi \quad \text{[Table 7B.1]},$$

where Λ^2 is an operator that contains derivatives with respect to θ and ϕ only.

Let $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$.

Substituting into the Schrödinger equation gives

$$-\frac{\hbar^2}{2m}\left(Y\frac{\partial^2 R}{\partial r^2} + \frac{2Y}{r}\frac{\partial R}{\partial r} + \frac{R}{r^2}\Lambda^2 Y\right) = ERY$$

Divide both sides by RY:

$$-\frac{\hbar^2}{2m}\left(\frac{1}{R}\frac{\partial^2 R}{\partial r^2} + \frac{2}{Rr}\frac{\partial R}{\partial r} + \frac{1}{Yr^2}\Lambda^2 Y\right) = E$$

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:

$$-\frac{\hbar^2}{2m}\left(\frac{r^2}{R}\frac{\partial^2 R}{\partial r^2} + \frac{2r}{R}\frac{\partial R}{\partial r} + \frac{1}{Y}\Lambda^2 Y\right) = Er^2$$

Put all of the terms involving angles on the right hand side and the terms involving distance on the left:

$$-\frac{\hbar^2}{2m}\left(\frac{r^2}{R}\frac{\partial^2 R}{\partial r^2} + \frac{2r}{R}\frac{\partial R}{\partial r}\right) - Er^2 = \frac{\hbar^2}{2mY}\Lambda^2 Y$$

Note that the right side depends only on θ and ϕ, while the left side depends on r. The only way that the two sides can be equal to each other for all r, θ, and ϕ is if they are both equal to a constant. Call that constant $-\dfrac{\hbar^2 l(l+1)}{2m}$ (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

$$-\frac{\hbar^2}{2m}\left(\frac{r^2}{R}\frac{\partial^2 R}{\partial r^2} + \frac{2r}{R}\frac{\partial R}{\partial r}\right) - Er^2 = -\frac{\hbar^2 l(l+1)}{2m}$$

After multiplying both sides by R / r^2 and rearranging, we get the desired radial equation

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 R}{\partial r^2} + \frac{2}{r}\frac{\partial R}{\partial r}\right) + \frac{\hbar^2 l(l+1)}{2mr^2}R = ER$$

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:

$$\frac{\partial^2 R}{\partial r^2}+\frac{2}{r}\frac{\partial R}{\partial r}=-\frac{2mER}{\hbar^2}$$

Form the following derivatives of the proposed solution:

$$\frac{\partial R}{\partial r}=(2\pi a)^{-1/2}\left[\frac{\cos(n\pi r/a)}{r}\left(\frac{n\pi}{a}\right)-\frac{\sin(n\pi r/a)}{r^2}\right]$$

and $$\frac{\partial^2 R}{\partial r^2}=(2\pi a)^{-1/2}\left[-\frac{\sin(n\pi r/a)}{r}\left(\frac{n\pi}{a}\right)^2-\frac{2\cos(n\pi r/a)}{r^2}\left(\frac{n\pi}{a}\right)+\frac{2\sin(n\pi r/a)}{r^3}\right]$$

Substituting into the left side of the rearranged radial equation yields

$$(2\pi a)^{-1/2}\left[-\frac{\sin(n\pi r/a)}{r}\left(\frac{n\pi}{a}\right)^2-\frac{2\cos(n\pi r/a)}{r^2}\left(\frac{n\pi}{a}\right)+\frac{2\sin(n\pi r/a)}{r^3}\right]$$

$$+(2\pi a)^{-1/2}\left[\frac{2\cos(n\pi r/a)}{r^2}\left(\frac{n\pi}{a}\right)-\frac{2\sin(n\pi r/a)}{r^3}\right]$$

$$=-(2\pi a)^{-1/2}\frac{\sin(n\pi r/a)}{r}\left(\frac{n\pi}{a}\right)^2=-\left(\frac{n\pi}{a}\right)^2 R$$

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

$$\left(\frac{n\pi}{a}\right)^2=\frac{2mE}{\hbar^2} \quad \text{so} \quad E=\left(\frac{n\pi}{a}\right)^2\frac{\hbar^2}{2m}=\frac{n^2\pi^2}{2ma^2}\left(\frac{h}{2\pi}\right)^2=\boxed{\frac{n^2h^2}{8ma^2}}$$

Integrated activities

8.2 The particle in a box can serve a model for many kinds of bound particles. Perhaps most relevant to chemistry, it is a model for π-electrons in linear systems of conjugated double bonds. See Example 8A.2, in which it is the basis for estimating the absorption wavelength for an electronic transition in the linear polyene β-carotene. Electrons in nanostructures such as quantum dots can be modeled as particles in a three-dimensional box or sphere. More crudely yet more fundamentally, the particle in a box model can provide order-of-magnitude excitation energies for bound particles such as an electron confined to an atom-sized box around a nucleus or even for a nucleon confined to a nucleus-sized box. The harmonic oscillator serves as the first approximation for describing molecular vibrations. The excitation energies for stretching and bending bonds are manifested in infrared and Raman spectroscopy.

8.4 **(a)** The ground state is $n = 1$. Expectation values for $\langle x\rangle$, $\langle x^2\rangle$, $\langle p\rangle$, and $\langle p^2\rangle$ were evaluated in Exercises 8A.5 and 8A.6.

$$\langle x\rangle=\frac{L}{2} \text{ for all } n\text{, including } n=1$$

$$\langle x^2\rangle=L^2\left(\frac{1}{3}-\frac{1}{2n^2\pi^2}\right)=L^2\left(\frac{1}{3}-\frac{1}{2\pi^2}\right)\ [n=1]$$

$$\Delta x=\left[L^2\left(\frac{1}{3}-\frac{1}{2n^2\pi^2}\right)-\frac{L^2}{4}\right]^{1/2}=L\left(\frac{1}{12}-\frac{1}{2\pi^2n^2}\right)^{1/2}=\boxed{L\left(\frac{1}{12}-\frac{1}{2\pi^2}\right)^{1/2}}\ [n=1]$$

$$\langle p\rangle=0 \text{ for all } n\text{, including } n=1$$

$$\langle p^2\rangle=\frac{n^2h^2}{4L^2}=\frac{h^2}{4L^2}\ [n=1]$$

$$\Delta p = \left(\frac{n^2h^2}{4L^2}\right)^{1/2} = \frac{nh}{2L} = \boxed{\frac{h}{2L}}\ [n=1]$$

$$\Delta p\Delta x = \frac{nh}{2L} \times L\left(\frac{1}{12} - \frac{1}{2\pi^2 n^2}\right)^{1/2} = \frac{nh}{2\sqrt{3}}\left(1 - \frac{1}{24\pi^2 n^2}\right)^{1/2} > \frac{\hbar}{2}$$

(b) The ground state is $v = 0$.

$\langle x \rangle = 0$ for all v, including $v = 0$ [8B.12a, or by symmetry]

and $$\langle x^2 \rangle = \left(v + \frac{1}{2}\right) \times \left(\frac{\hbar^2}{mk_\mathrm{f}}\right)^{1/2} \text{ [8B.12]} = \left(v + \frac{1}{2}\right) \times \frac{\hbar}{\omega m} \text{ [8B.4]} = \frac{\hbar}{2\omega m}\ [v=0]$$

so $$\Delta x = \left\{\left(v + \frac{1}{2}\right)\frac{\hbar}{\omega m}\right\}^{1/2} = \boxed{\left(\frac{\hbar}{2\omega m}\right)^{1/2}}\ [v=0]$$

$\langle p \rangle = 0$ [by symmetry, or by noting that the integrand is an odd function of x]

and $$\langle p^2 \rangle = 2m\langle E_\mathrm{k} \rangle = 2m\int_{-\infty}^{+\infty} \psi^* \hat{E}_\mathrm{k}\, \psi\ \mathrm{d}x$$

$$\hat{E}_\mathrm{k} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} \text{ [7C.5]} = -\frac{\hbar^2}{2m\alpha^2}\frac{\mathrm{d}^2}{\mathrm{d}y^2} = -\frac{\hbar\omega}{2}\frac{\mathrm{d}^2}{\mathrm{d}y^2}, \quad \left[x = \alpha y,\ \alpha^2 = \frac{\hbar}{m\omega}\right]$$

which implies that

$$\hat{E}_\mathrm{k}\psi = -\frac{\hbar\omega}{2}\left(\frac{\mathrm{d}^2\psi}{\mathrm{d}y^2}\right)$$

We then use $\psi = NH\mathrm{e}^{-y^2/2}$, and obtain

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}y^2} = N\frac{\mathrm{d}^2}{\mathrm{d}y^2}(H\mathrm{e}^{-y^2/2}) = N\{H'' - 2yH' - H + y^2H\}\mathrm{e}^{-y^2/2}$$

From Table 8B.1

$$H_v'' - 2yH_v' = -2vH_v$$

$$y^2H_v = y\left(\tfrac{1}{2}H_{v+1} + vH_{v-1}\right) = \tfrac{1}{2}\left(\tfrac{1}{2}H_{v+2} + (v+1)H_v\right) + v\left(\tfrac{1}{2}H_v + (v-1)H_{v-2}\right)$$

$$= \tfrac{1}{4}H_{v+2} + v(v-1)H_{v-2} + \left(v + \tfrac{1}{2}\right)H_v$$

Hence, $$\frac{\mathrm{d}^2\psi}{\mathrm{d}y^2} = N\left[\tfrac{1}{4}H_{v+2} + v(v-1)H_{v-2} - \left(v + \frac{1}{2}\right)H_v\right]\mathrm{e}^{-y^2/2}$$

Therefore,

$$\langle E_\mathrm{k} \rangle = N_v^{\,2}\left(-\frac{\hbar\omega}{2}\right)\int_{-\infty}^{+\infty} H_v\left\{\frac{1}{4}H_{v+2} + v(v-1)H_{v-2} - \left(v + \frac{1}{2}\right)H_v\right\}\mathrm{e}^{-y^2}\mathrm{d}x\ [\mathrm{d}x = \alpha\mathrm{d}y]\ \text{so}$$

$$= \alpha N_v^{\,2}\left(-\tfrac{1}{2}\hbar\omega\right)\left\{0 + 0 - \left(v + \tfrac{1}{2}\right)\pi^{1/2}2^v v!\right\} \text{[Hermite polynomials orthogonal]}$$

$$= \frac{1}{2}\left(v + \frac{1}{2}\right)\hbar\omega \quad \left[N_v^2 = \frac{1}{\alpha\pi^{1/2}2^v v!}, \text{ Example 8B.2}\right]$$

and $$\langle p^2 \rangle = \left(v + \frac{1}{2}\right)m\hbar\omega = \boxed{\frac{m\hbar\omega}{2}}\ [v = 0]$$

$$\Delta p = \left\{\left(v + \frac{1}{2}\right)\hbar\omega m\right\}^{1/2} = \boxed{\left(\frac{m\hbar\omega}{2}\right)^{1/2}}\ [v = 0]$$

$$\Delta p\Delta x = \left(v + \frac{1}{2}\right)\hbar \geq \frac{\hbar}{2}$$

Comment. Both results show a consistency with the uncertainty principle in the form $\Delta p\Delta q \geq \dfrac{\hbar}{2}$ as given in eqn 7C.13 (for all values of the quantum numbers, by the way).

8.6 **(a)** Notice in Figures I8.1(a) and I8.1(b) that regions of high probability and low probability alternate on an increasingly smaller scale as n increases. The distribution of the particle's probability becomes more uniform if one ignores the fluctuations or (what amounts to the same thing) if one looks for the probability of finding the particle in a region small compared to the box as a whole but large compared to the very short-wavelength $n=50$ state. For example, compare the probability of finding the particle in the central 10% of the box to the first 10% of the box. The different in probabilities is huge for the ground state and minuscule for the $n=50$ state. One more way to think of the distribution as becoming more uniform is that both regions of high probability and regions of low probability become more and more widely and evenly distributed.

Figure I8.1(a)

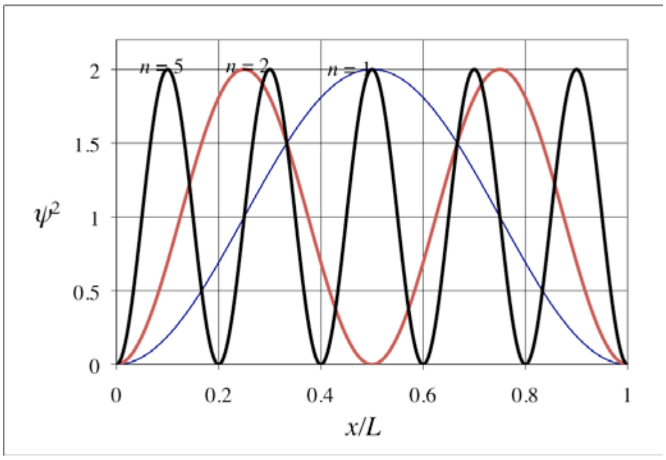
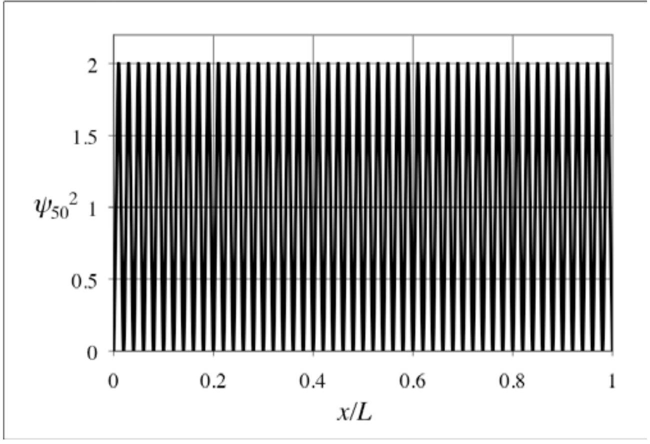
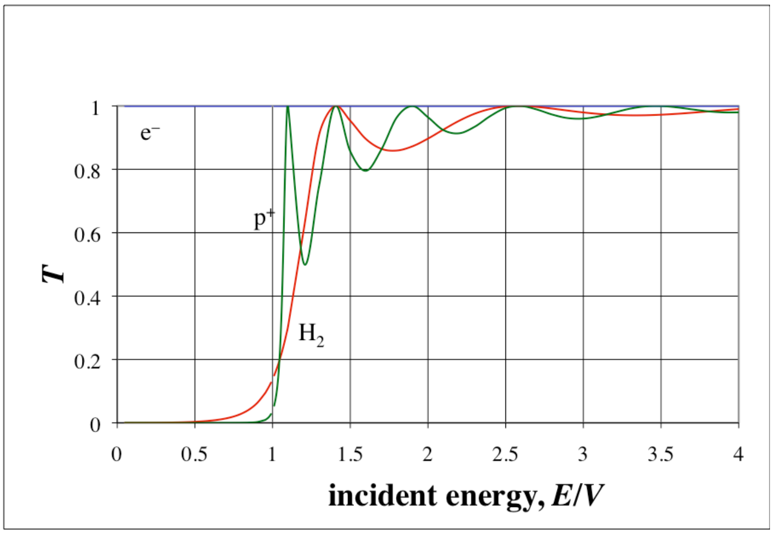


Figure I8.1(b)



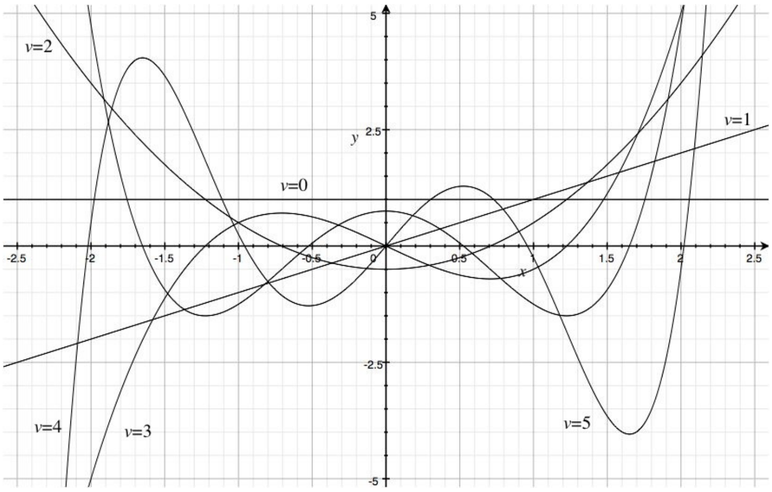
(**b**) Figure I8.2 is a plot like that of textbook Fig. 8A.12 of the main text. The curves in the figure differ in the value of $L(mV)^{1/2}/\hbar$, a measure of the size of the barrier (a combination of its width and "height"). Think of the curves in this plot as having the same value of L and V, but differing only in m. The values of L and V were chosen such that the proton and hydrogen molecule could exhibit "typical" tunnelling behavior: if the incident energy is small enough, there is practically no transmission, and if the incident energy is high enough, transmission is virtually certain. A barrier through which a proton and hydrogen molecule can tunnel with such behavior is practically no barrier for an electron: T for the electron is indistinguishable from 1 on this plot.

Figure I8.2



(c) In Figure I8.3, $y = H_v(x)$ is plotted against x. The quantum number v is equal to the number of nodes. Notice that the number of nodes increases as v increases and that the position of those nodes spreads out.

Figure I8.3



(d) The number of nodal lines (excluding those that fall on the boundaries) is n_1+n_2-2. The number of nodal lines for motion along a given axis is one less than n for that motion.

9 Atomic structure and spectra

9A Hydrogenic atoms

Answers to discussion questions

9A.2 (1) The principal quantum number, *n*, determines the energy of a hydrogenic atomic orbital through eqn 9A.9.

(2) The azimuthal quantum number, *l*, determines the magnitude of the angular momentum of a hydrogenic atomic orbital through the formula $\{l(l+1)\}^{1/2}\hbar$.

(3) The magnetic quantum number, m_l, determines the z-component of the angular momentum of a hydrogenic orbital through the formula $m_l\hbar$.

(4) The spin quantum number, *s*, determines the magnitude of the spin angular momentum through the formula $\{s(s+1)\}^{1/2}\hbar$. For hydrogenic atomic orbitals, *s* can only be $1/2$.

(5) The spin quantum number, m_s, determines the z-component of the spin angular momentum through the formula $m_s\hbar$. For hydrogenic atomic orbitals, m_s can only be $\pm 1/2$.

Solutions to exercises

9A.1(b) The degeneracy *g* of a hydrogenic atom with principal quantum number *n* is $g = n^2$. The energy *E* of hydrogenic atoms is

$$E = -\frac{hcZ^2\tilde{R}_\mathrm{N}}{n^2} = -\frac{hcZ^2\tilde{R}_\mathrm{N}}{g}$$

so the degeneracy is

$$g = -\frac{hcZ^2\tilde{R}_\mathrm{N}}{E}$$

(i) $$g = -\frac{hc(2)^2\tilde{R}_\mathrm{N}}{-4hc\tilde{R}_\mathrm{N}} = \boxed{1}$$

(ii) $$g = -\frac{hc(4)^2\tilde{R}_\mathrm{N}}{-\frac{1}{4}hc\tilde{R}_\mathrm{N}} = \boxed{64}$$

(iii) $$g = -\frac{hc(5)^2\tilde{R}_\mathrm{N}}{-hc\tilde{R}_\mathrm{N}} = \boxed{25}$$

.

9A.2(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

$$1 = 4\pi N^2\int_0^\infty e^{-r/a_0}(2-r/a_0)^2 r^2\mathrm{d}r$$

$$= 4\pi N^2\int_0^\infty e^{-r/a_0}(4-4r/a_0+r^2/a_0^2)r^2\mathrm{d}r = 4\pi N^2(8a_0^3)$$

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

9A.3(b) The radial wavefunction is [Table 9A.1]

$$R_{3,0} = A\left(6-2\rho+\tfrac{1}{9}\rho^2\right)\mathrm{e}^{-\rho/6} \text{where } \rho \equiv \frac{2Zr}{a_0}\text{, and } A \text{ is a collection of constants.}$$

[Note: for convenience ρ defined here is 3 × ρ as defined in table 9A.1]

Differentiating with respect to ρ yields

$$\frac{\mathrm{d}R_{3,0}}{\mathrm{d}\rho} = 0 = A(6-2\rho+\tfrac{1}{9}\rho^2)\times\left(-\tfrac{1}{6}\right)\mathrm{e}^{-\rho/6} + \left(-2+\tfrac{2}{9}\rho\right)A\mathrm{e}^{-\rho/6}$$

$$= A\mathrm{e}^{-\rho/6}\left(-\tfrac{\rho^2}{54}+\tfrac{5}{9}\rho-3\right)$$

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

$$\rho = \frac{-b\pm(b^2-4ac)^{1/2}}{2a} = 15\pm3\sqrt{7}$$

so $r = \boxed{\left(\frac{15}{2}\pm\frac{3\left(7^{1/2}\right)}{2}\right)\frac{a_0}{Z}}$.

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 $a_0 = 5.292\times10^{-11}$ 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.

9A.4(b) The radial distribution function varies as

$$P = 4\pi r^2\psi^2 = \frac{4}{a_0^3}r^2\mathrm{e}^{-2r/a_0}\ [9A.17]$$

The maximum value of P occurs at $r = a_0$ since

$$\frac{\mathrm{d}P}{\mathrm{d}r} \propto \left(2r - \frac{2r^2}{a_0}\right)\mathrm{e}^{-2r/a_0} = 0 \quad \text{at} \quad r = a_0 \text{ and } P_{\max} = \frac{4}{a_0}\mathrm{e}^{-2}$$

P falls to a fraction f of its maximum given by

$$f = \frac{\frac{4r^2}{a_0^3}\mathrm{e}^{-2r/a_0}}{\frac{4}{a_0}\mathrm{e}^{-2}} = \frac{r^2}{a_0^2}\mathrm{e}^2\mathrm{e}^{-2r/a_0}$$

and hence we must solve for r in

$$\frac{f^{1/2}}{\mathrm{e}} = \frac{r}{a_0}\mathrm{e}^{-r/a_0}$$

(i) $f = 0.50$

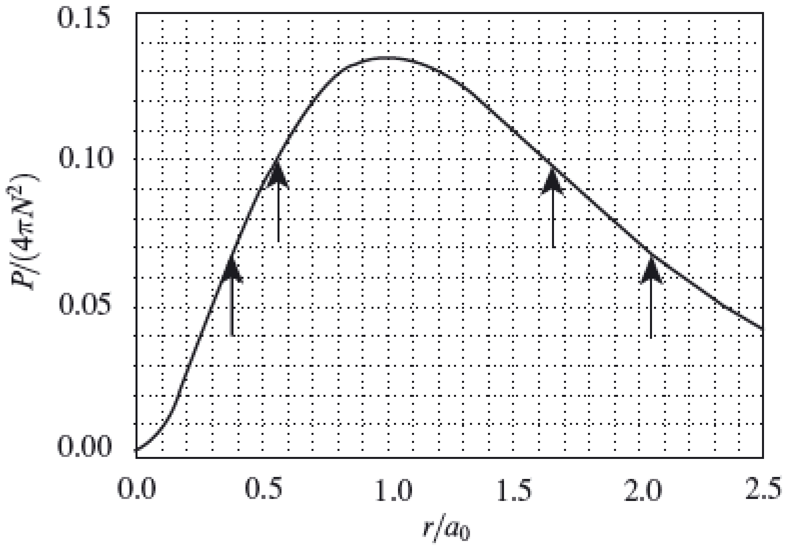
$$0.260 = \frac{r}{a_0}\mathrm{e}^{-r/a_0} \text{ solves to } r = 2.08a_0 = \boxed{110\,\text{pm}} \text{ and to } r = 0.380a_0 = \boxed{20.1\text{pm}}$$

(ii) $f = 0.75$

$$0.319=\frac{r}{a_0}\mathrm{e}^{-r/a_0} \text{ solves to } r=1.63a_0=\boxed{86\,\mathrm{pm}} \text{ and to } r=0.555a_0=\boxed{29.4\,\mathrm{pm}}$$

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 Fig. 9A.1.

Figure 9A.1



9A.5(b) The complete radial wavefunction, $R_{4,1}$ is not given in Table 9A.1; however, 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

$$\rho=0, \qquad \boxed{r=0}$$

and when

$$(20-10\rho+\rho^2)=0, \quad \text{with roots} \quad \rho=2.764, \quad \text{and} \quad \rho=7.236$$

$$\text{then } r=\frac{4\rho a_0}{2Z}=\frac{4\rho a_0}{2}=\frac{11.056a_0}{2}=\boxed{5.528a_0} \text{ and } \frac{28.944a_0}{2}=\boxed{14.472a_0}$$

$$\text{or } r=\boxed{2.92\times10^{-10}\ \mathrm{m}} \text{ and } \boxed{7.66\times10^{-10}\ \mathrm{m}}$$

9A.6(b) The average kinetic energy is

$$\langle\hat{E}_{\mathrm{K}}\rangle=\int\psi^*\hat{E}_{\mathrm{K}}\psi\,\mathrm{d}\tau$$

$$\text{where } \psi=N(2-\rho)\mathrm{e}^{-\rho/2} \text{ with } N=\frac{1}{4}\left(\frac{Z^3}{2\pi a_0^3}\right)^{1/2}.$$

[Note: ρ is defined here as in Table 9A.1]

$$\hat{E}_{\mathrm{K}}=-\frac{\hbar^2}{2m}\nabla^2 \qquad \mathrm{d}\tau=r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi=\frac{a_0^3\rho^2\sin\theta\,\mathrm{d}\rho\,\mathrm{d}\theta\,\mathrm{d}\phi}{Z^3}$$

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

$$\nabla^2\psi=\frac{\partial^2\psi}{\partial r^2}+\frac{2}{r}\frac{\partial\psi}{\partial r}=\frac{\partial^2\psi}{\partial\rho^2}\left(\frac{\partial\rho}{\partial r^2}\right)^2+\frac{2Z}{\rho a_0}\left(\frac{\partial\psi}{\partial\rho}\right)\frac{\partial\rho}{\partial r}=\left(\frac{Z}{a_0}\right)^2\times\left(\frac{\partial^2\psi}{\partial\rho^2}+\frac{2}{\rho}\frac{\partial\psi}{\partial\rho}\right)$$

$$\frac{\partial\psi}{\partial\rho}=N(2-\rho)\times\left(-\tfrac{1}{2}\right)\mathrm{e}^{-\rho/2}-N\,\mathrm{e}^{-\rho/2}=N\left(\tfrac{1}{2}\rho-2\right)\mathrm{e}^{-\rho/2}$$

$$\frac{\partial^2\psi}{\partial\rho^2}=N\left(\tfrac{1}{2}\rho-2\right)\times\left(-\tfrac{1}{2}\right)\mathrm{e}^{-\rho/2}+\tfrac{1}{2}N\,\mathrm{e}^{-\rho/2}=N\left(\tfrac{3}{2}-\tfrac{1}{4}\rho\right)\mathrm{e}^{-\rho/2}$$

$$\nabla^2\psi=\left(\frac{Z}{a_0}\right)^2N\mathrm{e}^{-\rho/2}(-4/\rho+5/2-\rho/4)$$

and

$$\left\langle\hat{E}_{\mathrm{K}}\right\rangle=\int_0^\infty\int_0^\pi\int_0^{2\pi}N(2-\rho)\mathrm{e}^{-\rho/2}\left(\frac{Z}{a_0}\right)^2\times\left(\frac{-\hbar^2}{2m}\right)$$

$$\times N\mathrm{e}^{-\rho/2}(-4/\rho+5/2-\rho/4)\frac{a_0^3\,\mathrm{d}\phi\sin\theta\,\mathrm{d}\theta\,\rho^2\,\mathrm{d}\rho}{Z^3}$$

The integrals over angles give a factor of 4π, so

$$\left\langle\hat{E}_{\mathrm{K}}\right\rangle=4\pi N^2\left(\frac{a_0}{Z}\right)\times\left(-\frac{\hbar^2}{2m}\right)\int_0^\infty(2-\rho)\times\left(-4+\tfrac{5}{2}\rho-\tfrac{1}{4}\rho^2\right)\rho\mathrm{e}^{-\rho}\,\mathrm{d}\rho$$

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

$$\left\langle\hat{E}_{\mathrm{K}}\right\rangle=4\pi\left(\frac{Z^3}{32\pi a_0^3}\right)\times\left(\frac{a_0}{Z}\right)\times\left(\frac{\hbar^2}{m}\right)=\boxed{\frac{\hbar^2Z^2}{8ma_0^2}}$$

The average potential energy is

$$\langle V\rangle=\int\psi^*V\psi\,\mathrm{d}\tau\quad\text{where}\quad V=-\frac{Ze^2}{4\pi\varepsilon_0r}=-\frac{Z^2e^2}{4\pi\varepsilon_0a_0\rho}$$

and $\langle V\rangle=\int_0^\infty\int_0^\pi\int_0^{2\pi}N(2-\rho)\mathrm{e}^{-\rho/2}\left(-\dfrac{Z^2e^2}{4\pi\varepsilon_0a_0\rho}\right)N(2-\rho)\mathrm{e}^{-\rho/2}\,\dfrac{a_0^3\rho^2\sin\theta\,\mathrm{d}\rho\,\mathrm{d}\theta\,\mathrm{d}\phi}{Z^3}$

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

$$\langle V\rangle=4\pi\left(\frac{Z^3}{32\pi a_0^3}\right)\times\left(-\frac{Z^2e^2}{4\pi\varepsilon_0a_0}\right)\times\left(\frac{a_0^3}{Z^3}\right)\times(2)=\boxed{-\frac{Z^2e^2}{16\pi\varepsilon_0a_0}}$$

9A.7(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 $\rho\equiv\dfrac{2Zr}{na_0}=\dfrac{2Zr}{3a_0}$ here.

But 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 which 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.

9A.8(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.

But 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 $(P_{3p})^{1/2}$

$$\frac{\mathrm{d}(P_{3p})^{1/2}}{\mathrm{d}\rho} = 0 = \frac{\mathrm{d}}{\mathrm{d}\rho}C\rho^2(4-\rho)\mathrm{e}^{-\rho/2}$$

$$=C[\rho(8-5\rho+\rho^2/2)]\mathrm{e}^{-\rho/2}$$

$$\text{so} \quad 8-5\rho+\rho^2/2=0$$

Numerical solution of this quadratic equation yields

$$\rho = 2,\ \text{and } 8$$

corresponding to

$$r = 3a_0/Z \text{ and } 12a_0/Z$$

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 which 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.

9A.9(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

(i) $n=4,\ l=2,\ \text{so}\langle \hat{L}^2 \rangle^{1/2} = 6^{1/2}\hbar = \boxed{2.45\times10^{-34}\,\text{J s}}$ $\boxed{2}$ angular nodes $\boxed{1}$ radial node

(ii) $n=2,\ l=1,\ \text{so}\langle \hat{L}^2 \rangle^{1/2} = 2^{1/2}\hbar = \boxed{1.49\times10^{-34}\,\text{J s}}$ $\boxed{1}$ angular nodes $\boxed{0}$ radial nodes

(iii) $n=3,\ l=1,\ \text{so}\langle \hat{L}^2 \rangle^{1/2} = 2^{1/2}\hbar = \boxed{1.49\times10^{-34}\,\text{J s}}$ $\boxed{1}$ angular node $\boxed{1}$ radial node

9A.10(b) The radial portion of the 4d orbital is proportional to (6 – ρ). Its position can be determined by setting (6 − ρ) = 0. Hence, ρ = 6 and $r = \boxed{12a_0/Z}$.

See Figs. 8C.9, 8C.11 and 9A.16 as well as Table 8C.1 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 makes the wavefunction zero.

d_{z^2} orbital: see eqn. 9A.23, Table 8C.1 and Figs. 8.35 and 9A.16. The nodal planes are difficult to picture. $\boxed{\theta = 0.95532}$ is the angular node for both planes.

d_{xy} orbital: see eqn. 9A.23, Table 8C.1 and Figs. 8.35 and 9A.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. 9A.23, Table 8C.1 and Figs. 8.35 and 9A.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. 9A.23, Table 8C.1 and Figs. 8.35 and 9A.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.

$\text{d}_{x^2-y^2}$ orbital: see eqn. 9A.23, Table 8C.1 and Figs. 8.35 and 9A.16. The two nodal planes are $\boxed{\text{planes at } \phi = \pi/4 \text{ and and } \phi = 3\pi/4}$, respectively, and $\boxed{\theta = 0}$ is the angular node of both of these planes.

Problems

9A.2 In each case we need to show that

$$\int_{\text{all space}} \psi_1^* \psi_2 \,\text{d}\tau = 0$$

(a) $$\int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{1\text{s}}\psi_{2\text{s}} r^2 \,\text{d}r \sin\theta \,\text{d}\theta \,\text{d}\phi \overset{?}{=} 0$$

$$\left.\begin{array}{l} \psi_{1s} = R_{1,0}Y_{0,0} \\ \psi_{2s} = R_{2,0}Y_{0,0} \end{array}\right\} Y_{0,0} = \left(\frac{1}{4\pi}\right)^{1/2} \quad [\text{Table 8}C.1]$$

Since $Y_{0,0}$ is a constant, the integral over the radial functions determines the orthogonality of the functions.

$$\int_0^\infty R_{1,0}R_{2,0}r^2 \,\text{d}r$$

$$R_{1,0} \propto \text{e}^{-\rho/2} = \text{e}^{-Zr/a_0} \qquad \left[\rho = \frac{2Zr}{a_0}\right]$$

$$R_{2,0} \propto (2-\rho/2)\text{e}^{-\rho/4} = \left(2 - \frac{Zr}{a_0}\right)\text{e}^{-Zr/2a_0} \qquad \left[\rho = \frac{2Zr}{a_0}\right]$$

$$\int_0^{\infty} R_{1,0}R_{2,0}r^2\,\mathrm{d}r \propto \int_0^{\infty} \mathrm{e}^{-Zr/a_0}\left(2-\frac{Zr}{a_0}\right)\mathrm{e}^{-Zr/2a_0}r^2\,\mathrm{d}r$$

$$=\int_0^{\infty} 2\mathrm{e}^{-(3/2)Zr/a_0}r^2\,\mathrm{d}r-\int_0^{\infty}\frac{Z}{a_0}\mathrm{e}^{-(3/2)Zr/a_0}r^3\,\mathrm{d}r$$

$$=\frac{2\times 2!}{\left(\frac{3}{2}\frac{z}{a_0}\right)^3}-\left(\frac{Z}{a_0}\right)\times\frac{3!}{\left(\frac{3}{2}\frac{z}{a_0}\right)^4}=\boxed{0}$$

Hence, the functions are orthogonal.

(b) We use the p_x and p_y orbitals in the form given in Section 9A.2(g), eqn 9A.22

$$\mathrm{p}_x \propto x, \qquad \mathrm{p}_y \propto y$$

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 variable 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 9A.2(g), eqn 9A.22)

$$\mathrm{p}_x = f(r)\sin\theta\cos\phi \quad \mathrm{p}_y = f(r)\sin\theta\sin\phi$$

$$\int_{\text{all space}} \mathrm{p}_x\mathrm{p}_y r^2\mathrm{d}r\sin\theta\;\mathrm{d}\theta\;\mathrm{d}\phi = \int_0^{\infty} f(r)^2r^2\mathrm{d}r\int_0^{\pi}\sin^2\theta\;\mathrm{d}\theta\int_0^{2\pi}\cos\phi\sin\phi\;\mathrm{d}\phi$$

The first factor is nonzero 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.

9A.4 We use the p_x and p_y orbitals in the form (Section 9A.2(g))

$$\mathrm{p}_x = rf(r)\sin\theta\cos\phi \qquad \mathrm{p}_y = rf(r)\sin\theta\sin\phi$$

and use $\cos\phi = \frac{1}{2}(\mathrm{e}^{\mathrm{i}\phi}+\mathrm{e}^{-\mathrm{i}\phi})$ and $\sin\phi = \frac{1}{2\mathrm{i}}(\mathrm{e}^{\mathrm{i}\phi}-\mathrm{e}^{-\mathrm{i}\phi})$ then

$$\mathrm{p}_x = \frac{1}{2}rf(r)\sin\theta\;(\mathrm{e}^{\mathrm{i}\phi}+\mathrm{e}^{-\mathrm{i}\phi}) \qquad \mathrm{p}_y = \frac{1}{2\mathrm{i}}rf(r)\sin\theta\;(\mathrm{e}^{\mathrm{i}\phi}-\mathrm{e}^{-\mathrm{i}\phi})$$

$$\hat{l}_z = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial\phi}$$

$$\hat{l}_z\mathrm{p}_x = \frac{\hbar}{2}rf(r)\sin\theta\;\mathrm{e}^{\mathrm{i}\phi}-\frac{\hbar}{2}rf(r)\sin\theta\;\mathrm{e}^{-\mathrm{i}\phi} = \mathrm{i}\hbar\mathrm{p}_y \neq \text{constant}\times\mathrm{p}_x$$

$$\hat{l}_z\mathrm{p}_y = \frac{\hbar}{2\mathrm{i}^2}rf(r)\sin\theta\;\mathrm{e}^{\mathrm{i}\phi}+\frac{\hbar}{2\mathrm{i}^2}rf(r)\sin\theta\;\mathrm{e}^{-\mathrm{i}\phi} = -\mathrm{i}\hbar\mathrm{p}_x \neq \text{constant}\times\mathrm{p}_y$$

Therefore, neither p_x nor p_y are eigenfunctions of $\hat{l}_z$. However, $\boxed{\mathrm{p}_x+\mathrm{i}\mathrm{p}_y \text{ and } \mathrm{p}_x-\mathrm{i}\mathrm{p}_y}$ are eigenfunctions

$$\mathrm{p}_x+\mathrm{i}\mathrm{p}_y = rf(r)\sin\theta\;\mathrm{e}^{\mathrm{i}\phi} \qquad \mathrm{p}_x-\mathrm{i}\mathrm{p}_y = rf(r)\sin\theta\;\mathrm{e}^{-\mathrm{i}\phi}$$

since both $\mathrm{e}^{\mathrm{i}\phi}$ and $\mathrm{e}^{-\mathrm{i}\phi}$ are eigenfunctions of $\hat{l}_z$ with eigenvalues $+h$ and $-h$.

9A.6
$$\psi_{1\mathrm{s}} = \left(\frac{1}{\pi a_0^3}\right)^{1/2}\mathrm{e}^{-r/a_0}$$

The probability of the electron being within a sphere of radius r' is

$$\int_0^{r'}\int_0^{\pi}\int_0^{2\pi}\psi_{1\mathrm{s}}^2r^2\,\mathrm{d}r\;\sin\theta\;\mathrm{d}\theta\;\mathrm{d}\phi$$

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

$$-\frac{a_0 r^2 e^{-2r/a_0}}{2}\Bigg|_0^{r'} + a_0\left[-\frac{a_0 r e^{-2r/a_0}}{2}\Bigg|_0^{r'} + \frac{a_0}{2}\left(-\frac{a_0 e^{-2r/a_0}}{2}\right)\Bigg|_0^{r'}\right]$$

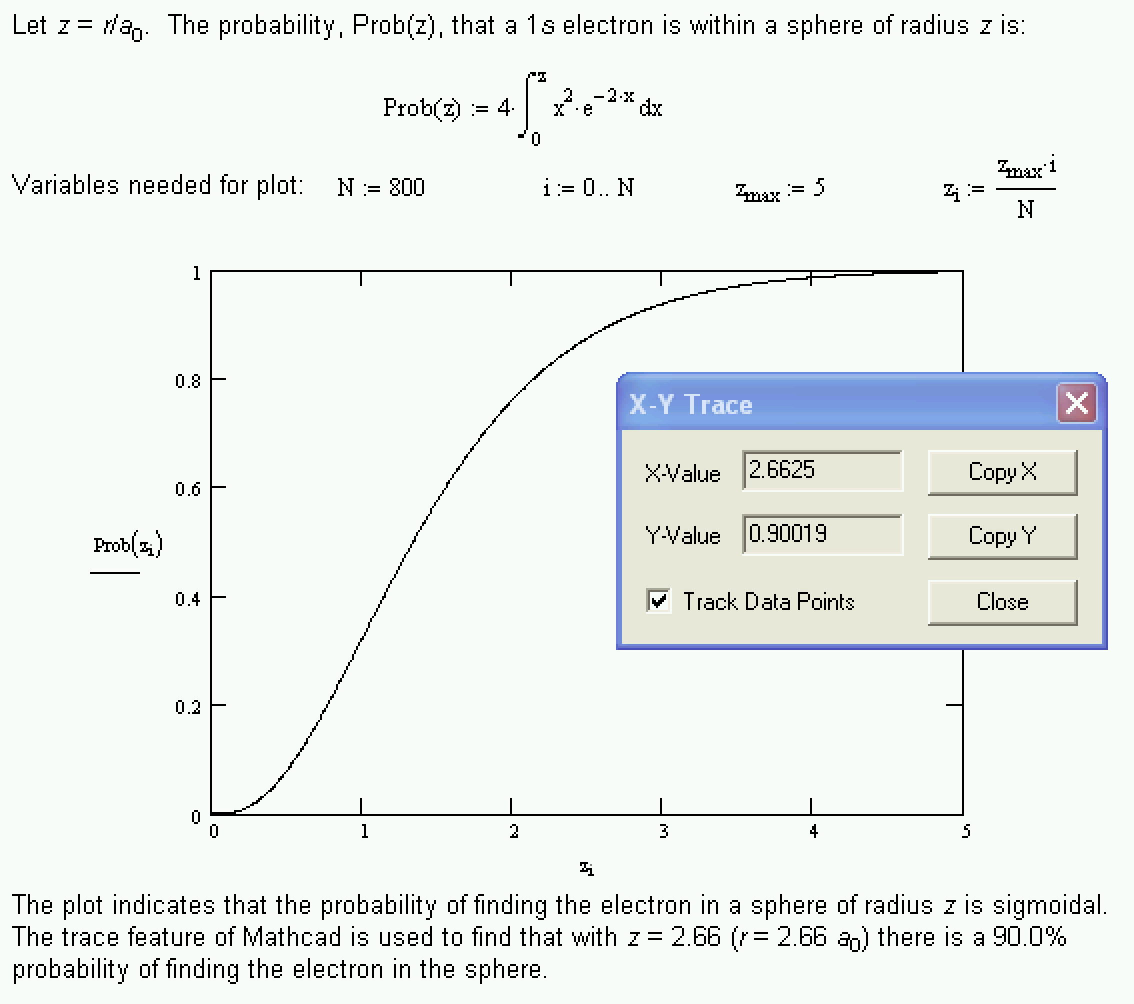
$$= -\frac{a_0 (r')^2 e^{-2r'/a_0}}{2} - \frac{a_0^2 r'}{2} e^{-2r'/a_0} - \frac{a_0^3}{4} e^{-2r'/a_0} + \frac{a_0^3}{4}$$

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: $N := 800$ $\quad i := 0..N$ $\quad z_{max} := 5$ $\quad z_i := \frac{z_{max}\cdot i}{N}$

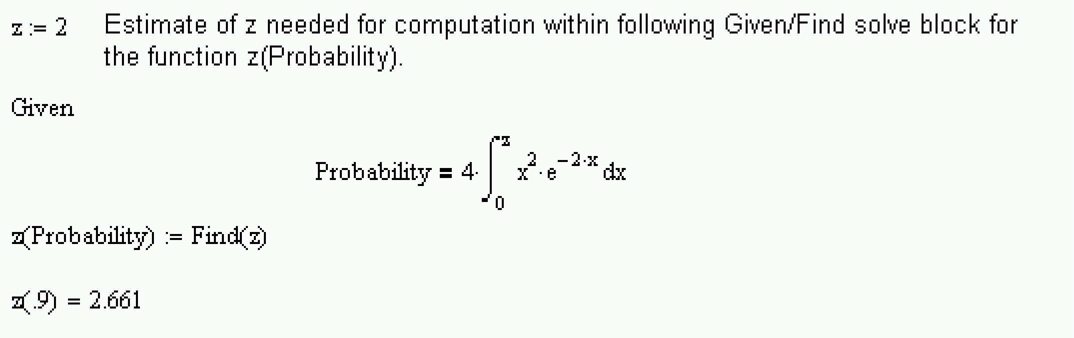
X-Value 2.6625

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

9A.8. The attractive Coulomb force $= \dfrac{Ze^2}{4\pi\varepsilon_0}\cdot\dfrac{1}{r^2}$

The repulsive centrifugal force $= \dfrac{(\text{angular momentum})^2}{m_\text{e}r^3} = \dfrac{(n\hbar)^2}{m_\text{e}r^3}$[postulated]

The two forces balance when

$$\frac{Ze^2}{4\pi\varepsilon_0}\times\frac{1}{r^2} = \frac{n^2\hbar^2}{m_\text{e}r^3},\quad \text{implying that}\quad r = \frac{4\pi n^2\hbar^2\varepsilon_0}{Ze^2m_\text{e}}$$

The total energy is

$$E = E_\text{K} + V = \frac{(\text{angular momentum})^2}{2I} - \frac{Ze^2}{4\pi\varepsilon_0}\times\frac{1}{r} = \frac{n^2\hbar^2}{2m_\text{e}r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}[\text{postulated}]$$

$$= \left(\frac{n^2\hbar^2}{2m_\text{e}}\right)\times\left(\frac{Ze^2m_\text{e}}{4\pi n^2\hbar^2\varepsilon_0}\right)^2 - \left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\times\left(\frac{Ze^2m_\text{e}}{4\pi n^2\hbar^2\varepsilon_0}\right) = \boxed{-\frac{Z^2e^4m_\text{e}}{32\pi^2\varepsilon_0^2\hbar^2}\times\frac{1}{n^2}}$$

9A.10 Refer to Problems 9C.8 and 9A.8 and their solutions.

$$\mu_\text{H} = \frac{m_\text{e}m_\text{p}}{m_\text{e}+m_\text{p}} \approx m_\text{e} \quad [m_\text{p} = \text{mass of proton}]$$

$$\mu_\text{Ps} = \frac{m_\text{e}m_\text{pos}}{m_\text{e}+m_\text{pos}} = \frac{m_\text{e}}{2} \quad [m_\text{pos} = \text{mass of proton} = m_\text{e}]$$

$$a_0 = r(n=1) = \frac{4\pi\hbar^2\varepsilon_0}{e^2m_\text{e}}[\text{9A.11a and Problem 9A.8}]$$

To obtain a_Ps the radius of the first Bohr orbit of positronium, we replace m_e with $\mu_\text{Ps} = \frac{m_e}{2}$; hence,

$$\boxed{a_\text{Ps} = 2a_0} = \frac{\pi\hbar^2\varepsilon_0}{e^2m_\text{e}}$$

The energy of the first Bohr orbit of positronium is

$$E_\text{1,Ps} = -hc\tilde{R}_\text{Ps} = -\frac{hc}{2}\tilde{R}_\infty \text{ [Problem 9C.8]}$$

Thus, $\boxed{E_\text{1,Ps} = \tfrac{1}{2}E_\text{1,H}}$

Question. What modifications are required in these relations when the finite mass of the hydrogen nucleus is recognized?

9B Many-electron atoms

Answers to discussion questions

9B.2 In period 2, the first ionization energies increase markedly from Li to Be, decrease slightly from Be to B, again increase markedly from B to N, again decrease slightly from N to O, and finally increase markedly from O to Ne. The general trend is an overall increase of I_1 with atomic number across the period. That is to be expected since the principal quantum number (electron shell) of the outer electron remains the same, while its attraction to the nucleus increases. The slight decrease from Be to B is a reflection of the outer electron being in a higher energy subshell (larger *l* value) in B than in Be. The slight decrease from N to O is due to the half-filled subshell effect; half-filled sub-shells have increased stability. O has one electron outside of the half-filled p subshell and that electron must pair with another resulting in strong electron–electron repulsions between them.

The same kind of variation is expected for the elements of period 3 because in both periods the outer shell electrons are only s and p.

Solutions to exercises

9B.1(b) Y: [Kr]$5s^2 4d^1$
Zr: [Kr]$5s^2 4d^2$
Nb: [Kr]$5s^2 4d^3$ or [Kr]$5s^1 4d^4$ (most probable)
Mo: [Kr]$5s^1 4d^5$
Tc: [Kr]$5s^2 4d^5$
Ru: [Kr]$5s^2 4d^6$ or [Kr]$5s^1 4d^7$ (most probable)
Rh: [Kr]$5s^1 4d^8$
Pd: [Kr]$5s^1 4d^9$ or [Kr]$4d^{10}$ (most probable)
Ag: [Kr]$5s^1 4d^{10}$
Cd: [Kr]$5s^2 4d^{10}$

9B.2(b) (i) $\mathrm{V}^{2+}: 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 = [\mathrm{Ar}]3d^3$

(ii) The only unpaired electrons are those in the 3d subshell. There are three.

$S = \boxed{\tfrac{3}{2}}$ and $\tfrac{3}{2} - 1 = \boxed{\tfrac{1}{2}}$.

For $S = \tfrac{3}{2}, M_S = \boxed{\pm\tfrac{1}{2} \text{ and } \pm\tfrac{3}{2}}$

for $S = \tfrac{1}{2}, M_S = \boxed{\pm\tfrac{1}{2}}$

9B.2 **(a)** The Slater wavefunction [9B.5a] is

$$\psi(1,2,3,\ldots,N) = \frac{1}{(N!)^{1/2}} \begin{vmatrix} \psi_a(1)\alpha(1) & \psi_a(2)\alpha(2) & \psi_a(3)\alpha(3) & \cdots & \psi_a(N)\alpha(N) \\ \psi_a(1)\beta(1) & \psi_a(2)\beta(2) & \psi_a(3)\beta(3) & \cdots & \psi_a(N)\beta(N) \\ \psi_b(1)\alpha(1) & \psi_b(2)\alpha(2) & \psi_b(3)\alpha(3) & \cdots & \psi_b(N)\alpha(N) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \psi_z(1)\beta(1) & \psi_z(2)\beta(2) & \psi_z(3)\beta(3) & \cdots & \psi_z(N)\beta(N) \end{vmatrix}$$

Interchanging any two columns or rows leaves the function unchanged except for a change in sign. For example, interchanging the first and second columns of the above determinant gives:

$$\psi(1,2,3,\ldots,N)=\frac{-1}{(N!)^{1/2}}\begin{vmatrix}\psi_a(2)\alpha(2) & \psi_a(1)\alpha(1) & \psi_a(3)\alpha(3) & \cdots & \psi_a(N)\alpha(N)\\ \psi_a(2)\beta(2) & \psi_a(1)\beta(1) & \psi_a(3)\beta(3) & \cdots & \psi_a(N)\beta(N)\\ \psi_b(2)\alpha(2) & \psi_b(1)\alpha(1) & \psi_b(3)\alpha(3) & \cdots & \psi_b(N)\alpha(N)\\ \vdots & \vdots & \vdots & \vdots & \vdots\\ \psi_z(2)\beta(2) & \psi_z(1)\beta(1) & \psi_z(3)\beta(3) & \cdots & \psi_z(N)\beta(N)\end{vmatrix}$$

$$=-\psi(2,1,3,\ldots,N)$$

This demonstrates that a Slater determinant is antisymmetric under particle exchange.

(b) The possibility that 2 electrons occupy the same orbital with the same spin can be explored by making any two rows of the Slater determinant identical, thereby, providing identical orbital and spin functions to two rows. Rows 1 and 2 are identical in the Slater wavefunction below. Interchanging these two rows causes the sign to change without in any way changing the determinant.

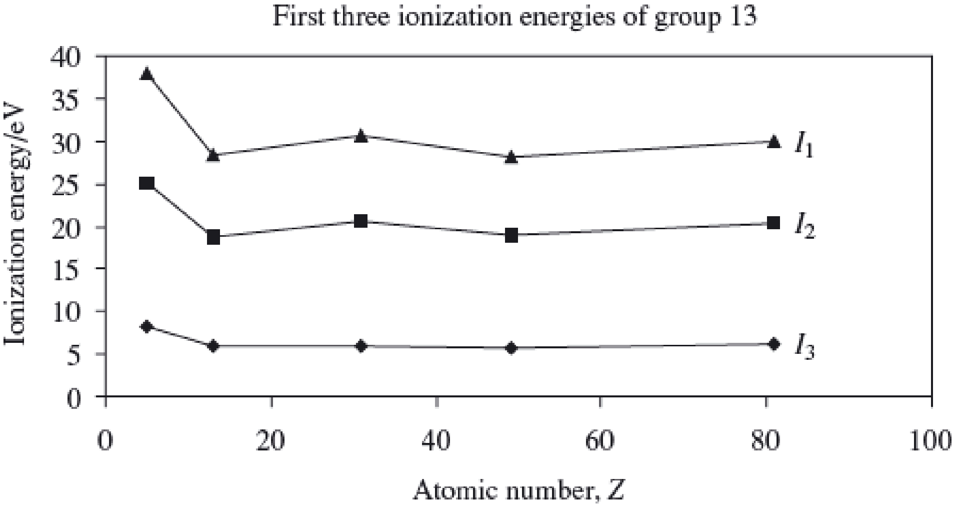
$$\psi(1,2,3,\ldots,N)=\frac{1}{(N!)^{1/2}}\begin{vmatrix}\psi_a(1)\alpha(1) & \psi_a(2)\alpha(2) & \psi_a(3)\alpha(3) & \cdots & \psi_a(N)\alpha(N)\\ \psi_a(1)\alpha(1) & \psi_a(2)\alpha(2) & \psi_a(3)\alpha(3) & \cdots & \psi_a(N)\alpha(N)\\ \psi_b(1)\alpha(1) & \psi_b(2)\alpha(2) & \psi_b(3)\alpha(3) & \cdots & \psi_b(N)\alpha(N)\\ \vdots & \vdots & \vdots & \vdots & \vdots\\ \psi_z(1)\beta(1) & \psi_z(2)\beta(2) & \psi_z(3)\beta(3) & \cdots & \psi_z(N)\beta(N)\end{vmatrix}$$

$$=-\psi(2,1,3,\ldots,N)=-\psi(1,2,3,\ldots,N)$$

Only the null function satisfies a relationship in which it is the negative of itself so we conclude that, since the null function is inconsistent with existence, the Slater determinant satisfies the Pauli exclusion principle. No two electrons can occupy the same orbital with the same spin.

9B.4 See Figure 9B.1

Figure 9B.1



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 aluminum 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.

9C Atomic spectra

Answers to discussion questions

9C.2 The selection rules are:

$$\Delta n = \pm 1, \pm 2, \cdots \qquad \Delta l = \pm 1 \qquad \Delta m_l = 0, \pm 1$$

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 $\Delta l = \pm 1$. 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 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.

Solutions to exercises

9C.1(b) Eqn. 9A.1 implies that the shortest wavelength corresponds to $n_2 = \infty$, and the longest to n_2= 6. Solve eqn. 9A.1 for λ.

$$\lambda = \frac{(1/n_1^2 - 1/n_2^2)^{-1}}{\tilde{R}_{\text{H}}}$$

Shortest: $$\lambda = \frac{(1/5^2 - 1/\infty^2)^{-1}}{109677\text{cm}^{-1}} = 2.279 \times 10^{-4}\ \text{cm}$$

Longest: $$\lambda = \frac{(1/5^2 - 1/6^2)^{-1}}{109677\text{cm}^{-1}} = 7.460 \times 10^{-4}\ \text{cm}$$

9C.2(b) For atoms N, eqn. 9A.9 may be rewritten in terms of the Rydberg constant R_{N} as

$$E_n = -\frac{Z^2 \mu_{\text{N}} hc\tilde{R}_{\text{Li}^{2+}}}{m_{\text{e}} n^2} \approx -\frac{Z^2 hc\tilde{R}_\infty}{n^2}$$

where to within 0.01% the ratio $\mu_{\text{N}}/m_{\text{e}}$ is unity. Eqn. 9A.1 can then be rewritten as

$$\tilde{\nu} = Z^2 \tilde{R}_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \qquad \lambda = \frac{1}{\tilde{\nu}} \qquad \nu = \frac{c}{\lambda}$$

$$\tilde{\nu} = 9 \times 109\ 737\ \text{cm}^{-1} \left(\frac{1}{4^2} - \frac{1}{5^2} \right) = \boxed{2.222 \times 10^4\ \text{cm}^{-1}}$$

$$\lambda = \boxed{4.500 \times 10^{-5}\text{cm}}$$

$$\nu = \frac{2.9978\times10^{10}\ \text{cm s}^{-1}}{4.500\times10^{-5}\ \text{cm}} = \boxed{6.662\times10^{14}\ \text{s}^{-1}}$$

9C.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

$$E_{\text{photon}} = I + E_{\text{kinetic}} \quad I = \text{ionization energy}$$

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

$$E_{\text{kinetic}} = \tfrac{1}{2}m_{\text{e}}s^2$$

So $\frac{hc}{\lambda} = I + \frac{1}{2}m_e s^2 \Rightarrow I = \frac{hc}{\lambda} - \frac{1}{2}m_e s^2$

$$I = \frac{(6.626\times10^{-34}\,\text{J s})\times(2.998\times10^{8}\,\text{m s}^{-1})}{58.4\times10^{-9}\,\text{m}}$$

$$-\tfrac{1}{2}(9.11\times10^{-31}\,\text{kg})\times(1.79\times10^{6}\,\text{m s}^{-1})^2$$

$$= \boxed{1.94\times10^{-18}\,\text{J}} = 12.1\ \text{eV}$$

9C.4(b) **(i)** 5d → 2s is $\boxed{\text{not}}$ an allowed transition, for $\Delta l = -2$ (Δl must equal ±1).

(ii) 5p → 3s is $\boxed{\text{allowed}}$, since $\Delta l = -1$.

(iii) 6p → 4f is $\boxed{\text{not}}$ allowed, for $\Delta l = +2$ (Δl must equal ±1).

9C.5(b) For $l > 0$, $j = l \pm 1/2$, so

(i) $l = 1$, so $j = \boxed{1/2 \text{ or } 3/2}$

(ii) $l = 5$, so $j = \boxed{9/2 \text{ or } 11/2}$

9C.6(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 $j_2 = 3$

$$J = \boxed{8, 7, 6, 5, 4, 3, 2}$$

9C.7(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.

9C.8(b) **(i)** 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.

(ii) 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.

9C.9(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

$$\boxed{{}^1\mathrm{F}_3;\ {}^3\mathrm{F}_4,\ {}^3\mathrm{F}_3,\ {}^3\mathrm{F}_2;\ {}^1\mathrm{D}_2;\ {}^3\mathrm{D}_3,\ {}^3\mathrm{D}_2,\ {}^3\mathrm{D}_1;\ {}^1\mathrm{P}_1,\ {}^3\mathrm{P}_2,\ {}^3\mathrm{P}_1,\ {}^3\mathrm{P}_0}\ .$$

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 $\boxed{{}^3\mathrm{F}_2}$

9C.10(b) **(i)** ${}^3\mathrm{D}$ has $S = 1$ and $L = 2$, so $J = \boxed{3,\ 2,\ \text{and}\ 1}$ are present. $J = 3$ has $\boxed{7}$ states, with $M_J = 0$, ± 1, ± 2, or ± 3; $J = 2$ has $\boxed{5}$ states, with $M_J = 0$, ± 1, or ± 2; $J = 1$ has $\boxed{3}$ states, with $M_J = 0$, or ± 1.

(ii) ${}^4\mathrm{D}$ 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 $M_J = \pm 7/2$, $\pm 5/2$, $\pm 3/2$ or $\pm 1/2$; $J = 5/2$ has $\boxed{6}$ possible states, with $M_J = \pm 5/2$ $\pm 3/2$ or $\pm 1/2$; $J = 3/2$ has $\boxed{4}$ possible states, with $M_J = \pm 3/2$ or $\pm 1/2$; $J = 1/2$ has $\boxed{2}$ possible states, with $M_J = \pm 1/2$.

(iii) ${}^2\mathrm{G}$ 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 $M_J = \pm 9/2,\ \pm 7/2,\ \pm 5/2,\ \pm 3/2$ or $\pm 1/2$, $J = 7/2$ has $\boxed{8}$ possible states, with $M_J = \pm 7/2$, $\pm 5/2$, $\pm 3/2$ or $\pm 1/2$.

9C.11(b) Closed shells and subshells do not contribute to either L or S and thus are ignored in what follows.

(i) $\mathrm{Sc[Ar]3d^1 4s^2}$: $S = \frac{1}{2}$, $L = 2$; $J = \frac{5}{2}, \frac{3}{2}$, so the terms are $\boxed{{}^2\mathrm{D}_{5/2}\ \text{and}\ {}^2\mathrm{D}_{3/2}}$

(ii) $\mathrm{Br[Ar]3d^{10} 4s^2 4p^5}$. 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 $\boxed{{}^2\mathrm{P}_{3/2}\ \text{and}\ {}^2\mathrm{P}_{1/2}}$

9C.12(b) See eqn. 9C.8 for the selection rules. (i) $\boxed{\text{allowed}}$, (ii) $\boxed{\text{allowed}}$, (iii) $\boxed{\text{forbidden}}$

Solutions to problems

9C.2 All lines in the hydrogen spectrum fit the Rydberg formula

$$\frac{1}{\lambda} = \tilde{R}_{\mathrm{H}}\left(\tfrac{1}{n_1^2} - \tfrac{1}{n_2^2}\right)\left[\text{9A.1, with } \tilde{\nu} = \frac{1}{\lambda}\right] \qquad \tilde{R}_{\mathrm{H}} = 109\ 677\,\mathrm{cm}^{-1}$$

Find n_1 from the value of $\lambda_{\max}$, which arises from the transition $n_1 + 1 \rightarrow n_1$

$$\frac{1}{\lambda_{\max}\tilde{R}_{\mathrm{H}}} = \frac{1}{n_1^2} - \frac{1}{(n_1+1)^2} = \frac{2n_1 + 1}{n_1^2(n_1+1)^2}$$

$$\lambda_{\max}\tilde{R}_{\mathrm{H}} = \frac{n_1^2(n_1+1)^2}{2n_1+1} = (656.46\times 10^{-9}\,\mathrm{m})\times(109677\times 10^2\,\mathrm{m}^{-1}) = 7.20$$

and hence $n_1 = 2$, as determined by trial and error substitution. Therefore, the transitions are given by

$$\tilde{\nu} = \frac{1}{\lambda} = (109677\,\mathrm{cm}^{-1})\times\left(\frac{1}{4} - \frac{1}{n_2^2}\right), \quad n_2 = 3, 4, 5, 6$$

The next line has $n_2 = 7$, and occurs at

$$\tilde{\nu} = \frac{1}{\lambda} = (109677\,\mathrm{cm}^{-1})\times\left(\frac{1}{4} - \frac{1}{49}\right) = \boxed{397.13\,\mathrm{nm}}$$

The energy required to ionize the atom is obtained by letting $n_2 \rightarrow \infty$. Then

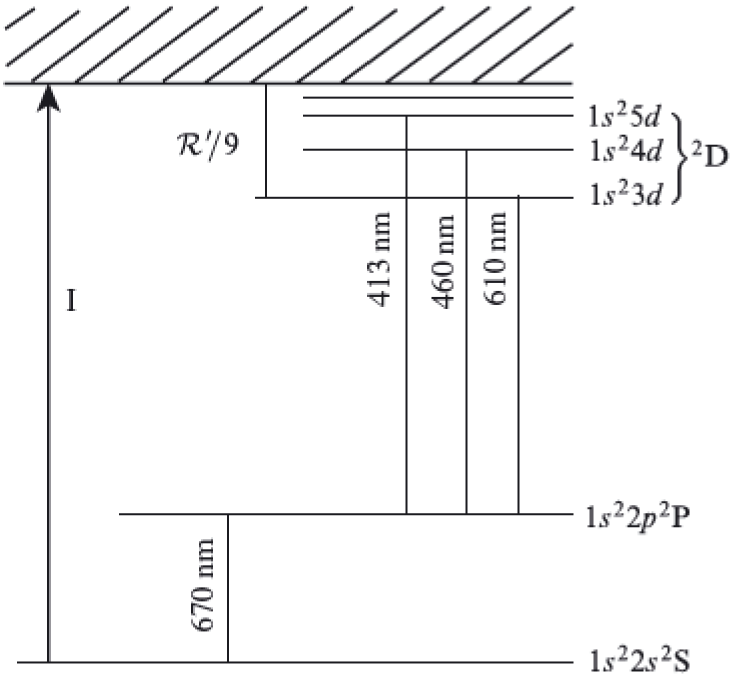
$$\tilde{\nu}_\infty = \frac{1}{\lambda_\infty} = (109677\ \text{cm}^{-1})\times\left(\frac{1}{4}-0\right) = 27419\ \text{cm}^{-1}, \quad \text{or} \quad \boxed{3.40\ \text{eV}}$$

(The answer, $3.40\ \text{eV}$, 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.

9C.4 The lowest possible value of n in $1s^2nd^1$ is 3; thus the series of ^2D terms correspond to $1s^2 3d$, $1s^2 4d$, etc. Figure 9C.1 is a description consistent with the data in the problem statement.

Figure 9C.1



If we assume that the energies of the d orbitals are hydrogenic we may write

$$E(1s^2nd^1, {}^2\text{D}) = -\frac{hc\tilde{R}_{\text{Li}}}{n^2} \quad [n = 3, 4, 5, \cdots]$$

Then for the $^2\text{D} \rightarrow {}^2\text{P}$ transitions

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{|E(1s^2 2p^1, {}^2\text{P})|}{hc} - \frac{\tilde{R}_{\text{Li}}}{n^2} \qquad \left[\Delta E = h\nu = \frac{hc}{\lambda} = hc\tilde{\nu},\ \tilde{\nu} = \frac{\Delta E}{hc}\right]$$

from which we can write

$$\frac{|E(1s^2 2p^1, {}^2\text{P})|}{hc} = \frac{1}{\lambda} + \frac{\tilde{R}_{\text{Li}}}{n^2} = \begin{cases} \dfrac{1}{610.36\times 10^{-7}\,\text{cm}} + \dfrac{\tilde{R}_{\text{Li}}}{9} & \text{(a)} \\[2ex] \dfrac{1}{460.29\times 10^{-7}\,\text{cm}} + \dfrac{\tilde{R}_{\text{Li}}}{16} & \text{(b)} \\[2ex] \dfrac{1}{413.23\times 10^{-7}\,\text{cm}} + \dfrac{\tilde{R}_{\text{Li}}}{25} & \text{(c)} \end{cases}$$

$$\text{Then}\ \left.\begin{aligned} &\text{(b)}-\text{(a) solves to } \tilde{R}_{\text{Li}} = 109886\ \text{cm}^{-1} \\ &\text{(a)}-\text{(c) solves to } \tilde{R}_{\text{Li}} = 109910\ \text{cm}^{-1} \\ &\text{(b)}-\text{(c) solves to } \tilde{R}_{\text{Li}} = 109963\ \text{cm}^{-1} \end{aligned}\right\}\ \text{Mean} = 109920\ \text{cm}^{-1}$$

The binding energies are therefore

$$E(1\text{s}^2\,3\text{d}^1,\,{}^2\text{D}) = -\frac{\tilde{R}_{\text{Li}}}{9} = -12213\,\text{cm}^{-1}$$

$$E(1\text{s}^2\,2\text{p}^1,\,{}^2\text{P}) = -\frac{1}{610.36\times10^{-7}\ \text{cm}} - 12213\ \text{cm}^{-1} = -28597\ \text{cm}^{-1}$$

$$E(1\text{s}^2\,2\text{s}^1,\,{}^2\text{S}) = -\frac{1}{670.78\times10^{-7}\ \text{cm}} - 28597\ \text{cm}^{-1} = -43505\ \text{cm}^{-1}$$

Therefore, the ionisation energy is

$$I(1\text{s}^2\,2\text{s}^1,\,{}^2\text{S}) = 43505\ \text{cm}^{-1},\quad \text{or}\quad \boxed{5.39\ \text{eV}}$$

9C.6 The ground term is $[\text{Ar}]4s^1\ {}^2\text{S}_{1/2}$ and the first excited is $[\text{Ar}]4\text{p}^1\ {}^2\text{P}$. 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 9C.2(b). Therefore, ascribe the transitions to $\boxed{{}^2\text{P}_{3/2} \rightarrow {}^2\text{S}_{1/2}}$ and $\boxed{{}^2\text{P}_{1/2} \rightarrow {}^2\text{S}_{1/2}}$ (since both are allowed). For these values of J, the splitting is equal to $\frac{3}{2}A$ (Example 9C.1). Hence, since

$$(766.70\times10^{-7}\ \text{cm})^{-1} - (770.11\times10^{-7}\ \text{cm})^{-1} = 57.75\,\text{cm}^{-1}$$

we can conclude that $A = \boxed{38.50\,\text{cm}^{-1}}$

9C.8 The Rydberg constant for positronium $(\tilde{R}_{\text{Ps}})$ is given by

$$\tilde{R}_{\text{Ps}} = \frac{\tilde{R}_\infty}{1+\frac{m_\text{e}}{m_\text{e}}} = \frac{\tilde{R}_\infty}{1+1} = \frac{1}{2}\tilde{R}_\infty \quad [\text{9A.15; also see Problem 9C.7; } m(\text{positron}) = m_\text{e}]$$

$$= 54\,869\ \text{cm}^{-1} \quad [\tilde{R}_\infty = 109\,737\,\text{cm}^{-1}]$$

Hence,

$$\tilde{\nu} = \frac{1}{\lambda} = (54869\ \text{cm}^{-1})\times\left(\frac{1}{4} - \frac{1}{n^2}\right),\quad n = 3, 4, \ldots$$

$$= \boxed{7621\ \text{cm}^{-1}}, \boxed{10\,288\ \text{cm}^{-1}}, \boxed{11522\ \text{cm}^{-1}}, \ldots$$

The binding energy of Ps is

$E = -hc\tilde{R}_{\text{Ps}}$, corresponding to $(-)54869\ \text{cm}^{-1}$

The ionization energy is therefore $54869\ \text{cm}^{-1}$, or $\boxed{6.80\,\text{eV}}$

9C.10 *Justification* 9C.1 noted that the transition dipole moment, μ_{fi} had to be non-zero for a transition to be allowed. The Justification examined conditions that allowed the *z* component of this quantity to be non-zero; now examine the *x* and *y* components.

$$\mu_{x,\text{fi}} = -e\int \psi_\text{f}^* x \psi_i \,\text{d}\tau \quad \text{and} \quad \mu_{y,\text{fi}} = -e\int \psi_\text{f}^* y \psi_i \,\text{d}\tau$$

As in the Justification, express the relevant Cartesian variables in terms of the spherical harmonics, $Y_{l,m}$. Start by expressing them in spherical polar coordinates:

$$x = r\sin\theta\cos\phi \quad \text{and} \quad y = r\sin\theta\sin\phi.$$

Note that $Y_{1,1}$ and $Y_{1,-1}$ have factors of $\sin\theta$. They also contain complex exponentials that can be related to the sine and cosine of ϕ through the identities

$$\cos\phi = 1/2(\text{e}^{\text{i}\phi} + \text{e}^{-\text{i}\phi}) \quad \text{and} \quad \sin\phi = 1/2i(\text{e}^{\text{i}\phi} - \text{e}^{-\text{i}\phi}).$$

These relations motivate us to try linear combinations $Y_{1,1} + Y_{1,-1}$ and $Y_{1,1} - Y_{1,-1}$ (from Table 8.2; note *c* here corresponds to the normalization constant in the table):

$$Y_{1,1} + Y_{1,-1} = -c\sin\theta(\text{e}^{\text{i}\phi} + \text{e}^{-\text{i}\phi}) = -2c\sin\theta\cos\phi = -2cx/r,$$

so $x = -(Y_{1,1} + Y_{1,-1})r/2c;$

$$Y_{1,1} - Y_{1,-1} = c\sin\theta(\mathrm{e}^{\mathrm{i}\phi} - \mathrm{e}^{-\mathrm{i}\phi}) = 2\mathrm{i}c\sin\theta\sin\phi = 2\mathrm{i}cy/r,$$

so $y = (Y_{1,1} - Y_{1,-1})r/2ic.$

Now we can express the integrals in terms of radial wavefunctions $R_{n,l}$ and spherical harmonics Y_{l,m_l}

$$\mu_{x,\mathrm{fi}} = \frac{e}{2c}\int_0^\infty R_{n_\mathrm{f},l_\mathrm{f}}\, r R_{n_\mathrm{i},l_\mathrm{i}}\, r^2\, dr \int_0^\pi \int_0^{2\pi} Y^*{}_{l_\mathrm{f},m_{l_\mathrm{f}}}(Y_{1,1} + Y_{1,-1})Y_{l_\mathrm{i},m_{l_\mathrm{i}}} \sin\theta \,\mathrm{d}\theta\,\mathrm{d}\phi.$$

The angular integral can be broken into two, one of which contains $Y_{1,1}$ and the other $Y_{1,-1}$. According to the “triple integral” relation (Section 8C), the integral

$$\int_0^\pi \int_0^{2\pi} Y^*{}_{l_f,m_{l_f}} Y_{1,1} Y_{l_i,m_{l_i}} \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$

vanishes unless $l_\mathrm{f} = l_\mathrm{i} \pm 1$ and $m_{l_f} = m_{l_i} \pm 1$. The integral that contains $Y_{1,-1}$ introduces no further constraints; it vanishes unless $l_\mathrm{f} = l_\mathrm{i} \pm 1$ and $m_{l_\mathrm{f}} = m_{l_\mathrm{i}} \pm 1$. Similarly, the *y* component introduces no further constraints, for it involves the same spherical harmonics as the *x* component. The whole set of selection rules, then, is that transitions are allowed only if

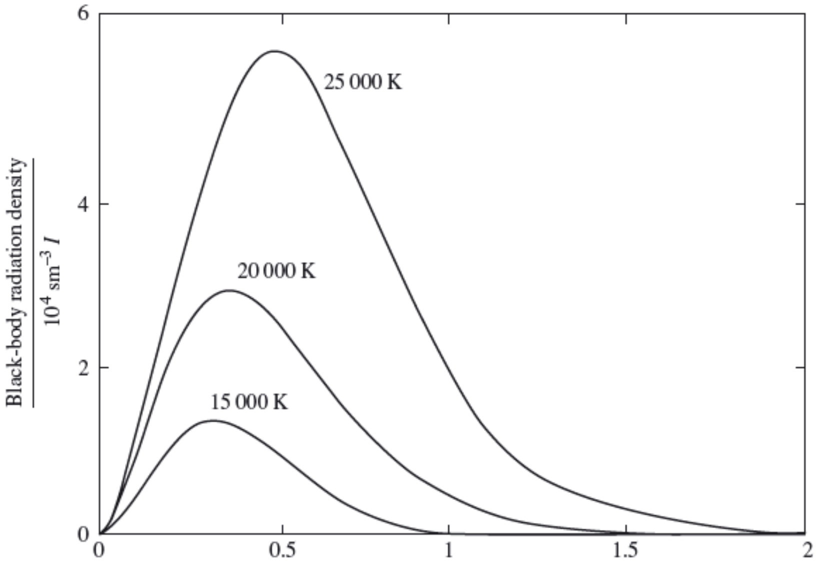
$$\boxed{\Delta l = \pm 1 \text{ and } \Delta m_l = 0 \text{ or } \pm 1}\,.$$

9C.12 A stellar surface temperature of 3000 K–4000 K, (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 15000 K – 20000 K. Both the kinetic energy and the blackbody 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 K – 10000 K has a temperature low enough to avoid complete hydrogen ionization but high enough for blackbody 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 blackbody radiation against *hν/I*, where *I* is the ionization eneregy, is shown below. (Fig. 9C.2)

Figure 9C.2



It is clearly seen that at 25000 K a large fraction of the radiation is able to ionize the hydrogen $(h\nu/I)$.

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:

$$K = \frac{p_{+}p_{-}}{p_{\mathrm{H}}p^{\ominus}} = \exp\left(\frac{-\Delta G^{\ominus}}{RT}\right) = \exp\left(\frac{-\Delta H^{\ominus}}{RT}\right)\times\exp\left(\frac{\Delta S^{\ominus}}{R}\right).$$

Clearly $\Delta S^{\ominus}$ is positive for ionization, which makes two particles out of one, and $\Delta H^{\ominus}$, which is close to the ionization energy, is also positive. At a sufficiently high temperature, ions will outnumber neutral molecules. Using concepts and equations developed in Chapters 15 and 21, one can compute the equilibrium constant; it turns out to be 60 (see below). Hence, there are relatively few undissociated H atoms in the equilibrium mixture that is consistent with the weak spectrum of neutral hydrogen observed.

The details of the calculation of the equilibrium constant based on the methods of Chapter 15 follows. Consider the equilibrium between hydrogen atoms and their component charged particles:

$$\mathrm{H} = \mathrm{H}^{+} + \mathrm{e}^{-}.$$

The equilibrium constant is:

$$K = \frac{p_{+}p_{-}}{p_{\mathrm{H}}p^{\ominus}} = \exp\left(\frac{-\Delta G^{\ominus}}{RT}\right).$$

Jump ahead to chapter 21 to use the statistical thermodynamic analysis of a dissociation equilibrium:

$$K = \frac{q_{+}^{\ominus}q_{-}^{\ominus}}{q_{\mathrm{H}}^{\ominus}N_{\mathrm{A}}}\mathrm{e}^{-\Delta_r E_0/RT}.$$

where $q^{\ominus} = \dfrac{gRT}{p^{\ominus}\Lambda^{3}}$ *and* $\Lambda = \left(\dfrac{h^{2}}{2\pi kTm}\right)^{1/2}$.

and where g is the degeneracy of the species. Note that $g_{+} = 2, g_{-} = 2$, and $g_{\mathrm{H}} = 4$. Consequently, these factors cancel in the expression for *K*.

So $K = \dfrac{RT}{p^{\ominus}N_{\mathrm{A}}}\left(\dfrac{2\pi kT}{h^{2}}\right)^{3/2}\left(\dfrac{m_{-}m_{+}}{m_{\mathrm{H}}}\right)^{3/2}\mathrm{e}^{-\Delta_r E_0/RT}$

Note that the Boltzmann, Avogadro, and perfect gas constants are related $(R = N_{\mathrm{A}}k)$, and collect powers of *kT*; note also that the product of masses is the reduced mass, which is approximately equal to the mass of the electron; note finally that the molar energy $\Delta_r E_0$ divided by *R* is the same as the atomic ionization energy (2.179×10^{-18} J) divided by *k*:

$$K = \frac{(kT)^{5/2}(2\pi m_{\mathrm{e}})^{3/2}}{p^{\ominus}h^{3}}\mathrm{e}^{-E/kT},$$

$$K = \frac{\left[\left(1.381\times10^{-23}\,\mathrm{JK}^{-1}\right)\left(25000\mathrm{K}\right)\right]^{5/2}\left[2\pi\left(9.11\times10^{-31}\mathrm{kg}\right)\right]^{3/2}}{\left(10^{5}\,\mathrm{Pa}\right)\left(6.626\times10^{-34}\,\mathrm{Js}\right)^{3}}$$

$$\times\exp\left(\frac{-2.179\times10^{-18}\mathrm{J}}{\left(1.381\times10^{-23}\mathrm{JK}^{-1}\right)\left(25000\mathrm{K}\right)}\right).$$

$$K = 60.$$

Thus, the equilibrium favors the ionized species, even though the ionization energy is greater than *kT*.

Integrated activities

9.2 $E_n = -\dfrac{hc\tilde{R}_{\mathrm{H}}}{n^2}$ where $\tilde{R}_{\mathrm{H}} = 109\,677\ \mathrm{cm^{-1}}$ [9A.14]

(a) $\Delta E = E_{n+1} - E_n = -hc\tilde{R}_{\mathrm{H}}\left(\dfrac{1}{(n+1)^2} - \dfrac{1}{n^2}\right)$

(b) For $n = 100$

$$\Delta E = E_{n+1} - E_n = -hc\tilde{R}_{\mathrm{H}}\left(\frac{1}{101^2} - \frac{1}{100^2}\right) = 1.97\times10^{-6}\,hc\tilde{R}_{\mathrm{H}}$$

$$\tilde{\nu} = \frac{\Delta E}{hc} = 1.97\times10^{-6}\,\tilde{R}_{\mathrm{H}} = \boxed{0.216\ \mathrm{cm^{-1}}}$$

$\langle r\rangle_{n,l} = n^2\left\{1+\frac{1}{2}\left(1-\frac{l(l+1)}{n^2}\right)\right\}\frac{a_0}{Z}$ [eqn 10.19, Atkins and de Paula, *Physical Chemistry*, 8th edition]

$$\langle r\rangle_{100} \approx \frac{3}{2}\frac{n^2 a_0}{Z} = \frac{3}{2}100^2 a_0 = \frac{3}{2}10^4 a_0 = \boxed{793\ \mathrm{nm}}$$

The radius of a Bohr orbit is $a_n \approx n^2 a_0$; hence the geometric cross-section $\pi a_n^2 \approx n^4\pi a_0^2$. For $n = 1$ this is $8.8\times10^{-21}\ \mathrm{m^2}$; for $n = 100$, it is $\boxed{8.8\times10^{-13}\ \mathrm{m^2}}$.

$$I = E_\infty - E_n = -E_n = \frac{hc\tilde{R}_{\mathrm{H}}}{n^2}$$

$$I_{100} = 10^{-4}\,hc\tilde{R}_{\mathrm{H}} \qquad \text{so} \qquad \boxed{\frac{I_{100}}{hc} = 10.9677\ \mathrm{cm^{-1}}}$$

(c) At $T = 25°\mathrm{C}$

$$\frac{kT}{hc} = \frac{(1.38\times10^{-23}\ \mathrm{J\,K^{-1}})\times(298\ \mathrm{K})\left(\frac{\mathrm{m}}{10^2\ \mathrm{cm}}\right)}{(6.63\times10^{-34}\ \mathrm{J\,s})\times(3.00\times10^8\ \mathrm{m\,s^{-1}})} = 207\,\mathrm{cm^{-1}}$$

so the thermal energy is readily available to ionize the state $n = 100$.

(d) Let $v_{\min}$ be the minimum speed required for collisional ionization. Then

$$\frac{1}{2}\frac{m_{\mathrm{H}}v_{\min}^2}{hc} = \frac{I_{100}}{hc}$$

$$v_{\min} = \left[\frac{2hc}{m_{\mathrm{H}}}\left(\frac{I_{100}}{hc}\right)\right]^{1/2}$$

$$= \sqrt{\frac{2(6.63\times10^{-34}\ \mathrm{J}\ s)\times(3.00\times10^8\ \mathrm{m\,s^{-1}})\times(10.97\ \mathrm{cm^{-1}})}{(1.008\times10^{-3}\ \mathrm{kg\,mol^{-1}})\times(6.022\times10^{23}\ \mathrm{mol^{-1}})^{-1}\times\left(\frac{\mathrm{m}}{10^2\,\mathrm{cm}}\right)}}$$

$\boxed{v_{\min} = 511\ \mathrm{m\,s^{-1}}}$ [very slow for an H atom]

(e) The geometric cross section calculated abov suggests that a neutral H atom in its ground state is likely to pass right by the $n = 100$ Rydberg atom, leaving it undisturbed, since it is largely empty space.

(f) The radial wavefunction for $n = 100$ will have 99 radial nodes and an extremely small amplitude above $\dfrac{r}{a_0} \approx 20$. For large values of n we expect the radial wavefunction [9A.12] to be governed largely by the product of ρ^{n-1} and $\mathrm{e}^{-\rho/2n}$ and thus to approach a smoothly decreasing function of distance, as the exponential will predominate over the power term.

10 Molecular structure

10A Valence-bond theory

Answers to discussion questions

10A.2 Promotion and hybridization are two modifications to what one might call "naïve" valence-bond (VB) theory, constructed to overcome obvious mismatches between predictions of that theory and observations. By "naïve" VB theory, I mean the assumption that the functions *A* and *B* that appear in a VB wavefunction [10A.2] are orbitals in free atoms occupied by unpaired electrons. Under that assumption, one would expect carbon normally to form only two bonds rather than the four bonds characteristic of it, because the electron configuration of carbon is $1s^22s^22p^2$ (with two unpaired electrons in two 2p orbitals). We can accommodate the tetravalence if we imagine that one of its 2s electrons is excited ("promoted") to the empty 2p orbital, giving a configuration of $1s^22s^12p^3$, which has four unpaired electrons (in the 2s and 2p orbitals) available for forming valence bonds. (There is, however, no actual excitation or promotion; it is just a convenient fiction.) Hybrid orbitals are invoked to account for the fact that valence bonds formed from the orbitals of free atoms would have different orientations in space (among other properties) than are commonly observed. For instance, the four bonds in CH_4 are observed to be equivalent and directed toward the corners of a regular tetrahedron. By contrast, bonds made from the three distinct 2p orbitals in carbon would be expected to be oriented at 90° angles from each other, and those three bonds would not be equivalent to the bond made from a 2s orbital. Hybrid atomic orbitals (in this case, sp^3 hybrids) are a sets of equivalent atomic orbitals formed by appropriate linear combinations of free-atom orbitals. Thus, the functions *A* and *B* in a VB wavefunction can be hybrid orbitals where appropriate.

It is worth remembering that molecules are different quantum mechanical systems than free atoms (obviously) and that there is, therefore, no *a priori* reason why the solution of the Schrödinger equation for molecules should have features in common with the solutions for free atoms. The experience of chemists developed before (and after) the advent of quantum mechanics, however, suggests that atoms really are building blocks of molecules. VB theory is a framework for generating approximate molecular wavefunctions consistent with chemists' concepts and experience.

10A.4 The part of the VB wavefunction that depends on spatial coordinates is given in eqn. 10A.2; let's call it $f(1,2)$:

$$f(1,2) = A(1)B(2) + A(2)B(1)$$

This function corresponds to the lowest-energy way for orbitals on two different atoms to share two electrons. The wavefunction is a product of spatial and spin portions:

$$\psi(1,2) = f(1,2)\sigma(1,2)$$

The Pauli principle requires that the wavefunction must be antisymmetric (*i.e.*, change sign) upon interchange of particle labels: $\psi(2,1) = -\psi(1,2)$. Because $f(2,1) = +f(1,2)$ (*i.e.*, the spatial factor is symmetric), the spin part must be antisymmetric

$$\sigma(2,1) = -\sigma(1,2)$$

The antisymmetric spin wavefunction has paired spins:

$$\sigma(1,2) = \{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}/2^{1/2}\,.$$

In summary, the lowest-energy VB wavefunction has a symmetric part that it depends on spatial coordinates, so it must have an antisymmetric spin part, which requires paired spins.

Solutions to exercises

10A.1(b) Each N atom has two sp-hybrid orbitals and two unhybridized orbitals. Label the orbitals on nitrogen nucleus A sp_{1A}, sp_{2A}, p_{xA}, and p_{yA}. The VB wavefunction that represents the triple bond in N_2 is

$$\boxed{\begin{aligned}\psi = {}&\{sp_{1A}(1)sp_{1B}(2) + sp_{1A}(2)sp_{1B}(1)\}\\ &\times \{p_{xA}(3)p_{xB}(4) + p_{xA}(4)p_{xB}(3)\} \times \{p_{yA}(5)p_{yB}(6) + p_{yA}(6)p_{yB}(5)\}\end{aligned}}$$

Or rather, the part of the wavefunction that depends on spatial coordinates depends on terms of this form. The full VB wavefunction would include spin terms and would be properly antisymmetric to account for the indistinguishability of electrons.

Comment. The lone pairs would be represented by paired electrons in the hybrid orbitals not used for bonding:

$$\{sp_{2\mathrm{A}}(7)sp_{2\mathrm{A}}(8)\} \times \{sp_{2\mathrm{B}}(9)sp_{2\mathrm{B}}(10)\}$$

10A.2(b) Each N atom has two sp-hybrid orbitals and two unhybridized orbitals. Label the orbitals on nitrogen nucleus A $sp_{1\mathrm{A}}$, $sp_{2\mathrm{A}}$, $p_{x\mathrm{A}}$, and $p_{y\mathrm{A}}$. The VB wavefunction that represents the triple bond in N_2 is

$$\psi_{\mathrm{VB}} = \{sp_{1\mathrm{A}}(1)sp_{1\mathrm{B}}(2) + sp_{1\mathrm{A}}(2)sp_{1\mathrm{B}}(1)\}$$
$$\times \{p_{x\mathrm{A}}(3)p_{x\mathrm{B}}(4) + p_{x\mathrm{A}}(4)p_{x\mathrm{B}}(3)\} \times \{p_{y\mathrm{A}}(5)p_{y\mathrm{B}}(6) + p_{y\mathrm{A}}(6)p_{y\mathrm{B}}(5)\}$$

Or rather, the part of the wavefunction that depends on spatial coordinates depends on terms of this form. The full VB wavefunction would include spin terms and would be properly antisymmetric to account for the indistinguishability of electrons. Call the wavefunction that corresponds to N^+N^- ψ_1:

$$\psi_1 = \{sp_{1\mathrm{A}}(1)sp_{1\mathrm{B}}(2) + sp_{1\mathrm{A}}(2)sp_{1\mathrm{B}}(1)\} \times \{p_{x\mathrm{A}}(3)p_{x\mathrm{B}}(4) + p_{x\mathrm{A}}(4)p_{x\mathrm{B}}(3)\} \times p_{y\mathrm{A}}(5)p_{y\mathrm{A}}(6\ )$$

Similarly, call the wavefunction that corresponds to N^+N^- ψ_2:

$$\psi_2 = \{sp_{1\mathrm{A}}(1)sp_{1\mathrm{B}}(2) + sp_{1\mathrm{A}}(2)sp_{1\mathrm{B}}(1)\} \times p_{x\mathrm{B}}(3)p_{x\mathrm{B}}(4) \times p_{y\mathrm{B}}(5)p_{y\mathrm{B}}(6\ )$$

(ψ_1 and ψ_2 would similarly also have terms that treat nuclei A and B equivalently, *i.e.*, that have the positive charges on nucleus B rather than A, as well as spin terms and proper antisymmetry with respect to interchanging electron labels.) The wavefunction corresponding to the resonance hybrid is

$$\boxed{\psi = a\psi_{\mathrm{VB}} + b\psi_1 + c\psi_2}$$

where *a, b,* and *c* are coefficients determined by the variation principle and normalization.

10A.3(b) In SO_2 there are two localized S–O σ bonds formed from S(3sp^2) and O(2sp^2) orbitals. There is a π bond that exhibits resonance and that can be described by the following superposition (properly antisymmetrized, of course):

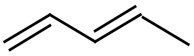
$$\psi(\pi\text{ bond}) = \mathrm{S3p}_z\ \mathrm{O2p}_{z,\mathrm{A}} + \mathrm{S3p}_z\ \mathrm{O2p}_{z,\mathrm{B}}$$

The sulfur also has a lone pair in a 3sp^2 hybrid orbital.

In SO_3, there are three localized S–O σ bonds formed from S(3sp^2) and O(2sp^2) orbitals. There is a π bond that exhibits resonance and that can be described by the superposition

$$\psi(\pi\text{ bond}) = \mathrm{S3p}_z\ \mathrm{O2p}_{z,\mathrm{A}} + \mathrm{S3p}_z\ \mathrm{O2p}_{z,\mathrm{B}} + \mathrm{S3p}_z\ \mathrm{O2p}_{z,\mathrm{C}}$$

10A.4(b) Carbon atoms 1-4 are sp^2 hybridized; the remaining C atom is sp^3 hybridized. The C–H σ bonds are formed by the overlap of carbon hybrid orbitals with H1s orbitals. The C–C σ bonds are formed by the overlap of carbon hybrid orbitals. The C–C π bonds are formed by the overlap of C2p orbitals. This description predicts double bonds between carbon atoms 1 & 2 and 3 & 4. Unlike a simple molecular-orbital description, this description attributes no double-bond character to the bond between carbons 2 & 3.



10A.5(b) Form the integral

$$\int h_1 {}^* h_2 \mathrm{d}\tau = \int \{(\sin\zeta)\mathrm{s} + (\cos\zeta)\mathrm{p}\}^*\{(\cos\zeta)\mathrm{s} - (\sin\zeta)\mathrm{p}\}\mathrm{d}\tau$$

If the integral vanishes, then the functions are orthogonal. (Note: the angle ζ is a parameter; it is not an angular coordinate in dτ.) Evaluating the integral yields

$$\int h_1 {}^* h_2 \mathrm{d}\tau = \sin\zeta\cos\zeta\int(|\mathrm{s}|^2 - |\mathrm{p}|^2)\mathrm{d}\tau + \cos^2\zeta\int \mathrm{p}^*\mathrm{s}\,\mathrm{d}\tau - \sin^2\zeta\int \mathrm{s}^*\mathrm{p}\,\mathrm{d}\tau$$

Because the s and p orbitals are themselves normalized, the integrals of $|\mathrm{s}|^2$ and $|\mathrm{p}|^2$ are one, so the first integral in this expression vanishes. Because the s and p orbitals are orthogonal, the other two orbitals also vanish.

10A.6(b) Normalization requires

$$\int \psi^*\psi\mathrm{d}\tau = 1$$

Let $\psi_1 = N_1 h_1 = N_1\{(\sin\zeta)\mathrm{s} + (\cos\zeta)\mathrm{p}\}$

Solve for the normalization constant N_1:

$$1 = N_1^{\ 2}\int\{(\sin\zeta)\mathrm{s} + (\cos\zeta)\mathrm{p}\}^*\{(\sin\zeta)\mathrm{s} + (\cos\zeta)\mathrm{p}\}\mathrm{d}\tau$$

so $$\frac{1}{N_1^{\,2}} = \sin^2\zeta\int|\mathrm{s}|^2\,\mathrm{d}\tau + \cos^2\zeta\int|p|^2\,\mathrm{d}\tau + \sin\zeta\cos\zeta\int(\mathrm{s}^*\mathrm{p}+\mathrm{p}^*\mathrm{s})\mathrm{d}\tau$$
$$= \sin^2\zeta + \cos^2\zeta = 1.$$

In the last step, we used the fact that the s and p orbitals are orthogonal and normalized. Thus

$\boxed{N_1 = 1}$ and $\boxed{\psi = (\sin\zeta)\mathrm{s} + (\cos\zeta)\mathrm{p}}$

Let $\psi_2 = N_2h_2 = N_2\{(\cos\zeta)\mathrm{s} - (\sin\zeta)\mathrm{p}\}$

Solve for the normalization constant N_2:

$$1 = N_2^{\,2}\int\{(\cos\zeta)\mathrm{s} - (\sin\zeta)\mathrm{p}\}^*\{(\cos\zeta)\mathrm{s} - (\sin\zeta)\mathrm{p}\}\mathrm{d}\tau$$

so $$\frac{1}{N_2^{\,2}} = \cos^2\zeta\int|\mathrm{s}|^2\,\mathrm{d}\tau + \sin^2\zeta\int|p|^2\,\mathrm{d}\tau - \sin\zeta\cos\zeta\int(\mathrm{p}^*\mathrm{s}+\mathrm{s}^*\mathrm{p})\mathrm{d}\tau$$
$$= \cos^2\zeta + \sin^2\zeta = 1$$

Thus

$\boxed{N_2 = 1}$ and $\boxed{\psi = (\cos\zeta)\mathrm{s} - (\sin\zeta)\mathrm{p}}$

In other words, the functions were already normalized.

Solutions to problem

10A.2 One approach is to construct the explicit forms of the orbitals and find the values of ϕ that maximize the squares of their magnitudes. We need the component unhybridized orbitals, put together from the radial and angular functions listed in Tables 9A.1 and 8C.1:

$$2\mathrm{s} = R_{20}Y_{00} = \frac{1}{8^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\times(2-\rho)\mathrm{e}^{-\rho/2}\times\left(\frac{1}{4\pi}\right)^{1/2} = \left(\frac{1}{32\pi}\right)^{1/2}\left(\frac{Z}{a}\right)^{3/2}(2-\rho)\mathrm{e}^{-\rho/2}$$

Use eqns. 9A.22 to write the p_x and p_y orbitals in terms of the complex hydrogenic orbitals defined in eqn. 9A.21:

$$2\mathrm{p}_x = -\frac{1}{2^{1/2}}R_{21}(Y_{1,+1} - Y_{1,-1})$$
$$= -\frac{1}{2^{1/2}}\times\frac{1}{24^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\rho\mathrm{e}^{-\rho/2}\times\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta(-\mathrm{e}^{+\mathrm{i}\phi} - \mathrm{e}^{-\mathrm{i}\phi})$$
$$= \left(\frac{1}{32\pi}\right)^{1/2}\left(\frac{Z}{a}\right)^{3/2}\rho\mathrm{e}^{-\rho/2}\sin\theta\cos\phi$$

$$2\mathrm{p}_y = \frac{\mathrm{i}}{2^{1/2}}R_{21}(Y_{1,+1} + Y_{1,-1})$$
$$= \frac{\mathrm{i}}{2^{1/2}}\times\frac{1}{24^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\rho\mathrm{e}^{-\rho/2}\times\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta(-\mathrm{e}^{+\mathrm{i}\phi} + \mathrm{e}^{-\mathrm{i}\phi})$$
$$= \left(\frac{1}{32\pi}\right)^{1/2}\left(\frac{Z}{a}\right)^{3/2}\rho\mathrm{e}^{-\rho/2}\sin\theta\sin\phi$$

where $\rho = \dfrac{2Zr}{2a} = \dfrac{Zr}{a}$ [9A.11a]

In forming each hybrid, we neglect the factor $\left(\dfrac{1}{32\pi}\right)^{1/2}\left(\dfrac{Z}{a}\right)^{3/2}\mathrm{e}^{-\rho/2}$ common to each component; an angle-independent multiplicative term cannot influence the angle at which the hybrid is maximal.

Next, form the hybrids, using eqn. 10A.7:

$h_1 = \mathrm{s} + 2^{1/2}\mathrm{p}_y = (2-\rho) + 2^{1/2}(\rho\sin\theta\sin\phi) = 2 + \rho(2^{1/2}\sin\theta\sin\phi - 1)$

$$h_2 = \mathrm{s} + \left(\frac{3}{2}\right)^{1/2} \mathrm{p}_x - \left(\frac{1}{2}\right)^{1/2} \mathrm{p}_y = (2-\rho) + \left(\frac{3}{2}\right)^{1/2} \rho\sin\theta\cos\phi - \left(\frac{1}{2}\right)^{1/2} \rho\sin\theta\sin\phi$$

$$= 2 + \rho\left(\frac{3^{1/2}\cos\phi - \sin\phi}{2^{1/2}}\sin\theta - 1\right)$$

and $$h_3 = \mathrm{s} - \left(\frac{3}{2}\right)^{1/2} \mathrm{p}_x - \left(\frac{1}{2}\right)^{1/2} \mathrm{p}_y = (2-\rho) - \left(\frac{3}{2}\right)^{1/2} \rho\sin\theta\cos\phi - \left(\frac{1}{2}\right)^{1/2} \rho\sin\theta\sin\phi$$

$$= 2 - \rho\left(\frac{3^{1/2}\cos\phi + \sin\phi}{2^{1/2}}\sin\theta + 1\right)$$

To find the angle ϕ at which the hybrids have maximum probability, differentiate with respect to ϕ, and set the derivative equal to zero, because positive maxima and negative minima in the hybrid orbitals correspond to maxima in the probability. Differentiation would work even for h_1, but it is unnecessary there. One can see by inspection that the function is maximized when $\sin\phi$ is maximal, namely at $\phi = \pi/2$ (90°). It should come as no surprise that this orbital points along the positive y-axis.

$$\frac{\partial h_2}{\partial\phi} = 0 = \left(\frac{\rho\sin\theta}{2^{1/2}}\right)(-3^{1/2}\sin\phi - \cos\phi)$$

so $$\frac{\sin\phi}{\cos\phi} = -\frac{1}{3^{1/2}} = \tan\phi \qquad \text{or} \qquad \phi = 5\pi/6 \text{ or } 11\pi/6 \ (150° \text{ or } 330°)\ .$$

Of these, $11\pi/6$ (330°) is a maximum and $5\pi/6$ a minimum. The larger amplitude is at the maximum ($11\pi/6$ or 330°). Finally

$$\frac{\partial h_3}{\partial\phi} = 0 = -\left(\frac{\rho\sin\theta}{2^{1/2}}\right)(-3^{1/2}\sin\phi + \cos\phi)$$

so $$\frac{\sin\phi}{\cos\phi} = \frac{1}{3^{1/2}} = \tan\phi \qquad \text{or} \qquad \phi = \pi/6 \text{ or } 7\pi/6 \ (30° \text{ or } 210°)\ .$$

Of these, $7\pi/6$ (210°) is a maximum and corresponds to the larger amplitude. The angles 90°, 210°, and 330° are 120° apart.

10B Principles of molecular orbital theory

Answers to discussion question

10B.2 The building-up principle for molecules is described in Topic 10C.1. That principle includes Hund's rule of maximum multiplicity, first introduced in the context of atomic orbitals in Topic 9B.2(a). Recall that Hund's rule says that configurations with parallel spins are lower in energy than configurations that have paired spins when the highest occupied orbitals are degenerate. In the case of atoms, most energy levels are degenerate (all except s orbitals), so parallel-spin configurations are common. Degenerate molecular orbitals are much less common, though. Therefore Hund's rule, though still valid for molecules, comes into play much less frequently.

Solutions to exercises

10B.1(b) $$\int \psi^2\,\mathrm{d}\tau = N^2\int (\psi_\mathrm{A} + \lambda\psi_\mathrm{B} + \lambda'\psi'_\mathrm{B})^2\,\mathrm{d}\tau = 1$$

$$= N^2\int \{\psi_\mathrm{A}^2 + \lambda^2\psi_\mathrm{B}^2 + (\lambda'\psi'_\mathrm{B})^2 + 2\lambda\psi_\mathrm{A}\psi_\mathrm{B} + 2\lambda'\psi_\mathrm{A}\psi'_\mathrm{B} + 2\lambda\lambda'\psi_\mathrm{B}\psi'_\mathrm{B}\}\mathrm{d}\tau$$

Defining $\int \psi_\mathrm{A}\psi_\mathrm{B}\mathrm{d}\tau = S$ and $\int \psi_\mathrm{A}\psi'_\mathrm{B}\mathrm{d}\tau = S'$

the normalization integral becomes

$$1 = N^2\{1 + \lambda^2 + (\lambda')^2 + 2\lambda S + 2\lambda' S'\}$$

Hence $\boxed{N=\left(\dfrac{1}{1+\lambda^2+(\lambda')^2+2\lambda S+2\lambda' S'}\right)^{1/2}}$

10B.2(b) Let $\psi_1 = N(0.727A + 0.144B)$ and $\psi_2 = aA + bB$

First, let us normalize ψ_1:

$$\int \psi_1{}^*\psi_1\mathrm{d}\tau = 1 = N^2\int(0.727A+0.144B)^*(0.727A+0.144B)\mathrm{d}\tau$$

$$0.529\int|A|^2\,\mathrm{d}\tau+0.0207\int|B|^2\,\mathrm{d}\tau+0.110\int B^*A\mathrm{d}\tau+0.110\int A^*B\mathrm{d}\tau=\frac{1}{N^2}$$

The first two integrals are 1 due to normalization and the latter two are the overlap integral, $S = 0.117$. So

$$0.529+0.0207+2\times0.110\times0.117=\frac{1}{N^2}=0.552$$

so $\boxed{N = 1.35}$ which makes $\boxed{\psi_1 = 0.979A + 0.194B}$

Orthogonality of the two molecular orbitals requires

$$\int \psi_1{}^*\psi_2\mathrm{d}\tau = 0 = N\int(0.727A+0.144B)^*(aA+bB)\mathrm{d}\tau$$

Dividing by N yields

$$0.727a\int|A|^2\,\mathrm{d}\tau+0.144b\int|B|^2\,\mathrm{d}\tau+0.144a\int B^*A\mathrm{d}\tau+0.727b\int A^*B\mathrm{d}\tau=0$$

$$0.727a + 0.144b + 0.144a\times0.117 + 0.727b\times0.117 = 0 = 0.744a + 0.229b$$

Normalization of ψ_2 requires

$$\int \psi_2{}^*\psi_2\mathrm{d}\tau = 1 = \int(aA+bB)^*(aA+bB)\mathrm{d}\tau$$

$$a^2\int|A|^2\,\mathrm{d}\tau+b^2\int|B|^2\,\mathrm{d}\tau+ab\int B^*A\mathrm{d}\tau+ab\int A^*B\mathrm{d}\tau=1$$

So $a^2 + b^2 + 2ab\times0.117 = 1 = a^2 + b^2 + 0.234ab$

We have two equations in the two unknown coefficients a and b. Solve the first equation for a in terms of b:

$$a = -0.229b/0.744 = -0.308b$$

Substitute this result into the second (quadratic) equation:

$$1 = (-0.308b)^2 + b^2 + 0.234(-0.308b)b = 1.022b^2$$

So $\boxed{b = 0.989}$ $\boxed{a = -0.304}$ and $\boxed{\psi_2 = -0.304A + 0.989B}$

10B.3(b) $E_{\mathrm{H}} = E_1 = -hc\tilde{R}_{\mathrm{H}}$ [9A.14]

Draw up the following table using the data in the question and using

$$\frac{e^2}{4\pi\varepsilon_0 R}=\frac{e^2}{4\pi\varepsilon_0 a_0}\times\frac{a_0}{R}=\frac{e^2}{4\pi\varepsilon_0\times(4\pi\varepsilon_0\hbar^2/m_{\mathrm{e}}e^2)}\times\frac{a_0}{R}$$

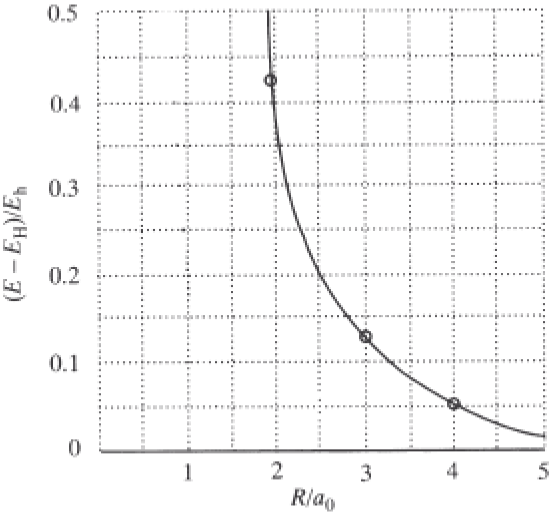
$$=\frac{m_{\mathrm{e}}e^4}{16\pi^2\varepsilon_0^2\hbar^2}\times\frac{a_0}{R}=E_{\mathrm{h}}\times\frac{a_0}{R}\quad\left[E_{\mathrm{h}}\equiv\frac{m_{\mathrm{e}}e^4}{16\pi^2\varepsilon_0^2\hbar^2}=2hc\tilde{R}_{\mathrm{H}}\right]$$

so that $\dfrac{e^2}{4\pi\varepsilon_0 R}\times\dfrac{1}{E_{\mathrm{h}}}=\dfrac{a_0}{R}$

Draw up the following table:

R / a_0	0	1	2	3	4	∞
$\dfrac{e^2}{4\pi\varepsilon_0 R}\times\dfrac{1}{E_{\mathrm{h}}}$	∞	1	0.500	0.333	0.250	0
$(V_1 - V_2)/ E_{\mathrm{h}}$	0	–0.007	0.031	0.131	0.158	0
$(E - E_{\mathrm{H}}) / E_{\mathrm{h}}$	∞	1.049	0.425	0.132	0.055	0

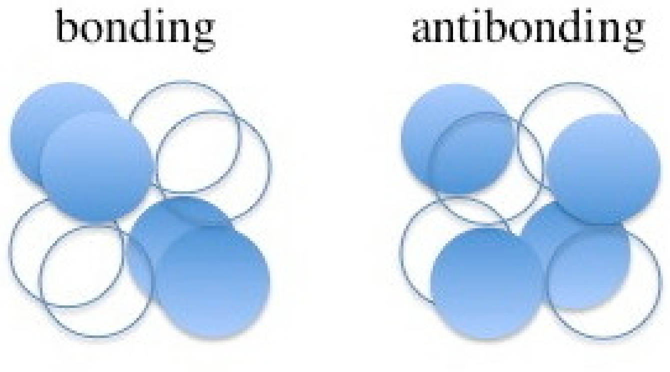
Figure 10B.1



The points are plotted in Figure 10B.1.

10B.4(b) Figure 10B.2 shows sketches of the orbitals in question. By inspection, one can see that the bonding orbital is even, $\boxed{\text{g}}$, with respect to inversion, and the antibonding orbital is odd, $\boxed{\text{u}}$.

Figure 10B.2



Solutions to problems

10B.2 $P = |\psi|^2\,\mathrm{d}\tau \approx |\psi|^2\,\delta\tau, \quad \delta\tau = 1.00\,\text{pm}^3$, where the wavefunction is [10B.2 and 9A.17]

$$\psi_\pm = N_\pm\left(\frac{1}{\pi a_0^3}\right)^{1/2}\{\mathrm{e}^{-|z|/a_0} \pm \mathrm{e}^{-|z-R|/a_0}\}$$

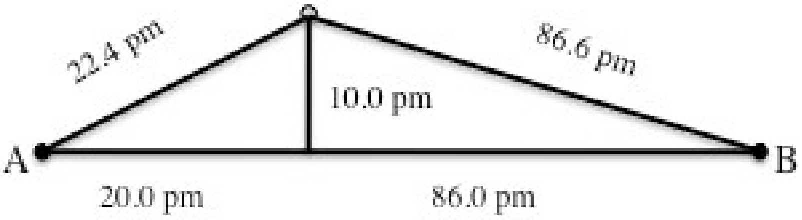
$$N_+ = \left(\frac{1}{2(1+S)}\right)^{1/2} = \left(\frac{1}{2(1+0.59)}\right)^{1/2} = 0.56$$

and $$N_- = \left(\frac{1}{2(1-S)}\right)^{1/2} = \left(\frac{1}{2(1-0.59)}\right)^{1/2} = 1.10 \ \text{[Example 10B.1]}$$

Hence $$P_\pm \approx N_\pm^2\left(\frac{1}{\pi a_0^3}\right)\{\mathrm{e}^{-r_\text{A}/a_0} \pm \mathrm{e}^{-r_\text{B}/a_0}\}^2\,\delta\tau$$

where r_A and r_B are measured from points A and B respectively, and A and B are 106 pm apart (Section 10B.1(b).) [Note: I am choosing to use the experimental equilibrium internuclear distance rather than that given by minimizing the approximate wavefunction. Using that internuclear distance is also a valid approach, one which would have R = 130 pm and would require using eqn. 10B.5a to compute S, which in turn would affect the normalization constants.] Point (d) is shown in Figure 10B.3 (with greater precision than the problem specifies).

Figure 10B.3



First, consider the bonding orbital, ψ_+

(a) $P_+ = (0.56)^2\left(\dfrac{1}{\pi(52.9\text{ pm})^3}\right)\{e^{-0/(52.9\text{ pm})} + e^{-106\text{ pm}/(52.9\text{ pm})}\}^2 \times 1.00\text{ pm}^3 = \boxed{8.7\times10^{-7}}$

(b) By symmetry (or by taking $z = 106$ pm), $P = \boxed{8.7\times10^{-7}}$

(c) $R/2 = 53$ pm, so $P_+\left(\frac{1}{2}R\right) = \boxed{3.6\times10^{-7}}$.

(d) From Figure 10.3, the point referred to lies at 22.4 pm from A and 86.6 pm from B.

Therefore, $P_+ = (0.56)^2\left(\dfrac{1}{\pi(52.9\text{ pm})^3}\right)(e^{-22.4/52.9} + e^{-86.6/52.9})^2 = \boxed{4.9\times10^{-7}}$

For the antibonding orbital, we proceed similarly.

(a) $P_- = (1.10)^2\left(\dfrac{1}{\pi(52.9\text{ pm})^3}\right)\{e^{-0/52.9} - e^{-106/52.9}\}^2 = \boxed{1.9\times10^{-6}}$

(b) By symmetry (or by taking $z = 106$ pm), $P = \boxed{1.9\times10^{-6}}$

(c) $\psi_-\left(\dfrac{1}{2}R\right) = 0$, so $P = \boxed{0}$

(d) $\psi_+^2 = (1.10)^2\left(\dfrac{1}{\pi(52.9\text{ pm})^3}\right)(e^{-22.4/52.9} - e^{-86.6/52.9})^2 = \boxed{5.5\times10^{-7}}$

10B.4 We are asked to compare, essentially, the energy difference between the bonding and antibonding molecular orbitals and the 1s hydrogenic atomic orbital. Let us call the first difference ΔE_{bond} and the latter ΔE_{anti}:

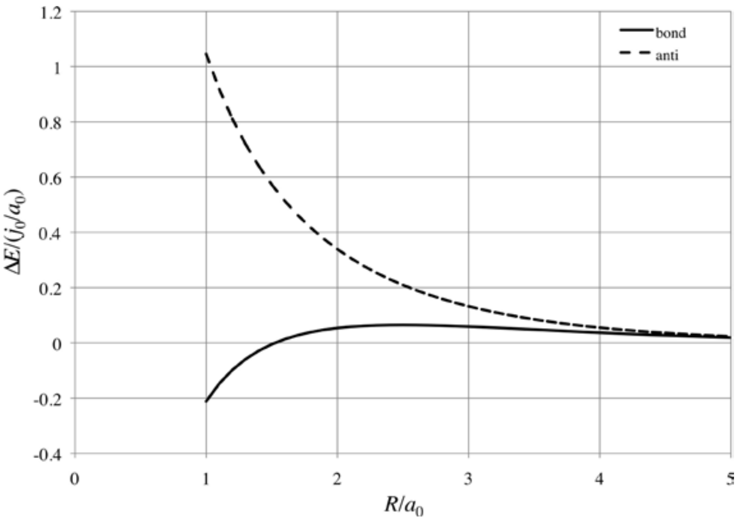
$$\Delta E_{\text{bond}} = E_{\text{H1s}} - E_{1\sigma} = \frac{j+k}{1+S} - \frac{j_0}{R} \quad [10\text{B}.4]$$

and
$$\Delta E_{\text{anti}} = E_{2\sigma} - E_{\text{H1s}} = -\frac{j+k}{1+S} + \frac{j_0}{R} \quad [10\text{B}.7]$$

Eqns. 10B.5 give expressions for j, k, and S as functions of R. One can draw up a spreadsheet computing j, k, and S as functions of R, and from those values form the energy differences. Here are selected values from the spreadsheet:

R/a_0	S	$\dfrac{j}{j_0/a_0}$	$\dfrac{k}{j_0/a_0}$	$\dfrac{\Delta E_{\text{bond}}}{j_0/a_0}$	$\dfrac{\Delta E_{\text{anti}}}{j_0/a_0}$
0	1	1	1	–∞	∞
1	0.858	0.729	0.736	–0.212	1.045
2	0.586	0.473	0.406	0.054	0.339
3	0.349	0.330	0.199	0.059	0.132
4	0.189	0.250	0.092	0.037	0.055
5	0.097	0.200	0.040	0.019	0.023
∞	0	0	0	0	0

Figure 10B.4



The points are plotted in Figure 10B.4. At all internuclear distances, the energy of the antibonding orbital is greater than that of an isolated hydrogen atom, so its effect on bonding is to destabilize the bond. Furthermore, the absolute value of $E - E_H$ is always greater for the antibonding orbital than for the bonding orbital so that occupancy of the antibonding orbital by one electron destabilizes a bond more than occupancy of the bonding orbital stabilizes it.

10B.6

$$\psi_{\pm} = N_{\pm}\left(\frac{1}{\pi a_0^3}\right)^{1/2}\{e^{-|z|/a_0} \pm e^{-|z-R|/a_0}\} \text{ [10B.2 and 9A.17]}$$

where $N_+ = \left(\frac{1}{2(1+S)}\right)^{1/2} = \left(\frac{1}{2(1+0.586)}\right)^{1/2} = 0.56$

and $N_- = \left(\frac{1}{2(1-S)}\right)^{1/2} = \left(\frac{1}{2(1-0.586)}\right)^{1/2} = 1.10$ [Example 10B.1]

We obtain the probability densities from ψ_+^2 and ψ_-^2. Hence

$$\psi_{\pm}^2 = N_{\pm}^2\left(\frac{1}{\pi a_0^3}\right)\{e^{-|z|/a_0} \pm e^{-|z-R|/a_0}\}^2$$

The "atomic" density is

$$\rho_{\text{atomic}} = \frac{1}{2}\left(\psi_{1\text{sA}}{}^2 + \psi_{1\text{sB}}\right)^2 = \frac{1}{2}\times\left(\frac{1}{\pi a_0^3}\right)(e^{-2r_A/a_0} + e^{-2r_B/a_0})$$

with z measured from A along the axis toward B.

The difference density is $\delta\psi_{\pm}^2 = \psi_{\pm}^2 - \rho_{\text{atomic}}$

We use a spreadsheet to draw the following table with R = 106 pm and a_0 = 52.9 pm:

z/pm	–100	–80	–60	–40	–20	0	20	40
$\psi_+ \times 10^4$ / pm$^{-3/2}$	1.41	2.06	3.01	4.39	6.40	9.35	7.26	6.23
$\psi_- \times 10^4$ / pm$^{-3/2}$	2.10	3.07	4.48	6.54	9.55	13.93	7.87	2.94
$\psi_+^2 \times 10^7$ / pm^{-3}	0.20	0.42	0.90	1.92	4.09	8.72	5.27	3.88
$\psi_-^2 \times 10^7$ / pm^{-3}	0.44	0.94	2.01	4.27	9.11	19.40	6.17	0.85
$\rho_{\text{atomic}} \times 10^7$ / pm^{-3}	0.25	0.53	1.13	2.41	5.15	10.93	5.47	3.26
$\delta\psi_+^2 \times 10^7$ / pm^{-3}	–0.05	–0.11	–0.23	–0.49	–1.05	–2.20	–0.20	0.62
$\delta\psi_-^2 \times 10^7$ / 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
$\psi_+ \times 10^4$ / pm$^{-3/2}$	6.10	6.85	8.59	7.17	4.91	3.37	2.31	1.58
$\psi_- \times 10^4$ / pm$^{-3/2}$	–1.57	–6.30	–11.95	–10.69	–7.33	–5.02	–3.44	–2.36
$\psi_+^2 \times 10^7$ / pm^{-3}	3.73	4.71	7.42	5.10	2.39	1.12	0.53	0.25

$\psi_-^2 \times 10^7$ / pm^{-3}	0.25	4.02	14.41	11.34	5.32	2.50	1.17	0.55
$\rho_{\text{atomic}} \times 10^7$ / pm^{-3}	3.01	4.58	8.88	6.40	3.00	1.41	0.66	0.31
$\delta\psi_+^2 \times 10^7$ / pm^{-3}	0.70	0.13	–1.46	–1.29	–0.61	–0.29	–0.14	–0.06
$\delta\psi_-^2 \times 10^7$ / pm^{-3}	–2.76	–0.56	5.54	4.95	2.33	1.09	0.51	0.24

The wavefunctions are plotted in Figure 10B.5(a), the densities in Figure 10.5(b), and the difference densities in Figure 10B.5(c).

Figure 10B.5(a)

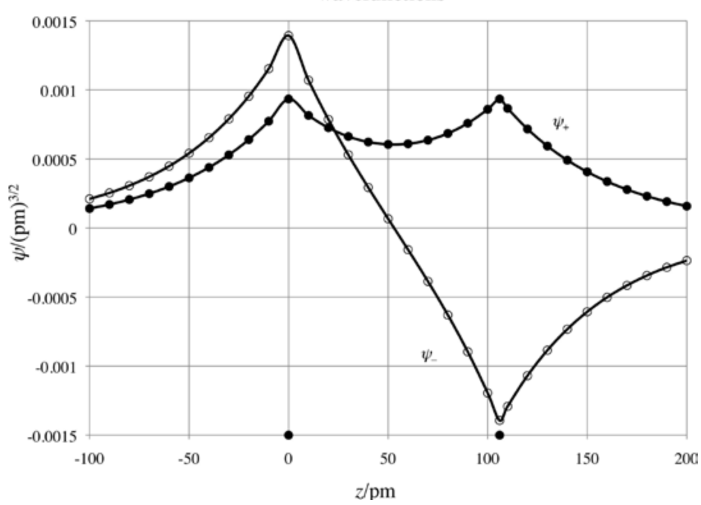


Figure 10B.5(b)

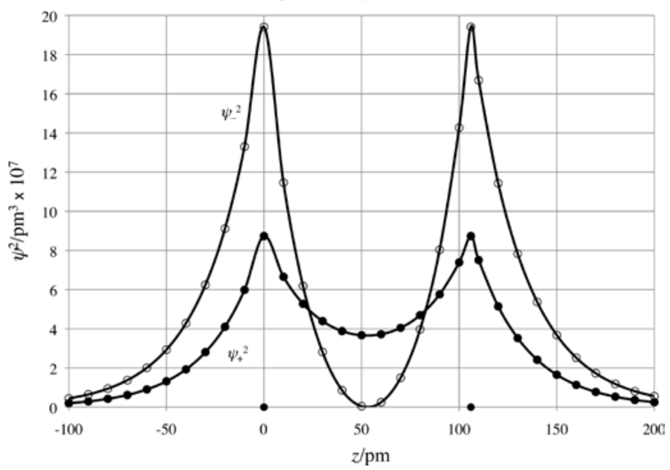
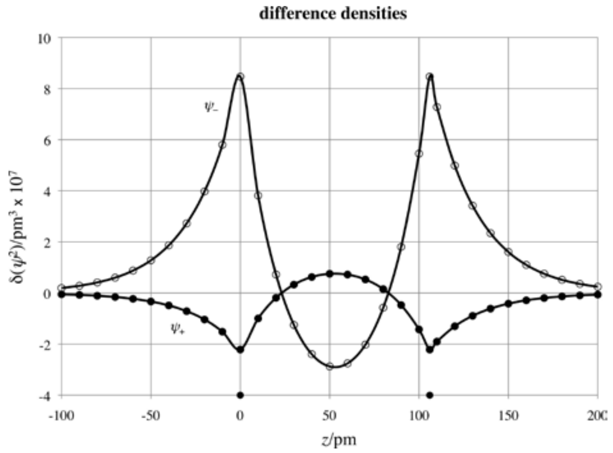


Figure 10B.5(c)



10C Homonuclear diatomic molecules

Answers to discussion questions

10C.2 The building-up principle for homonuclear diatomic molecules is essentially the same as for atoms, but the diatomic molecular orbitals used in the former are different in name and in nature than the atomic orbitals used in the latter. One needs a diagram of energy levels and degeneracies. (For diatomic molecules, these energy levels are either nondegenerate (for σ bonds) or doubly degenerate (for all others).) Populate the orbitals with electrons, placing each successive electron in the lowest-energy orbital available, no more than two electrons per orbital. Hund's rule tells us to singly populate different degenerate orbitals (with electrons that have parallel spins) before pairing two electrons in the same degenerate orbital.

10C.4 Molecular orbitals are made up of linear combinations of atomic orbitals of similar energy and symmetry. The s and p atomic orbitals have distinctly different energies, so the molecular orbitals that result from linear combinations primarily of s orbitals have very little character of the higher-energy p orbitals and vice versa. (In addition, only a p orbital along the internuclear axis has the right symmetry to combine with an s orbital to make a molecular orbital; the others have the wrong symmetry, even if they did have similar energy.)

Solutions to exercises

10C.1(b) Refer to Figure 10C.11 of the text. Place two of the valence electrons in each orbital starting with the lowest-energy orbital, until all valence electrons are used. Apply Hund's rule to the filling of degenerate orbitals.

(i) F_2^- (15 electrons) $\boxed{1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^4 2\sigma_u^1,\ b=0.5}$

(ii) N_2 (10 electrons) $\boxed{1\sigma_g^2 1\sigma_u^2 1\pi_u^4 2\sigma_g^2,\ b=3}$

(iii) O_2^{2-} (14 electrons) $\boxed{1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^4,\ b=1}$

10C.2(b) Refer to Figure 10C.11 of the text.

Li_2 (2 electrons):	$1\sigma_g^2$	$b=1$
Be_2 (4 electrons):	$1\sigma_g^2 1\sigma_u^2$	$b=0$

The bond orders of Li_2 and Be_2 are respectively 0 and 1; so $\boxed{Li_2}$ should have the greater bond dissociation energy. The experimental values are approximately and 110 and 59 kJ mol^{-1} respectively.

10C.3(b) Refer to Figure 10C.11 of the text.

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 $\mathrm{O_2^+}$ is added to an antibonding orbital, thus increasing the length. So the sequence $\boxed{\mathrm{O_2^+, O_2, O_2^-, O_2^{2-}}}$ has progressively longer bonds.

10C.4(b) Refer to Figure 10C.11 of the text.

$\mathrm{Li_2^+}$ (1 electrons):	$1\sigma_g^1$	$\boxed{b=0.5}$
$\mathrm{Be_2^+}$ (3 electrons):	$1\sigma_g^2 1\sigma_u^1$	$\boxed{b=0.5}$
$\mathrm{B_2^+}$ (5 electrons):	$1\sigma_g^2 1\sigma_u^2 1\pi_u^1$	$\boxed{b=0.5}$
$\mathrm{C_2^+}$ (7 electrons):	$1\sigma_g^2 1\sigma_u^2 1\pi_u^3$	$\boxed{b=1.5}$
$\mathrm{N_2^+}$ (9 electrons):	$1\sigma_g^2 1\sigma_u^2 1\pi_u^4 2\sigma_g^1$	$\boxed{b=2.5}$
$\mathrm{O_2^+}$ (11 electrons):	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^1$	$\boxed{b=2.5}$
$\mathrm{F_2^+}$ (13 electrons):	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^3$	$\boxed{b=1.5}$

$\mathrm{Li_2^-}$ (3 electrons):	$1\sigma_g^2 1\sigma_u^1$	$\boxed{b=0.5}$
$\mathrm{Be_2^-}$ (5 electrons):	$1\sigma_g^2 1\sigma_u^2 1\pi_u^1$	$\boxed{b=0.5}$
$\mathrm{B_2^-}$ (7 electrons):	$1\sigma_g^2 1\sigma_u^2 1\pi_u^3$	$\boxed{b=1.5}$
$\mathrm{C_2^-}$ (9 electrons):	$1\sigma_g^2 1\sigma_u^2 1\pi_u^4 2\sigma_g^1$	$\boxed{b=2.5}$
$\mathrm{N_2^-}$ (11 electrons):	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^1$	$\boxed{b=2.5}$
$\mathrm{O_2^-}$ (13 electrons):	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^3$	$\boxed{b=1.5}$
$\mathrm{F_2^-}$ (15 electrons):	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^4 2\sigma_u^1$	$\boxed{b=0.5}$

Comment. Note that each diatomic cation is isoelectronic with the diatomic anion of the next element, and has the same configuration and bond order.

10C.5(b) Refer to Figure 10C.11 of the text and to the configurations given in Exercise 10C.4b. The LUMO is the next energy level not included in the configuration.

$\mathrm{Li_2^+}$:	$\boxed{1\sigma_u}$	$\mathrm{Li_2^-}$:	$\boxed{1\pi_u}$
$\mathrm{Be_2^+}$:	$\boxed{1\pi_u}$	$\mathrm{Be_2^-}$:	$\boxed{2\sigma_g}$
$\mathrm{B_2^+}$:	$\boxed{2\sigma_g}$	$\mathrm{B_2^-}$:	$\boxed{2\sigma_g}$
$\mathrm{C_2^+}$:	$\boxed{2\sigma_g}$	$\mathrm{C_2^-}$:	$\boxed{1\pi_g}$
$\mathrm{N_2^+}$:	$\boxed{1\pi_g}$	$\mathrm{N_2^-}$:	$\boxed{2\sigma_u}$
$\mathrm{O_2^+}$:	$\boxed{2\sigma_u}$	$\mathrm{O_2^-}$:	$\boxed{2\sigma_u}$
$\mathrm{F_2^+}$:	$\boxed{2\sigma_u}$	$\mathrm{F_2^-}$:	$\boxed{3\sigma_g}$

Comment. Note that each diatomic cation is isoelectronic with the diatomic anion of the next element, and has the same configuration and LUMO.

10C.6(b) Energy is conserved, so when the photon is absorbed, its energy is transferred to the electron. Part of that energy overcomes the binding energy (ionization energy) and the remainder is manifest as the now freed electron's kinetic energy. Then the speed is obtained from the kinetic energy:

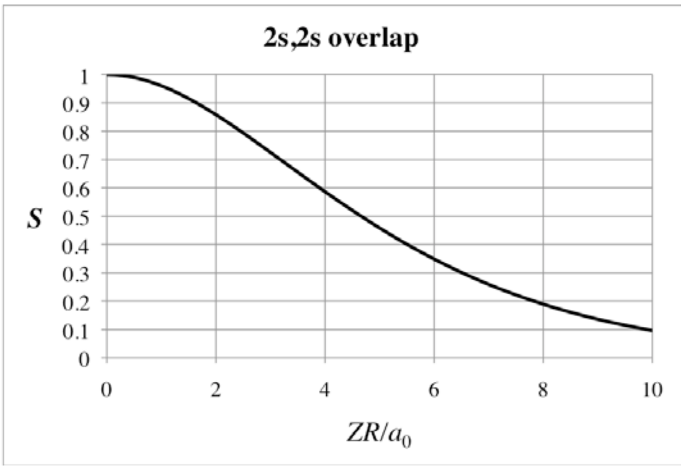
$$E_{\text{photon}} = I + E_{\text{kinetic}}$$

so
$$E_{\text{kinetic}} = E_{\text{photon}} - I = \frac{mv^2}{2}$$

$$v = \sqrt{\frac{2(E_{\text{photon}} - I)}{m}} = \sqrt{\frac{2(21-12)\ \text{eV}}{9.11\times10^{-31}\ \text{kg}} \times \frac{1.602\times10^{-19}\ \text{J}}{1\ \text{eV}}} = \boxed{1.8\times10^{6}\ \text{m s}^{-1}}$$

10C.7(b) The expression in *Brief illustration* 10C.2 cannot be solved analytically for R, but solving it numerically or graphically is fairly easy. In a spreadsheet, plot S as a function of ZR/a_0, and look for the value of ZR/a_0 where $S = 0.20$. One can change the scale of the plot and the spacing of grid points to find the graphical solution to arbitrary precision.

Figure 10C.1



By inspection of the plot (Figure 10C.1), $S = 0.20$ at approximately $ZR/a_0 = 7.8$. Or one could inspect the spreadsheet in the neighborhood of those points:

ZR/a_0	7.70	7.75	7.80	7.85	7.90
S	0.208	0.205	0.202	0.199	0.195

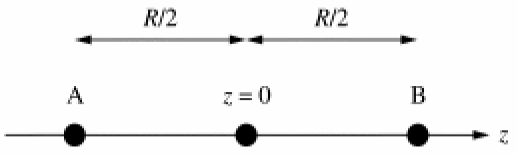
We can see that the value of S crosses $S = 0.20$ between the values of $ZR/a_0 = 7.80$ and 7.85. So to two significant figures, $ZR/a_0 = 7.8$, agreeing with the graphical estimate.

(i) For H_2, $Z = 1$, so $R = 7.8a_0/Z = 7.8\times5.29\times10^{-11}\ \text{m} / 1 = \boxed{4.1\times10^{-10}\ \text{m} = 0.41\ \text{nm}}$

(ii) For He_2, $Z = 2$, so $R = 7.8a_0/Z = 7.8\times5.29\times10^{-11}\ \text{m} / 2 = \boxed{2.1\times10^{-10}\ \text{m} = 0.21\ \text{nm}}$

Solutions to problems

10C.2 The question asks about bonding and antibonding LCAO-MOs made from 2p atomic orbitals.



(a) With spatial dimensions in units (multiples) of a_0, the atomic orbitals of atom A and atom B may be written in the form

$$\mathrm{p}_{z,\mathrm{A}} = \frac{1}{4(2\pi)^{1/2}}(z + R/2)\mathrm{e}^{-\left\{x^2+y^2+(z+R/2)^2\right\}^{1/2}/2}$$

and
$$\mathrm{p}_{z,\mathrm{B}} = \frac{1}{4(2\pi)^{1/2}}(z - R/2)\mathrm{e}^{-\left\{x^2+y^2+(z-R/2)^2\right\}^{1/2}/2}$$

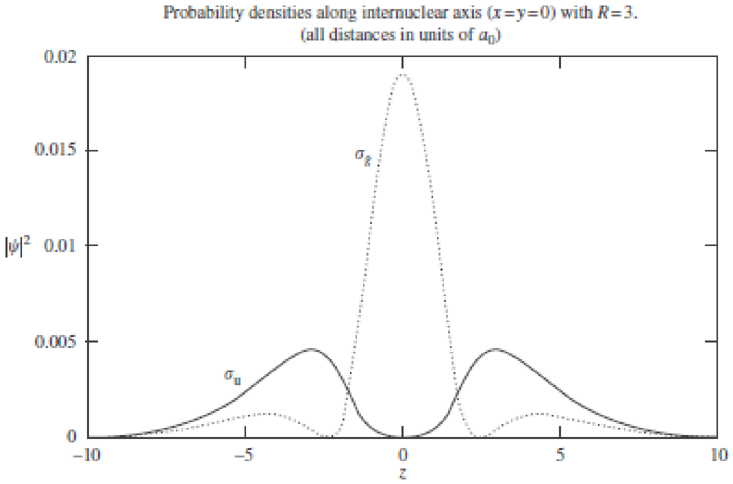
Following eqn. 10B.2 and Example 10B.1, we construct LCAO-MO's of the form:

$$\psi_{\sigma^*} = \frac{\mathrm{p}_{z,\mathrm{A}} + \mathrm{p}_{z,\mathrm{B}}}{\{2(1+S)\}^{1/2}}\ \text{[antibonding]} \quad \text{and} \quad \psi_{\sigma} = \frac{\mathrm{p}_{z,\mathrm{A}} - \mathrm{p}_{z,\mathrm{B}}}{\{2(1-S)\}^{1/2}}\ \text{[bonding]}$$

where
$$S = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{p}_{z,\mathrm{A}}\mathrm{p}_{z,\mathrm{B}}\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \quad [10\text{C}.3]$$

Computations and plots are readily prepared with mathematical software such as Mathcad. (See Figure 10C.2.)

Figure 10C.2



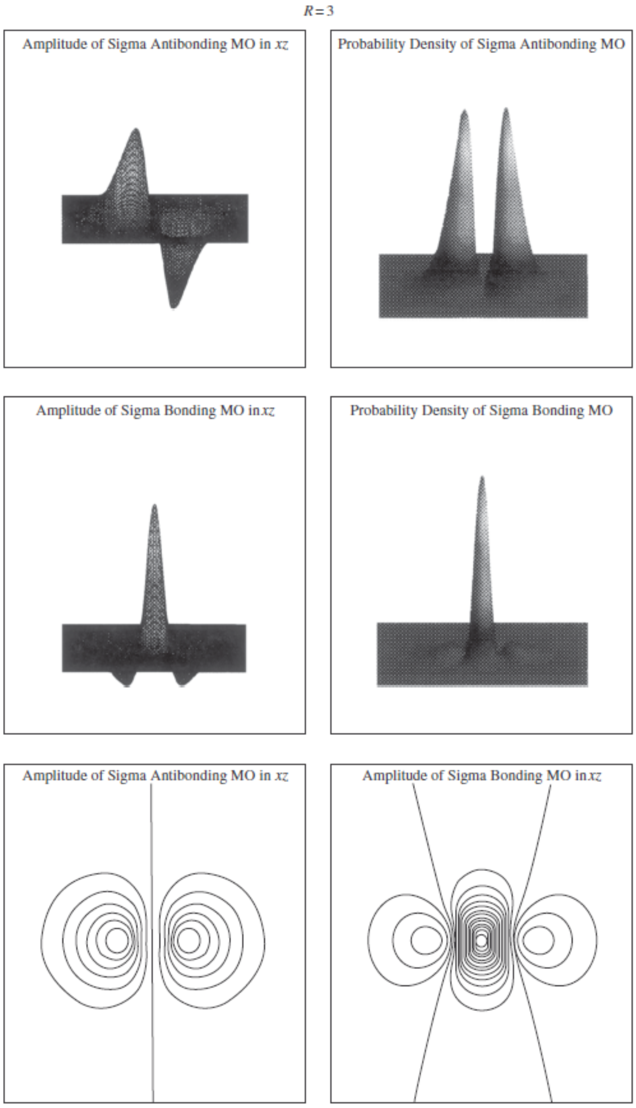
(b) With spatial dimensions in units of a_0, the atomic orbitals for the construction of π molecular orbitals are:

$$p_{x,\mathrm{A}} = \frac{1}{4(2\pi)^{1/2}} x\mathrm{e}^{-\left\{x^2+y^2+(z+R/2)^2\right\}^{1/2}/2}$$

$$p_{x,\mathrm{B}} = \frac{1}{4(2\pi)^{1/2}} x\mathrm{e}^{-\left\{x^2+y^2+(z-R/2)^2\right\}^{1/2}/2}$$

See Figures 10C.3 and 10C.4.

Figure 10C.3



Amplitude of Sigma Antibonding MO in xz

Probability Density of Sigma Antibonding MO

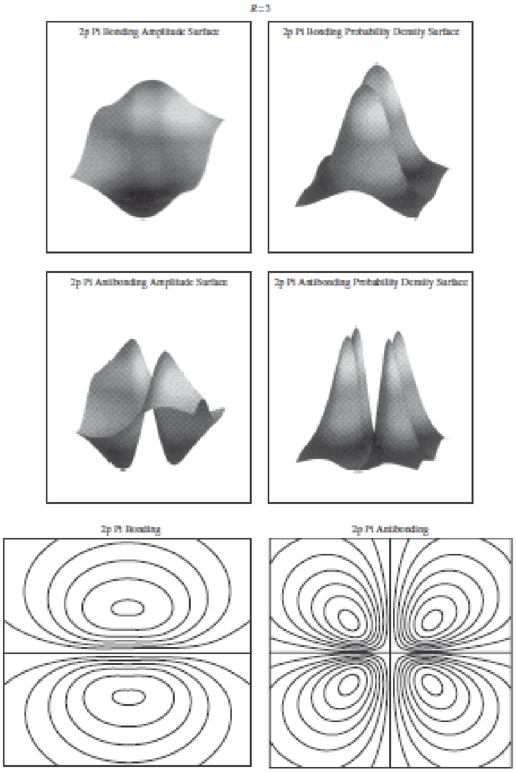
Amplitude of Sigma Bonding MO in xz

Probability Density of Sigma Bonding MO

Amplitude of Sigma Antibonding MO in xz

Amplitude of Sigma Bonding MO in xz

Figure 10C.4



The π MO's are:

$$\psi_{\pi} = \frac{\mathrm{p}_{x,\mathrm{A}} + \mathrm{p}_{x,\mathrm{B}}}{\{2(1+S)\}^{1/2}}\ \text{[bonding]} \quad \text{and} \quad \psi_{\pi^*} = \frac{\mathrm{p}_{x,\mathrm{A}} - \mathrm{p}_{x,\mathrm{B}}}{\{2(1-S)\}^{1/2}}\ \text{[antibonding]}$$

where $S = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{p}_{x,\mathrm{A}}\mathrm{p}_{x,\mathrm{B}}\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z$

The plots clearly show the constructive interference that makes a bonding molecular orbital. Nodal planes created by destructive interference are clearly seen in the antibonding molecular orbitals. When calculations and plots are produced for the $R = 10$ case, constructive and destructive interference is seen to be much weaker because of the weak atomic orbital overlap.

10C.4 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 now freed electron's kinetic energy.

$$E_{\text{photon}} = I + E_{\text{kinetic}} \qquad \text{so} \qquad I = E_{\text{photon}} - E_{\text{kinetic}}$$

so the first three ionization energies are:

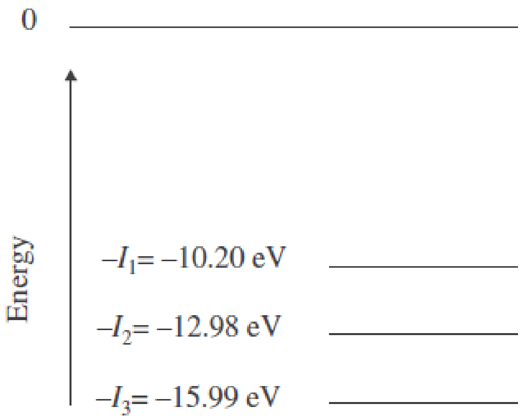
$I_1 = 21.21\ \text{eV} - 11.01\ \text{eV} = \boxed{10.20\ \text{eV}}$

$I_2 = 21.21\ \text{eV} - 8.23\ \text{eV} = \boxed{12.98\ \text{eV}}$

and $I_3 = 21.21\ \text{eV} - 5.22\ \text{eV} = \boxed{15.99\ \text{eV}}$

The energy level diagram is shown in Figure 10C.5.

Figure 10C.5



10D Heteronuclear diatomic molecules

Answers to discussion questions

10D.2 The difference in energy between an the cation X^+ of a free atom X and its anion X^- is the sum of the ionization energy (the energy required to detach an electron from X) and the electron affinity (the energy benefit of binding an additional electron to X). On the assumption that atoms in molecules retain at least some of their free-atom characteristics regarding electron binding energies, the energy difference between an unoccupied valence orbital of atom X in a molecule and that same orbital doubly occupied is also the sum of the ionization energy and electron affinity. See Topic 10D.1(a).

10D.4 The Coulomb integral is essentially the energy of an electron when it occupies an atomic orbital. (It would be the expectation value of the hamiltonian if the orbital function was a true wavefunction.) It is called a Coulomb integral because the energy of an electron in an atomic orbital is, at least semi-classically, the Coulombic energy of a negative charge distribution (essentially, the probability distribution of the electron in the orbital) and the atom's nucleus. The resonance integral is a non-classical contribution to the energy of a molecule that can be interpreted as an energy associated with an electron occupying an orbital on more than one nucleus at once. The electron ***does not*** "resonate" (vibrate, shuttle) between nuclei, however.

Solutions to exercises

10D.1(b) **(i)** For XeF, the relevant molecular orbitals (the only ones to which both atoms contribute significantly) are linear combinations of the atomic orbitals occupied by valence electrons.

Thus, $1\sigma = \text{F2s} + \text{Xe5s}$ $\quad 2\sigma = \text{F2s} - \text{Xe5s}$

$3\sigma = \text{F2p}_z + \text{Xe5p}_z$ $\quad 4\sigma = \text{F2p}_z - \text{Xe5p}_z$

$1\pi = \text{F2p}_x + \text{Xe5p}_x$ $\quad 2\pi = \text{F2p}_x - \text{Xe5p}_x$

(Note: each π molecular orbital is doubly degenerate; the other π orbital comes from p_y atomic orbitals.) Assume that the filling order is 3σ, 1π, 2π, 4σ, as it would be for OF. The configuration is

XeF (15 electrons) $\boxed{1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 2\pi^4 4\sigma^1}$

(ii) Likewise, for PN, the relevant molecular orbitals are linear combinations of valence atomic orbitals.

$1\sigma = \text{N2s} + \text{P3s}$ $\quad 2\sigma = \text{N2s} - \text{P3s}$

$3\sigma = \text{N2p}_z + \text{P3p}_z$ $\quad 4\sigma = \text{N2p}_z - \text{P3p}_z$

$1\pi = \text{N2p}_x + \text{P3p}_x$ $\quad 2\pi = \text{N2p}_x - \text{P3p}_x$ (each doubly degenerate, as in part (a))

Assume that the filling order is 1π, 3σ, as it would be for N_2. The configuration is

PN (10 electrons) $\boxed{1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2}$

(iii) For SO^-, the relevant molecular orbitals are.

$1\sigma = \text{S2s} + \text{O3s}$ $\quad 2\sigma = \text{S2s} - \text{O3s}$

$3\sigma = \text{S2p}_z + \text{O3p}_z$ $\quad 4\sigma = \text{S2p}_z - \text{O3p}_z$

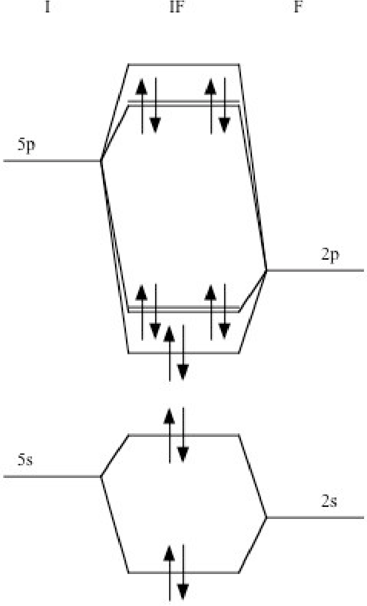
$1\pi = \text{S2p}_x + \text{O3p}_x$ $2\pi = \text{S2p}_x - \text{O3p}_x$ (each doubly degenerate, as in part (a))

Assume that the filling order is 3σ, 1π, 2π, 4σ, as it would be for O_2^-. The configuration is

O_2^- (13 electrons) $\boxed{1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 2\pi^3}$

10D.2(b) Figure 10D.1 is based on Figure 10C.12 of the text but with F orbitals lower than I orbitals. IF is likely to have a shorter bond length than IF^-, for the extra electron would go into an antibonding orbital. (The bond orders are 1 and 0.5 respectively.) IF^+ is likely to have a shorter bond length than IF, for the missing electron would be taken from an antibonding orbital. (The bond orders are 1.5 and 1 respectively.)

Figure 10D.1



10D.3(b) Form the electron configurations and find the bond order. See Figure 10C.11 of the main text.

SO^+ (11 electrons) $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 2\pi^1$ $b=2.5$

SO^- (13 electrons) $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 2\pi^3$ $b=1.5$

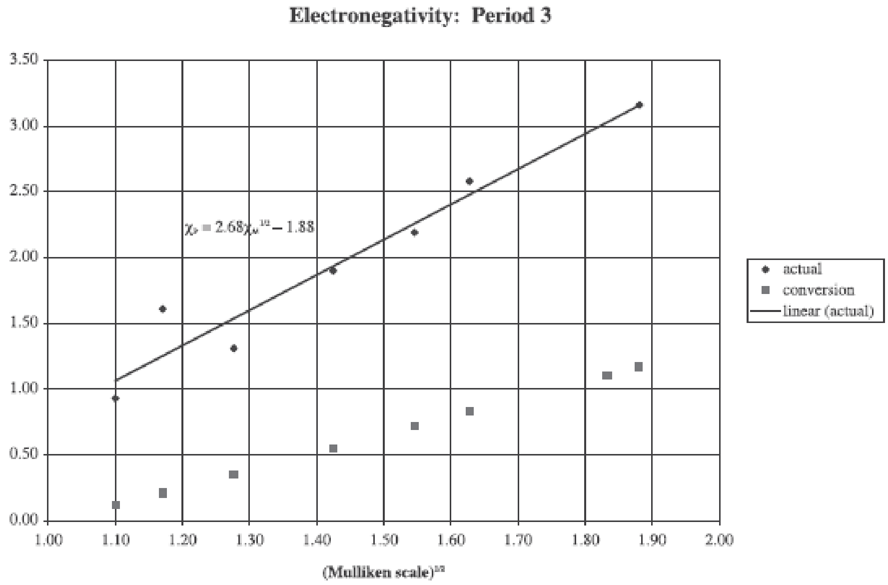
Based on the electron configurations, we would expect $\boxed{SO^+}$ to have the stronger and therefore the shorter bond.

10D.4(b) Draw up the following table using data from Table 10D.1:

element	Na	Mg	Al	Si	P	S	Cl	Ar
χ_M	1.21	1.63	1.37	2.03	2.39	2.65	3.54	3.36
$(\chi_M)^{1/2}$	1.10	1.28	1.17	1.42	1.55	1.63	1.88	1.83
χ_P (from table)	0.93	1.31	1.61	1.90	2.19	2.58	3.16	
χ_P (from formula)	0.12	0.35	0.21	0.55	0.72	0.83	1.17	1.10

A plot (Figure 10D.2(a) of the Pauling electronegativities (actual and from the formula) vs. the square root of the Mulliken electronegativities shows that the formula does a poor job. The formula consistently underestimates the Pauling electronegativity, and it underestimates the rise in electronegativity across the period.

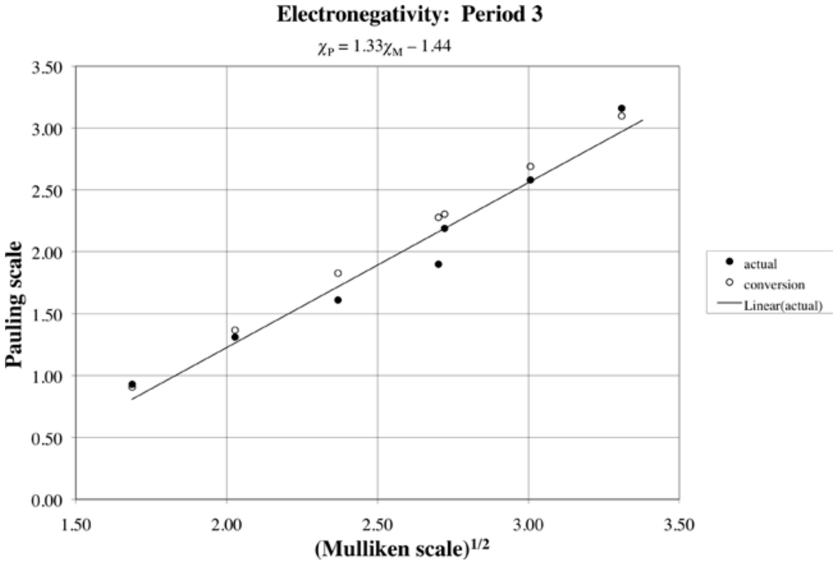
Figure 10D.2(a)



The problem is that the Mulliken electronegativities given in the table have already been scaled to the range of Pauling electronegativities ***using this very conversion***. That is, the Mulliken electronegativities given in Table 10D.1 are not defined by eqn. 10D.3, but rather by eqn. 10D.3 and then eqn. 10D.4. Using Mulliken electronegativities based on eqn. 10D.3 alone (the "intrinsic Mulliken electronegativities" also known as "Mulliken *a* parameters" from Steven G. Bratsch, "Revised Mulliken electronegativities: I. Calculation and conversion to Pauling units," *J. Chem. Educ.*, **1988**, *65*, 34-41).

element	Na	Mg	Al	Si	P	S	Cl	Ar
χ_M (Bratch *a*)	2.84	4.11	5.61	7.30	7.41	9.04	10.95	11.41
$(\chi_M)^{1/2}$	1.69	2.03	2.37	2.70	2.72	3.01	3.31	3.38
χ_P (from table)	0.93	1.31	1.61	1.90	2.19	2.58	3.16	
χ_P (from formula)	0.91	1.37	1.83	2.28	2.30	2.69	3.10	

Figure 10D.2



A plot (Figure 10D.2(b)) of actual Pauling electronegativities (from Table 10D.1; filled circles) vs. the square root of the intrinsic Mulliken electronegativities (from Table 5 of Bratch's article) yields quite a good regression line with an equation very close to that of eqn. 10D.4. The open circles on the same plot are the result of applying eqn. 10D.4 to the intrinsic Mulliken electronegativities from Bratch; these are essentially the "scaled"

Mulliken electronegativities. As you can see, they fall quite close to the best-fit line of the actual Pauling electronegativity values.

10D.5(b) Following *Brief Illustration* 10D.1, we draw up a table of ionization energies and electron affinities from Tables 9B.2 and 9B.3. The mean of those two energies is the estimated orbital energy for each atom.

	I/eV	E_{ea}/eV	$\tfrac{1}{2}(I+E_{ea})$ / eV
H	13.6	0.75	$\boxed{7.2}$
Br	11.8	3.4	$\boxed{7.6}$

10D.6(b) In the zero overlap approximation, the molecular orbital energies are given by eqn. 10D.8c:

$$E_\pm = \tfrac{1}{2}(\alpha_A+\alpha_B) \pm \tfrac{1}{2}(\alpha_A-\alpha_B)\left\{1+\left(\frac{2\beta}{\alpha_A-\alpha_B}\right)^2\right\}^{1/2}$$

Taking $\beta = -1.0$ eV (a typical value), we have

$$E_\pm \,/\, \text{eV} = \tfrac{1}{2}(-7.2-7.6) \pm \tfrac{1}{2}(-7.2+7.6)\left\{1+\left(\frac{2(-1)}{-7.2+7.6}\right)^2\right\}^{1/2} = \boxed{-6.4 \text{ or } -8.4}$$

10D.7(b) If overlap cannot be neglected, then the molecular orbital energies are given by eqn. 10D.8a:

$$E_\pm = \frac{\alpha_A+\alpha_B-2\beta S \pm \{(\alpha_A+\alpha_B-2\beta S)^2 - 4(1-S^2)(\alpha_A\alpha_B-\beta^2)\}^{1/2}}{2(1-S^2)}$$

Taking $\beta = -1.0$ eV (a typical value), we have

$$\frac{E_\pm}{\text{eV}} = \frac{-7.2-7.6+2(1.0)(0.20) \pm \{(-7.2-7.6+2(1.0)(0.20))^2 - 4(1-0.20^2)(7.2\times 7.6-1.0^2)\}^{1/2}}{2(1-0.20^2)}$$

so $E_\pm = \boxed{-4.8 \text{ or } -10.2 \text{ eV}}$

Solutions to problems

10D.2 At first blush, we simply have three terms rather than two. But the fact that two of the atomic orbitals belong to the same nucleus alters matters. Overlap, for instance, is zero for atomic orbitals on the same nucleus, because the orbitals are orthogonal. Also the resonance integral for different atomic orbitals on the same nucleus (which we would denote by β_{BC}) vanishes, as it must for orbitals that have zero overlap.

Thus $(\alpha_A - E)c_A + (\beta_{AB} - ES_{AB})c_B + (\beta_{AC} - ES_{AC})c_C = 0$

$(\beta_{AB} - ES_{AB})c_A + (\alpha_B - E)c_B = 0$

and $(\beta_{AC} - ES_{AC})c_A + (\alpha_C - E)c_C = 0$

10D.4 See the solution of Problem 10D.2 for the secular equations. For the case $S = 0$ (without, however, making the resonance integrals also vanish) the secular determinant—call it $f(E)$—is

$$f(E) = \begin{vmatrix} \alpha_A - E & \beta_{AB} & \beta_{AC} \\ \beta_{AB} & \alpha_B - E & 0 \\ \beta_{AC} & 0 & \alpha_C - E \end{vmatrix}$$

Solve for the energies by expanding the secular determinant and setting it equal to zero. Let us expand using the second row:

$$f(E) = \beta_{AB}\{\beta_{AB}(\alpha_C - E)\} - (\alpha_B - E)\{(\alpha_A - E)(\alpha_C - E) - \beta_{AC}^2\} = 0$$

$$0 = E^3 - (\alpha_A+\alpha_B+\alpha_C)E^2 + (\alpha_A\alpha_B+\alpha_A\alpha_C+\alpha_B\alpha_C-\beta_{AB}^2-\beta_{AC}^2)E + \alpha_B\beta_{AC}^2 + \alpha_C\beta_{AB}^2 - \alpha_A\alpha_B\alpha_C$$

Substituting in the parameters in Problem 10D.3, we have

$$0 = E^3 + (26.0 \text{ eV})E^2 + (221 \text{ eV}^2)E - 614 \text{ eV}^3$$

This cubic equation can be solved numerically and/or graphically. The following table shows the roots of the secular determinant for a variety of values of α_C while keeping all of the other parameters as specified in Problem 10D.4.

α_C/eV	–10.4	–8.4	–7.2	–6	–5	–4	–2	0
E_1/eV	–10.8	–10.7	–10.7	–10.7	–10.7	–10.7	–10.7	–10.7
E_2/eV	–10.4	–8.7	–7.8	–7.3	–7.2	–7.1	–7	–7
E_3/eV	–6.8	–6.6	–6.3	–5.6	–4.7	–3.8	–1.9	0.1

In all cases, the energies of the molecular orbitals (the roots of the secular determinant) are not terribly different from the energies of the input atomic orbitals (the Coulomb integrals α), with the lowest MO energy (E_1) lower in energy than the lowest α because of a bonding interaction and the highest MO energy (E_3) higher than the highest α because of a bonding interaction. The greatest bonding stabilization can be seen when the Coulomb integrals are closest in energy. (Notice that E_1 is lowest when $\alpha_C = \alpha_B = –10.4$ eV, and that E_2 shows a great deal of bonding stabilization when $\alpha_C = \alpha_A = –7.2$ eV.) When all three Coulomb integrals are within just a few eV of each other, both E_1 and E_2 show bonding character and only E_3 appears to be antibonding (*i.e.*, E_1 lower than the lowest α, E_2 at least as low as the next lowest α, and E_3 higher than the highest α). However, once α_C gets substantially higher than the other atomic orbitals, E_1 and E_2 start acting like a bonding-antibonding pair and stop changing much in energy, while E_3 increasingly closely matches α_C, becoming, in effect, an irrelevant non-bonding molecular orbital.

10E Polyatomic molecules

Answers to discussion questions

10E.2 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.

10E.4 Gaussian type orbitals (functions of the form e^{-r^2}) centred on atomic nuclei have the advantage over the slightly more realistic orbitals (functions of the form e^{-r}, also known as Slater-type orbitals) that the product of two Gaussian functions on different centres is equivalent to a single Gaussian function located at a point between the centres. Therefore, two-electron integrals on three and four different atomic centres (such as eqn. 10E.14a) can be reduced to integrals over two different centres (such as eqn 10E.14b), which are much easier to evaluate numerically.

Solutions to exercises

10E.1(b) In setting up the secular determinant we use the Hückel approximations outlined in Topic 10E.1:

$$\textbf{(i)}\quad \begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix} \qquad \textbf{(ii)}\quad \begin{vmatrix} \alpha-E & \beta & 0 & \beta \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ \beta & 0 & \beta & \alpha-E \end{vmatrix}$$

The atomic orbital basis is $1s_A$, $1s_B$, $1s_C$, $1s_D$ in each case; in linear H_4 we ignore A, D overlap because A and D are not neighboring atoms; in cyclic H_4 we include it because they are.

10E.2(b) See Self-test 10E.2 for part (i) and Example 10E.2 for part (ii).
(i) The energy levels are $E_1 = \alpha + 1.41\beta$, $E_2 = \alpha$, and $E_3 = \alpha - 1.41\beta$. There are three π electrons, so the configuration is $\psi_1^2\psi_2^1$ and the energy is

$$E_\pi = 2(\alpha + 1.41\beta) + \alpha = \boxed{3\alpha + 2.82\beta}$$

(ii) The energy levels are $E_1 = \alpha + 2\beta$, $E_2 = E_3 = \alpha$, and $E_4 = \alpha - 2\beta$. There are three π electrons, so the configuration is $\psi_1^2\psi_2^1$ and the energy is

$$E_\pi = 2(\alpha + 2\beta) + \alpha = \boxed{3\alpha + 4\beta}$$

10E.3(b) The π-bond formation energy is the difference between the π-electron binding energy and the Coulomb energies α [10E.12]:

$$E_{\text{bf}} = E_\pi - N_{\text{C}}\alpha$$

The delocalization energy is the difference between E_π and the energy of isolated π bonds:

$$E_{\text{delocal}} = E_\pi - N_{\text{C}}(\alpha + \beta)$$

(i) $E_\pi = 3\alpha + 2.82\beta$ [Exercise 10E.2(b)]

so $E_{\text{bf}} = 3\alpha + 2.82\beta - 3\alpha = \boxed{2.82\beta}$

and $E_{\text{delocal}} = 3\alpha + 2.82\beta - 3(\alpha + \beta) = \boxed{(2.82\text{–}3)\beta} = \boxed{-0.18\beta}$

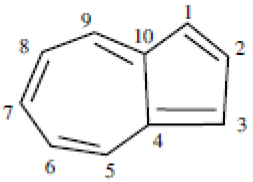
(ii) $E_\pi = 3\alpha + 4\beta$ [Exercise 10E.2(b)]

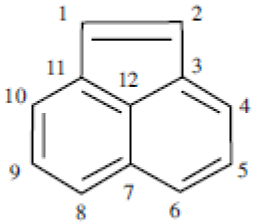
so $E_{\text{bf}} = 3\alpha + 4\beta - 3\alpha = \boxed{4\beta}$

and $E_{\text{delocal}} = 3\alpha + 4\beta - 3(\alpha + \beta) = \boxed{\beta}$

Comment. With an odd number of π electrons, we do not have a whole number of π bonds in the formula for delocalization energy. In effect, we compare the π-electron binding energy to the energy of 1.5 isolated π bonds—whatever that means. This result in (i) is a **de**stabilization, consistent with the observation from organic chemistry that cumulated double bonds (*i.e.*, adjacent double bonds) are unfavorable.

10E.4(b) The structures are numbered to match the row and column numbers shown in the determinants:





(i) The secular determinant of azulene in the Hückel approximation is:

	1	2	3	4	5	6	7	8	9	10
1	$\alpha - E$	β	0	0	0	0	0	0	0	β
2	β	$\alpha - E$	β	0	0	0	0	0	0	0
3	0	β	$\alpha - E$	β	0	0	0	0	0	0
4	0	0	β	$\alpha - E$	β	0	0	0	0	β
5	0	0	0	β	$\alpha - E$	β	0	0	0	0
6	0	0	0	0	β	$\alpha - E$	β	0	0	0
7	0	0	0	0	0	β	$\alpha - E$	β	0	0
8	0	0	0	0	0	0	β	$\alpha - E$	β	0
9	0	0	0	0	0	0	0	β	$\alpha - E$	β
10	β	0	0	β	0	0	0	0	β	$\alpha - E$

(ii) The secular determinant of acenaphthalene in the Hückel approximation is:

	1	2	3	4	5	6	7	8	9	10	11	12
1	$\alpha - E$	β	0	0	0	0	0	0	0	0	β	0
2	β	$\alpha - E$	β	0	0	0	0	0	0	0	0	0
3	0	β	$\alpha - E$	β	0	0	0	0	0	0	0	β
4	0	0	β	$\alpha - E$	β	0	0	0	0	0	0	0

5	0	0	0	β	$\alpha-E$	β	0	0	0	0	0	0
6	0	0	0	0	β	$\alpha-E$	β	0	0	0	0	0
7	0	0	0	0	0	β	$\alpha-E$	β	0	0	0	β
8	0	0	0	0	0	0	β	$\alpha-E$	β	0	0	0
9	0	0	0	0	0	0	0	β	$\alpha-E$	β	0	0
10	0	0	0	0	0	0	0	0	β	$\alpha-E$	β	0
11	β	0	0	0	0	0	0	0	0	β	$\alpha-E$	β
12	0	0	β	0	0	0	β	0	0	0	β	$\alpha-E$

10E.5(b) The secular determinants from Exercise 10E.4(b) can be diagonalized with the assistance of general-purpose mathematical software. Alternatively, programs specifically designed for Hückel calculations (such as the Simple Hückel Molecular Orbital Theory Calculator at the University of Calgary, http://www.chem.ucalgary.ca/SHMO/ or Hückel software in *Explorations in Physical Chemistry*, 2nd ed., by Julio de Paula, Valerie Walters, and Peter Atkins, http://ebooks.bfwpub.com/explorations.php) can be used.

(i) 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 $\boxed{10\alpha + 13.364\beta}$.

(ii) Acenaphthalene has 12 π electrons, which fill six orbitals. The energies of the filled orbitals are $\alpha + 2.471\beta$, $\alpha + 1.688\beta$, $\alpha + 1.683\beta$, $\alpha + \beta$, $\alpha + 0.831\beta$, and $\alpha + 0.638\beta$. Thus, the total π-electron binding energy is $\boxed{12\alpha + 16.619\beta}$.

10E.6(b) LiH^{2+} is a two-electron molecule. The hamiltonian for the electrons in LiH^{2+} is

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0 r_{1\mathrm{H}}} - \frac{e^2}{4\pi\varepsilon_0 r_{2\mathrm{H}}} - \frac{3e^2}{4\pi\varepsilon_0 r_{1\mathrm{Li}}} - \frac{3e^2}{4\pi\varepsilon_0 r_{2\mathrm{Li}}} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

The first two terms represent kinetic energy of the electrons, the next two attraction of the electrons to the H nucleus, the next two attraction of the electrons to the Li nucleus, and the last electron-electron repulsion. There is an additional term that does not enter into the Schrödinger equation of the electrons but into the total energy as a function of internuclear separation, namely a nuclear-nuclear repulsion term $\dfrac{3e^2}{4\pi\varepsilon_0 R}$.

Solutions to problems

10E.2 **(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 β is negative (as is α for that matter), 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, though, because there are only as many MOs as there were

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. (See also P10E.4.)

(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 three lowest-energy orbitals is doubly occupied, but the second level ($k = \pm 1$) 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, the first three orbitals are also doubly occupied:

$$E_\pi = 2(\alpha + 2\beta\cos\frac{\pi}{7}) + 2\left(\alpha + 2\beta\cos\frac{2\pi}{7}\right) + 2\left(\alpha + 2\beta\cos\frac{3\pi}{7}\right) = 6\alpha + 6.988\beta$$

so $E_{\text{deloc}} = \boxed{0.988\beta}$. Thus 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:

$$E_{\text{deloc}} = E_\pi - 8(\alpha+\beta) = 8\alpha + 9.657\beta - 8(\alpha+\beta) = \boxed{1.657\beta}$$

In linear octatetraene, the first four levels are doubly occupied:

$$\begin{aligned} E_\pi &= 2(\alpha + 2\beta\cos\frac{\pi}{9}) + 2\left(\alpha + 2\beta\cos\frac{2\pi}{9}\right) + 2\left(\alpha + 2\beta\cos\frac{3\pi}{9}\right) + 2\left(\alpha + 2\beta\cos\frac{4\pi}{9}\right) \\ &= 8\alpha + 9.518\beta \end{aligned}$$

so $E_{\text{deloc}} = \boxed{1.518\beta}$. Thus cycloocatetraene does not have much additional stabilitzation over the linear structure. Once again, though, 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 an example 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. 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.

10E.4 We use the Hückel approximation, neglecting overlap integrals.

The secular determinant of cyclobutadiene is $\begin{vmatrix} \alpha - E & \beta & 0 & \beta \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \beta & 0 & \beta & \alpha - E \end{vmatrix}$

Mathematical software (such as the Simple Hückel Molecular Orbital Theory Calculator at the University of Calgary, http://www.chem.ucalgary.ca/SHMO/) diagonalizes the hamiltonian matrix to

$$\boldsymbol{E} = \begin{pmatrix} \alpha+2\beta & 0 & 0 & 0 \\ 0 & \alpha & 0 & 0 \\ 0 & 0 & \alpha & 0 \\ 0 & 0 & 0 & \alpha-2\beta \end{pmatrix}$$

The secular determinant of benzene is $\begin{vmatrix} \alpha-E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha-E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha-E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha-E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha-E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha-E \end{vmatrix}$

The hamiltonian matrix is diagonalized to

$$\boldsymbol{E} = \begin{pmatrix} \alpha+2\beta & 0 & 0 & 0 & 0 & 0 \\ 0 & \alpha+\beta & 0 & 0 & 0 & 0 \\ 0 & 0 & \alpha+\beta & 0 & 0 & 0 \\ 0 & 0 & 0 & \alpha-\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & \alpha-\beta & 0 \\ 0 & 0 & 0 & 0 & 0 & \alpha-2\beta \end{pmatrix}$$

The secular determinant of cyclooctatetraene is

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 & \beta \\ \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 \\ 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 \\ 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 \\ 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 \\ 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 \\ 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta \\ \beta & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E \end{vmatrix}$$

The hamiltonian matrix is diagonalized to

$$\boldsymbol{E} = \begin{pmatrix} \alpha+2\beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \alpha+\sqrt{2}\beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \alpha+\sqrt{2}\beta & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \alpha & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \alpha & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \alpha-\sqrt{2}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \alpha-\sqrt{2}\beta & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \alpha-2\beta \end{pmatrix}$$

Recall that β is negative, so energies increase from the upper left to the lower right of the diagonalized matrices. In each of these examples, one can see by inspection that the first and last energy levels are non-degenerate (for there is no other energy value in the diagonalized $\boldsymbol{E}$ matrix equal to them) and that the other levels are two-fold degenerate (for those energy values occur in pairs).

10E.6 The secular determinant for an N-carbon linear polyene (call the determinant P_N) has the form

$$\begin{array}{c} \begin{array}{cccccccc} 1 & 2 & 3 & \dots & \dots & \dots & N-1 & N \end{array} \\ \hline \begin{vmatrix} x & 1 & 0 & 0 & 0 & \dots & 0 & 0 \\ 1 & x & 1 & 0 & 0 & \dots & 0 & 0 \\ 0 & 1 & x & 1 & 0 & \dots & 0 & 0 \\ 0 & 0 & 1 & x & 1 & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & 0 & \dots & x & 1 \\ 0 & 0 & 0 & 0 & 0 & \dots & 1 & x \end{vmatrix} = P_N \end{array}$$

where $x = \dfrac{\alpha - E}{\beta}$. The determinant can be expanded by cofactors; use the elements of the first row:

$$P_N = M_{11}c_{11} - M_{12}c_{12} + M_{13}c_{13} - \dots + (-1)^{N+1}M_{1N}c_{1N}$$

In this notation, M_{1n} is the element in the first row, n^{th} column of the determinant and c_{1n} is the cofactor of that element. The cofactor, c_{1n}, is a determinant whose elements are the elements of the original determinant with row 1 and column n removed. Note that the elements of the first row after M_{11} and M_{12} are zero, so $P_N = M_{11}c_{11} - M_{12}c_{12}$, $M_{11} = x$ and c_{11} is the secular determinant of an (N–1)-carbon polyene; that is, the c_{11} cofactor in P_N is P_{N-1}.
$M_{12} = 1$, so we are almost there:

$$P_N = xP_{N-1} - c_{12}$$

We need to examine c_{12}. As shown below, c_{12} is the determinant left after crossing out the elements in the original P_N determinant that are in the first row or the second column:

$$c_{12} = \begin{vmatrix} \cancel{x} & \boxed{\cancel{1}} & \cancel{0} & \cancel{0} & \cancel{0} & \cancel{\dots} & \cancel{0} & \cancel{0} \\ 1 & \cancel{x} & 1 & 0 & 0 & \dots & 0 & 0 \\ 0 & \cancel{1} & x & 1 & 0 & \dots & 0 & 0 \\ 0 & \cancel{0} & 1 & x & 1 & \dots & 0 & 0 \\ \vdots & \cancel{\vdots} & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \cancel{0} & 0 & 0 & 0 & \dots & x & 1 \\ 0 & \cancel{0} & 0 & 0 & 0 & \dots & 1 & x \end{vmatrix}.$$

Now c_{12} is not itself a secular determinant of a polyene; its first row has ones as its first two elements and no x elements. Its first *column*, though, has only one element, a one. Expanding this determinant by the elements and cofactors of its first *column* yields a one-term sum whose cofactor is illustrated here. We cross out elements in the original P_N determinant, not only those in the first row or second column, but also those in the same row or column as the single term in the first column of c_{12}:

$$c_{12} = 1\times \begin{vmatrix} \cancel{x} & \cancel{1} & \cancel{0} & \cancel{0} & \cancel{0} & \cancel{\dots} & \cancel{0} & \cancel{0} \\ \boxed{\cancel{1}} & \cancel{x} & \cancel{1} & \cancel{0} & \cancel{0} & \cancel{\dots} & \cancel{0} & \cancel{0} \\ \cancel{0} & \cancel{1} & x & 1 & 0 & \dots & 0 & 0 \\ \cancel{0} & \cancel{0} & 1 & x & 1 & \dots & 0 & 0 \\ \cancel{\vdots} & \cancel{\vdots} & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \cancel{0} & \cancel{0} & 0 & 0 & 0 & \dots & x & 1 \\ \cancel{0} & \cancel{0} & 0 & 0 & 0 & \dots & 1 & x \end{vmatrix} = 1\times P_{N-2} = P_{N-2}$$

That is, the cofactor involved in evaluating c_{12} is the secular determinant of an (N–2)-carbon polyene, *i.e.*, P_{N-2}. So $\boxed{P_N = xP_{N-1} - P_{N-2}}$.

10E.8 **(a)**

$$\begin{vmatrix} \alpha-E & \beta & \beta \\ \beta & \alpha-E & \beta \\ \beta & \beta & \alpha-E \end{vmatrix}=0$$

$$(\alpha-E)\begin{vmatrix} \alpha-E & \beta \\ \beta & \alpha-E \end{vmatrix}-\beta\begin{vmatrix} \beta & \beta \\ \beta & \alpha-E \end{vmatrix}+\beta\begin{vmatrix} \beta & \alpha-E \\ \beta & \beta \end{vmatrix}=0$$

$$(\alpha-E)\times\{(\alpha-E)^2-\beta^2\}-\beta\{\beta(\alpha-E)-\beta^2\}+\beta\{\beta^2-(\alpha-E)\beta\}=0$$

$$(\alpha-E)\times\{(\alpha-E)^2-\beta^2\}-2\beta^2\{\alpha-E-\beta\}=0$$

$$(\alpha-E)\times(\alpha-E+\beta)\times(\alpha-E-\beta)-2\beta^2(\alpha-E-\beta)=0$$

$$(\alpha-E-\beta)\times\{(\alpha-E)\times(\alpha-E+\beta)-2\beta^2\}=0$$

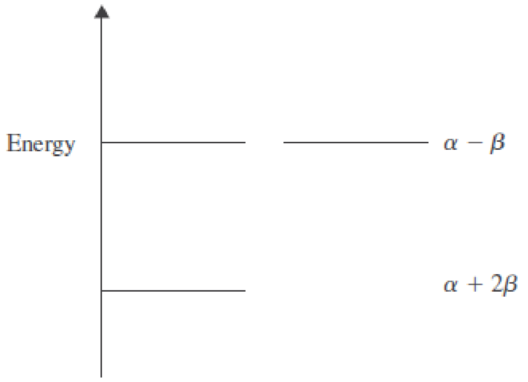
$$(\alpha-E-\beta)\times\{(\alpha-E)\times(\alpha-E+2\beta)-\beta(\alpha-E)-2\beta^2\}=0$$

$$(\alpha-E-\beta)\times\{(\alpha-E)\times(\alpha-E+2\beta)-\beta(\alpha-E+2\beta)\}=0$$

$$(\alpha-E-\beta)\times(\alpha-E+2\beta)\times(\alpha-E-\beta)=0$$

Therefore, the desired roots are $E=\boxed{\alpha-\beta,\ \alpha-\beta,\text{ and }\alpha+2\beta}$. The energy level diagram is shown in Figure 10E.1.

Figure 10E.1



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)

$H_3^+(g) \rightarrow 2H(g) + H^+(g)$ $\Delta H_1 = 849$ kJ mol^{-1}

$H^+(g) + H_2(g) \rightarrow H_3^+(g)$ $\Delta H_2 = ?$

$H_2(g) \rightarrow 2H(g)$ $\Delta H_3 = [2(217.97) - 0]$ kJ mol^{-1}

$\Delta H_2 = \Delta H_3 - \Delta H_1 = \{2(217.97) - 849\}$ kJ mol^{-1},

$\Delta H_2 = \boxed{-413\text{ kJ mol}^{-1}}$

This is only slightly less than the binding energy of H_2 (435.94 kJ mol^{-1})

(c) $2\alpha + 4\beta = -\Delta H_1 = -849$ 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	$3\alpha + 3\beta = 3\left(\alpha - \frac{\Delta H_1 + 2\alpha}{4}\right) = 3\left(\frac{1}{2}\alpha - \frac{\Delta H_1}{4}\right) = \boxed{3(\alpha/2) - 212\,\text{kJ mol}^{-1}}$
H_3^-	$4\alpha + 2\beta = 4\alpha - \frac{\Delta H_1 + 2\alpha}{2} = 3\alpha - \frac{\Delta H_1}{2} = \boxed{3\alpha - 425\,\text{kJ mol}^{-1}}$

As α is a negative quantity, all three of these species are expected to be stable.

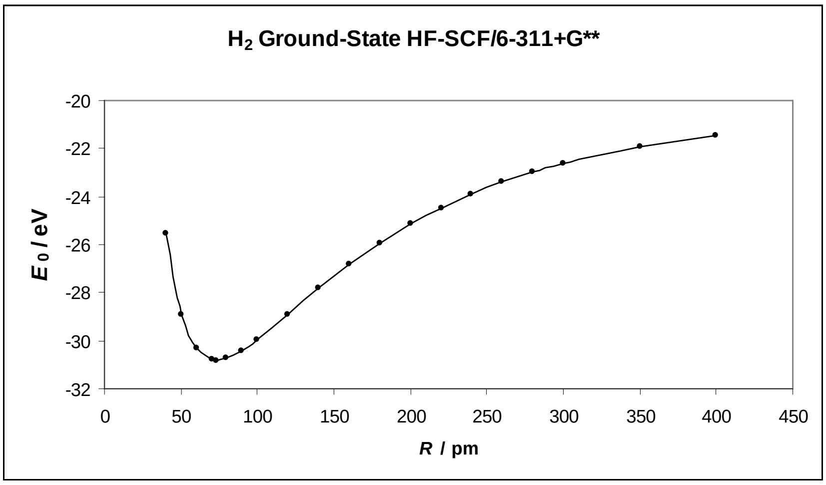
10E.10 For H_2 the 6-31G* basis set is equivalent to the 6-31G basis set because the star indicates that the basis set adds d-type polarization functions for each atom other than hydrogen. Consequently, we choose the basis sets **(a)** 6-31G* and **(b)** 6-311+G**. 1 au = 27.2114 eV. Since the calculated energy is with respect to the energy of widely separated stationary electrons and nuclei, the experimental ground electronic energy of dihydrogen is calculated as $D_e + 2I$.

Features Calculated with HF-SCF Method[*] Bond length (R) in pm and ground-state energy (E_0) in eV			
H_2	(a) 6-31G*	(b) 6-311+G**	exp
R	73.0	73.5	74.1
E_0	–30.6626	–30.8167	–32.06
F_2	(a) 3-31G*	(b) 6-311+G**	exp
R	134.5	132.9	141.8
E_0	–5406.30	–5407.92	
[*]Spartan '10™			

Both computational basis sets give satisfactory bond length agreement with the experimental value for H_2. However the 6-31G* basis set is not as accurate as the larger basis set as illustrated by consideration of both its higher ground-state energy and the variation principle that the energy of a trial wavefunction is never less than the true energy. That is, the energy provided by the 6-311+G** basis set is closer to the true energy. Figure 10E.2 shows the variation of the dihyrogen ground-state energy with the internuclear distance.

It is surprising that the 6-311+G** basis set gives a significantly shorter bond length for F_2. This might be an indication that the method should be used with caution when fluorine is present in a molecule.

Figure 10E.2



10E.12 **(a)** The standard enthalpy of formation $(\Delta_f H^\ominus / \text{kJ mol}^{-1})$ of ethene and the first few linear polyenes is listed below.

Species	Computed[*]	Experimental[†]	% error
C_2H_4	69.58	52.46694	32.6

C_4H_6	129.84	108.8 ± 0.79	19.3
C_6H_8	188.52	168. ± 3	12.2
C_8H_{10}	246.85	295.9[‡]	16.6

[*] Semi-empirical, PM3 level, Spartan ’10™

[†] http://webbook.nist.gov/chemistry/

[‡] Pedley, Naylor, and Kirby, Thermodynamic Data of Organic Compounds.

(b) The % error, shown in the table, is defined by:

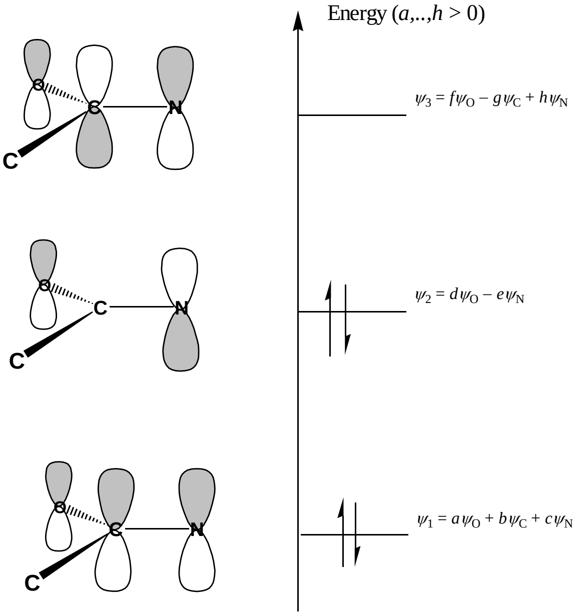
$$\%\ \text{error} = \left|\frac{\Delta_f H^\ominus(\text{calc}) - \Delta_f H^\ominus(\text{expt})}{\Delta_f H^\ominus(\text{expt})}\right| \times 100\%.$$

(c) For all of the molecules, the computed enthalpies of formation deviate from the experimental values by much more than the uncertainty in the experimental value. This observation serves to illustrate that molecular modeling software is not a substitute for experimentation when it comes to quantitative measures. It is also worth noting, however, that the experimental uncertainty can vary a great deal. The NIST database reports $\Delta_f H^\ominus$ for C_2H_4 to seven significant figures (with no explicit uncertainty). Even if the figure is not accurate to 1 part in 5000000, it is clearly a very precisely known quantity—as one should expect in such a familiar and well studied substance. The database lists two different determinations for $\Delta_f H^\ominus(C_4H_6)$, and the experimental values differ by more than the uncertainty claimed for each; a critical evaluation of the experimental data is called for. The uncertainty claimed for $\Delta_f H^\ominus(C_6H_8)$ is greater still (but still only about 2%). Finally, it should go without saying that not all of the figures reported by the molecular modeling software are physically significant.

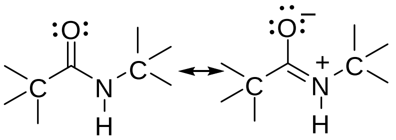
Integrated activities

10.2 **(a)** The orbitals are sketched in Figure I10.1(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 I10.1(a)



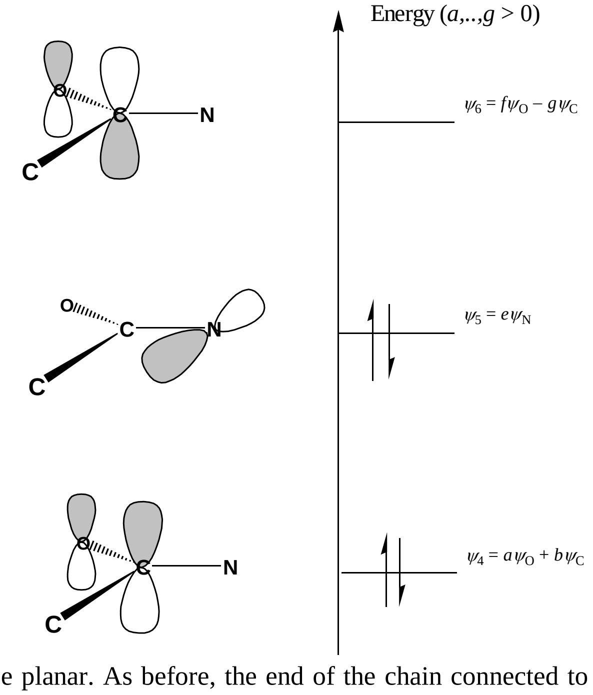
(b) This arrangement only works if the entire peptide link is coplanar. For starters, the O, C, and N atoms in the peptide link must be in the same plane (call it the *xy* plane) if all three atoms are to contribute unhybridized *p* orbitals (p_z orbitals) to make the three MOs sketched in Figure 10.15(a). And 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.



(c) The energy order of the orbitals and their occupancy are shown in Figure 10.15(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.

(d) The orbitals of the non-planar alternative are sketched in Figure I10.2(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.

Figure I10.2(b)



(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.

10.4 $$\psi_{\text{trial}} = N\mathrm{e}^{-\alpha r^2}$$

We must find the expectation value of the hydrogenic hamiltonian:

$$E_{\text{trial}} = \langle H \rangle = \int \psi_{\text{trial}} * \hat{H}\psi_{\text{trial}}\mathrm{d}\tau = \int N\mathrm{e}^{-\alpha r^2}\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right)N\mathrm{e}^{-\alpha r^2}\,\mathrm{d}\tau$$

The laplacian operator is

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2 .$$

Because Λ^2 contains derivatives with respect to angles only, we can ignore it in applying the laplacian to our trial function, which is independent of angles. Applying the kinetic energy operator to our trial function yields

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi_{\text{trial}} = \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)N\mathrm{e}^{-\alpha r^2} = \frac{\hbar^2\alpha N}{\mu}\left(\frac{\partial}{\partial r} + \frac{2}{r}\right)r\mathrm{e}^{-\alpha r^2}$$

$$= \frac{\hbar^2\alpha N}{\mu}\left(\mathrm{e}^{-\alpha r^2} - 2\alpha r^2\mathrm{e}^{-\alpha r^2} + 2\mathrm{e}^{-\alpha r^2}\right) = \frac{\hbar^2\alpha N}{\mu}(3 - 2\alpha r^2)\mathrm{e}^{-\alpha r^2}$$

Inserting this into the energy expectation yields:

$$E_{\text{trial}} = \int N\mathrm{e}^{-\alpha r^2}\left(\frac{\hbar^2\alpha N}{\mu}(3 - 2\alpha r^2)\mathrm{e}^{-\alpha r^2} - \frac{e^2 N\mathrm{e}^{-\alpha r^2}}{4\pi\varepsilon_0 r}\right)\mathrm{d}\tau$$

To actually evaluate the integral, we must write out $\mathrm{d}\tau$ and the limits of integration explicitly. Here $\mathrm{d}\tau = r^2 \sin\theta\,\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi$. Other than in $\mathrm{d}\tau$, there is no angular dependence in the integrand, so integrating over the angles yields 4π. Thus the integral becomes

$$E_{\text{trial}} = 4\pi N^2\int_0^\infty \mathrm{e}^{-2\alpha r^2}\left(\frac{3\hbar^2\alpha r^2}{\mu} - \frac{2\hbar^2\alpha^2 r^4}{\mu} - \frac{e^2 r}{4\pi\varepsilon_0}\right)\mathrm{d}r$$

Consult the integral table in the Resource section to find [G.7 and G.8]

$$\int_0^\infty x^{2n+1}\mathrm{e}^{-ax^2}\,\mathrm{d}x = \frac{n!}{2a^{n+1}}$$

$$\int_0^\infty x^{2n}\mathrm{e}^{-ax^2}\,\mathrm{d}x = \frac{(2n-1)!!}{2^{n+1}a^n}\left(\frac{\pi}{a}\right)^{1/2} \quad (2n-1)!! = 1\times3\times5\times\ldots\times(2n-1)$$

Apply these to the appropriate terms in the integral to obtain

$$E_{\text{trial}} = 4\pi N^2\left(\frac{3\hbar^2\alpha}{\mu}\times\frac{\pi^{1/2}}{2^2(2\alpha)^{3/2}} - \frac{2\hbar^2\alpha^2}{\mu}\times\frac{3\pi^{1/2}}{2^3(2\alpha)^{5/2}} - \frac{e^2}{4\pi\varepsilon_0}\times\frac{1}{2(2\alpha)}\right)$$

$$= 4\pi N^2\left(\frac{3\hbar^2\pi^{1/2}}{2^{9/2}\alpha^{1/2}\mu} - \frac{e^2}{16\pi\varepsilon_0\alpha}\right)$$

We must now evaluate $N(\alpha)$. Normalization requires

$$\int \psi * \psi\,\mathrm{d}\tau = 1 = N^2\int \mathrm{e}^{-2\alpha r^2}\,\mathrm{d}\tau = 4\pi N^2\int_0^\infty r^2\mathrm{e}^{-2\alpha r^2}\,\mathrm{d}r$$

$$1 = 4\pi N^2\times\frac{\pi^{1/2}}{2^{7/2}\alpha^{3/2}} \qquad \text{or} \qquad 4\pi N^2 = \frac{2^{7/2}\alpha^{3/2}}{\pi^{1/2}}$$

Thus, $$E_{\text{trial}} = \frac{2^{7/2}\alpha^{3/2}}{\pi^{1/2}}\left(\frac{3\hbar^2\pi^{1/2}}{2^{9/2}\alpha^{1/2}\mu} - \frac{e^2}{16\pi\varepsilon_0\alpha}\right) = \boxed{\frac{3\hbar^2\alpha}{2\mu} - \frac{e^2\alpha^{1/2}}{2^{1/2}\pi^{3/2}\varepsilon_0}} .$$

The variation principle says that the minimum energy is obtained by taking the derivative of the trial energy with respect to adjustable parameters, setting it equal to zero, and solving for the parameters:

$$\frac{\mathrm{d}E_{\text{trial}}}{\mathrm{d}\alpha} = \frac{3\hbar^2}{2\mu} - \frac{e^2}{2^{3/2}\pi^{3/2}\varepsilon_0\alpha^{1/2}} = 0$$

Solving for α yields

$$\frac{3\hbar^2}{2\mu} = \frac{e^2}{2^{3/2}\pi^{3/2}\varepsilon_0\alpha^{1/2}} \quad \text{so} \quad \alpha = \left(\frac{\mu e^2}{3\hbar^2\varepsilon_0}\right)^2\left(\frac{1}{2\pi^3}\right) = \frac{\mu^2 e^4}{18\pi^3\hbar^4\varepsilon_0^2}$$

Substituting this back into the energy expression yields the minimum energy for this trial wavefunction:

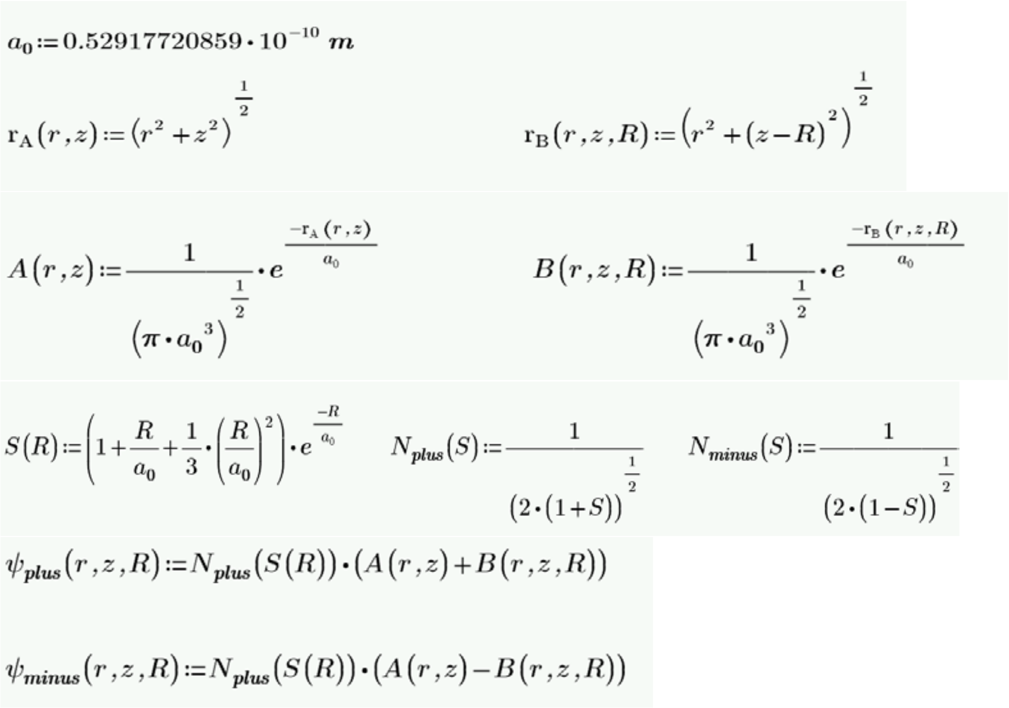
$$\begin{aligned} E_{\text{trial}} &= \frac{3\hbar^2}{2\mu}\left(\frac{\mu^2 e^4}{18\pi^3\hbar^4\varepsilon_0^2}\right) - \frac{e^2}{2^{1/2}\pi^{3/2}\varepsilon_0}\left(\frac{\mu^2 e^4}{18\pi^3\hbar^4\varepsilon_0^2}\right)^{1/2} \\ &= \frac{\mu e^4}{12\pi^3\varepsilon_0^2\hbar^2} - \frac{\mu e^4}{6\pi^3\varepsilon_0^2\hbar^2} = \boxed{\frac{-\mu e^4}{12\pi^3\varepsilon_0^2\hbar^2}} \end{aligned}$$

Notice that the above expression indicates that $\langle V\rangle = -2\langle E_{\text{k}}\rangle$ in accord with the virial theorem for a potential that goes as r^{-1}. Also, compare the above result to the actual hydrogenic energy:

$$E_{\text{H}} = \frac{-\mu e^4}{32\pi^2\varepsilon_0^2\hbar^2}$$

E_{trial} has 12π in the denominator where the true energy has 32. Thus, the trial energy is greater than (not as negative as) the true energy, consistent with the variation principle.

10.6 The equations for studying the amplitudes of the 1σ and 2σ* dihydrogen ion states are found in eqn. 10B2 and *Brief Illustration* 10B.1. This approximate method uses a linear combination of atomic 1s orbitals of the hydrogen atoms, which are label A and B. Atom A is placed at the point $(x,y,z) = (0,0,0)$ with atom B at $(x,y,z) = (0,0,R)$. Both LCAOs have cylindrical symmetrical around the internuclear z-axis so we examine amplitudes as they vary with z along a cylinder that is the perpendicular distance r from the z-axis where $r^2 = x^2 + y^2$. Calculations will be setup so that the user can select any desired r/a_0 ratio. Identical results are obtained should you wish to assign x and/or y to arbitrary values. A Mathcad Prime 2^{TM} setup and amplitude plots are shown below. Be sure to explore changes in the coefficients of both R and r and explain the observed effects. The antibonding orbital vanishes halfway between the nuclei, so we see antibonding associated with low internuclear electron density. Similarly, the bonding orbital is substantially non-zero between the nuclei (although not as large in value as at each nucleus), so we see bonding associated with high internuclear electron density.



$$a_0 := 0.52917720859 \cdot 10^{-10}\ m$$

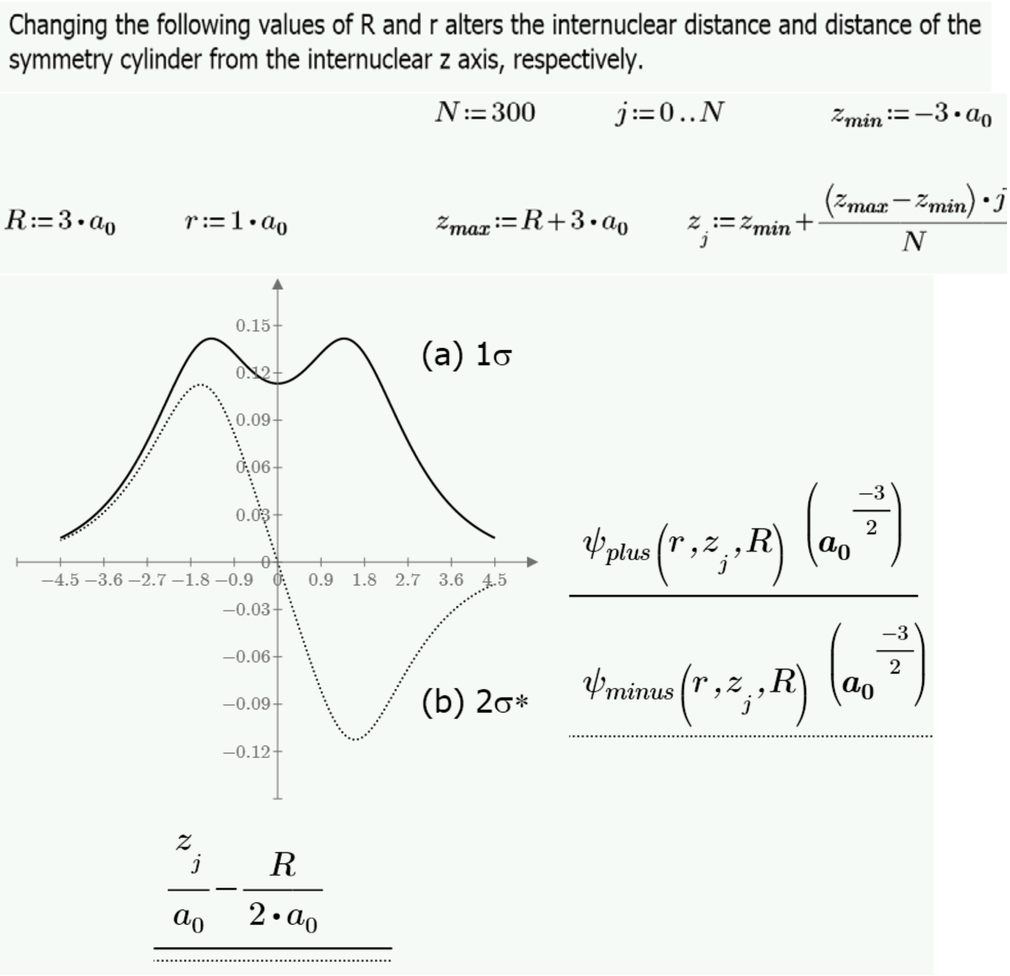
$$\mathrm{r_A}(r,z) := \left(r^2 + z^2\right)^{\frac{1}{2}} \qquad \mathrm{r_B}(r,z,R) := \left(r^2 + (z-R)^2\right)^{\frac{1}{2}}$$

$$A(r,z) := \frac{1}{\left(\pi \cdot {a_0}^3\right)^{\frac{1}{2}}} \cdot e^{\frac{-\mathrm{r_A}(r,z)}{a_0}} \qquad B(r,z,R) := \frac{1}{\left(\pi \cdot {a_0}^3\right)^{\frac{1}{2}}} \cdot e^{\frac{-\mathrm{r_B}(r,z,R)}{a_0}}$$

$$S(R) := \left(1 + \frac{R}{a_0} + \frac{1}{3}\cdot\left(\frac{R}{a_0}\right)^2\right)\cdot e^{\frac{-R}{a_0}} \qquad N_{plus}(S) := \frac{1}{(2\cdot(1+S))^{\frac{1}{2}}} \qquad N_{minus}(S) := \frac{1}{(2\cdot(1-S))^{\frac{1}{2}}}$$

$$\psi_{plus}(r,z,R) := N_{plus}(S(R))\cdot(A(r,z) + B(r,z,R))$$

$$\psi_{minus}(r,z,R) := N_{plus}(S(R))\cdot(A(r,z) - B(r,z,R))$$



Changing the following values of R and r alters the internuclear distance and distance of the symmetry cylinder from the internuclear z axis, respectively.

$N := 300 \qquad j := 0..N \qquad z_{min} := -3 \cdot a_0$

$R := 3 \cdot a_0 \qquad r := 1 \cdot a_0 \qquad z_{max} := R + 3 \cdot a_0 \qquad z_j := z_{min} + \frac{(z_{max} - z_{min}) \cdot j}{N}$

$\psi_{plus}(r, z_j, R) \left(a_0^{\frac{-3}{2}}\right)$

$\psi_{minus}(r, z_j, R) \left(a_0^{\frac{-3}{2}}\right)$

$\frac{z_j}{a_0} - \frac{R}{2 \cdot a_0}$

11 Molecular Symmetry

11A Symmetry Elements

Answers to discussion questions

11A.2

Symmetry operation	Symmetry element
Identity, *E*	The entire object
n-fold rotation	*n*-fold axis of symmetry, C_n
Reflection	Mirror plane, σ
Inversion	Centre of symmetry, *i*
n-fold improper rotation	*n*-fold improper rotation axis, S_n

There are three kinds of mirror planes. The **vertical mirror plane, σ_v**, is parallel to the principal axis while the **horizontal mirror plane, σ_h**, is perpendicular to the principal axis. A mirror plane that bisects the angle between two C_2 axes is called a **dihedral plane, σ_d**. A vertical mirror plane that bisects bonds is also given the σ_d designation.

11A.4 A molecule may be chiral, and therefore optically active, only if it does not possess an axis of improper rotation, S_n. An improper rotation is a rotation followed by a reflection and this combination of operations always converts a right-handed object into a left-handed object and *vice-versa*; hence an S_n axis guarantees that a molecule cannot exist in chiral forms. When discussing optical activity, it is helpful to remember that:
(a) the presence of both a C_n and a σ_h is equivalent to an S_n.
(b) $i = S_2$.
(c) $\sigma = S_1$.
Thus, a molecule cannot be optically active if it possesses a centre of symmetry or a mirror plane.

Solutions to exercises

11A.1(b) CCl_4 belongs to the point group T_d. It has $\boxed{\text{4 } C_3 \text{ axes}}$ (each C–Cl axis), $\boxed{\text{3 } C_2 \text{ axes}}$ (bisecting Cl–C–Cl angles), $\boxed{\text{3 } S_4 \text{ axes}}$ (the same as the C_2 axes), and $\boxed{\text{6 dihedral mirror planes}}$ (each Cl–C–Cl plane). A sample of each symmetry element is shown in Fig. 11A.1.

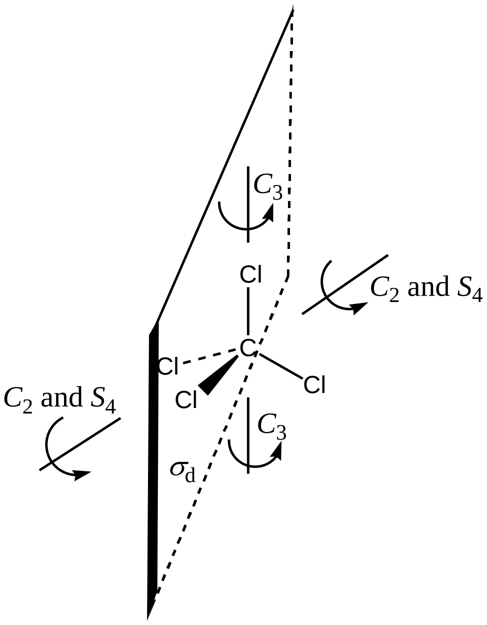


Figure 11A.1

11A.2(b) Anthracene belongs to the point group $\boxed{D_{2h}}$ and it has the symmetry elements shown in Fig. 11A.2. There are $\boxed{3C_2 \text{ axes}}$, $\boxed{\text{a centre of inversion}}$, and $\boxed{3\sigma_h \text{ mirror planes}}$.

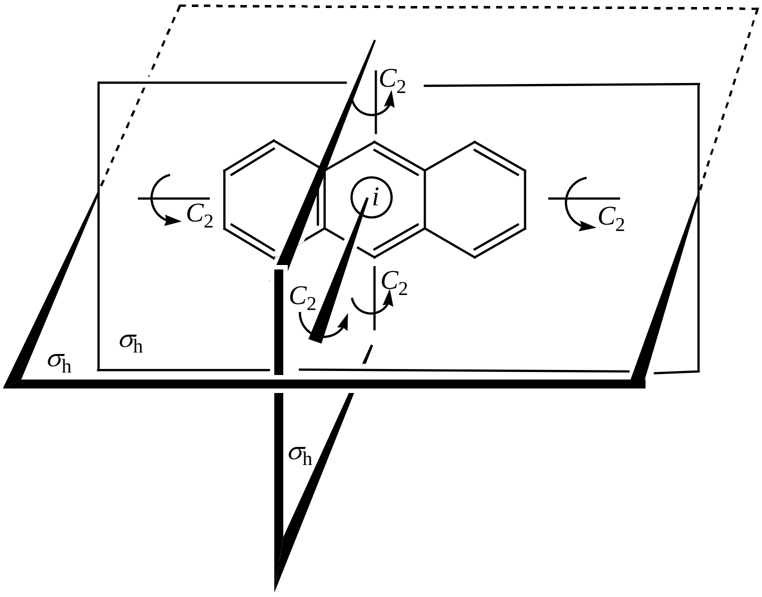


Figure 11A.2

11A.3(b) Sketch a figure of the object, identify symmetry elements, and use the flow diagram in Figure 11A.7 of the text when it simplifies the group assignment.

(i) Sharpened pencil: E, C_∞, σ_v ; therefore $\boxed{C_{\infty v}}$

(ii) Propellor: $E, C_3, 3C_2$; therefore $\boxed{D_3}$

(iii) Square table: $E, C_4, 4\sigma_v$; therefore $\boxed{C_{4v}}$; Rectangular table: $E, C_2, 2\sigma_v$; therefore $\boxed{C_{2v}}$

(iv) Person with left-right symmetry: E, σ ; therefore $\boxed{C_s}$

11A.4(b) Make a sketch of the molecule, identify symmetry elements, and use the flow diagram in Figure 11A.7 of the text when it simplifies the point group assignment.

(i) furan: E, C_2, σ_{v}, σ'_{v}; $\boxed{C_{2\mathrm{v}}}$

(ii) γ-pyran: E, C_2, σ_{v}, σ'_{v}; $\boxed{C_{2\mathrm{v}}}$

(iii) 1,2,5-trichlorobenzene: E, σ_{h}; $\boxed{C_{\mathrm{s}}}$

11A.3(b) Make a sketch of the molecule, identify symmetry elements, and use the flow diagram in Figure 11A.7 of the text when it simplifies the point group assignment.

(i) HF: linear, no i, so $\boxed{C_{\infty\mathrm{v}}}$

(ii) IF_7: pentagonal bipyramidal, E, C_5, $5C_2$, S_5, σ_{h}, σ_{v}; $\boxed{D_{5\mathrm{h}}}$

(iii) XeO_2F_2: see-saw, E, C_2, σ_{v}, σ'_{v}; $\boxed{C_{2\mathrm{v}}}$

(iv) $Fe_2(CO)_9$: E, C_3, $2C_2$, $3C_2'$, S_3, σ_{h}, σ_{v}; $\boxed{D_{3\mathrm{h}}}$

(v) Cubane (C_8H_8): E, $8C_3$, $6C_2$, $6C_4$, i, $6S_4$, $8S_6$, $3\sigma_{\mathrm{h}}$, $6\sigma_{\mathrm{d}}$; $\boxed{O_{\mathrm{h}}}$

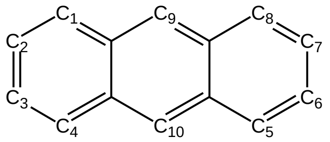
(vi) Tetrafluorocubane: E, $8C_3$, $3C_2$, $6S_4$, $6\sigma_{\mathrm{d}}$; $\boxed{T_{\mathrm{d}}}$

11A.4(b) Only molecules belonging to C_{s}, C_n, and $C_{n\mathrm{v}}$ groups may be polar, so …

(i) CH_3Cl ($C_{3\mathrm{v}}$) $\boxed{\text{polar}}$ along the C–Cl bond

(ii) $HW_2(CO)_{10}$ ($D_{4\mathrm{h}}$) $\boxed{\text{not polar}}$

(iii) $SnCl_4$ (T_{d}) $\boxed{\text{not polar}}$



11A.5(b) The parent of the dichloroanthracene isomers is shown to the right. Care must be taken when determining possible isomers because anthracene is a flat molecule that belongs to the point group $D_{2\mathrm{h}}$ as discussed in Exercise **11A.2(b)**. It has an inversion centre, mirror planes, and rotational axes that cause superficially distinct visual images to actually be the same molecule viewed from different angles. For example, Fig. 11A.3 structures are all 1,3-dichloroanthracene. By drawing figures that avoid the redundancy caused by the symmetry elements you will find a total of fifteen dichloroanthracene isomers.

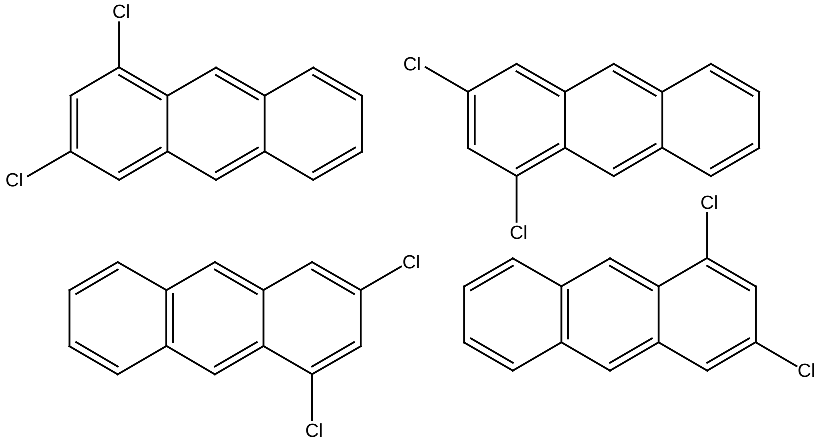


Figure 11A.3

The names and point groups of the fifteen isomers are summarized in the following table.

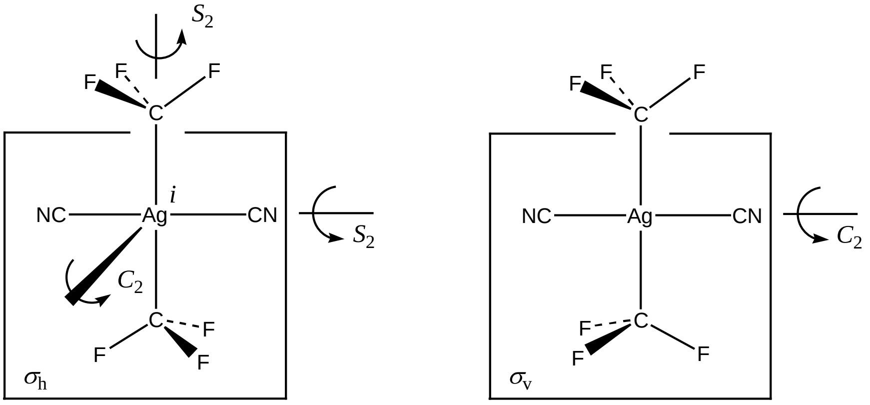
Isomers and Point Groups of *m*,*n*-Dichloroanthracene															
m,*n*	1,2	1,3	1,4	1,5	1,6	1,7	1,8	1,9	1,10	2,3	2,6	2,7	2,9	2,10	9,10
Point Group	C_s	C_s	C_{2v}	C_{2h}	C_s	C_s	C_{2v}	C_s	C_s	C_{2v}	C_{2h}	C_{2v}	C_s	C_s	D_{2h}

11A.6(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 $\boxed{\text{mirror planes } (= S_1)}$, which preclude chirality. The T_h group has, in addition, a centre of inversion (= S_2). Therefore, molecules belonging to these point groups cannot be chiral and cannot be optically active.

Solutions to problems

11A.2‡ (a) We work through the flow diagram in the text (Fig. 11A.7) first noting that this complex with freely rotating CF_3 groups is not linear, no C_n axes with $n > 2$. It does have three mutually perpendicular C_2 axes and each has a perpendicular mirror plane. Therefore, the point group is $\boxed{D_{2h}}$.

(b) The plane shown in Fig. 11A.4 below is a mirror plane so long as the CF_3 groups each have a CF bond in the plane. (i) If the CF_3 groups are staggered, then the Ag–CN axis is an S_2 axis. The Ag–CF_3 axis is also an S_2 axis, which means that the Ag atom is at an inversion centre. There is a C_2 axes perpendicular to the plane of the molecule and the plane of the molecule is a σ_h. So the point group is C_{2h}. (ii) If the CF_3 groups are eclipsed, then the axis through the Ag and perpendicular to the plane of the Ag bonds is no longer a C_2 axis; however, the Ag–CN axis is a C_2 axis. There is no σ_h but there are two σ_v planes (the plane shown and the plane perpendicular to it and through the Ag–CN bond). So the point group is $\boxed{C_{2v}}$.



(i) Staggered form, C_{2h} **(ii)** Eclipsed form, C_{2v}

Figure 11A.4

11B Group theory

Answers to discussion questions

11B.2 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.

11B.4 A representation is **reducible** when matrices of the set can be transformed (with a similarity transformation) into new matrices that are the direct sum of representations of smaller dimension. The transformation brings each matrix into block-diagonal form $\begin{pmatrix} \square & & 0 \\ & & 0 \\ 0 & 0 & \square \end{pmatrix}$ where only zero elements appear outside the blocks. The reduction of a three-dimensional representation to the direct sum of a two-dimensional and a one-dimensional representation is denoted symbolically by writing $\Gamma^{(3)} = \Gamma^{(2)} + \Gamma^{(1)}$. One-dimensional representations $\Gamma^{(1)}$ are necessarily **irreducible**.

An **irreducible representation** cannot be transformed into matrices that are a direct sum of representations of smaller dimension. The sums of their diagonal elements (the **traces**) are the **characters** of the representation symmetry operations. The set of characters for an irreducible representation is called the **symmetry species** of that representation.

Solutions to exercises

11B.1(b) Since the p_z orbitals are perpendicular to the molecular plane, we recognize that the set of p_z orbitals on each atom of BF_3 experience the C_3 change $(p_B, p_{F1}, p_{F2}, p_{F3})\boldsymbol{D}(C_3) = (p_B, p_{F3}, p_{F1}, p_{F2})$. Consequently, we find by inspection that

$$\boxed{\boldsymbol{D}(C_3) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix}}$$

11B.2(b) The matrix representations of the operations σ_h and C_3 are deduced in Exercises 11B.1(a) and 11B.1(b). According to the precepts of group theory, the successive application of these operations yields another member of the D_{3h} group to which BF_3 belongs and, in fact, by definition the operation $C_3\sigma_h$ should yield the S_3 symmetry operation. The matrix representation of S_3 can be found by matrix multiplication of the component operations.

$$\boldsymbol{D}(C_3)\boldsymbol{D}(\sigma_h) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix}\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} = \boxed{\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & -1 & 0 & 0 \end{pmatrix} = \boldsymbol{D}(S_3)}$$

The result may be checked by matrix operation on the p_z orbital vector where the effort should yield $(p_B, p_{F1}, p_{F2}, p_{F3})\boldsymbol{D}(S_3) = (-p_B, -p_{F3}, -p_{F1}, -p_{F2})$ and, as expected

$$(p_B, p_{F1}, p_{F2}, p_{F3})\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & -1 & 0 & 0 \end{pmatrix} = (-p_B, -p_{F3}, -p_{F1}, -p_{F2})$$

Also, the symmetry operations commute in this particular case.

11B.3(b) Consider the equilateral triangle $P_1P_2P_3$, which belongs to the D_{3h} point group (text Fig. 11A.8). The three C_2 axes and the three σ_v mirror planes of this triangle are shown in Fig. 11B.1.

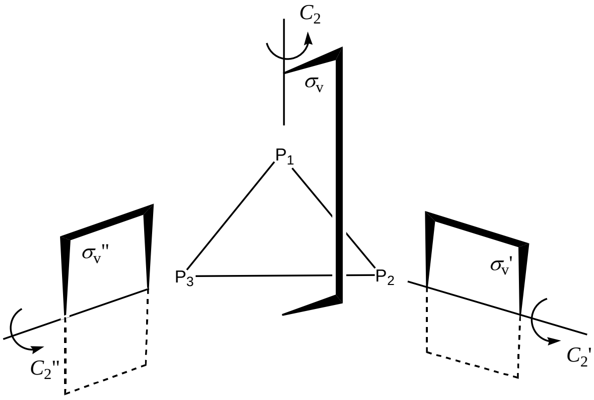


Figure 11B.1

The σ_v and σ'_v mirror planes belong to the same class if there it a member S of the group such that $\sigma'_v = S^{-1}\sigma_v S$ [11B.1] where S^{-1} is the inverse of S. We will work with $S = C''_2$, an operator for which $S^{-1} = C''_2$. By comparison of the action of $S^{-1}\sigma_v S$ upon the vector (P_1,P_2,P_3) with the action of σ'_v upon the same vector we can determine whether or not the equality of eqn. 11B.1 holds. If it does, σ_v and σ'_v mirror belong to the same class.

$$\begin{aligned} S^{-1}\sigma_v S(\mathrm{P}_1,\mathrm{P}_2,\mathrm{P}_3) &= C''_2\sigma_v C''_2(\mathrm{P}_1,\mathrm{P}_2,\mathrm{P}_3) \\ &= C''_2\sigma_v(\mathrm{P}_2,\mathrm{P}_1,\mathrm{P}_3) \\ &= C''_2(\mathrm{P}_2,\mathrm{P}_3,\mathrm{P}_1) \\ &= (\mathrm{P}_3,\mathrm{P}_2,\mathrm{P}_1) \qquad \text{(i)} \\ \sigma'_v(\mathrm{P}_1,\mathrm{P}_2,\mathrm{P}_3) &= (\mathrm{P}_3,\mathrm{P}_2,\mathrm{P}_1) \qquad \text{(ii)} \end{aligned}$$

Eqs. (i) and (ii) indicate that $\sigma'_v = S^{-1}\sigma_v S$ where $S = C''_2$ and we conclude that σ_v and σ'_v belong to the same class. By either using the same argument or seeing the necessities of symmetry we find that σ_v and σ''_v also belong to the same class. Consequently, σ_v, σ'_v and σ''_v all belong to the same class.

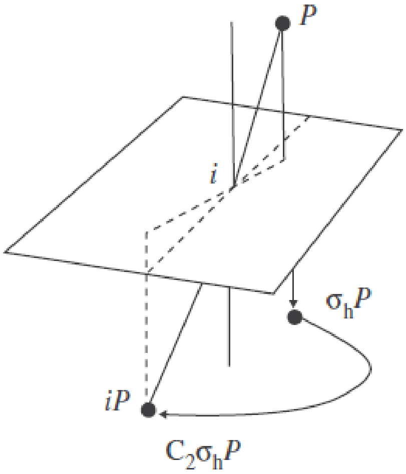
11B.4(b) Because the largest character is 5 in the column headed *E* in the *I* character table, we know that the maximum orbital degeneracy is 5.

11B.5(b) 1,4-Dichlorobenzene belongs to the D_{2h} point group. Because the largest character is 1 in the column headed *E* in the D_{2h} character table, we know that the orbitals are nondegenerate.

Solutions to problems

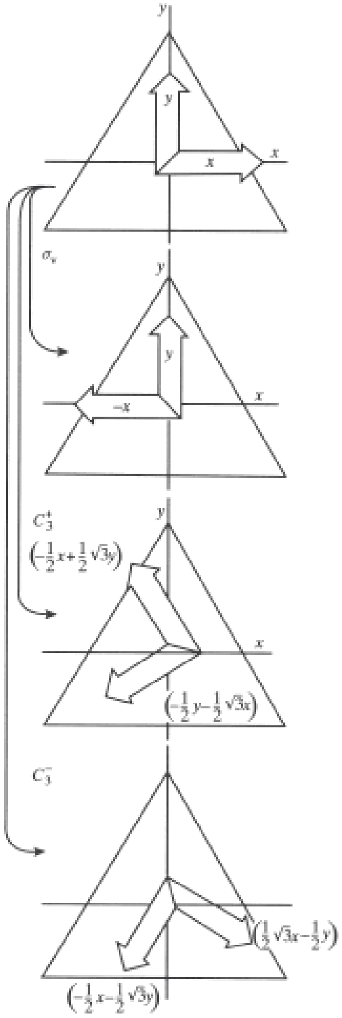
11B.1 Consider Fig. 11B.2. The effect of σ_h on a point P is to generate $\sigma_h P$, and the effect of C_2 on $\sigma_h P$ is to generate the point $C_2\sigma_h P$. The same point is generated from P by the inversion i, so $C_2\sigma_h P = iP$ for all points P. Hence, $\boxed{C_2\sigma_h = i}$, and i must be a member of the group.

Figure 11B.2



11B.4 We examine how the operations of the $C_{3\text{v}}$ group affect $l_z = xp_y - yp_x$ when applied to it. The transformation of x, y, and z, and by analogy p_x, p_y, and p_z components of momentum, are as follows (see Fig. 11B.3).

Figure 11B.3



$$E(x, y, z) \to (x, y, z)$$
$$\sigma_{\rm v}(x, y, z) \to (-x, y, z)$$
$$\sigma'_{\rm v}(x, y, z) \to (x, -y, z)$$
$$\sigma''_{\rm v}(x, y,z) \to (x, y, -z)$$
$$C_3^+(x,\ y,\ z) \to \left(-\tfrac{1}{2}x+\tfrac{1}{2}\sqrt{3}\,y, -\tfrac{1}{2}\sqrt{3}\,x -\tfrac{1}{2}y,\ z\right)$$
$$C_3^-(x, y, z) \to \left(-\tfrac{1}{2}x-\tfrac{1}{2}\sqrt{3}\,y,\ \tfrac{1}{2}\sqrt{3}\,x-\tfrac{1}{2}y, z\right)$$

The characters of all σ operations are the same, as are those of both C_3 operations (see the $C_{3\rm v}$ character table); hence we need consider only one operation in each class.

$$El_z = xp_y - yp_x = l_z$$
$$\sigma_{\rm v}l_z = -xp_y + yp_x = -l_z \quad [(x,\ y,\ z) \to (-x,\ y,\ z)]$$
$$C_3^+l_z = (-\tfrac{1}{2}x+\tfrac{1}{2}\sqrt{3}y)\times(-\tfrac{1}{2}\sqrt{3}p_x -\tfrac{1}{2}p_y) - (-\tfrac{1}{2}\sqrt{3}x-\tfrac{1}{2}y)\times(-\tfrac{1}{2}p_x+\tfrac{1}{2}\sqrt{3}p_y)$$
$$[(x,\ y,\ z) \to (-\tfrac{1}{2}x+\tfrac{1}{2}\sqrt{3}y, -\tfrac{1}{2}\sqrt{3}x-\tfrac{1}{2}y,\ z)]$$
$$= \tfrac{1}{4}(\sqrt{3}xp_x + xp_y - 3yp_x - \sqrt{3}yp_y - \sqrt{3}xp_x + 3xp_y - yp_x + \sqrt{3}yp_y)$$
$$= xp_y - yp_x = l_z$$

The representatives of E, $\sigma_{\rm v}$, and C_3^+ are therefore all one-dimensional matrices with characters 1, –1, 1, respectively. It follows that l_z is a basis for A_2 (see the $C_{3\rm v}$ character table).

11B.6 Using the symbolism defined in the solution for Problem 11B.5, we find:

$$\boldsymbol{D}\left(C_{3\rm A}^+\right)\boldsymbol{D}\left(C_{3\rm A}^-\right) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \boldsymbol{D}(E)$$

$$\boldsymbol{D}\left(S_{4\rm AB}^+\right)\boldsymbol{D}\left(C_{3\rm A}^+\right) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \end{pmatrix} = \boldsymbol{D}\left(S_{4\rm AC}^-\right)$$

$$\boldsymbol{D}\left(S_{4\rm AB}^+\right)\boldsymbol{D}\left(C_{3\rm C}^+\right) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \boldsymbol{D}\left(\sigma_{\rm dAC}\right)$$

11B.8 The *RR*' multiplication table, using $\sigma_0 = 1$, is

*R**R*'	σ_0	σ_x	σ_y	σ_z
σ_0	σ_0	σ_x	σ_y	σ_z
σ_x	σ_x	σ_0	$\mathrm{i}\,\sigma_z$	$-\mathrm{i}\,\sigma_y$
σ_y	σ_y	$-\mathrm{i}\,\sigma_z$	σ_0	$\mathrm{i}\,\sigma_x$
σ_z	σ_z	$\mathrm{i}\,\sigma_y$	$-\mathrm{i}\,\sigma_x$	σ_0

The matrices $\boxed{\text{do not form a group}}$ since the products $\mathrm{i}\sigma_z$, $\mathrm{i}\sigma_y$, $\mathrm{i}\sigma_x$ and their negatives are not among the four

Pauli spin matrices, **σ**.

11C Applications of symmetry

Answers to discussion questions

11C.2 Molecular orbitals of specified symmetry can be generated from an arbitrary basis or set of atomic orbitals by the application of group theory. The technique involves generating **symmetry-adapted linear combinations** (SALCs), which serve as building blocks of LCAO molecular orbitals. The method makes use of a **projection operator**, $P^{(\Gamma)}$, an operator that takes one of the basis orbitals and generates from it an SALC of the symmetry species Γ:

$$P^{(\Gamma)}=\frac{1}{h}\sum_{R}\chi^{(\Gamma)}(R)R \quad \text{for } \psi_m^{(\Gamma)}=P^{(\Gamma)}\chi_o \quad [11\text{C}.5]$$

To perform the projection:

- Write each basis orbital at the head of a column and in successive rows show the effect of each operation R on each orbital. Treat each operation individually.
- Multiply each member of the column by the character, $\chi^{(\Gamma)}(R)$, of the corresponding operation.
- Add together all the orbitals in each column with the factors as determined in (2).
- Divide the sum by the order of the group, h.

Text Example 11C.4 illustrates the construction method. We provide a further example by constructing the E symmetry-adapted linear combinations of H1s orbitals for NH_3, which belongs to the C_{3v} point group.

From the (s_N,s_A,s_B,s_C) basis in NH_3 we form the following table with each row showing the effect of the operation shown on the left.

	s_N	s_A	s_B	s_C
E	s_N	s_A	s_B	s_C
C_3^+	s_N	s_B	s_C	s_A
C_3^-	s_N	s_C	s_A	s_B
σ_v	s_N	s_A	s_C	s_B
σ_v'	s_N	s_B	s_A	s_C
σ_v''	s_N	s_C	s_B	s_A

To generate an E combination, we take the characters for E (2,−1,−1,0,0,0); then multiplication by the column under s_A leads to $\psi \propto 2s_A - s_B - s_C$. Multiplication by the column under s_B leads to the second E combination: $\psi \propto 2s_B - s_C - s_A$. Multiplication by the column under s_C leads to a combination that is a linear combination of the previous two so it gives no further information. Notice that the first SALC minus the second gives $\psi \propto s_A - s_B$ so, should we wish, the pair $\psi \propto 2s_A - s_B - s_C$ and $\psi \propto s_A - s_B$ can be chosen as the doubly degenerate e orbitals as shown in text Figure 11B.1.

Solutions to exercises

11C.1(b) The p_x orbital spans E' of the D_{3h} point group while z and p_z span A_2''. Following the Section 11C.1(a) procedure for deducing the symmetry species spanned by the product f_1f_2 and hence to see whether it does indeed span A_1, we write a table of the characters of each function and multiply the rows.

D_{3h}	E	σ_h	$2C_3$	$2S_3$	$3C_2'$	$3\sigma_v$
p_x	2	2	–1	–1	0	0
z	1	–1	1	–1	–1	1
p_z	1	–1	1	–1	–1	1
p_xzp_z	2	2	–1	–1	0	0

The characters of the product p_xzp_z are those of E' alone, so the integrand does not span A_1. It follows that the integral must be zero.

11C.2(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 [11C.6] have transition integrands that span $E_{2u} \times E_{1u} \times A_{1g}$ for the $A_{1g} \to E_{2u}$ transition. By inspection of the C_{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 $A_{1g} \to E_{2u}$ transition. Consequently, the z component of the transition integral must also equal zero and we conclude that the transition is 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 [11C.2]:

$$n(A_{1g}) = (4) + 2(-1) + 2(1) + (-4) + 3(0) + 3(0) + (4) + 2(-1) + 2(1) + (-4) + 3(0) + 3(0) = 0$$

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.

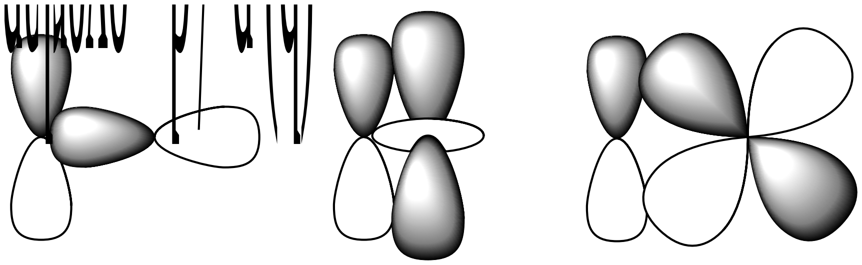
11C.3(b) The classes of operations for D_2 are: E, $C_2(x)$, $C_2(y)$, and $C_2(z)$. How does the function xyz behave under each kind of operation? E leaves it unchanged. $C_2(x)$ leaves x unchanged and takes y to $-y$ and z to $-z$, leaving the product xyz unchanged. $C_2(y)$ and $C_2(z)$ have similar effects, leaving one axis unchanged and taking the other two into their negatives. These observations are summarized as follows.

	E	$C_2(x)$	$C_2(y)$	$C_2(z)$
xyz	1	1	1	1

A look at the character table shows that this set of characters belongs to symmetry species $\boxed{A_1}$.

11C.4(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 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 only the valence p_z orbital of N may possibly have a nonzero overlap with this O combination. Furthermore, only the p_z, the d_{xz} and the d_{yz} orbitals of S may possibly have nonzero overlap in this π system. To see this, look for nonzero overlap between $p_z(O)$ and $p_x(N)$ orbitals in Fig. 11C.1(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 Fig. 11C.1(b). The p_z/d_{xz} overlap shown in Fig. 11C.1(c) yields a net nonzero overlap because both the overlap of positive lobes and the overlap of negative lobes results in constructive interference.



(a) p_z/p_x overlap (c) p_z/d_{xz} overlap

Figure 11C.1

Now, consider the non-normalized combination of oxygen p_z orbitals to be: $p_{z,\text{comb}} = a\times p_z(A) + b\times p_z(B) + c\times p_z(C)$ where a, b, and c are constants. The overlap integral of $p_{z,\text{comb}}$ with $p_z(N)$ is

$$\int p_{z,\text{comb}}\times p_z(\text{N})\,d\tau = \int\{a\times p_z(\text{A})+b\times p_z(\text{B})+c\times p_z(\text{C})\}\times p_z(\text{N})\,d\tau$$

$$= a\times\int p_z(\text{A})\times p_z(\text{N})\,d\tau + b\times\int p_z(\text{B})\times p_z(\text{N})\,d\tau + b\times\int p_z(\text{C})\times p_z(\text{N})\,d\tau$$

The three N─O bond lengths are equivalent so

$$\int p_z(\text{A})\times p_z(\text{N})\,d\tau = \int p_z(\text{B})\times p_z(\text{N})\,d\tau = \int p_z(\text{C})\times p_z(\text{N})\,d\tau$$

and the overlap integral becomes

$$\int p_{z,\text{comb}}\times p_z(\text{N})\,d\tau = (a+b+c)\times\int p_z(\text{A})\times p_z(\text{N})\,d\tau$$

$$\begin{cases} = 0 \text{ if } a+b+c=0 \text{ (as in this exercise, which has } a+b+c=2-1-1=0) \\ \neq 0 \text{ if } a+b+c\neq 2 \end{cases}$$

Thus, the overlap integral is generally nonzero but it is zero for the very specific combination $2p_z(A) - p_z(B) - p_z(C)$ because the AO's are in the specific ratio +2:−1:−1. We conclude that no orbital of the central N atom can have a nonzero overlap with the combination $2p_z(A) - p_z(B) - p_z(C)$ of the three O atoms but that the d_{xz} and d_{yz} orbitals of S may possibly have nonzero overlap in this π system. We now turn to the application of group theory and the use of symmetry-adapted linear combinations (SALCs) to gain a understanding of origin and symmetry species of the $2p_z(A) - p_z(B) - p_z(C)$ combination.

The symmetry species spanned by the oxygen $(p_z(A),p_z(B),p_z(C))$ basis is easily found with use of these quick rules for determining the character of the basis set under each symmetry operation of the group D_{3h}:

Count zero each time a basis function is changed by the operation but count 1 each time a basis function is left unchanged by the operation, because only these functions give a nonzero 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. Fig. 11C.2 is used to evaluate the effect of the operations on the oxygen $(p_z(A),p_z(B),p_z(C))$ basis.

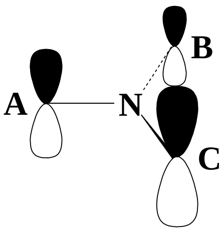


Figure 11C.2

Here is a tabulated summary of the characters:

D_{3h}	E	σ_h	$2C_3$	$2S_3$	$3C_2'$	$3\sigma_v$
$(p_z(A),p_z(B),p_z(C))$	3	–3	0	0	–1	1

Inspection of the D_{3h} character table reveals that the above characters of the oxygen (p_z(A),p_z(B),p_z(C)) basis spans $A_2'' + E''$ because the sum of the A_2'' and E'' characters yields those of the above 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, as expected, only p_z, d_{xz}, and d_{yz} orbitals of the central atom may possibly have nonzero overlap with symmetry-adapted basis formed from (p_z(A),p_z(B),p_z(C)).

We continue by finding the SALCs using the procedure of text Section 11C.2(b). In the process we find why the specific combination $2p_z(A) - p_z(B) - p_z(C)$ has been introduced in this exercise. We use the D_3 subgroup for convenience and the following table summarizes the effect of point group operations on members of the (p_z(A),p_z(B),p_z(C)) basis.

D_3, $h = 6$	p_z(A)	p_z(B)	p_z(C)
E	p_z(A)	p_z(B)	p_z(C)
C_3^+	p_z(C)	p_z(A)	p_z(B)
C_3^-	p_z(B)	p_z(C)	p_z(A)
$C_2'(A-N)$	$-p_z$(A)	$-p_z$(C)	$-p_z$(B)
$C_2'(B-N)$	$-p_z$(C)	$-p_z$(B)	$-p_z$(A)
$C_2'(C-N)$	$-p_z$(B)	$-p_z$(A)	$-p_z$(C)

To generate the A_2 combination take $\chi(A_2) = (1\ 1\ 1\ -1\ -1\ -1)$ and multiply by any column of table transformations, sum terms, and divide by 6. This gives the totally symmetric combination.

A_2'': $p_{z,\text{comb }1} = \tfrac{1}{3}\times(p_z(A) + p_z(B) + p_z(C))$

To generate the E combinations take $\chi(E) = (2\ -1\ -1\ 0\ 0\ 0)$ and multiply by each column of table transformations, sum terms for each, and divide each by 6. This gives three SALCs.

E'': $p_{z,\text{comb }2} = \tfrac{1}{6}\times(2p_z(A) - p_z(B) - p_z(C))$
$p_{z,\text{comb }3} = \tfrac{1}{6}\times(2p_z(B) - p_z(A) - p_z(C))$
$p_{z,\text{comb }4} = \tfrac{1}{6}\times(2p_z(C) - p_z(B) - p_z(A))$

$p_{z,\text{comb }4}$ is a linear combination of the previous two, $p_{z,\text{comb }4} = -(p_{z,\text{comb }2} + p_{z,\text{comb }3})$, so we discard it and are left with the double degenerate, orthogonal pair $p_{z,\text{comb }2}$ and $p_{z,\text{comb }3}$. In the process we have shown that the combination of the exercise, which is $p_{z,\text{comb }2}$, belongs to the E'' symmetry species of D_{3h}.

Finally, inspection of the D_{3h} character table tells us that p_z(N) belongs to the A_2'' symmetry species so the integrand of the overlap integral between p_z(N) and $p_{z,\text{comb }2}$ has the symmetry $A_2'' \times E'' = E'$. The integrand does not span the totally symmetric species A_1' so the overlap integral is necessarily zero.

11C.4(b) The product $\Gamma_f \times \Gamma(\mu) \times \Gamma_i$ must contain A_1 (Example 11C.5 of text). Then, since $\Gamma_i = B_1$ and $\Gamma(\mu) = \Gamma(y) = B_2$ of the 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 $A_2 \times A_2 = A_1$.

11C.5(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

$$n(\Gamma)=\frac{1}{h}\sum_R \chi^{(\Gamma)}(R)\chi(R) \qquad [11C.2] \qquad \text{where } \chi(R)=(6,-2,0,0)$$

$$n(A_1)=\tfrac{1}{4}\{1(1\times 6)+1(1\times(-2))+1(1\times 0)+1(1\times 0)\}=1$$

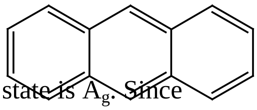
$$n(B_1)=\tfrac{1}{4}\{1(1\times 6)+1(1\times(-2))+1(-1\times 0)+1(-1\times 0)\}=1$$

$$n(B_2)=\tfrac{1}{4}\{1(1\times 6)+1(-1\times(-2))+1(1\times 0)+1(-1\times 0)\}=2$$

$$n(B_3)=\tfrac{1}{4}\{1(1\times 6)+1(-1\times(-2))+1(-1\times 0)+1(1\times 0)\}=2$$

Thus, this set of basis functions spans $\boxed{A_1 + B_1 + 2B_2 + 2B_3}$.

11C.6(b) (i) 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).

(ii) 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.

11C.8(b) The C_s character table indicates that x and y are invariant under the σ_h symmetry operation while the character of z is -1 under σ_h. Thus, the z-axis is perpendicular to the σ_h plane, the x and y axes are in the plane. The character table also indicates that x^2 belongs to the A' irrep so we surmise that $x\times x^2 = x^3$ also belongs to A' (because A'×A' = A') and that any polynomial in x must belong to the totally symmetric A' irrep. Thus, $\boxed{\text{the integral of any polynomial in } x \text{ may be non-zero}}$ when integrated over an object of C_s symmetry (methanol, bromochloromethane, O=N–Cl, etc.).

Now, consider the odd function $f(z) = f_1(z)\times f_2(z) = z\times(3z^2-1)$. Being perpendicular to the σ_h plane, the z dimension can exhibit a symmetrical integration interval from one side of the plane to the other side in a C_s object so we place the z-axis origin in the plane. The C_s character table indicates that z belongs to A" while z^2 belongs to the totally symmetric A' irrep. Thus, the function $z\times(3z^2-1)$ belongs to A'×A" = A" and, since it does not span the totally symmetric irrep, $\boxed{\text{integration of the function over a symmetric interval around } z = 0 \text{ is necessarily zero}}$:

$$I=\int_{-a}^{a} f_1(z)\times f_2(z)\,dz=\int_{-a}^{a} z\times(3z^2-1)\,dz=0$$

Solutions to problems

11C.2 (a) In C_{3v} symmetry the H1s orbitals span the same irreducible representations as in NH_3, which is A_1 +

A_1 + E. There is an additional A_1 orbital because a fourth H atom lies on the C_3 axis. In C_{3v}, the d orbitals span A_1 + E + E [see the final column of the C_{3v} character table]. Therefore, $\boxed{\text{all five d orbitals}}$ may contribute to the bonding.

(b) In C_{2v} symmetry the H1s orbitals span the same irreducible representations as in H_2O, but one “H_2O” fragment is rotated by 90° with respect to the other. Therefore, whereas in H_2O the H1s orbitals span $A_1 + B_2$ [$H_1 + H_2$, $H_1 - H_2$], in the distorted CH_4 molecule they span $A_1 + B_2 + A_1 + B_1$ [$H_1 + H_2$, $H_1 - H_2$, $H_3 + H_4$, $H_3 - H_4$]. In C_{2v} the d orbitals span $2A_1 + B_1 + B_2 + A_2$ [C_{2v} character table]; therefore, $\boxed{\text{all except } A_2(d_{xy})}$ may participate in bonding.
Note: The method used to solve Problem 11C.1 also works nicely.

11C.4‡ (a) For a photon to induce a spectroscopic transition, the transition moment (μ) must be nonzero. The transition moment is the integral $\int \psi_f^* \boldsymbol{\mu} \psi_i \, d\tau$, 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 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 the eqn. 11C.2 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. 11C.2, the little orthogonality theorem, gives the coefficient of A_1 in the integrand as

$$n(\mathrm{A}_1) = \frac{1}{h}\sum_R \chi^{(\mathrm{A}_1)}(R)\chi(R)$$

$$= \{12 + 12[-\tfrac{1}{2}(1+\sqrt{5})] + 12[-\tfrac{1}{2}(1-\sqrt{5})] + 20(0) + 15(0)\}/60 = 0$$

So the integrand does not contain A_1, and the transition to G would still be forbidden.

11C.6 Can the $\mathrm{E_u}$ excited state be reached by a dipole transition from the $\mathrm{A_{1g}}$ ground state? Only if the representation of the product $\psi_\mathrm{f}^*\boldsymbol{\mu}\psi_\mathrm{i}$ includes the totally symmetric species $\mathrm{A_{1g}}$. The *z* component of the dipole operator belongs to symmetry species $\mathrm{A_{2u}}$, and the *x* and *y* components belong to $\mathrm{E_u}$. So the products we must consider are $\mathrm{E_u}\times\mathrm{A_{2u}}\times\mathrm{A_{1g}}$ and $\mathrm{E_u}\times\mathrm{E_u}\times\mathrm{A_{1g}}$. For *z*-polarized transitions, the relevant characters are:

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_\mathrm{v}$	$2\sigma_\mathrm{d}$
$\mathrm{E_u}$	2	0	–2	0	0	–2	0	2	0	0
$\mathrm{A_{2u}}$	1	1	1	–1	–1	–1	–1	–1	1	1
$\mathrm{A_{1g}}$	1	1	1	1	1	1	1	1	1	1
$\mathrm{E_uA_{2u}A_{1g}}$	2	0	–2	0	0	2	0	–2	0	0

To see whether $\mathrm{E_u}\times\mathrm{A_{2u}}\times\mathrm{A_{1g}}$ contains $\mathrm{A_{1g}}$, we would multiply the characters of the $\mathrm{E_u}\times\mathrm{A_{2u}}\times\mathrm{A_{1g}}$ by the characters of $\mathrm{A_{1g}}$, sum those products, and divide the sum by the order *h* of the group; since the characters of $\mathrm{A_{1g}}$ are all 1, we can simply sum the characters of $\mathrm{E_u}\times\mathrm{A_{2u}}\times\mathrm{A_{1g}}$. Because they sum to zero, the product $\mathrm{E_u}\times\mathrm{A_{2u}}\times\mathrm{A_{1g}}$ does not contain $\mathrm{A_{1g}}$, and the $\boxed{z\text{-polarized transition is not allowed}}$.

For *x*- or *y*-polarized transitions:

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_\mathrm{v}$	$2\sigma_\mathrm{d}$
$\mathrm{E_u}$	2	0	–2	0	0	–2	0	2	0	0
$\mathrm{E_u}$	2	0	–2	0	0	–2	0	2	0	0
$\mathrm{A_{1g}}$	1	1	1	1	1	1	1	1	1	1
$\mathrm{E_uA_{2u}A_{1g}}$	4	0	4	0	0	4	0	4	0	0

Summing the characters of $\mathrm{E_u}\times\mathrm{A_{2u}}\times\mathrm{A_{1g}}$, yields 16, the order of the group. Therefore the product $\mathrm{E_u}\times\mathrm{A_{2u}}\times\mathrm{A_{1g}}$ does contain $\mathrm{A_{1g}}$, and the $\boxed{\text{transition is allowed}}$.

12 Rotational and vibrational spectra

Note: The masses of nuclides are listed in Table 0.2 of the *Resource section*.

12A General features of molecular spectroscopy

Answers to discussion questions

12A.2 *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 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. The shape of a Doppler-broadened spectral line reflects the Maxwell distribution of speeds in the sample at the temperature of the experiment; hence the line broadens as the temperature is increased because the molecules acquire a wider and higher range of speeds. Doppler broadening can be significant in gas-phase samples but it can be reduced by decreasing the sample temperature.

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 $\delta E \approx \hbar/\tau$ (eqn 12A.19) and is due to the finite lifetimes τ of the states involved in emission transitions. When τ is finite, the energy of the states is smeared out and hence the transition frequency is broadened. The rate of spontaneous emission cannot be changed; hence it is a natural limit to the breadth of a spectral line.

Pressure broadening or collisional broadening. **Collisional deactivation**, which arises from collisions between molecules and from collision of molecules with the walls of the container, affects the rate of transition from an upper to a lower energy state. Lowering the pressure can reduce this rate. For a gas phase **collisional lifetime** of τ_{col}, the mean time between collisions, the resulting collisional linewidth is $\delta E_{\text{col}} \sim \hbar/\tau_{\text{col}}$. Because $\tau_{\text{col}} = 1/z$ for gases where z is the collision frequency, the kinetic model of gases implies that z is proportional to the pressure and that linewidths are proportional to the gas pressure. Thus, gas phase linewidths can be reduced by decreasing the pressure. The collisional frequency of liquid phase molecules is more difficult to define but, since pressure has little effect upon liquid density and kinetic energy, we expect pressure to have little effect upon the linewidth of liquid samples. Estimating that a liquid-phase molecule experiences a deactivating collision in the period of a vibration, the collisional linewidth is something like $\delta E_{\text{col}} \sim \hbar/\tau_{\text{col}} \sim \hbar/(1.0\times10^{-13}\ \text{s}) \sim 1.1\times10^{-21}\ \text{J}$ or $\sim 53\ \text{cm}^{-1}/(\tau/\text{ps})$ [12A.19] as a wavenumber.

Solutions to exercises

12A.1(b) The ratio of Einstein coefficients A/B is

(i)
$$\frac{A}{B} = \frac{8\pi h\nu^3}{c^3}\ [12\text{A}.9] = \frac{8\pi\left(6.626\times10^{-34}\,\text{Js}\right)\times\left(500\times10^{6}\,\text{s}^{-1}\right)^3}{\left(2.998\times10^{8}\ \text{m s}^{-1}\right)^3} = \boxed{7.73\times10^{-32}\,\text{J m}^{-3}\text{s}}$$

(ii)
$$\nu = \frac{c}{\lambda}\ \text{so}\ \frac{A}{B} = \frac{8\pi h}{\lambda^3} = \frac{8\pi\left(6.626\times10^{-34}\,\text{J s}\right)}{\left(3.0\times10^{-2}\ \text{m}\right)^3} = \boxed{3.9\times10^{-28}\,\text{J m}^{-3}\ \text{s}}$$

12A.2(b) $\log\dfrac{I}{I_0} = -\log\dfrac{I_0}{I} = -\varepsilon[\mathrm{J}]L \quad [12\mathrm{A}.13 \text{ and } 12\mathrm{A}.14]$

$$= (-227\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}) \times (2.52\times10^{-3}\ \mathrm{mol\ dm^{-3}}) \times (0.200\ \mathrm{cm})$$
$$= -0.114$$

Hence, $\dfrac{I}{I_0} = 10^{-0.114} = 0.769$, and the reduction in intensity is $\boxed{23.1 \text{ per cent}}$.

12A.3(b) $\log\dfrac{I}{I_0} = -\log\dfrac{I_0}{I} = -\varepsilon[\mathrm{J}]L \quad [12\mathrm{A}.13 \text{ and } 12\mathrm{A}.14]$

$$\varepsilon = -\frac{1}{[\mathrm{J}]L}\log\frac{I}{I_0}$$
$$= \frac{-\log 0.615}{(7.17\times10^{-4}\ \mathrm{mol\ dm^{-3}})\times(0.25\,\mathrm{cm})} = 1.2\times10^{3}\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$$
$$= 1.2\times10^{6}\ \mathrm{cm^3\ mol^{-1}\ cm^{-1}} \quad [1\,\mathrm{dm} = 10\,\mathrm{cm}]$$
$$= \boxed{1.2\times10^{6}\ \mathrm{cm^2\ mol^{-1}}}$$

12A.4(b) $\log T = -A = -\varepsilon[\mathrm{J}]L \quad [12\mathrm{A}.12\text{-}14]$

$$[\mathrm{J}] = -\frac{1}{\varepsilon L}\log T = \frac{-\log(1-0.483)}{(423\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}})\times(0.650\ \mathrm{cm})}$$
$$= \boxed{1.04\ \mathrm{mmol\ dm^{-3}}}$$

12A.5(b) $\varepsilon = -\dfrac{1}{[\mathrm{J}]L}\log\dfrac{I}{I_0} \quad [12\mathrm{A}.13 \text{ and } 12\mathrm{A}.14] \quad \text{with } L = 0.20\ \mathrm{cm}$

We use this formula to draw up the following table.

[dye] / mol dm^{-3}	0.0010	0.0050	0.0100	0.0500
I / I_0	0.68	0.18	0.037	1.03×10^{-7}
ε / (dm^{-3} mol^{-1} cm^{-1})	670	596	573	559

The table indicates that as the dye concentration increases the molar absorption coefficient does not remain constant. Rather, it significantly decreases. The reason for this is not entirely evident but we may hypothesize that the dye molecules become associated at the higher concentrations and that the associated state exhibits a lower absorption coefficient than that of the unassociated dye molecule. Should this hypothesis be correct, the molar absorption coefficient at the low concentration, $\boxed{670\ \mathrm{dm^3\ mol^{-1}\ cm^{-2}}}$, is the molar absorption coefficient of the dye.

12A.6(b) $\varepsilon = -\dfrac{1}{[\mathrm{J}]L}\log\dfrac{I}{I_0} \quad [12\mathrm{A}.13,\ 12\mathrm{A}.14] = \dfrac{-1}{(0.0185\ \mathrm{mol\ dm^{-3}})\times(0.500\ \mathrm{cm})}\log(0.29) = \boxed{58\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}}$

$$T = \frac{I}{I_0} = 10^{-[\mathrm{J}]\varepsilon L} \quad [12\mathrm{A}.12\text{-}14]$$
$$= 10^{(-0.0185\ \mathrm{mol\ dm^{-3}})\times(58\ \mathrm{dm^3\ mol^{-1}cm^{-1}})\times(0.250\ \mathrm{cm})} = 10^{-0.27} = 0.54, \text{ or } \boxed{54 \text{ per cent}}$$

12A.7(b) $\log\dfrac{I}{I_0} = -\varepsilon[\mathrm{J}]L \quad \text{so} \quad L[\mathrm{J}] = -\dfrac{1}{\varepsilon}\log\dfrac{I}{I_0} \quad [12\mathrm{A}.13 \text{ and } 12\mathrm{A}.14]$

(i) $L[\mathrm{J}] = -\dfrac{1}{30\,\mathrm{dm^3\ mol^{-1}\ cm^{-1}}}\times\log\dfrac{1}{2} = \boxed{0.010\ \mathrm{mol\,dm^{-3}cm}}$

(ii) $L[\mathrm{J}] = -\dfrac{1}{30\,\mathrm{dm^3\ mol^{-1}\ cm^{-1}}}\times\log(0.10) = \boxed{0.033\ \mathrm{mol\,dm^{-3}cm}}$

12A.8(b) A parabolic lineshape, shown in Fig. 12.1 of the text, 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 $^2/_3$ × base width × height. Let $\tilde{\nu}_\mathrm{i}$ and $\tilde{\nu}_\mathrm{f}$ be the initial and final wavenumbers of the absorption band. Then, the base of the band has the width $\Delta\tilde{\nu}=\tilde{\nu}_\mathrm{f}-\tilde{\nu}_\mathrm{i}$ and the integrated absorption coefficient is the area given by

$$\mathcal{A}=\int_\mathrm{band}\varepsilon(\tilde{\nu})\,\mathrm{d}\tilde{\nu}\quad[\text{12A.15}]=\int_{\tilde{\nu}_\mathrm{i}}^{\tilde{\nu}_\mathrm{f}}\varepsilon(\tilde{\nu})\,\mathrm{d}\tilde{\nu}={}^2\!/_3\times(\tilde{\nu}_\mathrm{f}-\tilde{\nu}_\mathrm{i})\times\varepsilon_\mathrm{max}\quad\text{(See note below.)}$$

Since $\tilde{\nu}=\lambda^{-1}$ and $\tilde{\nu}/\mathrm{cm}^{-1}=10^7/(\lambda/\mathrm{nm})$, the initial and final wavenumbers of the absorption band are:
$\tilde{\nu}_\mathrm{i}/\mathrm{cm}^{-1}=10^7/(275)=3.64\times10^4$ and $\tilde{\nu}_\mathrm{f}/\mathrm{cm}^{-1}=10^7/(156)=6.41\times10^4$. So

$$\mathcal{A}={}^2\!/_3\times\left(6.41\times10^4\ \mathrm{cm}^{-1}-3.64\times10^4\ \mathrm{cm}^{-1}\right)\times\left(3.35\times10^4\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-1}\right)$$

$$=\boxed{6.19\times10^8\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-2}}$$

Note: The formula for the area of a parabola can be derived with the equation for a parabola (see Fig. 12.1 of the text):

$$\varepsilon(\tilde{\nu})=\varepsilon_\mathrm{max}\left\{1-\kappa(\tilde{\nu}-\tilde{\nu}_\mathrm{max})^2\right\}$$

The symmetry of the parabola means that $\tilde{\nu}_\mathrm{max}=\tilde{\nu}_\mathrm{i}+{}^1\!/_2\Delta\tilde{\nu}=\tilde{\nu}_\mathrm{f}-{}^1\!/_2\Delta\tilde{\nu}$. Because $\varepsilon(\tilde{\nu}_\mathrm{i})=\varepsilon(\tilde{\nu}_\mathrm{f})=0$, the constant κ is easily determined by examination of the parabola equation at either $\varepsilon(\tilde{\nu}_\mathrm{i})$ or $\varepsilon(\tilde{\nu}_\mathrm{f})$.

$$0=\varepsilon_\mathrm{max}\left\{1-\kappa(\tilde{\nu}_\mathrm{i}-\tilde{\nu}_\mathrm{max})^2\right\}=\varepsilon_\mathrm{max}\left\{1-\kappa(\tilde{\nu}_\mathrm{i}-\tilde{\nu}_\mathrm{i}-{}^1\!/_2\Delta\tilde{\nu})^2\right\}=\varepsilon_\mathrm{max}\left\{1-{}^1\!/_4\kappa\Delta\tilde{\nu}^2\right\}\qquad\text{or}\qquad\kappa=\frac{4}{\Delta\tilde{\nu}^2}$$

Thus,

$$\mathcal{A}=\int_\mathrm{band}\varepsilon(\tilde{\nu})\,\mathrm{d}\tilde{\nu}\quad[\text{12A.15}]=\int_{\tilde{\nu}_\mathrm{i}}^{\tilde{\nu}_\mathrm{f}}\varepsilon(\tilde{\nu})\,\mathrm{d}\tilde{\nu}$$

$$=\varepsilon_\mathrm{max}\int_{\tilde{\nu}_\mathrm{i}}^{\tilde{\nu}_\mathrm{f}}\left\{1-\frac{4}{\Delta\tilde{\nu}^2}(\tilde{\nu}-\tilde{\nu}_\mathrm{max})^2\right\}\mathrm{d}\tilde{\nu}=\varepsilon_\mathrm{max}\left[\tilde{\nu}-\frac{4}{3\Delta\tilde{\nu}^2}(\tilde{\nu}-\tilde{\nu}_\mathrm{max})^3\right]_{\tilde{\nu}=\tilde{\nu}_\mathrm{i}}^{\tilde{\nu}=\tilde{\nu}_\mathrm{f}}$$

$$=\varepsilon_\mathrm{max}\left\{\left[\tilde{\nu}_\mathrm{f}-\frac{4}{3\Delta\tilde{\nu}^2}(\tilde{\nu}_\mathrm{f}-\tilde{\nu}_\mathrm{max})^3\right]-\left[\tilde{\nu}_\mathrm{i}-\frac{4}{3\Delta\tilde{\nu}^2}(\tilde{\nu}_\mathrm{i}-\tilde{\nu}_\mathrm{max})^3\right]\right\}$$

$$=\varepsilon_\mathrm{max}\left\{\left[\tilde{\nu}_\mathrm{f}-\frac{4}{3\Delta\tilde{\nu}^2}\left(\tilde{\nu}_\mathrm{f}-(\tilde{\nu}_\mathrm{f}-{}^1\!/_2\Delta\tilde{\nu})\right)^3\right]-\left[\tilde{\nu}_\mathrm{i}-\frac{4}{3\Delta\tilde{\nu}^2}\left(\tilde{\nu}_\mathrm{i}-(\tilde{\nu}_\mathrm{i}+{}^1\!/_2\Delta\tilde{\nu})\right)^3\right]\right\}$$

$$=\varepsilon_\mathrm{max}\left\{\left[\tilde{\nu}_\mathrm{f}-\frac{\Delta\tilde{\nu}}{6}\right]-\left[\tilde{\nu}_\mathrm{i}+\frac{\Delta\tilde{\nu}}{6}\right]\right\}={}^2\!/_3\times\Delta\tilde{\nu}\times\varepsilon_\mathrm{max}$$

12A.9(b) The integrated absorption coefficient is the area under an absorption peak

$$\mathcal{A}=\int_\mathrm{band}\varepsilon(\tilde{\nu})\,\mathrm{d}\tilde{\nu}\quad[\text{12A.15}]$$

We are told that ε is a Gaussian function, i.e. a function of the form

$$\varepsilon=\varepsilon_\mathrm{max}\exp\left(\frac{-x^2}{a^2}\right)$$

where $x=\tilde{\nu}-\tilde{\nu}_\mathrm{max}$ and a is a parameter related to the width of the peak. The integrated absorption coefficient, then, is

$$\mathcal{A}=\int_{-\infty}^{\infty}\varepsilon_\mathrm{max}\exp\left(\frac{-x^2}{a^2}\right)\mathrm{d}x=\varepsilon_\mathrm{max}a\sqrt{\pi}$$

We must relate a to the half-width at half-height, $x_{1/2}$.

$$\tfrac{1}{2}\varepsilon_\mathrm{max}=\varepsilon_\mathrm{max}\exp\left(\frac{-x_{1/2}^2}{a^2}\right)\quad\text{so}\quad\ln\tfrac{1}{2}=\frac{-x_{1/2}^2}{a^2}\quad\text{and}\quad a=\frac{x_{1/2}}{\sqrt{\ln 2}}$$

So, $$\mathcal{A}=\varepsilon_\mathrm{max}x_{1/2}\left(\frac{\pi}{\ln 2}\right)^{1/2}=(1.54\times10^4\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-1})\times(4233\ \mathrm{cm}^{-1})\times\left(\frac{\pi}{\ln 2}\right)^{1/2}=\boxed{1.39\times10^8\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-2}}$$

12A.10(b) $v_{\text{approach}} = \left(\dfrac{1+s/c}{1-s/c}\right)^{1/2} v \quad [12\text{A}.16\text{a}]$

or $\qquad \lambda_{\text{approach}} = \left(\dfrac{1-s/c}{1+s/c}\right)^{1/2} \lambda \quad$ where $\quad c = 2.9979\times10^{8}\ \text{m s}^{-1} = 1.0793\times10^{9}\ \text{km h}^{-1}$

Solve for *s*.

$$s = \frac{\left(\lambda/\lambda_{\text{approach}}\right)^{2}-1}{\left(\lambda/\lambda_{\text{approach}}\right)^{2}+1}$$

$$= \left(\frac{\left(680/530\right)^{2}-1}{\left(680/530\right)^{2}+1}\right)c = \boxed{0.244\,c}$$

For this very large Doppler-shift the traffic light must be approached at 24.4% the speed of light in a vacuum.

12A.11(b) $\delta E \approx \hbar/\tau$ so, since $E = h\nu$, $\delta\nu = \left(2\pi\tau\right)^{-1}$. Solving for τ:

(i) $\qquad \tau = \left(2\pi\delta\nu\right)^{-1} = \left(2\pi\left(200\times10^{6}\ \text{s}^{-1}\right)\right)^{-1} = \boxed{0.796\ \text{ns}}$

(ii) $\qquad \tau = \left(2\pi\delta\nu\right)^{-1} = \left(2\pi c\,\delta\tilde{\nu}\right)^{-1} = \left(2\pi\left(2.9979\times10^{10}\ \text{cm s}^{-1}\right)\times\left(2.45\ \text{cm}^{-1}\right)\right)^{-1} = \boxed{2.17\ \text{ps}}$

12A.12(b) $\delta E \approx \hbar/\tau$ so, since $E = h\nu$, $\delta\nu = \left(2\pi\tau\right)^{-1} = \dfrac{\text{deactivation rate}}{2\pi}$ [i.e., $\tau = 1/$deactivation rate].

(i) $\qquad \delta\nu = \dfrac{1.0\times10^{9}\ \text{s}^{-1}}{2\pi} = \boxed{15\bar{9}\ \text{MHz}}$

(ii) $\qquad \delta\nu = \dfrac{1.0\times10^{9}\ \text{s}^{-1}}{2\pi\times10} = \boxed{16\ \text{MHz}}$

Solutions to problems

12A.2 Solutions that have identical transmittance must have identical values of the absorbance [12A.13] and identical values of ε[J]L [12A.14]. Consequently,

$$[\text{J}]_{\text{cell 2}} = [\text{J}]_{\text{cell 1}}\,L_{\text{cell 1}}/L_{\text{cell 2}}$$

$$= 25\ \mu\text{g dm}^{-3}\times\left(1.55\ \text{cm}\right)/\left(1.18\ \text{cm}\right) = \boxed{33\ \mu\text{g dm}^{-3}}$$

12A.4 The absorbance's A_1 and A_2 at wavelengths λ_1 and λ_2 are the sum of the individual absorbance's in the mixture of A and B.

$$A_1 = \varepsilon_{\text{A1}}L[\text{A}] + \varepsilon_{\text{B1}}L[\text{B}] \qquad \text{(i)}$$

$$A_2 = \varepsilon_{\text{A2}}L[\text{A}] + \varepsilon_{\text{B2}}L[\text{B}] \qquad \text{(ii)}$$

Solving (i) for [A] gives

$$[\text{A}] = \frac{A_1 - \varepsilon_{\text{B1}}L[\text{B}]}{\varepsilon_{\text{A1}}L} \qquad \text{(iii)}$$

Substitution of (iii) into (ii) and solving for [B] gives

$$A_2 = \varepsilon_{\text{A2}}L\left(\frac{A_1 - \varepsilon_{\text{B1}}L[\text{B}]}{\varepsilon_{\text{A1}}L}\right) + \varepsilon_{\text{B2}}L[\text{B}]$$

$$\varepsilon_{\text{A1}}A_2 = \varepsilon_{\text{A2}}A_1 - \varepsilon_{\text{A2}}\varepsilon_{\text{B1}}L[\text{B}] + \varepsilon_{\text{A1}}\varepsilon_{\text{B2}}L[\text{B}]$$

$$\boxed{[\text{B}] = \frac{\varepsilon_{\text{A1}}A_2 - \varepsilon_{\text{A2}}A_1}{\left(\varepsilon_{\text{A1}}\varepsilon_{\text{B2}} - \varepsilon_{\text{A2}}\varepsilon_{\text{B1}}\right)L}} \qquad \text{(iv)}$$

Substitution of (iv) into (iii) and simplifying gives

$$\varepsilon_{A1}L[A] = A_1 - \varepsilon_{B1}L\left\{\frac{\varepsilon_{A1}A_2 - \varepsilon_{A2}A_1}{(\varepsilon_{A1}\varepsilon_{B2} - \varepsilon_{A2}\varepsilon_{B1})L}\right\}$$

$$= \frac{(\varepsilon_{A1}\varepsilon_{B2} - \varepsilon_{A2}\varepsilon_{B1})A_1 - \varepsilon_{B1}(\varepsilon_{A1}A_2 - \varepsilon_{A2}A_1)}{(\varepsilon_{A1}\varepsilon_{B2} - \varepsilon_{A2}\varepsilon_{B1})}$$

$$= \frac{\varepsilon_{A1}\varepsilon_{B2}A_1 - \varepsilon_{A1}\varepsilon_{B1}A_2}{(\varepsilon_{A1}\varepsilon_{B2} - \varepsilon_{A2}\varepsilon_{B1})}$$

$$\boxed{[A] = \frac{\varepsilon_{B2}A_1 - \varepsilon_{B1}A_2}{(\varepsilon_{A1}\varepsilon_{B2} - \varepsilon_{A2}\varepsilon_{B1})L}} \qquad \text{(v)}$$

Equations (iv) and (v) are the desired results.

12A.6[‡] The integrated absorption coefficient is

$$\mathcal{A} = \int_{\text{band}} \varepsilon(\tilde{\nu})\,d\tilde{\nu} \quad [12\text{A}.15]$$

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. So, if $\ln\varepsilon = m\tilde{\nu} + b$, then

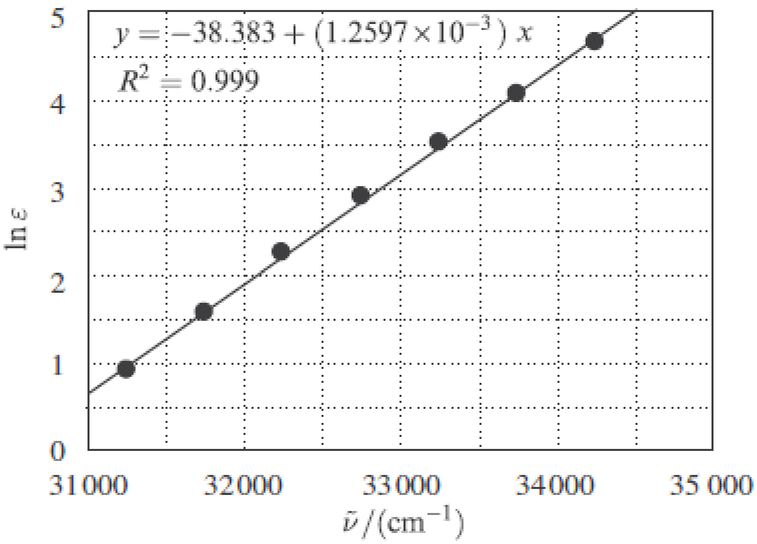
$$\varepsilon = \exp(m\tilde{\nu})\exp(b) \quad \text{and} \quad \mathcal{A} = (e^b/m)\{\exp(m\tilde{\nu}_f) - \exp(m\tilde{\nu}_i)\}$$

We draw up the following table, find the best-fit line, and make the plot of Fig. 12A.1. The linear regression fit yields the values of *m* and *b* for the computation of the integrated absorption coefficient.

λ/nm	ε/(dm^3 mol^{-1} cm^{-1})	$\tilde{\nu}$/cm^{-1}	$\ln\varepsilon$/(dm^3 mol^{-1} cm^{-1})
292.0	1512	34248	4.69
296.3	865	33748	4.13
300.8	477	33248	3.54
305.4	257	32748	2.92
310.1	135.9	32248	2.28
315.0	69.5	31746	1.61
320.0	34.5	31250	0.912

Figure 12A.1

[‡] These problems were supplied by Charles Trapp and Carmen Giunta.



So $$\mathcal{A} = \frac{\mathrm{e}^{-38.383}}{1.26\times10^{-3}\ \mathrm{cm}}\left[\exp\left(\frac{1.26\times10^{-3}\ \mathrm{cm}}{290\times10^{-7}\ \mathrm{cm}}\right) - \exp\left(\frac{1.26\times10^{-3}\ \mathrm{cm}}{320\times10^{-7}\ \mathrm{cm}}\right)\right]\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$$

$$= \boxed{1.24\times10^{5}\ \mathrm{dm^3\ mol^{-1}\ cm^{-2}}}$$

Gaussian distribution: $\varepsilon(\tilde{\nu}) = \varepsilon_{\max}\mathrm{e}^{-\frac{1}{2}\left(\frac{\tilde{\nu}-\mu}{\sigma}\right)^2}$ where μ is the mean of $\tilde{\nu}$ and σ is the standard deviation of the distribution. Dividing by $\varepsilon_{\max}$, taking the natural logarithm, and solving for $\tilde{\nu}-\mu$ gives

$$\tilde{\nu}-\mu = \pm\left(2\ln\frac{\varepsilon_{\max}}{\varepsilon}\right)^{1/2}\sigma$$

The width of the distribution at half-height, $\Delta\tilde{\nu}_{1/2}$, equals $2|\tilde{\nu}-\mu|$ evaluated at $\varepsilon = \varepsilon_{\max}/2$. Thus,

$$\Delta\tilde{\nu}_{1/2} = 2(2\ln 2)^{1/2}\sigma \quad \text{or} \quad \sigma = \frac{\Delta\tilde{\nu}_{1/2}}{2(2\ln 2)^{1/2}}$$

We can now evaluate the integrated absorption coefficient, $\mathcal{A}$, in terms of $\varepsilon_{\max}$ and $\Delta\tilde{\nu}_{1/2}$.

Let $$x = \frac{\tilde{\nu}-\mu}{\sigma} \quad \text{and} \quad \mathrm{d}x = \frac{1}{\sigma}\mathrm{d}\tilde{\nu} \quad \text{and} \quad \varepsilon = \varepsilon_{\max}\mathrm{e}^{-½x^2}$$

Then $$\mathcal{A} = \int_{-\infty}^{\infty}\varepsilon\,\mathrm{d}\tilde{\nu}\ [40.10] = \varepsilon_{\max}\sigma\int_{-\infty}^{\infty}\mathrm{e}^{-½x^2}\,\mathrm{d}x = (2\pi)^{1/2}\varepsilon_{\max}\sigma \quad \text{[standard integral]}$$

$$= \boxed{\frac{1}{2}\left(\frac{\pi}{\ln 2}\right)^{1/2}\varepsilon_{\max}\Delta\tilde{\nu}_{1/2}}$$

$$= 1.064467\,\varepsilon_{\max}\Delta\tilde{\nu}_{1/2}$$

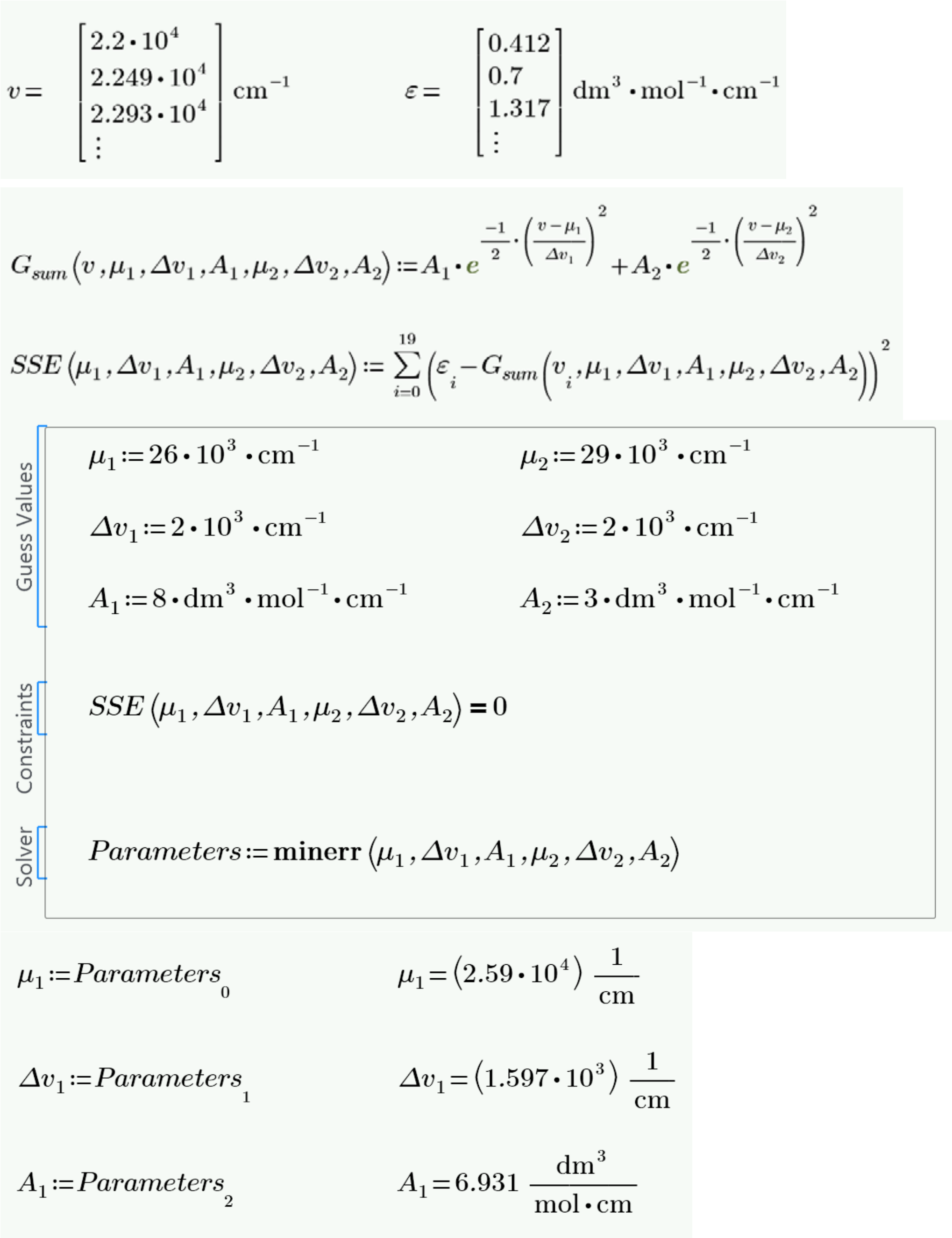
The Gaussian distribution is symmetric about the mean value of $\tilde{\nu}$, μ, which is the value of $\tilde{\nu}$ at the peak of the distribution. The absorption band of text Fig. 12.2 does not quite have this symmetry. It appears to be a skewed slightly toward the higher wavenumbers. Never the less, we estimate $\mathcal{A}$ by assuming that it can be approximated as a single Gaussian characterized by $\varepsilon_{\max}$ and $\Delta\tilde{\nu}_{1/2}$ values that are coarsely read off text Fig. F9.2.

Coarse estimate: $\mathcal{A} = 1.064467\,\varepsilon_{\max}\Delta\tilde{\nu}_{1/2} = 1.064467\times(10\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}})\times(5.4\times10^{3}\ \mathrm{cm^{-1}})$

$$= \boxed{5.7\times10^{4}\ \mathrm{dm^3\ mol^{-1}\ cm^{-2}}}$$

Let us now suppose that the slightly non-Gaussian shape exhibited by text Fig. 12.2 results from two separate absorption lines each of which has a molar absorption coefficient that is a Gaussian function of wavenumber. Text

Fig. 12.2 is then an 'apparent' molar absorption coefficient that is the sum of two independent Gaussians each characterized by an amplitude *A*, a mean value μ, and a standard deviation σ. That's a total of 6 parameters to be adjusted to fit the data of the figure. We label the 3 parameters of the predominate Gaussian, the one with the lower mean wavenumber, with a '1'; the low amplitude, higher mean distribution is labeled with a '2'. A lot of ($\tilde{v}$,ε) data pairs are needed to determine precise values of the parameters so we expanded text Fig. 12.2 and used Photoshop to read a total of 20 data pairs, several of which are displayed in the following Mathcad Prime 2 worksheet. Calling the sum of the two Gaussians G_{sum}, the worksheet uses guess values for the 6 parameters to calculate the difference $\varepsilon_{\text{obs}} - G_{\text{sum}}$ at each of the 20 $\tilde{v}_{\text{obs}}$, the difference is squared and summed over all data pairs, which the worksheet calls the 'sum of the squared errors' *SSE*. The idea is to systematically adjust the 6 parameters so as to minimize *SSE*. Mathcad performs the minimization process with the 'minerr()' function within a solve block. The symbol '*v*' is used to represent wavenumber within the worksheet.



$$v = \begin{bmatrix} 2.2 \cdot 10^4 \\ 2.249 \cdot 10^4 \\ 2.293 \cdot 10^4 \\ \vdots \end{bmatrix} \text{cm}^{-1} \qquad \varepsilon = \begin{bmatrix} 0.412 \\ 0.7 \\ 1.317 \\ \vdots \end{bmatrix} \text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$$

$$G_{sum}(v, \mu_1, \Delta v_1, A_1, \mu_2, \Delta v_2, A_2) := A_1 \cdot e^{\frac{-1}{2} \cdot \left(\frac{v-\mu_1}{\Delta v_1}\right)^2} + A_2 \cdot e^{\frac{-1}{2} \cdot \left(\frac{v-\mu_2}{\Delta v_2}\right)^2}$$

$$SSE(\mu_1, \Delta v_1, A_1, \mu_2, \Delta v_2, A_2) := \sum_{i=0}^{19} \left(\varepsilon_i - G_{sum}\left(v_i, \mu_1, \Delta v_1, A_1, \mu_2, \Delta v_2, A_2\right)\right)^2$$

$$\mu_1 := 26 \cdot 10^3 \cdot \text{cm}^{-1} \qquad \mu_2 := 29 \cdot 10^3 \cdot \text{cm}^{-1}$$

$$\Delta v_1 := 2 \cdot 10^3 \cdot \text{cm}^{-1} \qquad \Delta v_2 := 2 \cdot 10^3 \cdot \text{cm}^{-1}$$

$$A_1 := 8 \cdot \text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} \qquad A_2 := 3 \cdot \text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$$

$$SSE(\mu_1, \Delta v_1, A_1, \mu_2, \Delta v_2, A_2) = 0$$

$$Parameters := \mathbf{minerr}(\mu_1, \Delta v_1, A_1, \mu_2, \Delta v_2, A_2)$$

$$\mu_1 := Parameters_0 \qquad \mu_1 = \left(2.59 \cdot 10^4\right) \frac{1}{\text{cm}}$$

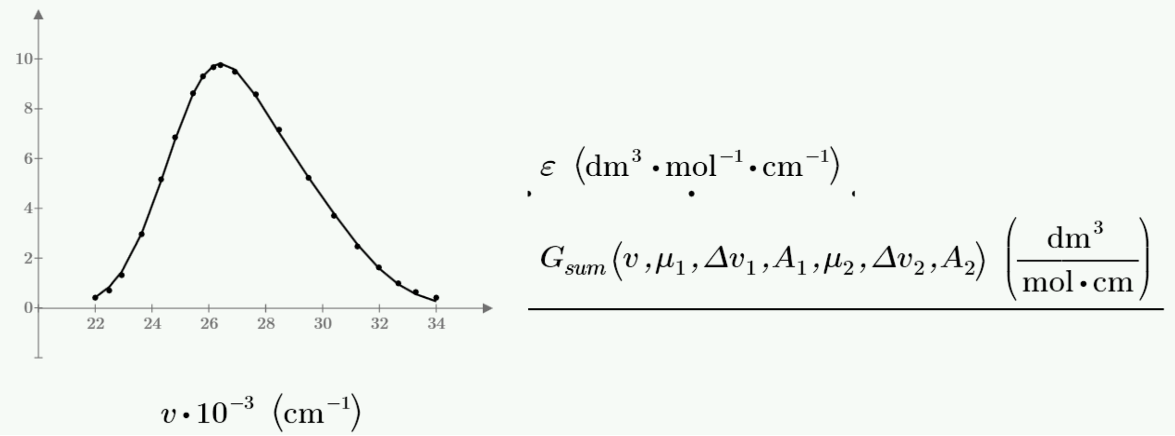
$$\Delta v_1 := Parameters_1 \qquad \Delta v_1 = \left(1.597 \cdot 10^3\right) \frac{1}{\text{cm}}$$

$$A_1 := Parameters_2 \qquad A_1 = 6.931 \frac{\text{dm}^3}{\text{mol} \cdot \text{cm}}$$

$\mu_2 := Parameters_3$ $\quad\mu_2 = \left(2.856\cdot 10^{4}\right)\ \frac{1}{\text{cm}}$

$\Delta v_2 := Parameters_4$ $\quad\Delta v_2 = \left(2.234\cdot 10^{3}\right)\ \frac{1}{\text{cm}}$

$A_2 := Parameters_5$ $\quad A_2 = 5.131\ \frac{\text{dm}^3}{\text{mol}\cdot\text{cm}}$



The plot shows that the sum of two Gaussians with adjusted parameters fits the data very nicely. The values of the six parameters are listed just above the plot. The following worksheet section uses the fitted function to calculate the integrated absorption coefficient with eqn 12A.15. The earlier, coarse estimate is seen to be rather close to the more precise calculation.

$$integrated\_absorption\_coeff := \int_{0\cdot\text{cm}^{-1}}^{10^{6}\cdot\text{cm}^{-1}} G_{sum}\left(v,\mu_1,\Delta v_1,A_1,\mu_2,\Delta v_2,A_2\right)\,dv$$

$$integrated\_absorption\_coeff = \left(5.649\cdot 10^{4}\right)\ \text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-2}$$

12A.8‡ **(a)** The integrated absorption coefficient is (specializing to a triangular lineshape)

$$\begin{aligned}\mathcal{A} &= \int_{\text{band}}\varepsilon\,\text{d}\tilde{\nu} = \tfrac{1}{2}\varepsilon_{\text{max}}\Delta\tilde{\nu}\\ &= \tfrac{1}{2}(150\,\text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1})\times(34\,483-31\,250)\,\text{cm}^{-1}\\ &= \boxed{2.42\times10^{5}\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-2}}\end{aligned}$$

(b) The concentration of gas under these conditions is

$$[\text{CH}_3\text{I}]_{\text{total}} = \frac{n}{V} = \frac{p}{RT} = \frac{2.4\,\text{Torr}}{(62.364\,\text{Torr}\,\text{dm}^3\ \text{mol}^{-1}\ \text{K}^{-1})\times(373\,\text{K})} = 1.03\times10^{-4}\ \text{mol dm}^{-3}$$

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

$$A = \varepsilon[\text{CH}_3\text{I}]L = (150\,\text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1})\times(1.03\times10^{-4}\ \text{mol dm}^{-3})\times(12.0\ \text{cm}) = \boxed{0.185}.$$

(c) The concentration of gas under these conditions is

$$[\mathrm{CH_3I}]_{\mathrm{total}} = \frac{n}{V} = \frac{p}{RT} = \frac{100\,\mathrm{Torr}}{(62.364\,\mathrm{Torr\,dm^3\,mol^{-1}\,K^{-1}})\times(373\,\mathrm{K})} = 4.30\times10^{-3}\,\mathrm{mol\,dm^{-3}}$$

Because 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 dm^{-3}. Beer's law is

$$A = \varepsilon[\mathrm{CH_3I}]L = (150\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}})\times(3.87\times10^{-3}\,\mathrm{mol\,dm^{-3}})\times(12.0\,\mathrm{cm}) = \boxed{6.97}$$

If this absorbance were measured, the molar absorption coefficient inferred from it without consideration of the dimerization would be

$$\varepsilon = A/([\mathrm{CH_3I}]L) = 6.97/((4.30\times10^{-1}\,\mathrm{mol\,dm^{-3}})\times(12.0\,\mathrm{cm}))$$
$$= \boxed{135\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}}$$

an apparent drop of 10% compared to the low-pressure value.

12A.10 According to eqn 12A.16a, the Doppler effect obeys

$$\nu_{\mathrm{receding}} = \nu f \quad \text{where} \quad f = \left(\frac{1-s/c}{1+s/c}\right)^{1/2}$$

This can be rearranged to yield:

$$s = \frac{1-f^2}{1+f^2}c\,.$$

We are given wavelength data, so we use:

$$f = \frac{\nu_{\mathrm{star}}}{\nu} = \frac{\lambda}{\lambda_{\mathrm{star}}}.$$

The ratio is:

$$f = \frac{654.2\ \mathrm{nm}}{706.5\ \mathrm{nm}} = 0.9260,$$

so $$s = \frac{1-0.9260^2}{1+0.9260^2}c = \boxed{0.0768\,c} = \boxed{2.30\times10^7\,\mathrm{m\,s^{-1}}}$$

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 12A.17 relates the observed linewidth to temperature:

$$\delta\lambda_{\mathrm{obs}} = \frac{2\lambda}{c}\left(\frac{2kT\ln 2}{m}\right)^{1/2} \quad \text{so} \quad T = \left(\frac{c\delta\lambda}{2\lambda}\right)^2 \frac{m}{2k\ln 2},$$

$$T = \left(\frac{(2.998\times10^8\,\mathrm{m\,s^{-1}})\times(61.8\times10^{-12}\ \mathrm{m})}{2(654.2\times10^{-9}\ \mathrm{m})}\right)^2 \left[\frac{(47.95\ \mathrm{u})(1.661\times10^{-27}\ \mathrm{kg\,u^{-1}})}{2(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\ln 2}\right],$$

$$\boxed{T = 8.34\times10^5\,\mathrm{K}}$$

12A.12 On the assumption that every collision deactivates the molecule we may write

$$\tau_{\mathrm{col}} \approx \frac{1}{z} = \boxed{\frac{kT}{4\sigma p}\left(\frac{\pi m}{kT}\right)^{1/2}} = \frac{kT}{4\sigma p}\left(\frac{\pi M}{RT}\right)^{1/2}$$

For HCl, with $M_{\mathrm{HCl}} = 36$ g mol^{-1},

$$\tau_{\mathrm{col}} = \left(\frac{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\ \mathrm{K})}{(4)\times(0.30\times10^{-18}\ \mathrm{m^2})\times(1.013\times10^5\ \mathrm{Pa})}\right)\times\left(\frac{\pi\times(36\times10^{-3}\ \mathrm{kg\,mol^{-1}})}{(8.315\ \mathrm{J\,K^{-1}\ mol^{-1}})\times(298\ \mathrm{K})}\right)^{1/2}$$
$$= 2.3\times10^{-10}\ \mathrm{s}$$

$$\delta E = h\,\delta\nu = \frac{\hbar}{\tau}$$

The width of the collision-broadened line is therefore approximately

$$\delta\nu_{\text{col}} = \frac{1}{2\pi\tau_{\text{col}}} = \frac{1}{(2\pi)\times(2.3\times10^{-10}\ \text{s})} \approx \boxed{700\,\text{MHz}}$$

To calculate the Doppler width we need the relation

$$\delta\nu_{\text{dop}} = \frac{2\nu}{c}\left(\frac{2kT\ln 2}{m}\right)^{1/2} = \frac{2\nu}{c}\left(\frac{2RT\ln 2}{M}\right)^{1/2} \quad [40.12,\ M_{\text{HCl}} \approx 36\ \text{g mol}^{-1}]$$

$$= \frac{2}{\left(2.998\times10^{8}\ \text{m s}^{-1}\right)} \times \left(\frac{2\times\left(8.315\ \text{J K}^{-1}\ \text{mol}^{-1}\right)\times\left(298\ \text{K}\right)\times\ln\left(2\right)}{36\times10^{-3}\ \text{kg mol}^{-1}}\right)^{1/2} \nu$$

$$= 2.1\times10^{-6}\nu$$

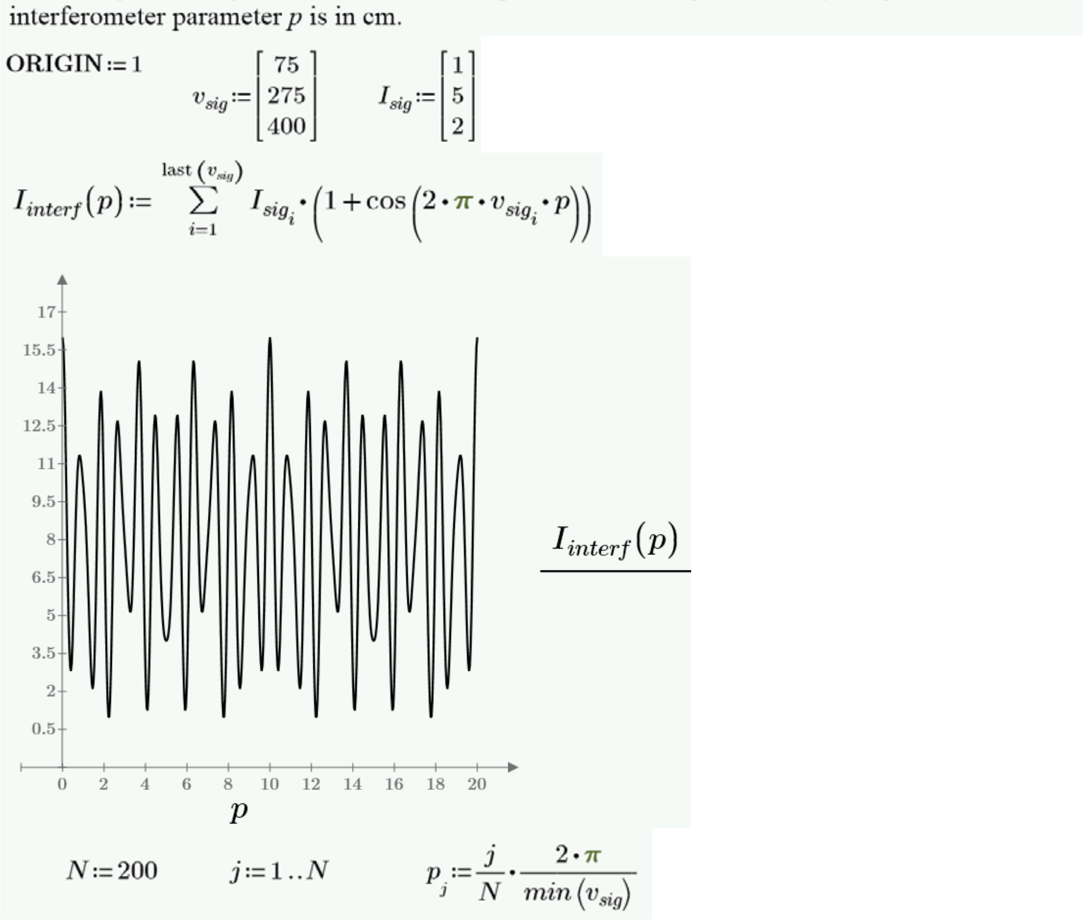
HCl exhibits a microwave, rotational transition at $\lambda \approx 0.016$ cm ($\nu \approx 1.9 \times 10^{12}$ Hz) so the Doppler width is estimated to be

$$\delta\nu_{\text{dop}} = \left(2.1\times10^{-6}\right)\times\left(1.9\times10^{12}\ \text{Hz}\right)$$

$$= \boxed{4.0\ \text{MHz}}$$

Since the collision width is proportional to p $[\delta\nu \propto 1/\tau$ and $\tau \propto 1/p]$ and, the pressure must be reduced by a factor of about 4.0/700 = 0.006 before Doppler broadening begins to dominate collision broadening. Hence, the pressure must be reduced to below $(0.006)\times(760\,\text{Torr}) = \boxed{5\ \text{Torr}}$

12A.14 Our study uses the discrete forms of eqns 12A.21 and 12A.22 for the signal and Fourier transformation. These are described in text Example 12A.2. Here's a Mathcad Prime 2 worksheet that is suitable for the study.



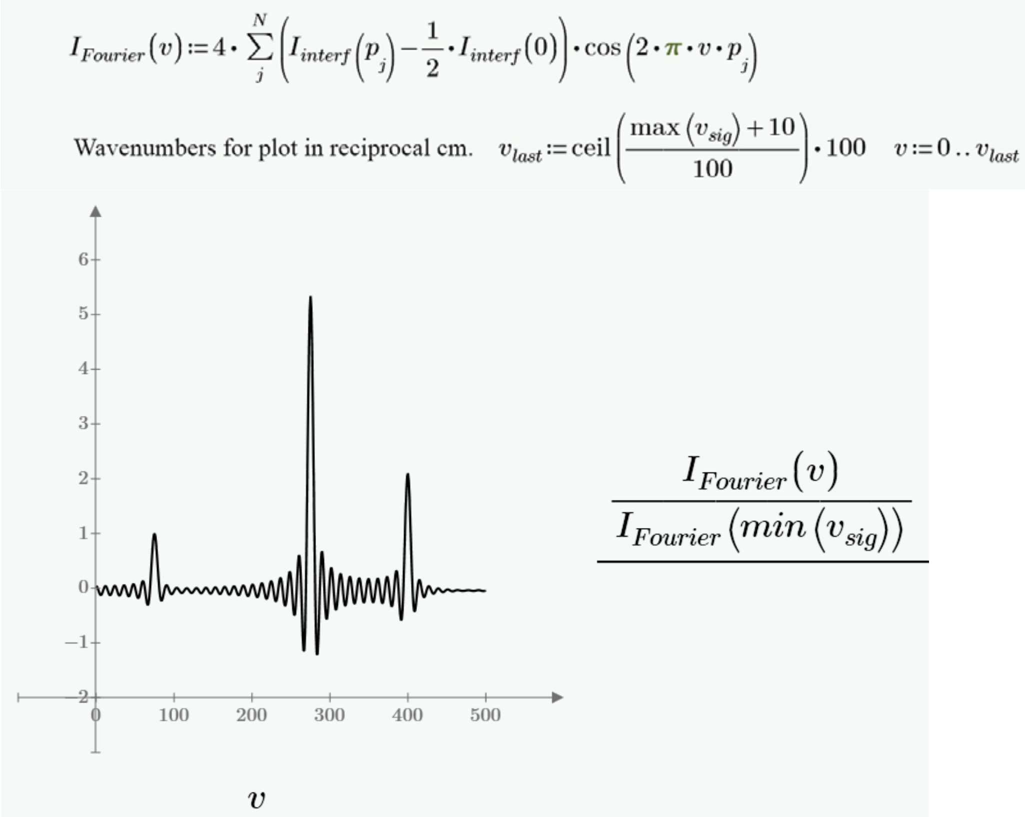
Data. v(sig) is the signal wavenumber in reciprocal cm. The signal intensity I(sig) is unitless. The interferometer parameter p is in cm.

ORIGIN := 1

$$v_{sig} := \begin{bmatrix} 75 \\ 275 \\ 400 \end{bmatrix} \qquad I_{sig} := \begin{bmatrix} 1 \\ 5 \\ 2 \end{bmatrix}$$

$$I_{interf}(p) := \sum_{i=1}^{\text{last}\left(v_{sig}\right)} I_{sig_i} \cdot \left(1 + \cos\left(2 \cdot \pi \cdot v_{sig_i} \cdot p\right)\right)$$

$$N := 200 \qquad j := 1\,..\,N \qquad p_j := \frac{j}{N} \cdot \frac{2 \cdot \pi}{min\left(v_{sig}\right)}$$



$$I_{Fourier}(v) := 4\cdot\sum_{j}^{N}\left(I_{interf}\left(p_j\right)-\frac{1}{2}\cdot I_{interf}(0)\right)\cdot\cos\left(2\cdot\pi\cdot v\cdot p_j\right)$$

Wavenumbers for plot in reciprocal cm. $v_{last} := \mathrm{ceil}\left(\frac{\max\left(v_{sig}\right)+10}{100}\right)\cdot 100 \quad v := 0\,..\,v_{last}$

By changing the values of the signal wavenumbers and intensities it is found that the Fourier transform of the interferometer output faithfully reproduces the signal. There is, however, an exception. If the interferometer number of *p* values, *N*, is set too low (try 20), the Fourier transform becomes a very bad distortion of the original signal and spurious peaks appear.

12B Molecular rotation

Answers to discussion questions

12B.2 A molecule has three principal axes of rotation; label them *a*, *b*, and *c*. The corresponding moments of inertia are I_a, I_b, and I_c. A prolate symmetric rotor has $I_a \neq I_b = I_c$ with $I_a = I_{\parallel} < I_b = I_c = I_{\perp}$. An oblate symmetric rotor has $I_a = I_b \neq I_c$ with $I_a = I_b = I_{\perp} < I_c = I_{\parallel}$. An American football and a cigar are prolate symmetric rotors, a discus and pancake are oblate symmetric rotors. CH_3Cl and CH_3CCH are prolate. PF_3, benzene, C_6H_6, and BCl_3 are oblate.

Solutions to exercises

12B.1(b) PH_3 is a symmetric rotor similar to NH_3; we use

$$I_{\|} = 2m_{\mathrm{H}}(1-\cos\theta)R^2 \ \text{[Table 12B.1]}$$

$$= 2\times 1.0079\ m_{\mathrm{u}} \times 1.66054\times 10^{-27}\ \mathrm{kg}/m_{\mathrm{u}} \times (1-\cos 93.5^{\circ})\times(1.42\times 10^{-10})^2$$

$$= \boxed{7.161\times 10^{-47}\ \mathrm{kg\ m^2}}$$

The corresponding rotational constant is

$$\tilde{A} = \frac{\hbar}{4\pi c I_{\|}} = \frac{1.05447\times 10^{-34}\ \mathrm{J\ s}}{4\pi\times 2.998\times 10^{8}\ \mathrm{m\ s^{-1}}\times 7.161\times 10^{-47}\ \mathrm{kg\ m^2}} = 390.9\ \mathrm{m^{-1}} = \boxed{3.909\ \mathrm{cm^{-1}}}$$

12B.2(b) In order to conform to the symbols used in the first symmetric rotor figure of Table 12B.1, we will use the molecular formula BA_4. $I_{\|}$ is along the internuclear axis, the unique A—B bond, and $I_{\perp}$ is perpendicular to both $I_{\|}$ and a molecular face that does not contain $I_{\|}$ (see the symmetric rotor of text Fig. 12B.3). For our molecule, $m_{\mathrm{C}} = m_{\mathrm{A}}$ and $\theta = \theta_{\mathrm{tetra}} = \pi/2 + \sin^{-1}(1/3)$ where θ_{tetra} is the tetrahedral angle (approx. 109.471°). You can demonstrate that $\cos(\theta_{\mathrm{tetra}}) = -\tfrac{1}{3}$ and, using the definition $\rho = R_{\mathrm{AB}}'/R_{\mathrm{AB}} = R_{\mathrm{AB}}'/R$, the equations of Table 12B.1 simplify to

$$I_{\|}/m_{\mathrm{A}}R^2 = 2(1-\cos\theta_{\mathrm{tetra}}) = \tfrac{8}{3}$$

$$I_{\perp}/m_{\mathrm{A}}R^2 = \tfrac{4}{3} + (m_{\mathrm{A}}+m_{\mathrm{B}})/3m + \{(3m_{\mathrm{A}}+m_{\mathrm{B}})\rho + 2m_{\mathrm{A}}\}\rho/m \text{ where } m = 4m_{\mathrm{A}} + m_{\mathrm{B}}.$$

The $I_{\|}/m_{\mathrm{A}}R^2$ moment of inertia ratio does not depend upon either atomic masses or bond lengths. It is a constant $^{8}/_{3}$ for all symmetric rotors with tetrahedral angles. However, the $I_{\perp}/m_{\mathrm{A}}R^2$ moment of inertia ratio does have a specific atomic mass dependency so we will plot its ρ dependence for CH_4, an important fuel and powerful greenhouse gas. The computational equation is

$$I_{\perp}/m_{\mathrm{A}}R^2 = \tfrac{77}{48} + (15\rho+2)\rho/16$$

and its plot is found in Fig. 12B.1. As ρ increases, the atom on the axis of $I_{\|}$ moves away from the axis of $I_{\perp}$, thereby, increasing the moment of inertia around this axis.

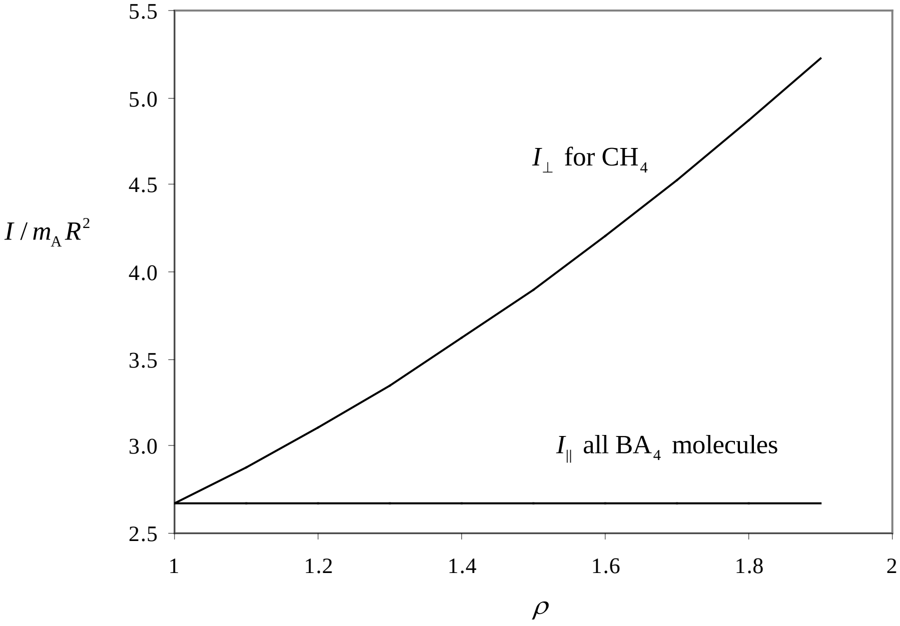


Figure 12B.1

12B.3(b)(i) asymmetric, **(ii)** oblate symmetric, **(iii)** asymmetric, **(iv)** linear

12B.4(b) This exercise is analogous to Exercise 12B.4(a), but here our solution will employ a slightly different algebraic technique. Let $R = R_{\mathrm{OC}}, R' = R_{\mathrm{CS}}, \mathrm{O} = {}^{16}\mathrm{O}, \mathrm{C} = {}^{12}\mathrm{C}$.

$$I = \frac{\hbar}{4\pi B} \text{ [See the comment in the solution to Exercise 12B.4(a)]}$$

$$I\left(\mathrm{OC}^{32}\mathrm{S}\right) = \frac{1.05457\times10^{-34}\,\mathrm{J\,s}}{(4\pi)\times\left(6.0815\times10^{9}\ \mathrm{s}^{-1}\right)} = 1.3799\times10^{-45}\,\mathrm{kg\,m^2} = 8.3101\times10^{-19}\ m_{\mathrm{u}}\ \mathrm{m}^2$$

$$I\left(\mathrm{OC}^{34}\mathrm{S}\right) = \frac{1.05457\times10^{-34}\,\mathrm{J\,s}}{(4\pi)\times\left(5.9328\times10^{9}\ \mathrm{s}^{-1}\right)} = 1.4145\times10^{-45}\,\mathrm{kg\,m^2} = 8.5184\times10^{-19}\ m_{\mathrm{u}}\ \mathrm{m}^2$$

The expression for the moment of inertia given in Table 12B.1 may be rearranged as follows.

$$\begin{aligned} Im &= m_{\mathrm{A}} m R^2 + m_{\mathrm{C}} m R'^2 - \left(m_{\mathrm{A}} R - m_{\mathrm{C}} R'\right)^2 \\ &= m_{\mathrm{A}} m R^2 + m_{\mathrm{C}} m R'^2 - m_{\mathrm{A}}^2 R^2 + 2 m_{\mathrm{A}} m_{\mathrm{C}} R R' - m_{\mathrm{C}}^2 R'^2 \\ &= m_{\mathrm{A}} \left(m_{\mathrm{B}} + m_{\mathrm{C}}\right) R^2 + m_{\mathrm{C}} \left(m_{\mathrm{A}} + m_{\mathrm{B}}\right) R'^2 + 2 m_{\mathrm{A}} m_{\mathrm{C}} R R' \end{aligned}$$

Let $m_{\mathrm{C}} = m_{^{32}\mathrm{S}}$ and $m'_{\mathrm{C}} = m_{^{34}\mathrm{S}}$

$$\frac{Im}{m_{\mathrm{C}}} = \frac{m_{\mathrm{A}}}{m_{\mathrm{C}}}\left(m_{\mathrm{B}} + m_{\mathrm{C}}\right) R^2 + \left(m_{\mathrm{A}} + m_{\mathrm{B}}\right) R'^2 + 2 m_{\mathrm{A}} R R' \qquad \text{(a)}$$

$$\frac{I'm'}{m'_{\mathrm{C}}} = \frac{m_{\mathrm{A}}}{m'_{\mathrm{C}}}\left(m_{\mathrm{B}} + m'_{\mathrm{C}}\right) R^2 + \left(m_{\mathrm{A}} + m_{\mathrm{B}}\right) R'^2 + 2 m_{\mathrm{A}} R R' \qquad \text{(b)}$$

Subtracting

$$\frac{Im}{m_{\mathrm{C}}} - \frac{I'm'}{m'_{\mathrm{C}}} = \left[\left(\frac{m_{\mathrm{A}}}{m_{\mathrm{C}}}\right)\left(m_{\mathrm{B}} + m_{\mathrm{C}}\right) - \left(\frac{m_{\mathrm{A}}}{m'_{\mathrm{C}}}\right)\left(m_{\mathrm{B}} + m'_{\mathrm{C}}\right)\right] R^2$$

Solving for R^2

$$R^2 = \frac{\left(\frac{Im}{m_{\mathrm{C}}} - \frac{I'm'}{m'_{\mathrm{C}}}\right)}{\left[\left(\frac{m_{\mathrm{A}}}{m_{\mathrm{C}}}\right)\left(m_{\mathrm{B}} + m_{\mathrm{C}}\right) - \left(\frac{m_{\mathrm{A}}}{m'_{\mathrm{C}}}\right)\left(m_{\mathrm{B}} + m'_{\mathrm{C}}\right)\right]} = \frac{m'_{\mathrm{C}} Im - m_{\mathrm{C}} I'm'}{m_{\mathrm{B}} m_{\mathrm{A}} (m'_{\mathrm{C}} \text{-} m_{\mathrm{C}})}$$

Substituting the masses, with $m_{\mathrm{A}} = m_{\mathrm{O}}, m_{\mathrm{B}} = m_{\mathrm{C}}, m_{\mathrm{C}} = m_{32_{\mathrm{S}}}$, and $m'_{\mathrm{C}} = m_{34_{\mathrm{S}}}$

$$m = (15.9949 + 12.0000 + 31.9721)\ m_{\mathrm{u}} = 59.9670\ m_{\mathrm{u}}$$

$$m' = (15.9949 + 12.0000 + 33.9679)\ m_{\mathrm{u}} = 61.9628\ m_{\mathrm{u}}$$

$$\begin{aligned} R^2 &= \frac{(33.9679\ m_{\mathrm{u}})\times(8.3101\times10^{-19}\ m_{\mathrm{u}}\ \mathrm{m}^2)\times(59.9670\ m_{\mathrm{u}})}{(12.0000\ m_{\mathrm{u}})\times(15.9949\ m_{\mathrm{u}})\times(33.9679\ m_{\mathrm{u}} - 31.9721\ m_{\mathrm{u}})} \\ &\quad - \frac{(31.9721\ m_{\mathrm{u}})\times(8.5184\times10^{-19}\ m_{\mathrm{u}}\ \mathrm{m}^2)\times(61.9628\ m_{\mathrm{u}})}{(12.0000\ m_{\mathrm{u}})\times(15.9949\ m_{\mathrm{u}})\times(33.9679\ m_{\mathrm{u}} - 31.9721\ m_{\mathrm{u}})} \\ &= \frac{51.6446\times10^{-19}\mathrm{m}^2)}{383.071} = 1.3482\times10^{-20}\,\mathrm{m}^2 \end{aligned}$$

$$R = 1.161\bar{1}\times10^{-10}\,\mathrm{m} = \boxed{116.1\ \mathrm{pm}} = R_{\mathrm{OC}}$$

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

$$R' = 1.559\times10^{-10}\,\text{m} = \boxed{155.9\text{ pm}} = R_{\text{CS}}$$

12B.5(b) The centrifugal distortion constant is given by

$$\tilde{D}_J = \frac{4\tilde{B}^3}{\tilde{\nu}^2} \text{ [12B.17, also see Integrated Activity I12.2]}$$

$$\tilde{D}_J = \frac{4\times(0.0809\text{ cm}^{-1})^3}{(323.2\text{ cm}^{-1})^2} = \boxed{2.028\times10^{-8}\text{ cm}^{-1}}$$

$$\tilde{D}_J \propto \tilde{B}^3 \quad \tilde{B}\propto\frac{1}{I} \quad I\propto m_{\text{Br}} \text{ [Table 12B.1]}$$

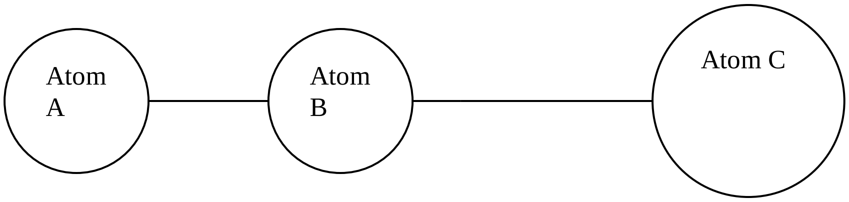
$$\text{Therefore, } \tilde{D}_J \propto \frac{1}{m_{\text{Br}}^3} \text{ and } \frac{\tilde{D}_J(^{81}\text{Br})}{\tilde{D}_J(^{79}\text{Br})} = \frac{m^3_{^{79}\text{Br}}}{m^3_{^{81}\text{Br}}} = \frac{(78.9183\,m_{\text{u}})^3}{(80.9163\,m_{\text{u}})^3} = \boxed{0.9277}$$

We have assumed that the internuclear distance remains constant upon substitution.

Solutions to problems

12B.2

Figure 12B.2



Let us assume atom C is the most massive. Then the center of mass, CM, will be located at a distance, D, from atom B. In the notation of Table 12B.1, we must have the relation

$m_{\text{A}}(R+D) + m_{\text{B}}D = m_{\text{C}}(R'-D)$, which may be rearranged into

$$D(m_{\text{A}}+m_{\text{B}}+m_{\text{C}}) = m_{\text{C}}R' - m_{\text{A}}R$$

Solving for D, we obtain $D = \dfrac{m_C R' - m_A R}{m}$, where $m = m_A + m_B + m_C$. Expanding $I = \sum_i m_i r_i^2$[12B.1] gives

$$
\begin{aligned}
I &= m_A R^2 + m_A D^2 + 2RDm_A + m_B D^2 + m_C R'^2 + m_C D^2 - 2R'Dm_C \\
&= m_A R^2 + m_C R'^2 + D^2(m_A + m_B + m_C) + 2D(m_A R - m_C R')
\end{aligned}
$$

After substituting the above formula for D, and using $m = m_A + m_B + m_C$ we obtain

$$
\begin{aligned}
I &= m_A R^2 + m_C R'^2 + m\left(\frac{m_C R' - m_A R}{m}\right)^2 + 2\left(\frac{m_C R' - m_A R}{m}\right) \times (m_A R - m_C R') \\
&= m_A R^2 + m_C R'^2 + \frac{1}{m}(m_C R' - m_A R)^2 - \frac{2}{m}(m_C R' - m_A R)^2 \\
&= m_A R^2 + m_C R'^2 - \frac{1}{m}(m_C R' - m_A R)^2 \\
&= \boxed{m_A R^2 + m_C R'^2 - \frac{1}{m}(m_A R - m_C R')^2}
\end{aligned}
$$

QED

12C Rotational spectroscopy

Answers to discussion questions

12C.2 (1) *Rotational Raman spectroscopy*. The gross selection rule is that the molecule must be anisotropically polarizable, which is to say that its polarizability, α, depends upon the direction of the electric field relative to the molecule. Non-spherical rotors satisfy this condition. Therefore, linear and symmetric rotors are rotationally Raman active.

(2) *Vibrational Raman spectroscopy*. The gross selection rule is that the polarizability of the molecule must change as the molecule vibrates. All diatomic molecules satisfy this condition as the molecules swell and contract during a vibration, the control of the nuclei over the electrons varies, and the molecular polarizability changes. Hence both homonuclear and heteronuclear diatomics are vibrationally Raman active. In polyatomic molecules it is usually quite difficult to judge by inspection whether or not the molecule is anisotropically polarizable; hence group theoretical methods are relied on for judging the Raman activity of the various normal modes of vibration. The procedure is discussed in Section 12D.5 and demonstrated in *Brief Illustration* 12D.5.

12C.4 Hydrogen molecules can exist in two forms: the *para*- form has antiparallel nuclear spins and the *ortho*- form has parallel nuclear spins. Because of these arrangements of the nuclear spins the *ortho*- form must have rotational wavefunctions restricted to odd J values only as discussed in detail in Section 12C.3. *Ortho*-hydrogen cannot exist in the $J = 0$ state. Hence, the lowest energy level of *ortho*-hydrogen has $J = 1$ and therefore a zero-point energy. The conversion between the two forms is very slow.

Solutions to Exercises

12C.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, $C_{n\text{v}}$, and C_s may be polar, and in the case of C_n and $C_{n\text{v}}$, that dipole must lie along the rotation axis. Hence all are polar molecules.

Their point group symmetries are

(i) H_2O, $C_{2\text{v}}$, (ii) H_2O_2, C_2, (iii) NH_3, $C_{3\text{v}}$, (iv) N_2O, $C_{\infty\text{v}}$

$\boxed{\text{All}}$ show a pure rotational spectrum.

12C.2(b) The frequency of the transition is related to the rotational constant by

$$h\nu = \Delta E = hc\Delta\tilde{F} = hc\tilde{B}\left[J(J+1)-(J-1)J\right] = 2hc\tilde{B}J$$

where J here refers to the upper state $(J=2)$. The rotational constant is related to molecular structure by

$$\tilde{B} = \frac{\hbar}{4\pi cI} = \frac{\hbar}{4\pi c m_\text{eff} R^2}$$

where I is moment of inertia, m_eff is effective mass, and R is the bond length. Putting these expressions together yields

$$\nu = 2c\tilde{B}J = \frac{\hbar J}{2\pi m_\text{eff} R^2}$$

The reciprocal of the effective mass is

$$m_\text{eff}^{-1} = m_\text{C}^{-1} + m_\text{O}^{-1} = \frac{(12m_\text{u})^{-1} + (15.9949m_\text{u})^{-1}}{1.66054\times10^{-27}\ \text{kg}\ m_\text{u}^{-1}} = 8.78348\times10^{25}\ \text{kg}^{-1}$$

$$\text{So } \nu = \frac{(8.78348\times10^{25}\ \text{kg}^{-1})\times(1.0546\times10^{-34}\,\text{J s})\times(2)}{2\pi(112.81\times10^{-12}\,\text{m})^2} = \boxed{2.3169\times10^{11}\ \text{s}^{-1}}$$

When centrifugal distortion is taken into account the frequency decreases as can be seen by considering eqn. 12C.8b.

12C.3(b) The wavenumber of the transition is related to the rotational constant by

$$hc\tilde{\nu} = \Delta E = hc\Delta\tilde{F} = hc\tilde{B}\left[J(J+1)-(J-1)J\right] = 2hc\tilde{B}J$$

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

$$\tilde{\nu} = 2\tilde{B}J = \frac{\hbar J}{2\pi cI} \quad \text{so} \quad I = \frac{\hbar J}{2\pi c\tilde{\nu}} = \frac{(1.0546\times10^{-34}\,\text{J s})\times(1)}{2\pi(2.998\times10^{10}\ \text{cm s}^{-1})\times(16.93\ \text{cm}^{-1})}$$

$$I = 3.307\times10^{-47}\ \text{kg m}^2$$

The moment of inertia is related to the bond length by

$$I = m_\text{eff}R^2 \ \text{ so } \ R = \left(\frac{I}{m_\text{eff}}\right)^{1/2}$$

$$m_{\text{eff}}^{-1} = m_{\text{H}}^{-1} + m_{\text{Br}}^{-1} = \frac{(1.0078\ m_{\text{u}})^{-1} + (80.9163\ m_{\text{u}})^{-1}}{1.66054\times10^{-27}\ \text{kg}\ m_{\text{u}}^{-1}} = 6.0494\times10^{26}\ \text{kg}^{-1}$$

$$\text{and } R = \left\{(6.0494\times10^{26}\ \text{kg}^{-1})\times(3.307\times10^{-47}\ \text{kg m}^2)\right\}^{1/2}$$

$$= 1.414\times10^{-10}\,\text{m} = \boxed{141.4\text{pm}}$$

12C.4(b) The wavenumber of the transition is related to the rotational constant by

$$hc\tilde{\nu} = \Delta E = hc\Delta\tilde{F} = hc\tilde{B}\left[J(J+1)-(J-1)J\right] = 2hc\tilde{B}J$$

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.

$$\text{So } I = \frac{(1.0546\times10^{-34}\ \text{J s})}{2\pi(2.9979\times10^{10}\ \text{cm s}^{-1})\times(1.033\ \text{cm}^{-1})} = \boxed{5.420\times10^{-46}\ \text{kg m}^2}$$

The moment of inertia is related to the bond length by

$$I = m_{\text{eff}}R^2 \quad \text{so} \quad R = \left(\frac{I}{m_{\text{eff}}}\right)^{1/2}$$

$$m_{\text{eff}}^{-1} = m_{\text{F}}^{-1} + m_{\text{Cl}}^{-1} = \frac{(18.9984\ m_{\text{u}})^{-1} + (34.9688\ m_{\text{u}})^{-1}}{1.66054\times10^{-27}\ \text{kg}\ m_{\text{u}}^{-1}} = 4.89196\times10^{25}\ \text{kg}^{-1}$$

$$\text{and } R = \left\{(4.89196\times10^{25}\ \text{kg}^{-1})\times(5.420\times10^{-46}\ \text{kg m}^2)\right\}^{1/2}$$

$$= 1.628\times10^{-10}\,\text{m} = \boxed{162.8\ \text{pm}}$$

12C.5(b) See eqn 12C.9 and problem 12C.9.The most highly populated rotational level is given by

$$J_{\max} \approx \left(\frac{kT}{2hc\tilde{B}}\right)^{1/2} - \frac{1}{2} \quad [12\text{C}.9]$$

For Br_2 after substituting for the constants this expression becomes

$$J_{\max} \approx \left(\frac{T/\text{K}}{0.2328}\right)^{1/2} - \frac{1}{2}$$

(i) At 25°C = 298.15 K, $J_{\max} \approx \left(\frac{298.15/\text{K}}{0.2328}\right)^{1/2} - \frac{1}{2} \approx \boxed{36}$

(ii) At 100°C = 373.15 K, $J_{\max} \approx \left(\frac{373.15/\text{K}}{0.2328}\right)^{1/2} - \frac{1}{2} \approx \boxed{40}$

Answers are rounded off to the nearest integer.

12C.6(b) A molecule must be anisotropically polarizable to show a rotational Raman spectrum; all molecules except spherical rotors have this property. So $\boxed{\text{(i)}CH_2Cl_2}$, $\boxed{\text{(ii)}CH_3CH_3}$, and $\boxed{\text{(iv)}N_2O}$ can display rotational Raman spectra; SF_6 cannot.

12C.7(b) The wavenumber of a Stokes line in rotational Raman is

$$\tilde{\nu}_{\text{Stokes}} = \tilde{\nu}_{\text{i}} - 2\tilde{B}(2J+3) \text{ [12C.15]}$$

where J is the initial (lower) rotational state. So

$$\tilde{\nu}_{\text{Stokes}} = 20623 \text{ cm}^{-1} - 2(1.4457 \text{ cm}^{-1}) \times [2(2)+3] = \boxed{20603 \text{ cm}^{-1}}$$

12C.8(b) The separation of lines is $4\tilde{B}$, so $\tilde{B} = \frac{1}{4} \times (3.5312 \text{ cm}^{-1}) = 0.88280 \text{ cm}^{-1}$

Then we use $R = \left(\dfrac{\hbar}{4\pi m_{\text{eff}} cB}\right)^{1/2}$ [Exercise 12C.8(a)]

with $m_{\text{eff}} = \frac{1}{2} m\left({}^{19}\text{F}\right) = \frac{1}{2} \times (18.9984\ m_{\text{u}}) \times (1.6605 \times 10^{-27} \text{ kg } m_{\text{u}}^{-1}) = 1.57734\overline{2} \times 10^{-26} \text{ kg}$

$$R = \left(\frac{1.0546 \times 10^{-34} \text{ J s}}{4\pi(1.577342 \times 10^{-26} \text{ kg}) \times (2.998 \times 10^{10} \text{ cm s}^{-1}) \times (0.88280 \text{ cm}^{-1})}\right)^{1/2}$$

$$= 1.4178\overline{5} \times 10^{-10} \text{ m} = \boxed{141.78 \text{ pm}}$$

12C.9(b) For ${}^{12}C^{32}S_2$, all nuclei are spin-0. The symmetry considerations are identical to those of ${}^{12}C^{16}O_2$ discussed in the text; $\boxed{\text{only even values of J are permissible}}$. For ${}^{13}C^{32}S_2$, the symmetry of the molecule is unchanged, so again $\boxed{\text{only even values of J are permissible.}}$

Solutions to problems

12C.2 The separations between neighbouring lines are

$$20.81,\ 20.60,\ 20.64,\ 20.52,\ 20.34,\ 20.37,\ 20.26 \quad \text{mean:} 20.51 \text{cm}^{-1}$$

$$\tilde{B} = \left(\tfrac{1}{2}\right) \times (20.51 \text{cm}^{-1}) = 10.26 \text{cm}^{-1} \text{ and}$$

$$I = \frac{\hbar}{4\pi c\tilde{B}} = \frac{1.05457 \times 10^{-34} \text{ Js}}{(4\pi) \times (2.99793 \times 10^{10} \text{ cm s}^{-1}) \times (10.26 \text{ cm}^{-1})} = \boxed{2.728 \times 10^{-47} \text{ kg m}^2}$$

$$R = \left(\frac{I}{m_{\text{eff}}}\right)^{1/2} \text{ [Table 12B.1] with } m_{\text{eff}} = 1.6266 \times 10^{-27} \text{ kg [Exercise 12C.3(a)]}$$

$$= \left(\frac{2.728 \times 10^{-47} \text{ kg m}^2}{1.6266 \times 10^{-27} \text{ kg}}\right)^{1/2} = \boxed{129.5 \text{ pm}}$$

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 $\tilde{B} \propto \dfrac{1}{I}$ and $I \propto m_{\text{eff}}$, $\tilde{B} \propto \dfrac{1}{m_{\text{eff}}}$. Hence, the corresponding lines in ${}^{2}H^{35}Cl$ 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. Therefore, we expect lines at

$\boxed{42.23,\ 52.79, 63.34,\ 73.90,\ 84.46,\ 95.02,\ \text{and } 105.57\ \text{cm}^{-1}.}$

12C.4 $R=\left(\dfrac{\hbar}{4\pi\mu c\tilde{B}}\right)^{1/2}$ and $\nu=2c\tilde{B}(J+1)$ [12C.8a, with $\nu=c\tilde{\nu}$]

We use $\mu(\text{CuBr})\approx\dfrac{(63.55)\times(79.91)}{(63.55)+(79.91)}m_{\text{u}}=35.40\ m_{\text{u}}$

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

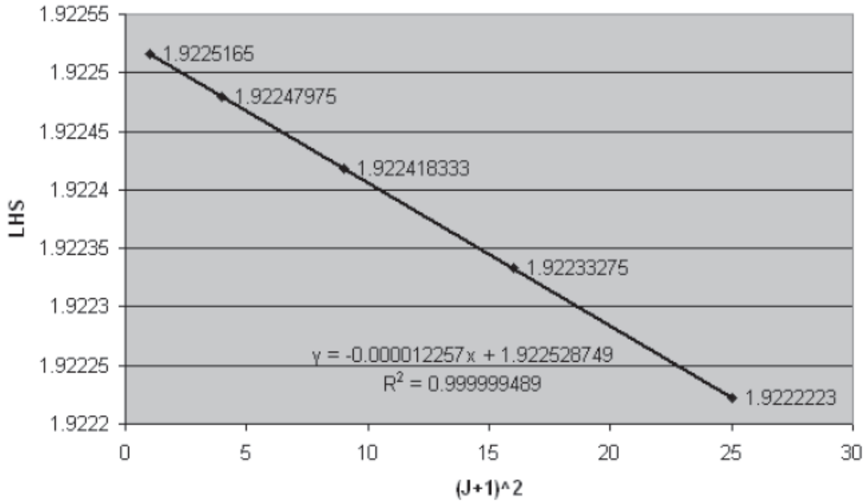
Hence, $R=\left(\dfrac{1.05457\times10^{-34}\,\text{J s}}{(4\pi)\times(35.40)\times(1.6605\times10^{-27}\,\text{kg})\times(2.9979\times10^{10}\,\text{cm}\,\text{s}^{-1})\times(0.10057\,\text{cm}^{-1})}\right)^{1/2}$

$=\boxed{218\ \text{pm}}$

12C.6 The data given is analyzed in the Excel® worksheet below in which a linear regression is performed on the left hand side of the equation provided in the problem. See Fig. 12C.1 below:

J	$(J+1)$	$2(J+1)$	$(J+1)^2$	$\nu(J+1\leftarrow J)/\text{cm}^{-1}$	$\nu(J+1\leftarrow J)/2(J+1)/\text{cm}^{-1}$
0	1	2	1	3.845033	1.9225165
1	2	4	4	7.689919	1.92247975
2	3	6	9	11.53451	1.922418333
3	4	8	16	15.378662	1.92233275
4	5	10	25	19.222223	1.9222223

Figure 12C.1



The intercept $\boxed{1.9225287\ \text{cm}^{-1}}$ is the value of the rotational constant $\tilde{B}$. The slope $-1.2257 \times 10^{-5}\ \text{cm}^{-1}$ gives $-2\tilde{D}_J$. Therefore $\boxed{\tilde{D}_J = 6.1285 \times 10^{-6}\ \text{cm}^{-1}}$. The equilibrium bond length is calculated from $R = \left(\dfrac{\hbar}{4\pi\mu c\tilde{B}}\right)^{1/2}$. We use $\mu(^{12}\text{C}^{16}\text{O}) = \dfrac{(12.0000)\times(15.9949)}{(12.0000)+(15.9949)}\,m_\text{u} = 6.8562\,m_\text{u}$

$= 1.13850 \times 10^{-26}\ \text{kg}$

$$\text{Hence, } R = \left(\frac{1.05457\times10^{-34}\,\text{Js}}{(4\pi)\times(1.13850\times10^{-26}\,\text{kg})\times(2.99793\times10^{10}\,\text{cm s}^{-1})\times(1.9225287\,\text{cm}^{-1})}\right)^{1/2}$$

$$= \boxed{113.09\ \text{pm}}$$

Comment: these values for the rotational constant are slightly different from the values given in data table 12D.1.

12C.8 If we apply the selection rules $\Delta J = \pm 1,\ \Delta K = 0$ to the formula for the rotational terms given in the problem we obtain for the frequencies of the allowed transitions the expression

$$\nu_{J+1,K\leftarrow J,K} = F(J+1,K) - F(J,K) = 2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2$$

In terms of wavenumbers, the expression is similar

$$\tilde{\nu}_{J+1,K\leftarrow J,K} = \tilde{F}(J+1,K) - \tilde{F}(J,K) = 2\tilde{B}(J+1) - 4\tilde{D}_J(J+1)^3 - 2\tilde{D}_{JK}(J+1)K^2$$

To work with the latter expression one must convert the data given in frequency units to wavenumbers. Here we solve the problem in frequency units using the former expression. We note that A and D_K drop out of the expression for the transition frequencies, hence these constants cannot be determined from the data given.

Examination of the data suggests that the identification of the transitions as shown in the table below can be made.

transition	1	2	3	4	5
transition frequency, ν/GHz	51.0718	102.1426	102.1408	153.2103	153.2076

transition quantum numbers	$K=0$ $J=0\rightarrow 1$	$K=0$ $J=1\rightarrow 2$	$K=1$ $J=1\rightarrow 2$	$K=0$ $J=2\rightarrow 3$	$K=1$ $J=2\rightarrow 3$
transition frequency expression	$2B-4D_J$	$4B-32D_J$	$4B-32D_J-4D_{JK}$	$6B-108D_J$	$6B-108D_J-6D_{JK}$

Examination of these expressions reveals that the difference in transition frequencies between transitions 3 and 2 and between transitions 5 and 4 yield the value of D_{JK} directly.

$$\boxed{D_{JK} = 4.5\times 10^{2}\ \text{kHz}}$$

B and D_J can be found from simultaneous solution of the equations for transitions 1 and 2 and also from transitions 2 and 4. The average value of D_J obtained in this way is $\boxed{D_J = 56\ \text{kHz}}$. The value of B obtained from transition 1 is then $\boxed{B = 25.5360\ \text{GHz}}$. If desired, these results in frequency units, Hz, can be converted to units of wavenumber, cm^{-1}, by division by c, the velocity of light, expressed in units of cm s^{-1}.

12C.10 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 upon which one has a rotational spectrum that best spans blackbody radiation of 2.726 K. Given $\tilde{B}_0(\text{CH}) = 14.190\ \text{cm}^{-1}$, 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 $^{12}\text{C}^{14}\text{N}$ 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.

$$\tilde{B}_0 = B/c = \frac{\nu}{2c(J+1)} = \frac{\nu}{4c}$$
$$= 1.892\ \text{cm}^{-1}$$

Blackbody radiation at 2.726 K may be plotted against radiation wavenumber with suitable transformation of the equation for $\rho(\lambda,T)$ in section 7A.2(b)

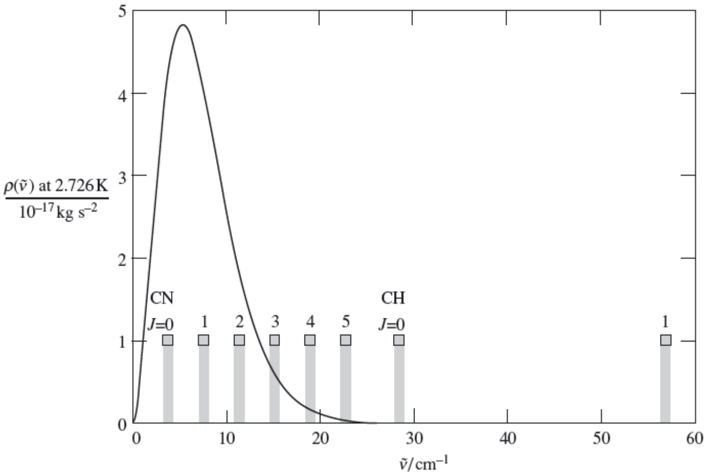
$$\rho(\tilde{\nu}) = \frac{8\pi hc\tilde{\nu}^3}{e^{hc\tilde{\nu}/kT}-1}$$

Spectral absorption lines of $^{12}\text{C}^{14}\text{N}$ and $^{12}\text{C}^{1}\text{H}$ are calculated with eqn 12C.8a.

$$\tilde{\nu}\left(J+1 \leftarrow J\right) = 2\tilde{B}\left(J+1\right) \qquad J = 0,\ 1,\ 2,\ 3.......$$

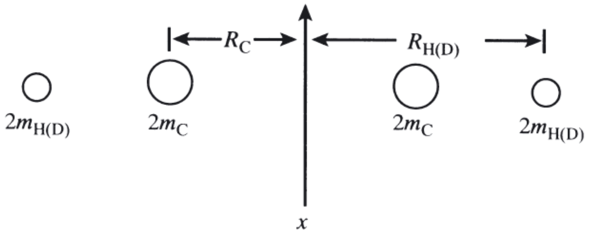
The cosmic background radiation and molecular absorption lines are shown in the graph, Fig. 12C.2. It is evident that only CN spans the background radiation.

Figure 12C.2



12C.12 Rotation about any axis perpendicular to the C_6 axis may be represented in its essentials by rotation of the pseudolinear molecule in Fig. 12.3(a) about the x-axis in the figure.

Figure 12C.3(a)



The data allow for a determination of R_C and $R_{H(D)}$ which may be decomposed into R_{CC} and $R_{CH(D)}$.

$$I_H = 4m_H R_H^2 + 4m_C R_C^2 = 147.59\times10^{-47}\,\text{kg m}^2$$

$$I_D = 4m_D R_D^2 + 4m_C R_C^2 = 178.45\times10^{-47}\,\text{kg m}^2$$

Subtracting I_H from I_D $\left(\text{assume } R_H = R_D\right)$ yields

$$4\left(m_D - m_H\right)R_H^2 = 30.86\times10^{-47}\,\text{kg m}^2$$

$$4\left(2.01410\ m_u - 1.0078\ m_u\right)\times\left(1.66054\times10^{-27}\ \text{kg}\ m_u^{\ -1}\right)\times\left(R_H^2\right) = 30.86\times10^{-47}\,\text{kg m}^2$$

$$R_H^2 = 4.616\overline{9}\times10^{-20}\,\text{m}^2 \qquad R_H = 2.149\times10^{-10}\,\text{m}$$

$$R_C^2 = \frac{(147.59\times10^{-47}\ \text{kg m}^2) - (4m_H R_H^2)}{4m_C}$$

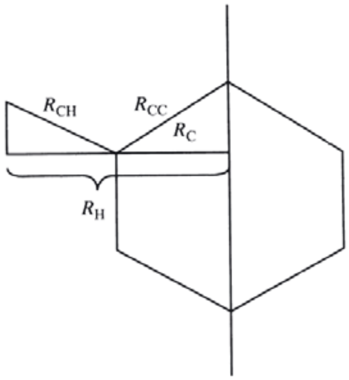
$$= \frac{(147.59\times10^{-47}\ \text{kg m}^2) - (4)\times(1.0078\,m_u)\times(1.66054\times10^{-27}\ \text{kg}\,m_u^{\ -1})\times(4.616\overline{9}\times10^{-20}\ \text{m}^2)}{(4)\times(12.011\,m_u)\times(1.66054\times10^{-27}\ \text{kg}\,m_u^{\ -1})}$$

$$= 1.4626\times10^{-20}\ \text{m}^2$$

$$R_C = 1.209\times10^{-10}\ \text{m}$$

Figure 12C.3(b) shows the relation between R_H, R_C, R_{CC}, and R_{CH}.

Figure 12C.3(b)



$$R_{CC} = \frac{R_C}{\cos 30^\circ} = \frac{1.209 \times 10^{-10}\,\text{m}}{0.8660} = 1.396 \times 10^{-10}\,\text{m} = \boxed{139.6\ \text{pm}}$$

$$R_{CH} = \frac{R_H - R_C}{\cos 30^\circ} = \frac{0.940 \times 10^{-10}}{0.8660} = 1.08\overline{5} \times 10^{-10} = \boxed{108.\overline{5}\ \text{pm}}$$

$$R_{CD} = R_{CH}$$

Comment. These values are very close to the interatomic distances quoted by Herzberg in *Electronic Spectra and Electronic Structure of Polyatomic Molecules,* p 666, which are 139.7 and 108.4 pm respectively.

12D Vibrational spectroscopy of diatomic molecules

Answers to discussion questions

12D.2 The rotational constants in vibrationally excited states are smaller than in the vibrational ground state and continue to get smaller as the vibrational level increases. Any anharmonicity in the vibration causes a slight extension of the bond length in the excited state. This results in an increase in the moment of inertia, and a consequent decrease in the rotational constant. The equation that describes how the rotational constant of a diatomic molecule changes with increasing vibrational level is $\tilde{B}_v = \tilde{B}_e - a(v + \frac{1}{2})$, where $\tilde{B}_e$ is a constant and $\tilde{B}_v$ is the rotational constant in level *v*.

12D.4 Isotopic substitution can change the spin of the nuclei in the molecule and 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. See Section 12C.3 and *Brief Illustration* 12C.2.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. But not all vibrational frequencies are necessarily changed by isotopic substitution. 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

12D.1(b) The angular frequency is

$$\omega=\left(\frac{k_{\mathrm{f}}}{m}\right)^{1/2}=2\pi\nu \quad \text{so} \quad k_{\mathrm{f}}=(2\pi\nu)^2 m=(2\pi)^2\times(3.0\ \mathrm{s}^{-1})^2\times(2.0\times10^{-3}\ \mathrm{kg})$$

$$k_{\mathrm{f}}=\boxed{0.71\ \mathrm{N\ m^{-1}}}$$

12D.2(b) $$\omega=\left(\frac{k_{\mathrm{f}}}{m_{\mathrm{eff}}}\right)^{1/2} \qquad \omega'=\left(\frac{k_{\mathrm{f}}}{m'_{\mathrm{eff}}}\right)^{1/2} \quad [\text{prime} = {}^{2}\mathrm{H}^{37}\mathrm{CI}]$$

The force constant, *k*, 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 $\boxed{28.4\ \text{per cent}}$

12D.3(b) The fundamental vibrational frequency is

$$\omega=\left(\frac{k_{\mathrm{f}}}{m_{\mathrm{eff}}}\right)^{1/2}=2\pi\nu=2\pi c\tilde{\nu} \quad \text{so} \quad k_{\mathrm{f}}=(2\pi c\tilde{\nu})^2 m_{\mathrm{eff}}$$

We need the effective mass

$$m_{\mathrm{eff}}^{-1}=m_{1}^{-1}+m_{2}^{-1}=(78.9183\ m_{\mathrm{u}})^{-1}+(80.9163\ m_{\mathrm{u}})^{-1}=0.0250298\ m_{\mathrm{u}}^{-1}$$

$$k_{\mathrm{f}}=\frac{[2\pi(2.998\times10^{10}\ \mathrm{cm\ s^{-1}})\times(323.2\ \mathrm{cm^{-1}})]^2\times(1.66054\times10^{-27}\ \mathrm{kg}\ m_{\mathrm{u}}^{-1})}{0.0250298\ m_{\mathrm{u}}^{-1}}$$

$$=\boxed{245.9\ \mathrm{N\ m^{-1}}}$$

12D.4(b) The relation between vibrational frequency and wavenumber is

$$\omega=\left(\frac{k}{m_{\mathrm{eff}}}\right)^{1/2}=2\pi\nu=2\pi c\tilde{\nu} \quad \text{so} \quad \tilde{\nu}=\frac{1}{2\pi c}\left(\frac{k}{m_{\mathrm{eff}}}\right)^{1/2}=\frac{\left(km_{\mathrm{eff}}^{-1}\right)^{1/2}}{2\pi c}$$

The reduced masses of the hydrogen halides are very similar, but not identical

$$m_{\mathrm{eff}}^{-1}=m_{\mathrm{D}}^{-1}+m_{\mathrm{X}}^{-1}$$

We assume that the force constants as calculated in Exercise 12D.4(a) are identical for the deuterium halide and the hydrogen halide.

For DF

$$m_{\text{eff}}^{-1}=\frac{\left(2.0140m_{\text{u}}\right)^{-1}+\left(18.9984m_{\text{u}}\right)^{-1}}{1.66054\times10^{-27}\,\text{kg}\;m_{\text{u}}^{-1}}=3.3071\times10^{26}\ \text{kg}^{-1}$$

$$\tilde{\nu}=\frac{\left\{\left(3.3071\times10^{26}\ \text{kg}^{-1}\right)\times\left(967.04\,\text{kg}\,\text{s}^{-2}\right)\right\}^{1/2}}{2\pi\left(2.9979\times10^{10}\ \text{cm}\,\text{s}^{-1}\right)}=\boxed{3002.3\,\text{cm}^{-1}}$$

For DCl

$$m_{\text{eff}}^{-1}=\frac{\left(2.0140m_{\text{u}}\right)^{-1}+\left(34.9688m_{\text{u}}\right)^{-1}}{1.66054\times10^{-27}\,\text{kg}\;m_{\text{u}}^{-1}}=3.1624\times10^{26}\ \text{kg}^{-1}$$

$$\tilde{\nu}=\frac{\left\{(3.1624\times10^{26}\ \text{kg}^{-1})\times(515.59\,\text{kg}\,\text{s}^{-2})\right\}^{1/2}}{2\pi(2.9979\times10^{10}\ \text{cm}\,\text{s}^{-1})}=\boxed{2143.7\,\text{cm}^{-1}}$$

For DBr

$$m_{\text{eff}}^{-1}=\frac{(2.0140m_{\text{u}})^{-1}+(80.9163m_{\text{u}})^{-1}}{1.66054\times10^{-27}\,\text{kg}\;m_{\text{u}}^{-1}}=3.0646\times10^{26}\ \text{kg}^{-1}$$

$$\tilde{\nu}=\frac{\left\{(3.0646\times10^{26}\ \text{kg}^{-1})\times(411.75\,\text{kg}\,\text{s}^{-2})\right\}^{1/2}}{2\pi(2.9979\times10^{10}\ \text{cm}\,\text{s}^{-1})}=\boxed{1885.8\,\text{cm}^{-1}}$$

For DI

$$m_{\text{eff}}^{-1}=\frac{(2.0140m_{\text{u}})^{-1}+(126.9045m_{\text{u}})^{-1}}{1.66054\times10^{-27}\,\text{kg}\;m_{\text{u}}^{-1}}=3.0376\times10^{26}\ \text{kg}^{-1}$$

$$\tilde{\nu}=\frac{\left\{(3.0376\times10^{26}\ \text{kg}^{-1})\times(314.21\,\text{kg}\,\text{s}^{-2})\right\}^{1/2}}{2\pi(2.9979\times10^{10}\ \text{cm}\,\text{s}^{-1})}=\boxed{1640.1\,\text{cm}^{-1}}$$

12D.5(b) The ratio of the population of the second excited state (N_2) to the first excited state (N_1) is

$$\frac{N_2}{N_1}=\exp\left(\frac{-h\nu}{kT}\right)=\exp\left(\frac{-hc\tilde{\nu}}{kT}\right)$$

(i) $$\frac{N_2}{N_1}=\exp\left(\frac{-\left(6.626\times10^{-34}\,\text{J}\,s\right)\times\left(2.998\times10^{10}\ \text{cm}\,\text{s}^{-1}\right)\times\left(321\,\text{cm}^{-1}\right)}{\left(1.381\times10^{-23}\,\text{J}\,\text{K}^{-1}\right)\times\left(298\,\text{K}\right)}\right)=\boxed{0.212}$$

(ii) $$\frac{N_2}{N_1}=\exp\left(\frac{-\left(6.626\times10^{-34}\,\text{J}\,\text{s}\right)\times\left(2.998\times10^{10}\ \text{cm}\,\text{s}^{-1}\right)\times\left(321\,\text{cm}^{-1}\right)}{\left(1.381\times10^{-23}\,\text{J}\,\text{K}^{-1}\right)\times\left(800\,\text{K}\right)}\right)=\boxed{0.561}$$

12D.6(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.

$$\Delta\widetilde{G}(v=1\leftarrow0)=\tilde{\nu}-2\tilde{\nu}x_{\text{e}}=2329.91\ \text{cm}^{-1}\ \text{[12D.14]}$$

$$\Delta\widetilde{G}(v=2\leftarrow0)=2\tilde{\nu}-6\tilde{\nu}x_{\text{e}}=4631.20\ \text{cm}^{-1}\ \text{[12D.15]}$$

Multiply the first equation by 3, then subtract the second.

$$\tilde{\nu}=(3)\times(2329.91\ \text{cm}^{-1})-(4631.20\ \text{cm}^{-1})=\boxed{2358.53\ \text{cm}^{-1}}$$

Then from the first equation

$$x_{\text{e}}=\frac{\tilde{\nu}-2329.91\ \text{cm}^{-1}}{2\tilde{\nu}}=\frac{(2358.53-2329.91)\text{cm}^{-1}}{(2)\times(2358.53\ \text{cm}^{-1})}=\boxed{6.067\times10^{-3}}$$

x_e data are usually reported as $x_e\tilde{\nu}$ which is

$$x_e\tilde{\nu} = 14.31\ \text{cm}^{-1}$$

$$\Delta\widetilde{G}(v = 3 \leftarrow 0) = 3\tilde{\nu} - 12vx_e = (3)\times(2358.53\ \text{cm}^{-1}) - (12)\times(14.31\ \text{cm}^{-1})$$

$$= 6903.87\ \text{cm}^{-1}$$

Very close to the given experimental value.

12D.7(b) $\Delta\widetilde{G}_{v+1/2} = \tilde{\nu} - 2(v+1)x_e\tilde{\nu}$ [12D.14] where $\Delta\widetilde{G}_{v+1/2} = \widetilde{G}(v+1) - \widetilde{G}(v)$

Therefore, since

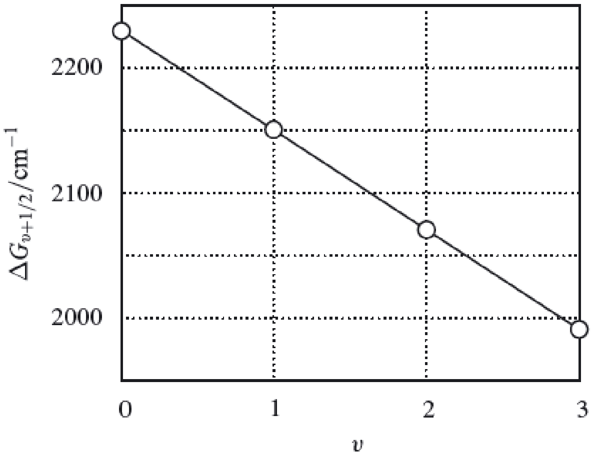
$$\Delta\widetilde{G}_{v+1/2} = (1-2x_e)\tilde{\nu} - 2vx_e\tilde{\nu}$$

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
$\widetilde{G}(v)/\text{cm}^{-1}$	1144.83	3374.90	5525.51	7596.66	9588.35
$\Delta\widetilde{G}_{v+1/2}/\text{cm}^{-1}$	2230.07	2150.61	2071.15	1991.69	

The points are plotted in Fig. 12D.1.

Figure 12D.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 $\widetilde{D}_e$ in the expression for the potential is an adequate first approximation for it. Then

$$\widetilde{D}_e = \frac{\tilde{\nu}}{4x_e}[\text{12D.12}] = \frac{\tilde{\nu}^2}{4x_e\tilde{\nu}} = \frac{(2310.16\ \text{cm}^{-1})^2}{(4)\times\left(39.83\ \text{cm}^{-1}\right)} = 33.50\times10^3\ \text{cm}^{-1} = 4.15\ \text{eV}$$

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

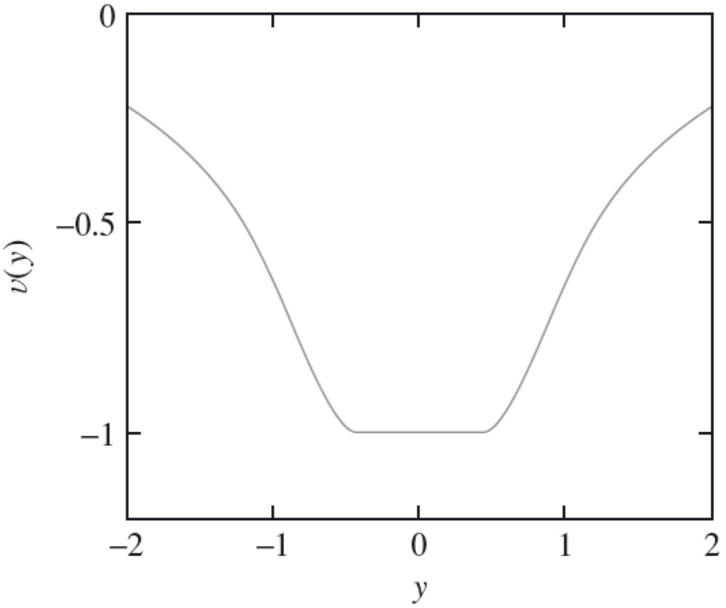
$$\widetilde{D}_0 = \widetilde{D}_e - \frac{1}{2}\tilde{\nu} = (33.50\times10^3\ \text{cm}^{-1}) - \left(\tfrac{1}{2}\right)\times(2310.16\ \text{cm}^{-1})$$

$$= \boxed{3.235\times10^4\ \text{cm}^{-1}} = \boxed{4.01\ \text{eV}}$$

Solutions to problems

12D.2 In order to plot this potential function define the variable $y \equiv x/a$ and rewrite the potential function as $v(y) = \dfrac{V(y)}{V_0} = \left(e^{-1/y^2} - 1\right)$. Figure 12D.2 shows a plot of this function against y.

Figure 12D.2



Note that for small displacements from $y = 0$ ($x = 0$) the potential energy function is flat (independent of x). Therefore the first and second derivatives of $V(x)$ are zero and the force constant is zero. There is no restoring force for small displacements from the equilibrium position. The particle $\boxed{\text{cannot undergo simple harmonic motion}}$.

12D.4 $\widetilde{D}_0 = \widetilde{D}_e - \tilde{\nu}'$ with $\tilde{\nu}' = \tfrac{1}{2}\tilde{\nu} - \tfrac{1}{4}x_e\tilde{\nu}$ [Section 12D.3]

(a) ^{1}HCl: $\tilde{\nu}' = \left\{(1494.9) - \left(\tfrac{1}{4}\right)\times(52.05)\right\},\text{cm}^{-1} = 1481.8\,\text{cm}^{-1}$, or $0.184\,\text{eV}$

Hence, $\widetilde{D}_0 = 5.33 - 0.18 = \boxed{5.15\ \text{eV}}$

(b) ^{2}HCl: $\dfrac{2m_{\text{eff}}\,\omega x_{\text{e}}}{\hbar} = a^2$ [12D.12], so $\tilde{\nu}x_{\text{e}} \propto \dfrac{1}{m_{\text{eff}}}$ as a is a constant. We also have $\tilde{D}_{\text{e}} = \dfrac{\tilde{\nu}^2}{4x_{\text{e}}\tilde{\nu}}$; so $\tilde{\nu}^2 \propto \dfrac{1}{m_{\text{eff}}}$, implying $\tilde{\nu} \propto \dfrac{1}{m_{\text{eff}}^{1/2}}$. Reduced masses were calculated in Exercises 12D.4(a) and 12D.4(b), and we can write

$$\tilde{\nu}(^{2}\text{HCl}) = \left(\frac{m_{\text{eff}}\,(^{1}\text{HCl})}{m_{\text{eff}}\,(^{2}\text{HCl})}\right)^{1/2} \times \tilde{\nu}(^{1}\text{HCl}) = (0.7172)\times(2989.7\,\text{cm}^{-1}) = 2144.2\,\text{cm}^{-1}$$

$$x_{\text{e}}\tilde{\nu}(^{2}\text{HCl}) = \left(\frac{m_{\text{eff}}\,(^{1}\text{HCl})}{m_{\text{eff}}\,(^{2}\text{HCl})}\right) \times x_{\text{e}}\tilde{\nu}(^{1}\text{HCl}) = (0.5144)\times(52.05\,\text{cm}^{-1}) = 26.77\,\text{cm}^{-1}$$

$$\tilde{\nu}'(^{2}\text{HCl}) = \left(\tfrac{1}{2}\right)\times(2144.2) - \left(\tfrac{1}{4}\right)\times(26.77\,\text{cm}^{-1}) = 1065.4\,\text{cm}^{-1}, \quad 0.132\,\text{eV}$$

Hence, $\tilde{D}_0\,(^{2}\text{HCl}) = (5.33 - 0.132)\,\text{eV} = \boxed{5.20\text{ eV}}$

12D.6 **(a)** In the harmonic approximation

$$\tilde{D}_{\text{e}} = \tilde{D}_0 + \tfrac{1}{2}\tilde{\nu} \quad \text{so} \quad \tilde{\nu} = 2(\tilde{D}_{\text{e}} - \tilde{D}_0)$$

$$\tilde{\nu} = \frac{2(1.51\times10^{-23}\,\text{J} - 2\times10^{-26}\,\text{J})}{(6.626\times10^{-34}\,\text{J s})\times(2.998\times10^{8}\,\text{m s}^{-1})} = \boxed{152\text{ m}^{-1}}$$

The force constant is related to the vibrational frequency by

$$\omega = \left(\frac{k_{\text{f}}}{m_{\text{eff}}}\right)^{1/2} [12\text{D}.7] = 2\pi\nu = 2\pi c\tilde{\nu} \quad \text{so} \quad k_{\text{f}} = (2\pi c\tilde{\nu})^2 m_{\text{eff}}$$

The effective mass is

$$m_{\text{eff}} = \tfrac{1}{2}m = \tfrac{1}{2}(4.003\,m_{\text{u}})\times(1.66\times10^{-27}\,\text{kg}\,m_{\text{u}}{}^{-1}) = 3.32\times10^{-27}\,\text{kg}$$

$$k_{\text{f}} = \left[2\pi(2.998\times10^{8}\ \text{ms}^{-1})\times(152\ \text{m}^{-1})\right]^2 \times (3.32\times10^{-27}\,\text{kg})$$

$$= \boxed{2.72\times10^{-4}\,\text{kg s}^{-2}}$$

The moment of inertia is

$$I = m_{\text{eff}}R_{\text{e}}^2 = (3.32\times10^{-27}\,\text{kg})\times(297\times10^{-12}\,\text{m})^2 = \boxed{2.93\times10^{-46}\,\text{kg m}^2}$$

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

$$x_{\text{e}} = \frac{\tilde{\nu}}{4\tilde{D}_{\text{e}}} \text{ and } \tilde{D}_{\text{e}} = \tilde{D}_0 + \frac{1}{2}\left(1 - \frac{1}{2}x_{\text{e}}\right)\tilde{\nu} = \tilde{D}_0 + \frac{1}{2}\left(1 - \frac{\tilde{\nu}}{8\tilde{D}_{\text{e}}}\right)\tilde{\nu}$$

This rearranges to a quadratic equation in $\tilde{\nu}$

$$\frac{\tilde{\nu}^2}{16\tilde{D}_{\text{e}}} - \frac{1}{2}\tilde{\nu} + \tilde{D}_{\text{e}} - \tilde{D}_0 = 0 \text{ so } \tilde{\nu} = \frac{\frac{1}{2} - \sqrt{\left(\frac{1}{2}\right)^2 - \frac{4(\tilde{D}_{\text{e}} - \tilde{D}_0)}{16\tilde{D}_{\text{e}}}}}{2(16\tilde{D}_{\text{e}})^{-1}}$$

$$\tilde{\nu} = 4\widetilde{D}_e\left(1-\sqrt{\frac{\widetilde{D}_0}{\widetilde{D}_e}}\right)$$

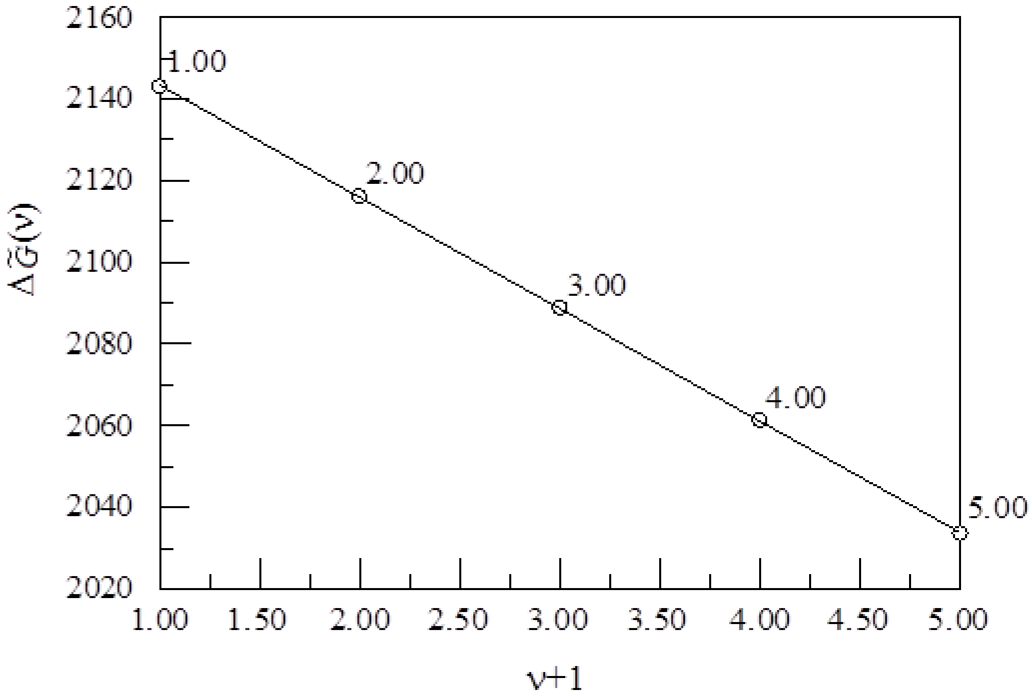
$$= \frac{4(1.51\times10^{-23}\,\mathrm{J})}{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{8}\ \mathrm{m\,s^{-1}})}\left(1-\sqrt{\frac{2\times10^{-26}\,\mathrm{J}}{1.51\times10^{-23}\,\mathrm{J}}}\right)$$

$$= \boxed{293\ \mathrm{m^{-1}}}$$

and $x_e = \dfrac{(293\ \mathrm{m^{-1}})\times(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{8}\,\mathrm{m\,s^{-1}})}{4(1.51\times10^{-23}\,\mathrm{J})} = \boxed{0.96}$

12D.8 See Fig. 12D.3 for a plot of $\Delta\widetilde{G}(v) = \tilde{\nu} - 2(v+1)x_e\tilde{\nu}$ [12D.14] against $v + 1$.

Figure 12D.3



The intercept gives $\boxed{\tilde{\nu} = 2170.8\ \mathrm{cm^{-1}}}$ and the slope gives $2x_e\tilde{\nu}$ = 27.4 cm^{-1}; thus, $\boxed{x_e\tilde{\nu} = 13.7\ \mathrm{cm^{-1}}.}$

12D.10 We note first that only two data are provided; yet we have four distances to calculate: R(CC), for both C_2H_2 and C_2D_2, R(CH), and R(CD). Consequently we must make some reasonable approximations in order to solve this problem. We will assume that the CC and CH distances are the same in both molecules. Our procedure will be first to calculate the moments of inertia of the molecules from the given rotational constants and then from the moments of inertia and the known masses of the atoms to calculate the interatomic distances.

$$\tilde{B} = \frac{\hbar}{4\pi cI} \text{ hence } I = \frac{\hbar}{4\pi c\tilde{B}}$$

The formulas for the moments of inertia in terms of the masses and distances are:

$$I(\mathrm{C_2H_2}) = 2m_{\mathrm{C}}a^2 + 2m_{\mathrm{H}}b^2 \text{ (eqn 1) and } I(\mathrm{C_2D_2}) = 2m_{\mathrm{C}}a^2 + 2m_{\mathrm{D}}b^2 \text{ (eqn 2)}$$

where a is the distance from the center of mass to the C atom, which is half the CC interatomic distance, and b is the distance from the center of mass to the H or D atom.

$$\tilde{B}(\mathrm{C_2H_2}) = \frac{2.352\ \mathrm{cm^{-1}}}{2} = 1.176\ \mathrm{cm^{-1}} \text{ and } \tilde{B}(\mathrm{C_2D_2}) = \frac{1.696\ \mathrm{cm^{-1}}}{2} = 0.848\mathrm{cm^{-1}}$$

Therefore,

$$I(\mathrm{C_2H_2}) = \frac{\hbar}{4\pi c \times 1.176\ \mathrm{cm^{-1}}} = 2.3804\times10^{-46}\ \mathrm{kg\ m^2} \text{ and}$$

$$I(\mathrm{C_2D_2}) = \frac{\hbar}{4\pi c \times 0.848\ \mathrm{cm^{-1}}} = 3.3010\times10^{-46}\ \mathrm{kg\ m^2}$$

The masses are m_{C} = 12.0000 u, m_{H} = 1.0078 u, and m_{D} = 2.0140 u; u is the atomic mass unit. Substituting these values into eqns. 1 and 2 above and solving the equations simultaneously for distances a and b we obtain:

$$a = 0.6049\times10^{-10}\ \mathrm{m} \text{ and } b = 1.6598\times10^{-10}\ \mathrm{m}$$

$$R(\mathrm{CC}) = 2a = 1.2098\times10^{-10}\ \mathrm{m} = \boxed{121.0\ \mathrm{pm}} \text{ and}$$

$$R(\mathrm{CH}) = R(\mathrm{CD}) = b - a = 1.055\times10^{-10}\ \mathrm{m}\ = \boxed{105.5\ \mathrm{pm}}$$

12D.12 Here we make use of results that have been obtained in Chapter 8 for the average value of $x = R - R_{\mathrm{e}}$ and $x^2 = (R - R_{\mathrm{e}})^2$.

$$\langle x\rangle = 0 \qquad \langle x^2\rangle = (v+\tfrac{1}{2})\frac{\hbar}{(mk)^{1/2}} \quad [\text{8B.12a \& b}]$$

Consider first $1/\langle R\rangle^2$. We need to evaluate $\langle R\rangle$.

$$\langle R\rangle = \langle R_{\mathrm{e}} + x\rangle\ [R_{\mathrm{e}} \text{ is a constant}] = \langle R_{\mathrm{e}}\rangle + \langle x\rangle = R_{\mathrm{e}} + 0 = R_{\mathrm{e}}$$

$$\boxed{1/\langle R\rangle^2 = 1/R_{\mathrm{e}}{}^2}$$

Next consider $1/\langle R^2\rangle$. We need to evaluate $\langle R^2\rangle$. $1/\langle R^2\rangle$ is the reciprocal of this quantity.

$$\langle R^2\rangle = \langle (R_{\mathrm{e}}+x)^2\rangle = \langle R_{\mathrm{e}}{}^2 + 2xR_{\mathrm{e}} + x^2\rangle = \langle R_{\mathrm{e}}{}^2\rangle + \langle 2xR_{\mathrm{e}}\rangle + \langle x^2\rangle = R_{\mathrm{e}}{}^2 + 2R_{\mathrm{e}}\langle x\rangle + \langle x^2\rangle = R_{\mathrm{e}}{}^2 + \langle x^2\rangle$$

$$\boxed{1/\langle R^2\rangle = \frac{1}{R_{\mathrm{e}}{}^2}\left(\frac{1}{1+\langle x^2\rangle/R_{\mathrm{e}}{}^2}\right)}$$

Finally consider $\langle 1/R^2\rangle$. We need to evaluate $1/R^2$ and then take the average of this quantity.

$$\frac{1}{R^2}=\frac{1}{(R_{\mathrm{e}}+x)^2}=\frac{1}{R_{\mathrm{e}}^{\,2}\left(1+\frac{x}{R_{\mathrm{e}}}\right)^2}=\frac{1}{R_{\mathrm{e}}^{\,2}}\left(1-2\frac{x}{R_{\mathrm{e}}}+3\frac{x^2}{R_{\mathrm{e}}^{\,2}}+\ldots\right)$$

We have expanded $\left(1+\frac{x}{R_{\mathrm{e}}}\right)^{-2}$ in a binomial series and dropped terms beyond the second power of $\frac{x}{R_{\mathrm{e}}}$.

Noting again that $\langle x\rangle=0$ we finally obtain $\boxed{\left\langle\frac{1}{R^2}\right\rangle=\frac{1}{R_{\mathrm{e}}^{\,2}}\left(1+3\frac{\langle x^2\rangle}{R_{\mathrm{e}}^{\,2}}\right)}$. Examination of these three results shows that $\left\langle\frac{1}{R^2}\right\rangle>\frac{1}{\langle R\rangle^2}>\frac{1}{\langle R\rangle^2}$.

12D.14 For IF, the rotational constant $\tilde{B}_{\mathrm{e}}$ = 0.27971 cm^{-1} and a = 0.187 m^{-1} = 0.00187 cm^{-1}. Values for $\tilde{B}_0$ and $\tilde{B}_1$ are calculated from $\tilde{B}_v=\tilde{B}_{\mathrm{e}}-a(v+\tfrac{1}{2})$.

$$\tilde{B}_0=\tilde{B}_{\mathrm{e}}-\tfrac{1}{2}a=0.27971\ \mathrm{cm^{-1}}-\tfrac{1}{2}(0.00187\ \mathrm{cm^{-1}})=\boxed{0.27877\overline{5}\ \mathrm{cm^{-1}}}$$

$$\tilde{B}_1=\tilde{B}_{\mathrm{e}}-\tfrac{3}{2}a=0.27971\ \mathrm{cm^{-1}}-\tfrac{3}{2}(0.00187\ \mathrm{cm^{-1}})=\boxed{0.27690\overline{5}\ \mathrm{cm^{-1}}}$$

The wavenumbers of the $J'\rightarrow 3$ transitions of the P and R branches of the spectrum are given by eqns. 12D.18 & 12D.19a.

$$\tilde{\nu}_{\mathrm{P}}(J)=\tilde{\nu}-(\tilde{B}_1+\tilde{B}_0)J+(\tilde{B}_1-\tilde{B}_0)J^2 \text{ and } \tilde{\nu}_{\mathrm{R}}(J)=\tilde{\nu}+(\tilde{B}_1+\tilde{B}_0)(J+1)+(\tilde{B}_1-\tilde{B}_0)(J+1)^2$$

When anharmonicities are present $\tilde{\nu}$ in the formulas above is replaced by

$$\Delta\tilde{G}(v)=\tilde{\nu}-2(v+1)x_{\mathrm{e}}\tilde{\nu}\ [12\mathrm{D}.14].$$

For v = 0,

$$\Delta\tilde{G}(v)=\tilde{\nu}-2x_{\mathrm{e}}\tilde{\nu}=610.258\ \mathrm{cm^{-1}}-2\times3.141\ \mathrm{cm^{-1}}=603.976\ \mathrm{cm^{-1}}$$

For the P branch J' = J = 4, and for the R branch J' = J = 2. Substituting all of these values into eqns 12D.18 & 12D.19a we obtain

$$\tilde{\nu}_{\mathrm{P}}(J)=\Delta\tilde{G}(v)-(\tilde{B}_1+\tilde{B}_0)J+(\tilde{B}_1-\tilde{B}_0)J^2=\boxed{601.723\ \mathrm{cm^{-1}}}$$

$$\tilde{\nu}_{\mathrm{R}}(J)=\Delta\tilde{G}(v)+(\tilde{B}_1+\tilde{B}_0)(J+1)+(\tilde{B}_1-\tilde{B}_0)(J+1)^2=\boxed{605.626\ \mathrm{cm^{-1}}}$$

The dissociation energy of the IF molecule may be obtained from $\tilde{D}_{\mathrm{e}}=\dfrac{\tilde{\nu}^2}{4x_{\mathrm{e}}\tilde{\nu}}[12\mathrm{D}.12]$ and the relation

$$\tilde{D}_0=\tilde{D}_{\mathrm{e}}-\tfrac{1}{2}\tilde{\nu}+\tfrac{1}{4}x_{\mathrm{e}}\tilde{\nu}\quad \text{if a Morse potential energy is assumed.}$$

Substituting the values given for $\tilde{\nu}$ and $\tilde{\nu}x_{\mathrm{e}}$ we obtain

$\tilde{D}_{\mathrm{e}}=29641\ \mathrm{cm^{-1}}$ and $\boxed{\tilde{D}_0=29337\ \mathrm{cm^{-1}}}$

12D.16 We work with eqns. 12D.22 which give the transition energies for the S and O branches of the vibrational Raman spectra. Transitions having $\tilde{\nu}_{\mathrm{S}}(J-2)$ and $\tilde{\nu}_{\mathrm{O}}(J+2)$ have a common upper state; hence the corresponding combination difference, Δ_0, is a function of B_0 only. Likewise, transitions $\tilde{\nu}_{\mathrm{S}}(J)$ and $\tilde{\nu}_{\mathrm{O}}(J)$ have a common lower state and the combination difference, Δ_1, is a function of B_1 only. Using eqns. 12D.22 we obtain

$$\tilde{\nu}_S(J-2) = \tilde{\nu}_i - \tilde{\nu} - 4\widetilde{B_0}(J-2) - 6\widetilde{B}_0$$
$$\tilde{\nu}_O(J+2) = \tilde{\nu}_i - \tilde{\nu} + 4\widetilde{B_0}(J+2) - 2\widetilde{B}_0$$

Taking the difference between $\tilde{\nu}_O(J+2)$ and $\tilde{\nu}_S(J-2)$ we obtain for the combination difference

$$\boxed{\Delta_0 = \tilde{\nu}_O(J+2) - \tilde{\nu}_S(J-2) = 8\widetilde{B}_0(J+\tfrac{1}{2})}\ .$$

In a similar manner we can obtain

$$\boxed{\Delta_1 = \tilde{\nu}_O(J) - \tilde{\nu}_S(J) = 8\widetilde{B}_1(J+\tfrac{1}{2})}$$

12E Vibrational spectroscopy of polyatomic molecules

Answers to discussion questions

12E.2 The gross selection rule is that the polarizability of the molecule must change as the molecule vibrates. All diatomic molecules satisfy this condition as the molecules swell and contract during a vibration, the control of the nuclei over the electrons varies, and the molecular polarizability changes. Hence both homonuclear and heteronuclear diatomics are vibrationally Raman active. In polyatomic molecules it is usually quite difficult to judge by inspection whether or not the molecule is anisotropically polarizable; hence group theoretical methods are relied on for judging the Raman activity of the various normal modes of vibration. The procedure is discussed in Section 12E.4 and demonstrated in the *Brief Illustration* in that section.

Solutions to exercises

12E.1(b) See Section 12E.2. 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

(i) CH_3 CH_3 **(ii)**CH_4 **(iii)** CH_3Cl

Comment. A more powerful method for determining infrared activity based on symmetry considerations is described in Section 12E.4(a).

12E.2(b) A nonlinear molecule has $3N-6$ normal modes of vibration, where N is the number of atoms in the molecule; a linear molecule has $3N-5$.

(i) C_6H_6 has $3(12)-6=\boxed{30}$ normal modes.

(ii) $C_6H_6CH_3$ has $3(16)-6=\boxed{42}$ normal modes.

(iii) $HC\equiv C-C\equiv CH$ is linear; it has $3(6)-5=\boxed{13}$ normal modes.

12E.3(b) This molecule is linear, and the number of vibrational modes is 3N-5. N = 36 in this case; therefore, the number of vibrational modes is $\boxed{103\ .}$

12E.4(b) $\tilde{G}_q(v) = (v+\tfrac{1}{2})\tilde{\nu}_q \qquad \tilde{\nu}_q = \dfrac{1}{2\pi c}\left(\dfrac{k_q}{m_q}\right)^{1/2}$ [12E.1]

The lowest energy term is $\tilde{\nu}_2$ corresponding to the normal mode for bending. For this mode the sulfur atom may be considered to remain stationary and the effective mass is approximately $m_q = \dfrac{2m_{\mathrm{O}}m_{\mathrm{S}}}{2m_{\mathrm{O}}+m_{\mathrm{S}}}$.

For the other modes the effective mass expression is more complicated and is beyond the scope of this text. SO_2, like H_2O, is a bent molecule so it has three normal modes ($3N - 6 = 3$) that have the same motions as the normal modes of H_2O shown in text Fig. 12E.3. However, because of differences in bond strengths and effective masses, the wavenumbers of the two molecules differ. In the ground vibrational state all normal modes have $\upsilon = 0$. Thus, like H_2O, the ground vibrational term of SO_2 is the sum of eqn. 12E.1 normal mode terms:

$$\tilde{G}_{\text{ground}} = \tilde{G}_1(0)+\tilde{G}_2(0)+\tilde{G}_3(0) = \boxed{\tfrac{1}{2}(\tilde{\nu}_1+\tilde{\nu}_2+\tilde{\nu}_3)}$$

12E.5(b) (i) A planar AB_3 molecule belongs to the D_{3h} 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_{3h}. 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_{3h}	E	σ_h	$2C_3$	$2S_3$	$3C_2'$	$3\sigma_v$
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 $\boxed{A_2'' \text{ and } E' \text{ are IR active.}}$ We also see from the character table that E' and A_1' correspond to the quadratic terms; hence $\boxed{A_1' \text{ and } E' \text{ are Raman active.}}$

(ii) A trigonal pyramidal AB_3 molecule belongs to the group C_{3v}. In a manner similar to the analysis in part (i) we obtain

C_{3V}	E	$2C_3$	$3\sigma_V$
χ(total)	12	0	2
χ(vibration)	6	–2	2

χ (vibration) corresponds to $2\mathrm{A}_1 + 2\mathrm{E}$. We see from the character table that $\boxed{\mathrm{A}_1 \text{ and } \mathrm{E}}$ are IR active and that $\boxed{\mathrm{A}_1 + \mathrm{E}}$ are also Raman active. Thus all modes are observable in both the IR and the Raman spectra.

12E.6(b) (i) 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 $\boxed{\text{IR active}}$.

(ii) Since benzene has a centre of inversion, the exclusion rule applies: a mode which is IR active (such as this one) must be $\boxed{\text{Raman inactive}}$.

12E.7(b) The displacements span $\mathrm{A}_{1g} + 2\mathrm{A}_{1u} + 2\mathrm{E}_{1u} + \mathrm{E}_{1g}$. The rotations R_x and R_y span E_{1g}, and the translations span $\mathrm{E}_{1u} + \mathrm{A}_{1u}$. So the vibrations span $\boxed{\mathrm{A}_{1g} + \mathrm{A}_{1u} + \mathrm{E}_{1u}}$

12E.8(b) CS_2 is a linear AB_2 molecule similar to CO_2; therefore (see the solution to Exercise 12E.5(a)); the symmetric stretch, A_{1g}, is infrared inactive but Raman active. The antisymmetric stretch, A_{1u}, is infrared active, and (by the exclusion rule) Raman inactive. The two bending modes, E_{1u}, are infrared active and therefore Raman inactive.

Solutions to problems

12E.2 The Lewis structure is

$$[\ddot{\underset{\cdot\cdot}{\mathrm{O}}}=\mathrm{N}=\ddot{\underset{\cdot\cdot}{\mathrm{O}}}]^+$$

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 (Fig. 12E.2 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 $\mathrm{cm}^{-1} \approx$ 3735 cm^{-1}, which shows a weak intensity in the infrared.

12E.4 Summarize the six observed vibrations according to their wavenumbers $(\tilde{\nu}/\mathrm{cm}^{-1})$:

IR	870	1370	2869	3417
Raman	877	1408	1435	3407.

(i) If H_2O_2 were linear, it would have $3N - 5 = \boxed{7}$ vibrational modes.

(ii) Follow the flow chart in Fig. 11.7. Structure **1** is not linear, there is only one C_n axis (a C_2), and there is a σ_h; the point group is $\boxed{C_{2\mathrm{h}}}$ Structure **2** is not linear, there is only one C_n axis (a C_2), no σ_h, but two σ_v; the point group is $\boxed{C_{2\mathrm{v}}}$. Structure 3 is not linear, there is only one C_n axis (a C_2), no σ_h, no σ_v; the point group is $\boxed{C_2}$.

(iii) The exclusion rule applies to structure **1** because it has a center of inversion: no vibrational modes can be both IR and Raman active. So $\boxed{\text{structure } \mathbf{1} \text{ is inconsistent with observation.}}$ The vibrational modes of structure **2** span $3\mathrm{A}_1 + \mathrm{A}_2 + 2\mathrm{B}_2$. (The full basis of 12 cartesian coordinates spans $4\mathrm{A}_1 + 2\mathrm{A}_2 + 2\mathrm{B}_1 + 4\mathrm{B}_2$; remove translations and rotations.) The $C_{2\mathrm{v}}$ character table says that five of these modes are IR active $(3\mathrm{A}_1 + 2\mathrm{B}_2)$ and all are Raman active. All of the modes of structure **3** are both IR and Raman active. (A look at the character table shows that both symmetry species are IR and Raman active, so determining the symmetry species of the normal modes does not help here.) Both structures **2** and **3** have more active modes than were observed. This is consistent with the observations. After all, group theory can only tell us whether the transition moment *must* be zero by symmetry; it does not tell us whether the transition moment is sufficiently strong to be observed under experimental conditions.

Integrated activities

12.2 Because the centrifugal force and the restoring force balance,

$$k_\mathrm{f}\,(r_\mathrm{c} - r_\mathrm{e}) = m_\mathrm{eff}\,\omega^2 r_\mathrm{c},$$

we can solve for the distorted bond length as a function of the equilibrium bond length:

$$r_\mathrm{c} = \frac{r_\mathrm{e}}{1 - m_\mathrm{eff}\,\omega^2 / k_\mathrm{f}}$$

Classically, then, the energy would be the rotational energy plus the energy of the stretched bond:

$$E = \frac{J^2}{2I} + \frac{k_\mathrm{f}\,(r_\mathrm{c} - r_\mathrm{e})^2}{2} = \frac{J^2}{2I} + \frac{k_\mathrm{f}^{\,2}\,(r_\mathrm{c} - r_\mathrm{e})^2}{2k} = \frac{J^2}{2I} + \frac{(m_\mathrm{eff}\,\omega^2 r_\mathrm{c})^2}{2k_\mathrm{f}}.$$

How is the energy different form the rigid-rotor energy? Besides the energy of stretching of the bond, the larger moment of inertia alters the strictly rotational piece of the energy. Substitute $m_\mathrm{eff}\, r_\mathrm{c}^2$ for I and substitute for r_c in terms of r_e throughout:

So $$E = \frac{J^2 (1 - m_\mathrm{eff}\,\omega^2 / k_\mathrm{f})^2}{2m_\mathrm{eff}\, r_\mathrm{e}^2} + \frac{m_\mathrm{eff}^{\,2}\,\omega^4 r_\mathrm{e}^2}{2k_\mathrm{f}\,(1 - m_\mathrm{eff}\,\omega^2 / k_\mathrm{f})^2}.$$

Assuming that $m_\mathrm{eff}\,\omega^2/k_\mathrm{f}$ is small (a reasonable assumption for most molecules), we can expand the expression and discard squares or higher powers of $m_\mathrm{eff}\,\omega^2/k_\mathrm{f}$:

$$E \approx \frac{J^2 (1 - 2m_\mathrm{eff}\,\omega^2 / k_\mathrm{f})}{2m_\mathrm{eff}\, r_\mathrm{e}^{\,2}} + \frac{m_\mathrm{eff}^{\,2}\,\omega^4 r_\mathrm{e}^2}{2k_\mathrm{f}}.$$

(Note that the entire second term has a factor of $m_\mathrm{eff}\,\omega^2/k_\mathrm{f}$ even before squaring and expanding the denominator, so we discard all terms of that expansion after the first.) Begin to clean up the expression by using classical definitions of angular momentum:

$$J = I\omega = m_\mathrm{eff}\, r^2 \omega \quad \text{so} \quad \omega = J / m_\mathrm{eff}\, r_\mathrm{e}^{\,2},$$

which allows us to substitute expressions involving J for all ω s:

$$E \approx \frac{J^2}{2m_\mathrm{eff}\, r_\mathrm{e}^{\,2}} - \frac{J^4}{m_\mathrm{eff}^{\,2}\, r_\mathrm{e}^{\,6} k_\mathrm{f}} + \frac{J^4}{2m_\mathrm{eff}^{\,2}\, r_\mathrm{e}^{\,6} k_\mathrm{f}}.$$

(At the same time, we have expanded the first term, part of which we can now combine with the last term.) Continue to clean up the expression by substituting I/m_eff for r^2, and then carry the expression over to its quantum mechanical equivalent by substituting $J(J+1)\hbar^2$ for J^2:

$$E \approx \frac{J^2}{2I} - \frac{J^4 m_{\text{eff}}}{2I^3 k_{\text{f}}} \Rightarrow E \approx \frac{J(J+1)\hbar^2}{2I} - \frac{J^2(J+1)^2 \hbar^4 m_{\text{eff}}}{2I^3 k_{\text{f}}}.$$

Dividing by hc gives the rotational term, $\widetilde{F}(J)$:

$$\widetilde{F}(J) \approx \frac{J(J+1)\hbar^2}{2hcI} - \frac{J^2(J+1)^2 \hbar^4 m_{\text{eff}}}{2hcI^3 k_{\text{f}}} = \frac{J(J+1)\hbar}{4\pi cI} - \frac{J^2(J+1)^2 \hbar^3 m_{\text{eff}}}{4\pi cI^3 k_{\text{f}}},$$

where we have used $\hbar = h/2\pi$ to eliminate a common divisor of h. Now use the definition of the rotational constant,

$$\widetilde{B} = \frac{\hbar}{4\pi cI} \Rightarrow \widetilde{F}(J) \approx J(J+1)\widetilde{B} - J^2(J+1)^2 \widetilde{B}^3 \frac{16\pi^2 c^2 m_{\text{eff}}}{k_{\text{f}}}.$$

Finally, use the relationship between the force constant and vibrational wavenumber:

$$\left(\frac{k_{\text{f}}}{m_{\text{eff}}}\right)^{1/2} = \omega_{\text{vib}} = 2\pi\nu = 2\pi c\tilde{\nu} \quad \text{so} \quad \frac{m_{\text{eff}}}{k_{\text{f}}} = \frac{1}{4\pi^2 c^2 \tilde{\nu}^2}$$

leaving $\widetilde{F}(J) \approx \widetilde{B}J(J+1) - \frac{4\widetilde{B}^3}{\tilde{\nu}^2} J^2(J+1)^2 = \widetilde{B}J(J+1) - \widetilde{D}_J J^2(J+1)^2$ where $\boxed{\widetilde{D}_J = \frac{4\widetilde{B}^3}{\tilde{\nu}^2}}$.

12.4 Figure I12.1 is a plot of the total electronic energy (w/r/t the free atoms) profile for each of the hydrogen halides. Calculations are performed with Spartan '10 using the MP2 method with the 6-311++G** basis set. In a 6-311G basis set each atomic core basis function is expanded as a linear combination of six Gaussian functions. Valence orbitals are split into three basis set functions consisting of three, one, and one Gaussians. The 6-311++G basis set adds both an s-type and three p-type diffuse functions for each atom other than hydrogen and one s-type diffuse function for each hydrogen atom. The 6-311++G** basis set adds a set of five d-type polarization functions for each atom other than hydrogen and a set of three p-type polarization functions for each hydrogen atom.

The plot clearly shows that in going down the halogens from HI to HBr to HCl to HF the equilibrium bond length decreases and the depth of the potential well decreases. The equilibrium properties of each molecule are summarized in the following table. The calculated bond lengths and enthalpies of formation are in excellent agreement with experimental values. The dipole moments of HCl, HBr, and HI are surprisingly high.

Equilibrium Properties of Hydrogen Halides Calculated with Spartan '10 using MP2/6-311++G**				
	HF	HCl	HBr	HI
R_{e} / pm	91.7	127.3	141.3	161.2
R_{e}(exp) / pm	91.680	127.45	141.44	160.92
$\tilde{\nu}$ / cm^{-1}	4198.162	3086.560	2729.302	2412.609
E_{LUMO} / eV	1.16	1.09	1.14	1.50
E_{HOMO} / eV	–17.72	–12.99	–11.83	–10.54
$\Delta_{\text{f}}H^0$ / kJ mol^{-1}	–272.55	–92.31	–36.44	+26.36
$\Delta_{\text{f}}H^0$(exp) / kJ mol^{-1}	–271.1	–92.31	–36.40	+26.48
Dipole / D	1.97	1.38	1.10	0.79
Dipole(exp) / D	1.91	1.08	0.80	0.42

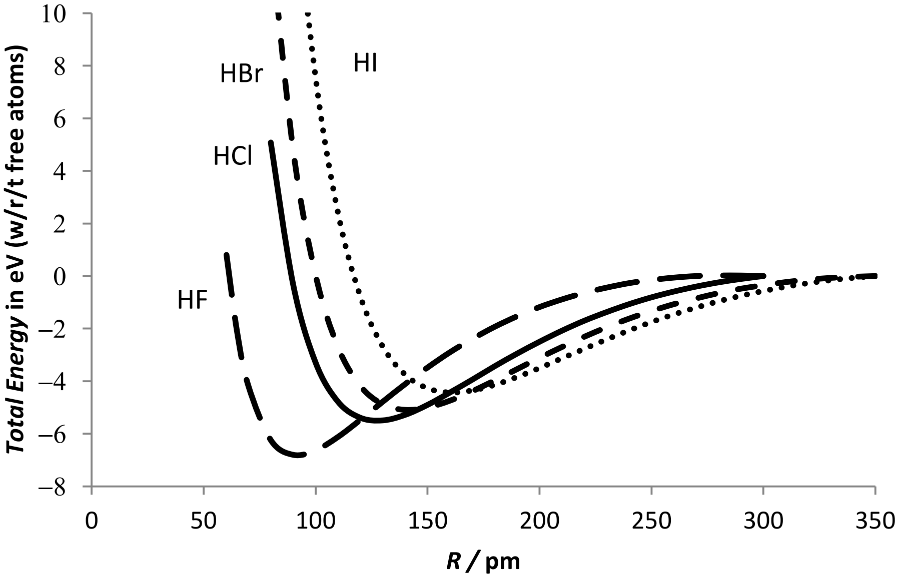


Figure I12.1

(b) The calculated fundamental vibrational wavenumbers, reported in the above table, increase in going down the halogens from HI to HBr to HCl to HF. Since the bonding force constant k_f is proportional to $\tilde{v}^2$ by eqn 43.8, k_f and the bond strength also increase in going down the halogens from HI to HBr to HCl to HF.

12.6 These calculations were performed with Spartan ’06 using the both MP2 and DFT(B3LYP) methods with both 6-31G* and 6-311G* basis sets (see problems F9.4 and F9.5 for an explanation of these basis sets).

(a) and **(b)** The following tables summarize the calculated equilibrium properties of H_2O and CO_2 and present experimental values for comparison.

H_2O Ground State					
	MP2/6-31G*	MP2/6-311G*	DFT/6-31G*	DFT/6-311G*	Exp.
Basis fns	19	24	19	24	
R / pm	96.9	95.7	96.8	96.3	95.8
E_0 / eV	–2073.4	–2074.5	–2074.6	–2079.9	
Angle / °	104.00	106.58	103.72	105.91	104.45
$\tilde{v}_1$ / cm^{-1}	3774.25	3858.00	3731.72	3764.70	3652
$\tilde{v}_2$ / cm^{-1}	1735.35	1739.88	1709.79	1705.47	1595
$\tilde{v}_3$ / cm^{-1}	3915.76	3994.30	3853.53	3877.60	3756
μ / D	n.s.	n.s.	2.0950	2.2621	1.854

CO_2 Ground State					
	MP2/6-31G*	MP2/6-311G*	DFT/6-31G*	DFT/6-311G*	Exp.
Basis fns	45	54	45	54	
R / pm	118.0	116.9	116.9	116.0	116.3
E_0 / eV	–5118.7	–5121.2	–5131.6	–5133.2	
Angle / °	180.00	180.00	180.00	180.00	180
$\tilde{v}_1$ / cm^{-1}	1332.82	1341.46	1373.05	1376.55	1388
$\tilde{v}_2$ / cm^{-1}	636.22	657.60	641.47	666.39	667
$\tilde{v}_3$ / cm^{-1}	2446.78	2456.16	2438.17	2437.85	2349
μ / D	n.s.	n.s.	0.0000	0.0000	0

(c) Except for the dipole moment, all calculations are typically within a reasonable 1-3% of the experimental value.

The dipole moment is very sensitive to the distribution of charge density. The significant difference between the dipole moment calculations and the experimental dipole moment may indicate that the computation methods do not adequately account for charge distribution in the very polar water molecule.

12.8 $\tilde{S}(\upsilon, J) = \left(\upsilon + \frac{1}{2}\right)\tilde{\nu} + \tilde{B}J(J+1)$ [12D.18]

$$\Delta\tilde{S}_J^{\mathrm{O}} = \tilde{\nu} - 2\tilde{B}(2J-1) \quad [\Delta\upsilon = 1, \Delta J = -2]$$

$$\Delta\tilde{S}_J^{\mathrm{S}} = \tilde{\nu} + 2\tilde{B}(2J+3) \quad [\Delta\upsilon = 1, \Delta J = +2]$$

The transition of maximum intensity corresponds, approximately, to the transition with the most probable value of J, which was calculated in Problem 12C.9.

$$J_{\max} = \left(\frac{kT}{2hc\tilde{B}}\right)^{1/2} - \frac{1}{2}$$

The peak-to-peak separation is then

$$\Delta\tilde{S} = \Delta\tilde{S}_{J_{\max}}^{\mathrm{S}} - \Delta\tilde{S}_{J_{\max}}^{\mathrm{O}} = 2\tilde{B}(2J_{\max}+3) - \{-2\tilde{B}(2J_{\max}-1)\} = 8\tilde{B}\left(J_{\max} + \tfrac{1}{2}\right)$$

$$= 8\tilde{B}\left(\frac{kT}{2hc\tilde{B}}\right)^{1/2} = \left(\frac{32\tilde{B}kT}{hc}\right)^{1/2}$$

To analyze the data we rearrange the relation to

$$\tilde{B} = \frac{hc(\Delta\tilde{S})^2}{32kT}$$

and convert to a bond length using $\tilde{B} = \frac{\hbar}{4\pi cI}$, with $I = 2m_{\mathrm{X}}R^2$ (Table 12B.1) for a linear rotor. This gives

$$R = \left(\frac{\hbar}{8\pi c m_{\mathrm{X}}\tilde{B}}\right)^{1/2} = \left(\frac{1}{\pi c\Delta\tilde{S}}\right) \times \left(\frac{2kT}{m_{\mathrm{X}}}\right)^{1/2}$$

We can now draw up the following table.

	$HgCl_2$	$HgBr_2$	HgI_2
T / K	555	565	565
m_{X} / u	35.45	79.1	126.90
$\Delta\tilde{S}$ / cm^{-1}	23.8	15.2	11.4
R / pm	227.6	240.7	253.4

Hence, the three bond lengths are approximately $\boxed{230,\ 240,\ \text{and}\ 250\,\text{pm}}$.

13 Electronic transitions

13A Electronic spectra

Answers to discussion questions

13A.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 (Fig. 13A.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 Franck–Condon factors. These 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 (Fig. 13A.7) of the two electronic potential energy curves. The most probable transitions are those to excited vibrational states with wavefunctions having a large amplitude at the internuclear position R_e.

13A.4 Color 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 color of the object will be that of the emitted radiation, and it may be an additive color resulting from the emission of more than one wavelength of radiation. When a substance absorbs radiation its color 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 color.

Solutions to exercises

13A.1(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 13C.11); each with two electrons. Although Hund's rule does not apply to excited states, we examine the state of maximum spin multiplicity. Thus, $S = ½ + ½ + ½ + ½ = 2$ 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 = $\boxed{\text{g}}$.

13A.2(b) The electronic spectrum selection rules concerned with changes in angular momentum are (eqn 13A.4): $\Delta\Lambda = 0, \ \pm 1 \quad \Delta S = 0 \quad \Delta\Sigma = 0 \quad \Delta\Omega = 0, \ \pm 1$ 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 +↔+ or –↔– (i.e., +↔– is forbidden). The **Laporte selection rule** states that for a centrosymmetric molecule (those with a center of inversion) the only allowed transitions are transitions that are accompanied by a change of parity: u↔g.

(i) 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 $\boxed{\text{allowed}}$.

(ii) 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 $\boxed{\text{allowed}}$.

(iii) The transition $\pi^* \leftrightarrow \text{n}$ is $\boxed{\text{forbidden}}$. For example, in a carbonyl group, where 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.

13A.3(b) We begin by evaluating the normalization constants N_0 and N_v.

$$N_0^2 = \frac{1}{\int_{-\infty}^{\infty} \mathrm{e}^{-2ax^2}\,\mathrm{d}x} = \left(\frac{2a}{\pi}\right)^{1/2} \text{ (standard integral);}\quad N_0 = \left(\frac{2a}{\pi}\right)^{1/4}$$

Likewise, $$N_\upsilon^2 = \frac{1}{\int_{-\infty}^{\infty} x^2\mathrm{e}^{-2b(x-x_0)^2}\,\mathrm{d}x} = \frac{(2b)^{3/2}}{\Gamma(3/2)} = \frac{(2b)^{3/2}}{\pi^{1/2}/2};\quad N_\upsilon = \left(\frac{2(2b)^{3/2}}{\pi^{1/2}}\right)^{1/2}$$

Furthermore, we can easily check that

$$ax^2 + b(x-x_0)^2 = z^2 + \frac{ab}{a+b}x_0^2 \quad\text{where}\quad z = (a+b)^{1/2}x - \frac{b}{(a+b)^{1/2}}x_0 \quad\text{and}\quad \mathrm{d}x = \frac{1}{(a+b)^{1/2}}\mathrm{d}z$$

Then, the vibration overlap integral between the vibrational wavefunction in the upper and lower electronic states is:

$$\begin{aligned}
S(\upsilon,0) &= \langle \upsilon\,|\,0\rangle = N_0 N_\upsilon \int_{-\infty}^{\infty} x\mathrm{e}^{-ax^2}\,\mathrm{e}^{-b(x-x_0)^2}\,\mathrm{d}x = N_0 N_\upsilon \int_{-\infty}^{\infty} x\mathrm{e}^{-\left\{ax^2+b(x-x_0)^2\right\}}\mathrm{d}x \\
&= \frac{N_0 N_\upsilon}{a+b}\int_{-\infty}^{\infty}\left\{\frac{bx_0}{(a+b)^{1/2}} + z\right\}\mathrm{e}^{-\left\{z^2+\frac{ab}{a+b}x_0^2\right\}}\mathrm{d}z \\
&= \frac{N_0 N_\upsilon \mathrm{e}^{-\frac{ab}{a+b}x_0^2}}{a+b}\left\{\frac{bx_0}{(a+b)^{1/2}}\int_{-\infty}^{\infty}\mathrm{e}^{-z^2}\mathrm{d}z + \int_{-\infty}^{\infty} z\mathrm{e}^{-z^2}\mathrm{d}z\right\} \\
&= \frac{N_0 N_\upsilon \mathrm{e}^{-\frac{ab}{a+b}x_0^2}}{a+b}\left\{bx_0\left(\frac{\pi}{a+b}\right)^{1/2} + \int_{-\infty}^{\infty} z\mathrm{e}^{-z^2}\mathrm{d}z\right\}
\end{aligned}$$

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, u × g = u and the integral over the complete *z* axis of an ungerade function equals zero.

$$\begin{aligned}
S(\upsilon,0) &= \frac{N_0 N_\upsilon b x_0 \mathrm{e}^{-\frac{ab}{a+b}x_0^2}}{a+b}\left(\frac{\pi}{a+b}\right)^{1/2} = \left(\frac{2a}{\pi}\right)^{1/4}\left(\frac{2(2b)^{3/2}}{\pi^{1/2}}\right)^{1/2}\frac{bx_0\mathrm{e}^{-\frac{ab}{a+b}x_0^2}}{a+b}\left(\frac{\pi}{a+b}\right)^{1/2} \\
&= \left(\frac{2}{a+b}\right)^{3/2} a^{1/4} b^{7/4} x_0 \mathrm{e}^{-\frac{ab}{a+b}x_0^2}
\end{aligned}$$

For the case *b* = *a*/2, this simplifies to

$$S(\upsilon,0) = \left(\frac{4}{3a}\right)^{3/2} a^{1/4}\left(\frac{a}{2}\right)^{7/4} x_0 \mathrm{e}^{-ax_0^2/3} = \left(\frac{32}{729}\right)^{1/4} a^{1/2} x_0 \mathrm{e}^{-ax_0^2/3}$$

The Franck-Condon factor is

$$|S(\upsilon,0)|^2 = \boxed{\left(\frac{32}{729}\right)^{1/2} a x_0^2 \mathrm{e}^{-2ax_0^2/3}}$$

13A.4(b) $\psi_0 = \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{\pi x}{L}\right)$ for $0 \le x \le L$ and 0 elsewhere.

$$\psi_v = \left(\frac{2}{L}\right)^{1/2}\sin\left\{\frac{\pi}{L}\left(x - \frac{L}{2}\right)\right\} \quad\text{for } \frac{L}{2} \le x \le \frac{3L}{2} \text{ and 0 elsewhere.}$$

$$S(v,0) = \langle v\,|\,0\rangle = \frac{2}{L}\int_{L/2}^{L}\sin\left(\frac{\pi x}{L}\right)\sin\left\{\frac{\pi}{L}\left(x - \frac{L}{2}\right)\right\}\mathrm{d}x$$

The above integral is recognized as the standard integral (see math handbook):

$\int \sin(ax)\sin(ax+b)\,\mathrm{d}x = \frac{x}{2}\cos(b) - \frac{\sin(2ax+b)}{4a}$ with the transformations $a = \pi/L$ and $b = -\pi/2$. Thus,

$$S(v,0) = \frac{2}{L}\left[\frac{x}{2}\cos\left(-\frac{\pi}{2}\right) - \frac{\sin(2\pi x/L - \pi/2)}{4\pi/L}\right]_{x=L/2}^{x=L} = \frac{2}{L}\left[-\frac{\sin(2\pi x/L - \pi/2)}{4\pi/L}\right]_{x=L/2}^{x=L}$$

$$= -\frac{1}{2\pi}\left[\sin(3\pi/2) - \sin(\pi/2)\right]$$

$$= \frac{1}{\pi}$$

The Franck-Condon factor is

$$|S(v,0)|^2 = \boxed{\frac{1}{\pi^2}}$$

13A.5(b) R branch $(\Delta J = +1)$: $\tilde{\nu}_{\mathrm{R}}(J) = \tilde{\nu} + (\tilde{B}' + \tilde{B})(J+1) + (\tilde{B}' - \tilde{B})(J+1)^2$ [13A.8c]

When the bond is longer in the excited state than in the ground state, $\tilde{B}' < \tilde{B}$ and $\tilde{B}' - \tilde{B}$ is negative. In this case, the lines of the R branch appear at successively increasing energies as *J* increases, begin to converge, go through a head at J_{head}, begin to decrease with increasing *J*, and become smaller than $\tilde{\nu}$ when $(J+1) > (\tilde{B}' + \tilde{B})/|(\tilde{B}' - \tilde{B})|$ (see Section 13A.1(d) and Discussion question 13A.3; the quadratic shape of the $\tilde{\nu}_{\mathrm{P}}$ against *J* curve is called the Fortrat parabola). This means that $\tilde{\nu}_{\mathrm{R}}(J)$ is a maximum when $J = J_{\text{head}}$. It is reasonable to deduce that J_{head} is the closest integer to $\boxed{\tfrac{1}{2}(\tilde{B}' + \tilde{B})/|(\tilde{B}' - \tilde{B})| - 1}$ because it takes twice as many *J* values to reach the maximum line of the R branch and to return to $\tilde{\nu}$. We can also find J_{head} by finding the maximum of the Fortrat parabola: $\mathrm{d}\tilde{\nu}_{\mathrm{R}}/\mathrm{d}J = 0$ when $J = J_{\text{head}}$.

$$\frac{\mathrm{d}\tilde{\nu}_{\mathrm{R}}}{\mathrm{d}J} = \frac{\mathrm{d}}{\mathrm{d}J}\left\{\tilde{\nu} + (\tilde{B}' + \tilde{B})(J+1) - |(\tilde{B}' - \tilde{B})|(J+1)^2\right\} = +(\tilde{B}' + \tilde{B}) - 2|(\tilde{B}' - \tilde{B})|(J+1)$$

$$(\tilde{B}' + \tilde{B}) - 2|(\tilde{B}' - \tilde{B})|(J_{\text{head}} + 1) = 0$$

$$J_{\text{head}} = \frac{(\tilde{B}' + \tilde{B})}{2|(\tilde{B}' - \tilde{B})|} - 1$$

13A.6(b) Since $\tilde{B}' > \tilde{B}$ and $\tilde{B}' - \tilde{B}$ is positive, the P branch shows a head at the closest integer to the value of $\boxed{\tfrac{1}{2}(\tilde{B}' + \tilde{B})/(\tilde{B}' - \tilde{B})}$ (see Exercise 13A.5(a)).

$$\frac{(\tilde{B}' + \tilde{B})}{2(\tilde{B}' - \tilde{B})} = \frac{(10.470 + 10.308)}{2(10.470 - 10.308)} = 64.2$$

$$J_{\text{head}} = \boxed{64}$$

13A.7(b) When the P branch has a head, J_{head} is the closest integer to $\boxed{\tfrac{1}{2}(\tilde{B}' + \tilde{B})/(\tilde{B}' - \tilde{B})}$ (see Exercise 13A.5(a)).

Thus, if we are only given that $J_{\text{head}} = 25$ and $\tilde{B} = 5.437\ \mathrm{cm}^{-1}$, 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 $\tfrac{1}{2}(\tilde{B}' + \tilde{B})/(\tilde{B}' - \tilde{B})$ calculation must be rounded-off to give the integer value J_{head}. Algebraic manipulation of the inequality yields

$$\frac{\{2(24.5)+1\}\tilde{B}}{\{2(24.5)-1\}} > \tilde{B}' > \frac{\{2(25.5)+1\}\tilde{B}}{\{2(25.5)-1\}}$$

$$1.042\tilde{B} > \tilde{B}' > 1.040\tilde{B}$$

$$\boxed{5.665\ \text{cm}^{-1} > \tilde{B}' > 5.654\ \text{cm}^{-1}}$$

When $\tilde{B}' > \tilde{B}$, the bond length in the electronically excited state is $\boxed{\text{shorter}}$ than that in the ground state.

Below 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. 13A.8(a) 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. 13A.8(a) into this inequality yields the relationship $\tilde{B}' < J_{\text{head}}\tilde{B}/(J_{\text{head}}-1)$. Consequently, $(J_{\text{head}}+1)\tilde{B}/J_{\text{head}} < \tilde{B}' < J_{\text{head}}\tilde{B}/(J_{\text{head}}-1)$.

13A.8(b) The transition wavenumber is $\tilde{\nu} = \dfrac{1}{\lambda} = \dfrac{1}{305\ \text{nm}} = 32.8\times10^{3}\ \text{cm}^{-1}$.

The cyano ligand (CN^-) is a strong ligand field splitter, so we expect the d^5 electrons of Fe^{3+} to have the $\text{t}_{2\text{g}}^5$ 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 $\text{t}_{2\text{g}}$ 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 $P < \Delta_{\text{O}}$ where P is the energy of repulsion for pairing two electrons in an orbital.

Hypothesis 1. A d–d transition to the $\text{t}_{2\text{g}}^4\text{e}_{\text{g}}^1$ octahedral excited state with $S = 1/2$ 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 $\text{t}_{2\text{g}}$ orbital that has paired electrons in the ground state. Thus, $\tilde{\nu} = \Delta_{\text{O}} - P$ and $\Delta_{\text{O}} = \tilde{\nu} + P$. Using the typical value $P \sim 28 \times 10^3\ \text{cm}^{-1}$ yields the estimate $\Delta_{\text{O}} \sim 63 \times 10^3\ \text{cm}^{-1}$. See F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., (New York: Wiley-Interscience Publishers, 1980), p. 646, 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 $\text{t}_{2\text{g}}$ orbitals of Fe^{3+} to produce complex-wide MOs that drastically reduce the electron pairing energy. Assuming that CN^- has a ground electronic configuration that is similar to that of N_2, $1\sigma^2 2\sigma^{*2} 1\pi^4 2\sigma^2 1\pi^{*0}$ (see text Fig. 10C.12), we see that the cyanide ligand has an antibonding $1\pi^*$ MO LUMO that has the correct symmetry to form a π bond with an Fe^{3+} $\text{t}_{2\text{g}}$ orbital. This possibility is depicted in Fig. 13A.1 with the LUMO polarized toward the carbon as expected for an antibonding MO. Fig. 13A.2 depicts a reasonable energy level diagram for the Fe^{3+}–CN^- π bond.

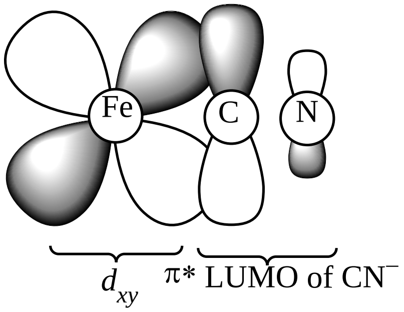


Figure 13A.1

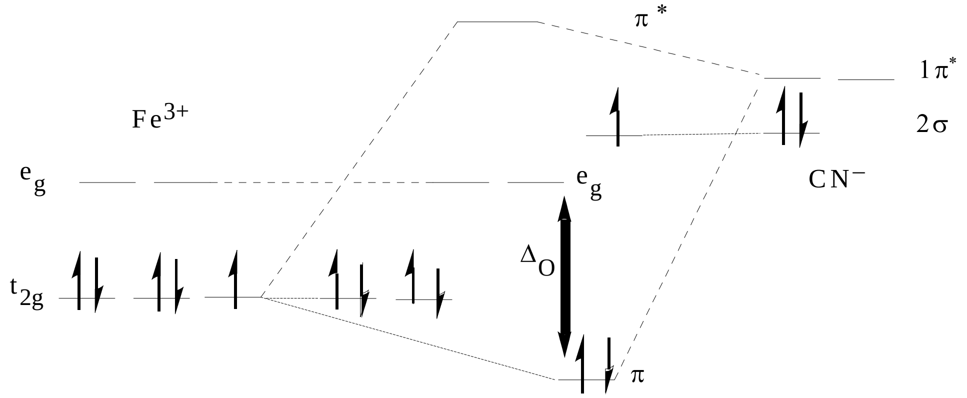


Figure 13A.2

Since the Fe^{3+}–CN^{-} π bond electron pair are more disperse than either a t_{2g} electron or a 2σ ligand electron, it now seems reasonable to assume that the electron pairing energy is small enough to ignore yielding the estimate $\boxed{\Delta_O \sim 33 \times 10^3\ \text{cm}^{-1}}$. This value seems acceptable.

13A.9(b) The normalized wavefunctions are:

$$\psi_i = \left(\frac{1}{a}\right)^{1/2} \quad \text{for } 0 \le x \le a \text{ and 0 elsewhere.}$$

$$\psi_f = \left(\frac{1}{a-ca}\right)^{1/2} \quad \text{for } ca \le x \le a \text{ and 0 elsewhere; } 0 \le c < 1$$

$$\int \psi_f x \psi_i \,\mathrm{d}x = \left(\frac{1}{a}\right)^{1/2}\left(\frac{1}{a(1-c)}\right)^{1/2}\int_{ca}^{a} x\,\mathrm{d}x = \left(\frac{1}{a}\right)^{1/2}\left(\frac{1}{a(1-c)}\right)^{1/2}\left.\frac{x^2}{2}\right|_{x=ca}^{x=a}$$

$$= \left(\frac{1}{a}\right)^{1/2}\left(\frac{1}{a(1-c)}\right)^{1/2}\left\{\frac{a^2}{2}\left(1-c^2\right)\right\} = \boxed{\frac{a}{2}\frac{\left(1-c^2\right)}{\left(1-c\right)^{1/2}}}$$

Thus, the dipole transition integral is a concave-down function of c with a maximum at $c = 1/3$.

13A.10(b) The normalized wavefunctions are:

$$\psi_i = \left(\frac{1}{a\sqrt{\pi}}\right)^{1/2} \mathrm{e}^{-x^2/2a^2} \quad \text{for } -\infty \le x \le \infty \text{ and width } a.$$

$$\psi_f = \left(\frac{2}{a\sqrt{\pi}}\right)^{1/2} \mathrm{e}^{-2x^2/a^2} \quad \text{for } -\infty \le x \le \infty \text{ and width } a/2.$$

$$\int \psi_f x \psi_i \,\mathrm{d}x = \left(\frac{2^{1/2}}{a\sqrt{\pi}}\right)\int_{-\infty}^{\infty} x\,\mathrm{e}^{-x^2/2a^2}\,\mathrm{e}^{-2x^2/a^2}\,\mathrm{d}x = \left(\frac{2^{1/2}}{a\sqrt{\pi}}\right)\int_{-\infty}^{\infty} x\,\mathrm{e}^{-5x^2/2a^2}\,\mathrm{d}x$$

The factors within the integral have ungerade and gerade symmetry. Because u × g = u, the integrand has ungerade symmetry and the dipole transition integral is necessarily $\boxed{\text{zero}}$ (the integral of an ungerade function over a symmetric interval equals zero).

13A.11(b) The weak absorption at 320 nm is typical of a carbonyl chromophore of an enol. The assignment is π*←n where a non-bonding electron comes from one of the two lone pair of the oxygen valence. The two lone pair 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, thereby, producing a low value for the dipole transition integral and a low molar absorption coefficient.

The strong absorption at 213 nm has the π*←π assignment. The conjugation of the π bonds of the ethenic chromophore and the carbonyl chromophore causes this transition to be shifted to lower energies w/r/t both the π*←π transition of ethene (165 nm) and the π*←π 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 Fig. 10E.2 and the simple MO energy diagram for C=C─C=O in Fig. 13A.3 below. The figure demonstrates a broad principle: the difference between neighboring energy levels becomes smaller as the number of adjacent, overlapping orbitals becomes larger.

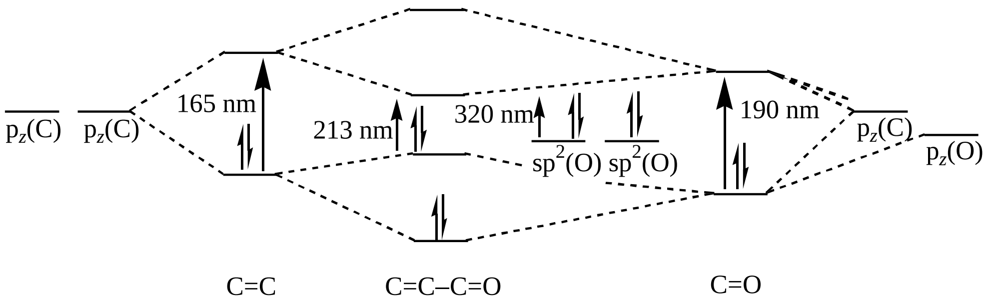


Figure 13A.3

Problems

13A.2 The potential energy curves for the $X\,^3\Sigma_g^-$ and $B\,^3\Sigma_u^-$ electronic states of O_2 are represented schematically in Fig. 13A.4 along with the notation used to represent the energy separation of this problem. Curves for the other electronic states of O_2 are not shown. Ignoring rotational structure and anharmonicity we may write

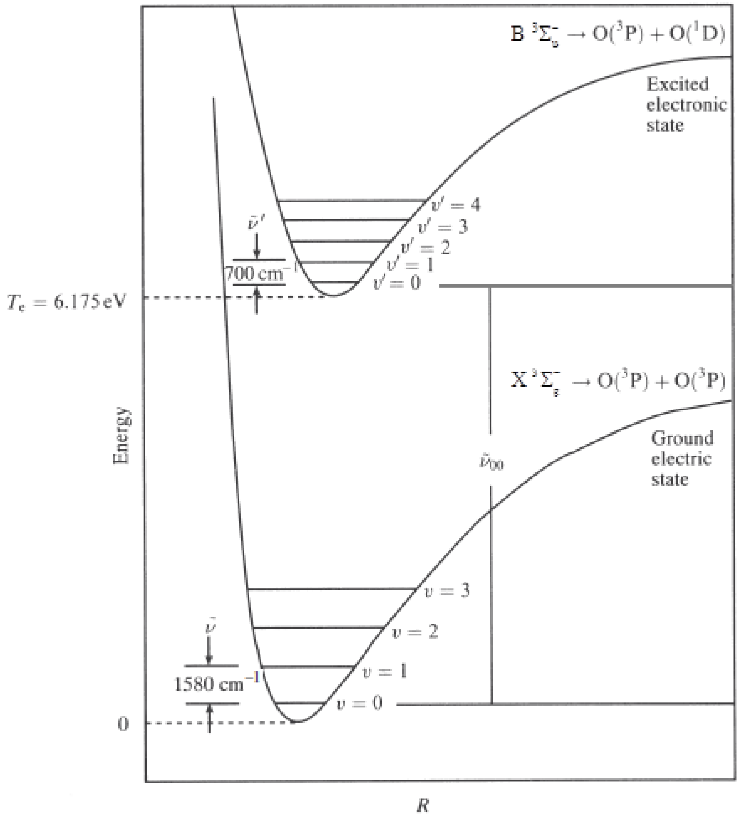
$$\tilde{\nu}_{00} \approx T_e + \tfrac{1}{2}(\tilde{\nu}' - \tilde{\nu}) = 6.175\ \text{eV} \times \left(\frac{8065.5\ \text{cm}^{-1}}{1\ \text{eV}}\right) + \tfrac{1}{2}(700 - 1580)\ \text{cm}^{-1}$$

$$\approx \boxed{49\,36\bar{4}\ \text{cm}^{-1}}$$

Comment: Note that the selection rule Δ*v* = ±1 does not apply to vibrational transitions between different electronic states.

Question**:** What is the percentage change in $\tilde{\nu}_{00}$ if the anharmonicity constants $x_e\tilde{\nu}$, $12.0730\ \text{cm}^{-1}$ and $8.002\ \text{cm}^{-1}$ for the ground and excited states, respectively, are included in the analysis?

Figure 13A.4



13A.4 The ionization is $HBr \rightarrow HBr^+ + e^-$ with the accompanying electronic energy change given by the equation $h\nu = \tfrac{1}{2} m_e v^2 + I_i + \Delta E_{\upsilon'\leftarrow\upsilon=0}$. This modified form of eqn 10C.6 accounts for the possibility of an excitation change in the vibrational energy in going from the ground electronic vibrational state $v = 0$, in which a majority of molecules start, to the ionized electronic vibrational state $v' = 0,1,2...$ The vibrational transition $v'=0 \leftarrow v=0$ is called an **adiabatic transition**. Fig. 13A.5 shows the potential energy relationships between the ground electronic state and two possible ionized electronic states.

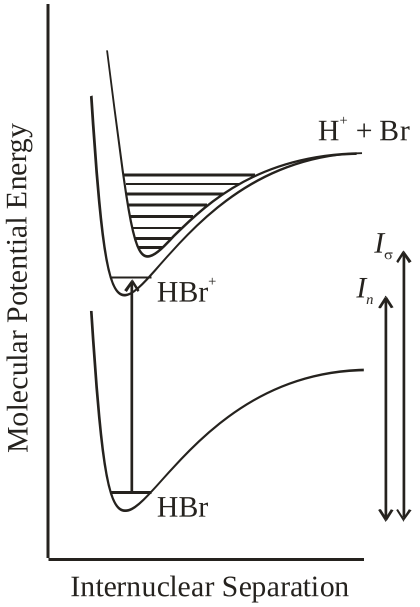


Figure 13A.5

(a) The photoelectron spectrum band between 15.2 eV and 16.2 eV is the ejection of a bonding σ electron of HBr (see text Fig. 13.1). Loss of this electron reduces the bond order from 1 to ½, reduces the magnitude of the bond force constant, and lengthens the equilibrium bond length of the ionized molecule. The electronic transition is labeled as I_σ in Fig. 13A.5. The longer bond length of the ionized state cause the Franck-Condon factor for the adiabatic transition ($v'=0 \leftarrow v=0$) to be small. This is the lowest energy transition of the band at about 15.3 eV. The increasing spectral intensity for the $v'=1 \leftarrow v=0$ and $v'=2 \leftarrow v=0$ transitions indicates that these vertical transitions have successively larger Franck-Condon factors. The separation of lines (~0.162 eV) corresponds to an ionized vibrational wavenumber of about 1300 cm^{-1}, which is considerably lower than the 2648.98 cm^{-1} of the neutral ground state. The presence of one unpaired electron in the bonding σ orbital means that the ionized molecule is in a $^2\Sigma^+$ state.

(b) The lines between 11.6 eV and 12.3 eV involve transitions of a non-bonding electron of the chlorine p valence subshell to two very closely spaced electronic states of the ionized molecule. The ionization energy of these states is labeled as I_n in Figure 13A.5. The unpaired electron of the ionized state makes it a doublet with spin-orbit coupling producing $j = |l+s|,...,|l-s| = |1 + ½|, |1 - ½| = {}^3/_2, {}^1/_2$. Consequently, the term symbols of these states are $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ and Hund's rule predicts that $^2\Pi_{3/2}$ is lowest in energy because the subshell is more than half-filled. Excitation of a non-bonding electron does not affect the molecular bond, nor does it affect the bonding force constant or the equilibrium bond length. Only the vertical, adiabatic transition ($v'=0 \leftarrow v=0$) has an appreciable Franck-Condon factor. The transition $v'=1 \leftarrow v=0$ of the $^2\Pi_{3/2}$ transition has a very small vertical, vibrational overlap integral; it cannot be seen in the spectrum because it lies below the $^2\Pi_{1/2}$ adiabatic transition at 12.0 ev. The transition $v'=1 \leftarrow v=0$ of the $^2\Pi_{1/2}$ transition has a very small vertical, vibrational overlap integral and it is located at 12.3 eV. The 0.3 eV line separation corresponds to an ionized vibrational wavenumber of about 2400 cm^{-1}. This is consistent with the vibrational wavenumber of the ground state (2648.98 cm^{-1}) and confirms the expectation that excitation of a non-bonding electron does not affect the σ bond.

13A.6 The spectrum gives the peak and half-height points:

$$\varepsilon_{\text{peak}} = 250 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1},\ \lambda_{\text{peak}} = 284 \text{ nm} \left(\tilde{v} = 35200 \text{ cm}^{-1}\right)$$

$$\varepsilon_{1/2} = 125 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1},\ \lambda_{1/2} = 305 \text{ nm} \left(\tilde{v} = 32800 \text{ cm}^{-1}\right) \text{ and } \lambda_{1/2} = 265 \text{ nm} \left(\tilde{v} = 37700 \text{ cm}^{-1}\right)$$

We estimate that the wavenumber band has a normal Gaussian shape:

$$\varepsilon = \varepsilon_{\text{max}} \mathrm{e}^{-\left(\tilde{\nu}-\tilde{\nu}_{\text{peak}}\right)^2/a^2} \quad \text{where } a \text{ is a constant related to the half-width } \Delta\tilde{\nu}_{1/2} = \left(37700-32800\right)\ \text{cm}^{-1} = 4900\ \text{cm}^{-1}$$

$$\mathcal{A} = \int_{\text{band}} \varepsilon\left(\tilde{\nu}\right)\ \mathrm{d}\tilde{\nu} \quad [12\,\text{A}.15] = \varepsilon_{\text{max}} \int_{-\infty}^{\infty} \mathrm{e}^{-\left(\tilde{\nu}-\tilde{\nu}_{\text{peak}}\right)^2/a^2}\ \mathrm{d}\tilde{\nu}$$

$$= \varepsilon_{\text{max}} a\sqrt{\pi} \quad \text{(standard integral)}$$

The relationship between the half-width and a is found by evaluation of the line shape at $\varepsilon(\tilde{\nu}_{1/2}) = \varepsilon_{\text{max}}/2$.

$$\varepsilon_{\text{max}}/2 = \varepsilon_{\text{max}} \mathrm{e}^{-\left(\tilde{\nu}_{1/2}-\tilde{\nu}_{\text{peak}}\right)^2/a^2}$$

$$\ln(1/2) = -\left(\tilde{\nu}_{1/2} - \tilde{\nu}_{\text{peak}}\right)^2/a^2$$

$$a^2 = \frac{\left(\tilde{\nu}_{1/2} - \tilde{\nu}_{\text{peak}}\right)^2}{\ln(2)} = \frac{\left(\Delta\tilde{\nu}_{1/2}/2\right)^2}{\ln(2)}$$

$$a = \frac{\Delta\tilde{\nu}_{1/2}}{2\sqrt{\ln 2}}$$

Thus,

$$\mathcal{A} = \boxed{\tfrac{1}{2}\Delta\tilde{\nu}_{1/2}\varepsilon_{\text{max}}\sqrt{\pi/\ln(2)}} = 1.0645\,\Delta\tilde{\nu}_{1/2}\varepsilon_{\text{max}}$$

$$\mathcal{A} = \tfrac{1}{2}\left(4900\ \text{cm}^{-1}\right)\times\left(250\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}\right)\sqrt{\pi/\ln(2)} = \boxed{1.3\bar{0}\times10^6\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-2}}$$

Since the dipole moment components transform as $\text{A}_1(z)$, $\text{B}_1(x)$, and $\text{B}_2(y)$, excitations from A_1 to A_1, B_1, and B_2 terms are allowed.

13A.8 Modeling the π electrons of 1,3,5-hexatriene as free electrons in a linear box yields non-degenerate energy levels of

$$E_n = \frac{n^2h^2}{8m_\text{e}L^2} \quad [8\text{A}.7\text{b}]$$

The molecule has six π electrons, so the lowest energy transition is from $n = 3$ to $n = 4$. The length of the box is 5 times the $\text{C}-\text{C}$ bond distance R. So

$$\Delta E_{\text{linear}} = \frac{(4^2-3^3)h^2}{8m_\text{e}(5R)^2}$$

Modeling the π electrons of benzene as free electrons on a ring of radius R yields energy levels of

$$E_{m_l} = \frac{m_l^2\hbar^2}{2I} \quad [8\text{C}.5] \quad \text{where the moment of inertion is } I = m_\text{e}R^2$$

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 $m_l = 2$

$$\Delta E_{\text{ring}} = \frac{(2^2-1^2)\hbar^2}{2m_\text{e}R^2} = \frac{(2^2-1^2)h^2}{8\pi^2m_\text{e}R^2}$$

Comparing the two shows

$$\Delta E_{\text{linear}} = \frac{7}{25}\left(\frac{h^2}{8m_\text{e}R^2}\right) < \Delta E_{\text{ring}} = \frac{3}{\pi^2}\left(\frac{h^2}{8m_\text{e}R^2}\right)$$

Therefore, the lowest-energy absorption will $\boxed{\text{rise}}$ in energy when the molecule is converted from a linear to a ring structure.

13A.10 Tryptophan (Trp) and tyrosine (Tyr) show the characteristic absorption of a phenyl group at about 280 nm. Cysteine (Cys) and glycine (Gly) lack the phenyl group as is evident from their spectra.

13B Decay of excited states

Answers to discussion questions

13B.2 The characteristics of fluorescence which are consistent with the accepted mechanism are: (1) it ceases as soon as the source of illumination is removed; (2) the time scale of fluorescence, ~10^{-9} s, is typical of a process in which the rate determining step is a spontaneous radiative transition between states of the same multiplicity; slower than a stimulated transition, but faster than phosphorescence; (3) it occurs at longer wavelength (lower frequency) than the inducing radiation; (4) its vibrational structure is characteristic of that of a transition from the ground vibrational level of the excited electronic state to the vibrational levels of the ground electronic state; and (5) the observed shifting and in some instances quenching of the fluorescence spectrum by interactions with the solvent.

Solutions to exercises

13B.1(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.

13B.2(b) When the steeply repulsive section of the H_2 potential energy curve for the excited state lies slightly toward the short side of the equilibrium bond length and the minimum of the excited state lies to the longer side (as shown in text Fig. 13B.7), a great many excited vibrational states overlap with the lowest energy vibration of the ground state thereby making the **Franck-Condon factor** appreciable for many vertical transitions (see text Fig. 13A.7). This, combined with continuous absorption above the dissociation limit, yields a relatively broad absorption band. Furthermore, predissociation to the unbound ${}^1\Sigma_u^+$ state shortens the lifetime of excited vibrational states. This causes the high resolution lines of rotational transitions to be broad through the Heisenberg uncertainty principle $\Delta E \Delta t \geq \hbar / 2$.

13C Lasers

Answers to discussion questions

13C.2 Strong and short radiation pulses from a *Q*-switched or mode-locked laser can be used to study ultrafast chemical reactions by promoting a molecule A to an excited state A*, which may either emit a photon or react with another molecule B to form an intermediate species AB. AB may even be an activated complex. A second pulse of radiation that is synchronized to pass through the sample at a specific time after the excitation pulse is used to monitor the appearance and disappearance of the various species. Reaction progress and rates on the nanosecond-to-picosecond scale can be examined by varying the time delay between the excitation pulse and the monitor pulse.

Text 13C.10 is a schematic of a time-resolved absorption spectrometer. A beamsplitter directs a portion of the excitation beam to a continuum generator, which converts the monochromatic laser pulse to a wide-frequency pulse suitable for monitoring reaction species. The time delay is selected by changing the position of the motorized stage in the directions shown by the double arrow. The monitor pulse is directed through the sample to the monochromator along a path, which avoids coincidence with the intense excitation pulse, to the monchromator and detector.

Solutions to exercises

13C.1(b) Only an integral number of half-wavelengths fit into the cavity. These are the **resonant modes**.

$\lambda = 2L / n$ [13C.1] 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 3.0 m cavity are $\boxed{\lambda = 6.0\ \text{m}\ (\nu = 50.0\ \text{MHz})}$.

13C.2(b) Referring to Example 13C.1, we have

$$P_{\text{peak}} = E_{\text{pulse}}/t_{\text{pulse}} \quad \text{and} \quad P_{\text{average}} = E_{\text{total}}/t = E_{\text{pulse}} \times \nu_{\text{repetition}}$$

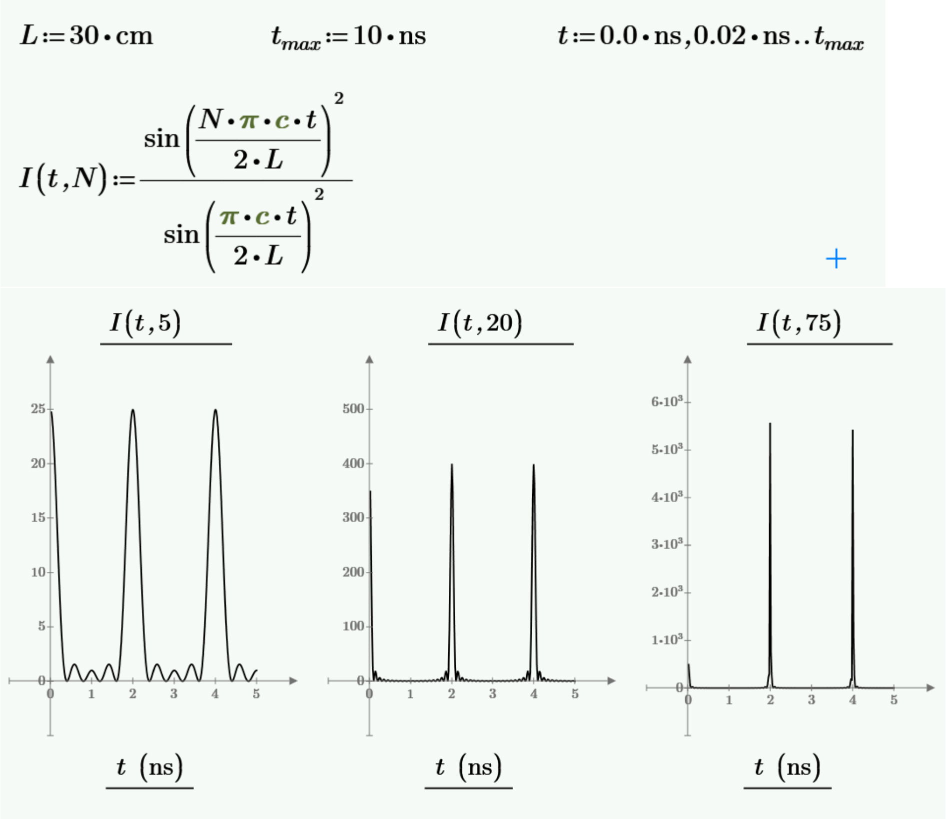
where $\nu_{\text{repetition}}$ is the pulse repetition rate.

$$t_{\text{pulse}} = E_{\text{pulse}}/P_{\text{peak}} = \frac{20\ \mu\text{J}}{100\ \text{kW}} = \boxed{200\ \text{ps}}$$

$$\nu_{\text{repetition}} = P_{\text{average}}/E_{\text{pulse}} = \frac{0.40\ \text{mW}}{20.0\ \mu\text{J}} = \boxed{20\ \text{Hz}}$$

Solutions to problems

13C.2 This Mathcad Prime 2 worksheet simulates the output of a mode-locked laser. The radiation intensity is analyzed in text Justification 13C.1 and we take the constant of proportionality to equal 1 (see eqn 13C.3). The worksheet plots for N = 5, 20, and 75 demonstrate that the superposition of many modes creates very narrow spikes separated by $t = 2L/c$ = 2 nm.



$L := 30 \cdot \text{cm} \qquad t_{max} := 10 \cdot \text{ns} \qquad t := 0.0 \cdot \text{ns}, 0.02 \cdot \text{ns} .. t_{max}$

$$I(t,N) := \frac{\sin\left(\frac{N \cdot \pi \cdot c \cdot t}{2 \cdot L}\right)^2}{\sin\left(\frac{\pi \cdot c \cdot t}{2 \cdot L}\right)^2}$$

Integrated activities

13.2 (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 $\boxed{\text{forbidden}}$.

13.4 E_{HOMO} calculations, performed with Spartan '10 using the DFT/B3LYP/6-31G* method, are reported in the following table along with the energy of experimentally determined I_2–aromatic hydrocarbon charge transfer bands. Figure 13.1 is a plot of the charge transfer energy against E_{HOMO} along with the linear regression fit.

Hydrocarbon	$h\nu_{\text{max}}$(exp) / eV	E_{HOMO} / eV
Benzene	4.184	−6.70
Biphenyl	3.654	−5.91
Naphthalene	3.452	−5.78
Phenanthrene	3.288	−5.73
Pyrene	2.989	−5.33
Anthracene	2.890	−5.23

The plot shows a clear correlation between the energy of charge transfer and the HOMO of hydrocarbon electron donor: as E_{HOMO} increases, the energy of charge transfer decreases. The correlation appears to be linear and the correlation coefficient ($R = 0.988$) indicates that about 98.8% of the variation is explained by the linear correlation. This supports the hypothesis that for π-donor hydrocarbons $h\nu_{\text{max}} = E_{\text{LUMO}}(I_2) - E_{\text{HOMO}}(\pi)$.

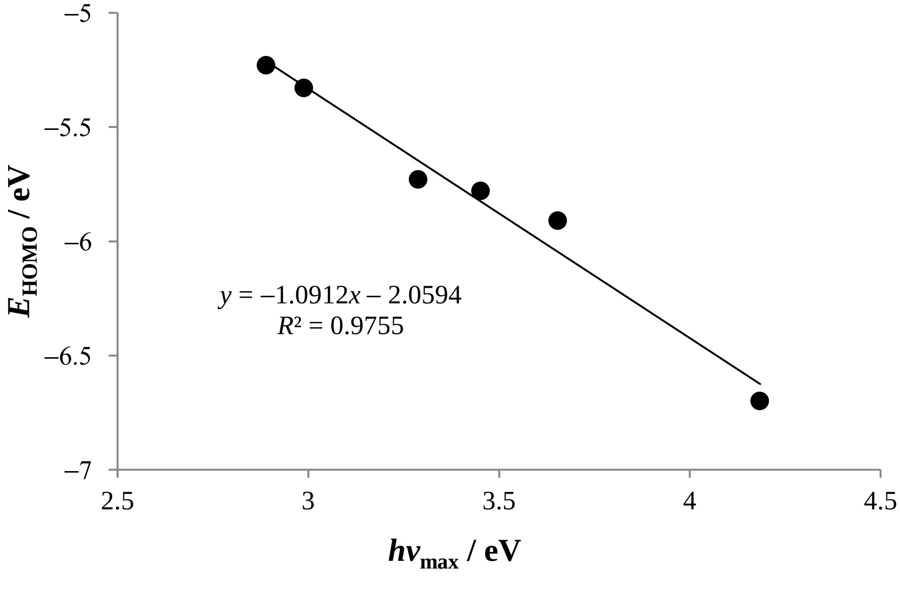


Figure 13.1

14 Magnetic Resonance

14A General principles

Answers to discussion questions

D14A.2 The magnetogyric ratio of the electron is much larger in magnitude than the magnetogyric ratios of nuclei; therefore, the magnetic moment of the electron is much larger than the magnetic moments of nuclei. Compare the Bohr magneton to the nuclear magneton. Hence the energy of interaction of an electron with a magnetic field is much greater than the energies of interaction of nuclei with a magnetic field, on the order of magnitude by a factor of 1000.

Solutions to exercises

E14A.1(b) Since $\mu_{\mathrm{N}} = e\hbar/2m_{\mathrm{p}} = 5.051\times10^{-27}\ \mathrm{J\,T^{-1}}$ and knowing the SI base units of $e,\ \hbar,$ and m_{p}, we can solve for the units of T in terms of the base units of the SI system. In terms of units, the above equation for μ_{N} can be written

(A s J s)/kg = (J T^{-1}). Or T = kg s^{-2} A^{-1}. In the solution to E47.1(a) it is shown that $\gamma_{\mathrm{N}} = \mathrm{s^{-1}T^{-1}}$; therefore, $\gamma_{\mathrm{N}} = \boxed{\mathrm{A\ s\ kg^{-1}}}$

E14A.2(b) The magnitude of the angular momentum is given by $\{I(I+1)\}^{1/2}\hbar$. For a $^{14}\mathrm{N}$ nucleus I = 1, hence

Magnitude = $\sqrt{2}\hbar = \boxed{1.491\times10^{-34}\ \mathrm{J\ s}}$. The components along the z – axis are

$0,\ \pm\hbar = \boxed{0,\ \pm1.055\times10^{-34}\ \mathrm{J\ s}}$. The angles that the projections of the angular momentum make with the z-axis are

$$\theta = 0,\ \pm\cos^{-1}\frac{\hbar}{\sqrt{2}\hbar} = \boxed{0,\ \pm0.7854\ \mathrm{rad} = 0^{\circ},\ \pm45^{\circ}}$$

E14A.3(b) For $^{19}\mathrm{F}$, $\dfrac{\mu}{\mu_{\mathrm{N}}} = 2.62887,\ g = 5.2567$

$$\nu = \nu_{\mathrm{L}} = \frac{\gamma_{\mathrm{N}}\mathcal{B}_0}{2\pi} \text{ with } \gamma_{\mathrm{N}} = \frac{g_I\mu_{\mathrm{N}}}{\hbar}$$

Hence, $$\nu = \frac{g_I\mu_{\mathrm{N}}\mathcal{B}_0}{h} = \frac{(5.2567)\times(5.0508\times10^{-27}\ \mathrm{J\,T^{-1}})\times(17.1\mathrm{T})}{(6.626\times10^{-34}\ \mathrm{J\,s})}$$

$$= 6.85\times10^{8}\ \mathrm{s^{-1}} = \boxed{685\ \mathrm{MHz}}$$

E14A.4(b) $E_{m_I} = -\gamma_{\mathrm{N}}\hbar\mathcal{B}_0 m_I = -g_I\mu_{\mathrm{N}}\mathcal{B}_0 m_I$ [eqns 14A.4c, $\gamma_{\mathrm{N}}\hbar = g_I\mu_{\mathrm{N}}$]

$m_I = 1, 0,\ -1$

$$E_{m_I} = -(0.404)\times(5.0508\times10^{-27}\ \mathrm{J\,T^{-1}})\times(10.50\,\mathrm{T})m_I$$

$$= -\left(2.14\overline{25}\times10^{-26}\ \mathrm{J}\right)m_I$$

$$\boxed{= -2.14\times10^{-26}\ \mathrm{J}, 0, +2.14\times10^{-26}\ \mathrm{J}}$$

E14A.5(b) The energy separation between the two levels is

$$\Delta E = h\nu \quad \text{where}\,\nu = \frac{\gamma_{\rm N}\mathcal{B}_0}{2\pi} = \frac{(1.93\times10^{7}\,T^{-1}\,s^{-1})\times(14.4T)}{2\pi}$$
$$= 4.42\times10^{7}\,s^{-1} = \boxed{44.2\text{ MHz}}$$

E14A.6(b) A 600 MHz NMR spectrometer means 600 MHz is the resonance field for protons for which the magnetic field is 14.1 T. In high-field NMR it is the field, not the frequency, that is fixed.

(i) A ^{14}N nucleus has three energy states in a magnetic field corresponding to $m_I = +1, 0, -1$. But $\Delta E(+1 \to 0) = \Delta E(0 \to -1)$

$$\Delta E = E_{m_I'} - E_{m_I} = -\gamma_{\rm N}\hbar\mathcal{B}_0 m_I' - (-\gamma_{\rm N}\hbar\mathcal{B}_0 m_I)$$
$$= -\gamma_{\rm N}\hbar\mathcal{B}_0(m_I' - m_I) = -\gamma_{\rm N}\hbar\mathcal{B}_0\Delta m_I$$

The allowed transitions correspond to $\Delta_{m_I} = \pm1$; hence

$$\Delta E = h\nu = \gamma_{\rm N}\hbar\mathcal{B}_0 = g_I\mu_N\mathcal{B}_0 = (0.4036)\times\left(5.051\times10^{-27}\,\text{JT}^{-1}\right)\times(14.1\text{ T})$$
$$= \boxed{2.88\times10^{-26}\text{ J}}$$

(ii) We assume that the electron *g*-value in the radical is equal to the free electron *g*-value, $g_{\rm e}$ = 2.0023. Then

$$\Delta E = h\nu = g_{\rm e}\mu_{\rm B}\mathcal{B}_0\ [14\text{A}.12] = (2.0023)\times(9.274\times10^{-24}\,\text{J}\,\text{T}^{-1})\times(0.300\,\text{T})$$
$$= \boxed{5.57\times10^{-24}\text{ J}}$$

Comment. The energy level separation for the electron in a free radical in an ESR 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.

E14A.7(b) The relative population difference for spin $\frac{1}{2}$ nuclei is given by

$$\frac{\delta N}{N} = \frac{N_\alpha - N_\beta}{N_\alpha + N_\beta} \approx \frac{\gamma\hbar\mathcal{B}_0}{2kT} = \frac{g_I\mu_{\rm N}\mathcal{B}_0}{2kT} \quad [\textit{Justification}\ 14\text{A}.1 \text{ and E14A.7(a)}]$$
$$= \frac{1.405\left(5.05\times10^{-27}\,\text{J T}^{-1}\right)\mathcal{B}_0}{2\left(1.381\times10^{-23}\,\text{JK}^{-1}\right)\times(298\text{ K})} = 8.62\times10^{-7}\left(\mathcal{B}_0/T\right)$$

(i) For 0.50 T $\frac{\delta N}{N} = (8.62\times10^{-7})\times(0.50) = \boxed{4.3\times10^{-7}}$

(ii) For 2.5 T $\frac{\delta N}{N} = (8.62\times10^{-7})\times(2.5) = \boxed{2.2\times10^{-6}}$

(iii) For 15.5 T $\frac{\delta N}{N} = (8.62\times10^{-7})\times(15.5) = \boxed{1.34\times10^{-5}}$

E14A.8(b)

$$\delta N \approx \frac{Ng_I\mu_{\rm N}\mathcal{B}_0}{2kT}[\text{Exercises 14A.7(a) \& (b)}] = \frac{Nh\nu}{2kT}$$

Thus, $\delta N\ \alpha\ \nu$

$$\frac{\delta N(450\text{MHz})}{\delta N(60\text{MHz})} = \frac{450\text{MHz}}{60\text{MHz}} = \boxed{7.5}$$

This ratio is not dependent on the nuclide as long as the approximation $\Delta E \ll kT$ holds. (Exercise 14A.7(a))

E14A.9(b) $$\mathcal{B}_0 = \frac{h\nu}{g_e\mu_B} = \frac{hc}{g_e\mu_B\lambda}$$

$$= \frac{(6.626\times10^{-34}\ \mathrm{J\,s})\times(2.998\times10^{8}\ \mathrm{m\,s^{-1}})}{(2.0023)\times(9.274\times10^{-24}\ \mathrm{J\,T^{-1}})\times(8\times10^{-3}\ \mathrm{m})} = \boxed{1.\bar{3}\,\mathrm{T}}$$

Solutions to problems

P14A.2 (a) $\mu = g_I\mu_N\,|I|\quad[\mu_N = 5.05079\times10^{-27}\ \mathrm{JT^{-1}}]$

Using the formulas

$$\text{Sensitivity ratio}(\nu) = \frac{R_\nu(\text{nuclide})}{R_\nu({}^1\mathrm{H})} = \frac{2}{3}(I+1)\left[\frac{\mu(\text{nuclide})}{\mu({}^1\mathrm{H})}\right]$$

$$\text{Sensitivity ratio}(\mathcal{B}\,) = \frac{R_{\mathcal{B}}(\text{nuclide})}{R_{\mathcal{B}}({}^1\mathrm{H})} = \frac{1}{6}\left(\frac{I+1}{I^2}\right)\left[\frac{\mu(\text{nuclide})}{\mu({}^1\mathrm{H})}\right]^3$$

We construct the following table:

Nuclide	Spin I	μ/μ_N	Sensitivity ratio(ν)	Sensitivity ratio ($\mathcal{B}$)
^{2}H	1	0.85745	0.409	0.00965
^{13}C	$\frac{1}{2}$	0.7023	0.251	0.01590
^{14}N	1	0.40356	0.193	0.00101
^{19}F	$\frac{1}{2}$	2.62835	0.941	0.83350
^{31}P	$\frac{1}{2}$	1.1317	0.405	0.06654
^{1}H	$\frac{1}{2}$	2.79285		

(b) $\mu = \gamma_N\hbar I = g_I\mu_N\,|I|$

Hence $\gamma_N = \dfrac{\mu}{\hbar I}$

At constant frequency

$R_\nu \propto (I+1)\mu\omega_0^2$ or $R_\nu \propto (I+1)\mu\quad[\omega_0$ is constant between the nuclei]

Thus

$$\text{Sensitivity ratio}(\nu) = \frac{R_\nu(\text{nuclide})}{R_\nu({}^1\mathrm{H})}$$

$$= \tfrac{2}{3}(I+1)\left[\frac{\mu(\text{nuclide})}{\mu({}^1\mathrm{H})}\right] = \tfrac{2}{3}(I+1)\left[\frac{\mu(\text{nuclide})/\mu_N}{\mu({}^1\mathrm{H})/\mu_N}\right]$$

as above. Substituting $\omega_0 = \gamma_N B_0$ and $\gamma_N = \dfrac{\mu}{\hbar I}$, $\omega_0 = \dfrac{\mu B_0}{\hbar I}$ so

$$R_B \propto \frac{(I+1)\mu^3 B_0^2}{I^2}$$

$$\text{Sensitivity ratio}(\mathcal{B}) = \frac{R_{\mathcal{B}}(\text{nuclide})}{R_{\mathcal{B}}(^1\text{H})} = \tfrac{1}{6}\left(\frac{I+1}{I^2}\right)\left[\frac{\mu(\text{nuclide})}{\mu(^1\text{H})}\right]^3$$

$$= \tfrac{1}{6}\left(\frac{I+1}{I^2}\right)\left[\frac{\mu(\text{nuclide})/\mu_\text{N}}{\mu(^1\text{H})/\mu_\text{N}}\right]^3$$

as in part (a).

14B Features of NMR spectra

Answers to discussion questions

D14B.2 Detailed discussions of the origins of the local, neighbouring group, and solvent contributions to the shielding constant can be found in Sections 14B.2(a), (b), and (c) 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 $\sigma(\text{local}) = \sigma_\text{d} + \sigma_\text{p}$. 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 which mixes in excited electronic states into the ground state and any theoretical calculation of the effect requires detailed knowledge of the excited state wave functions. 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 in 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 18) of the neighbouring group as shown in eqn 14B.10(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.

D14B.4 See Section 14B.3(d) for a detailed discussion of chemical and magnetic equivalence as applied to NMR and the distinction between them. Here we will summarize the basic concepts. Two nuclei are chemically equivalent if they are related by a symmetry operation of the molecule. Symmetrically equivalent nuclei will have the same resonance frequency, i.e. the same chemical shift. Examples are the protons in benzene and the protons *meta*- to each other (H-2, H-6 and H-3, H-5) in *para*-nitrophenol. In benzene the protons are related by a C_6 operation (as well as others) and in *para*-nitrophenol the protons are related by a plane of symmetry and a C_2 operation. Two nuclei are magnetically equivalent if in addition to being chemically equivalent they have identical spin-spin interactions with all other magnetic nuclei in the molecule. Examples are CH_2CF_2 and 1,2,3-trichlorobenzene. Chemical equivalence does not imply magnetic equivalence. In the case of para-nitrophenol, the protons H-2 and H-6, though chemically equivalent, are not magnetically equivalent because the coupling of H-2 to H-3 is different from the coupling of H-6 to H-3.

Solutions to exercises

E14B.1(b) See the solution to Exercise 14B.1(a).

(i) δ is $\boxed{\text{independent}}$ of both $\mathcal{B}$ and ν.

(ii) Rearranging [48.4] we see $\nu - \nu^{\circ} = \nu^{\circ}\delta \times 10^{-6}$ and the relative chemical shift is

$$\frac{\nu-\nu^{\circ}(450\text{ MHz})}{\nu-\nu^{\circ}(60\text{ MHz})}=\frac{(450\text{ MHz})}{(60\text{ MHz})}=\boxed{7.5}$$

E14B.2(b) $\mathcal{B}_{\mathrm{loc}} = (1-\sigma)\mathcal{B}_0$

$$|\Delta\mathcal{B}_{\mathrm{loc}}| = |(\Delta\sigma)|\mathcal{B}_0 \approx |[\delta(\mathrm{CH_3})-\delta(\mathrm{CH_2})]| \times 10^{-6}\mathcal{B}_0$$
$$= |1.16-3.36| \times 10^{-6}\mathcal{B}_0 = 2.20\times10^{-6}\mathcal{B}_0$$

(i) $\mathcal{B}_0 = 1.9\,\mathrm{T},| \quad \Delta\mathcal{B}_{\mathrm{loc}}| = (2.20\times10^{-6})\times(1.9\,\mathrm{T}) = \boxed{4.2\times10^{-6}\,\mathrm{T}}$

(ii) $\mathcal{B}_0 = 16.5\,\mathrm{T}, \quad |\Delta\mathcal{B}_{\mathrm{loc}}| = (2.20\times10^{-6})\times(16.5\,\mathrm{T}) = \boxed{3.63\times10^{-5}\,\mathrm{T}}$

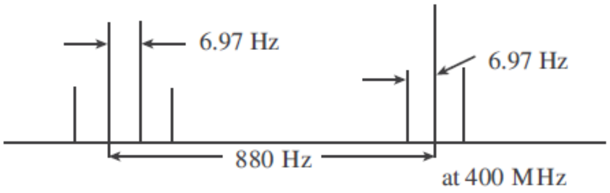
E14B.3(b) $\nu - \nu^{\circ} = \nu^{\circ}\delta \times 10^{-6}$

$$|\Delta\nu| \equiv (\nu-\nu^{\circ})(\mathrm{CH_2})-(\nu-\nu^{\circ})(\mathrm{CH_3}) = \nu(\mathrm{CH_2})-\nu(\mathrm{CH_3})$$
$$= \nu^{\circ}[\delta(\mathrm{CH_2})-\delta(\mathrm{CH_3})]\times10^{-6}$$
$$= (3.36-1.16)\times10^{-6}\nu^{\circ} = 2.20\times10^{-6}\nu^{\circ}$$

(i) $\nu^{\circ} = 400\,\mathrm{MHz} \qquad |\Delta\nu| = (2.20\times10^{-6})\times(400\,\mathrm{MHz}) = 880\,\mathrm{Hz}$ [Fig.14B.1]

(ii) $\nu^{\circ} = 650\,\mathrm{MHz} \qquad |\Delta\nu| = (2.20\times10^{-6})\times(650\,\mathrm{MHz}) = 1.43\,\mathrm{kHz}$

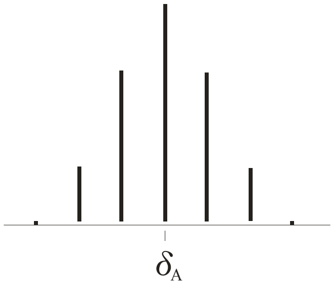
Figure 14B.1



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

E14B.4(b) See section 14B.3 of the text for the splitting pattern of the A resonance of an $\mathrm{AX_n}$ NMR spectrum. Here A = ^{31}P and n = 6. The 6 fluorine nuclei split the A resonance into a septet of lines with intensities in the ratio 1:6:15:20:15:6:1. See Fig. 14B.2.

Figure 14B.2



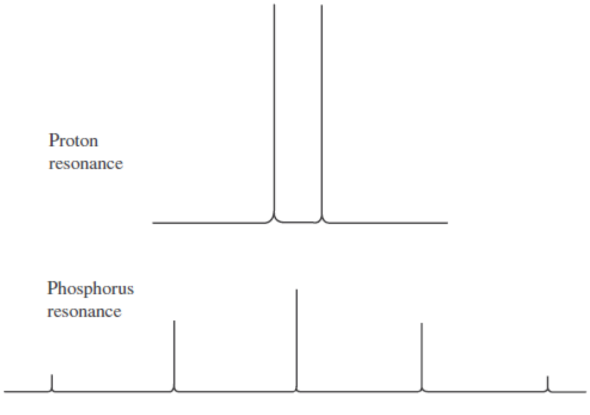
E14B.5(b) $\nu = \dfrac{g_I \mu_N \mathcal{B}_0}{h}$ [Solution to exercises 14A.3(a) & (b)]

Hence, $\dfrac{\nu(^{31}\mathbf{P})}{\nu(^{1}\mathbf{H})} = \dfrac{g(^{31}\mathbf{P})}{g(^{1}\mathbf{H})}$

or $\nu(^{31}\text{P}) = \dfrac{2.2634}{5.5857} \times 500\,\text{MHz} = \boxed{203\text{MHz}}$

The proton resonance consists of 2 lines $(2\times\frac{1}{2}+1)$ and the ^{31}P resonance of 5 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 48.3). 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 Fig. 14B.3.

Figure 14B.3

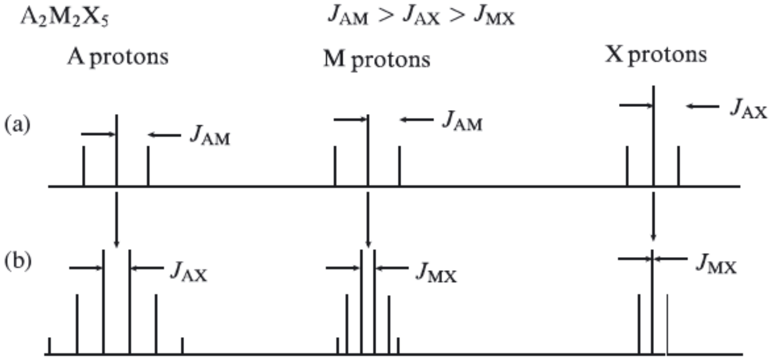


E14B.6(b) See Section 14B.3(a), Example 14B.3 and Figs. 14B.12 and 14B.13 for the approach to the solution to this exercise. Also see Example 14D.1 and Figs. 14D.4 and 14D.5. That latter example and those figures are applied specifically to EPR spectra, but the process of determining the intensity pattern 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 3 spin-5/2 nuclei. Each number in the table is the sum of the six (I = 5/2, 2I + 1 = 6) numbers above it (3 to the right and 3 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

E14B.7(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 Fig. 14B.4.) Only the splitting of the central peak of Fig. 14B.4(a) is shown in Fig. 14B.4(b).

Figure 14B.4



E14B.8(b) **(i)** 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.

(ii) Rapid rotation of the PH_3 groups about the Mo–P axes makes the P and H nuclei chemically and magnetically equivalient in both the *cis*- and *trans*-forms.

E14B.9(b) $\tau \approx \dfrac{\sqrt{2}}{\pi\Delta\nu}$[4B.16, with $\delta\nu$ written as $\Delta\nu$]

$\Delta\nu = \nu^{o}(\delta' - \delta)\times10^{-6}$ [Exercise 14B.3(a)]

Then

$$\tau \approx \frac{\sqrt{2}}{\pi\nu_0(\delta' - \delta)\times10^{-6}}$$

$$\approx \frac{\sqrt{2}}{(\pi)\times(350\times10^{6}\,\text{Hz})\times(5.5-4.2)\times10^{-6}} \approx 9.9\times10^{-4}\,\text{s}$$

Therefore, the signals merge when the lifetime of each isomer is less than about $\boxed{0.99\ \text{ms}}$, corresponding to a conversion rate of about $\boxed{1.0\times10^{3}\,\text{s}^{-1}}$

Solutions to problems

P14B.2 See Figures 14B.5(a), 14B.5(b), and 14B.5(c). In Figure 14B.5(a), J_1 has A = +7.0 Hz, B = −1.0 Hz, and C = +5.0 Hz. These are the suggested initial values of the parameters A, B, and C. For J_2 in the figure, we have changed C to +6.0 Hz. We see that a small change in C makes a relatively large change in J, but the overall shape of the curve remains similar; the crossover point remains at π/2. In Figure 14B.5(b), we have changed B from its initial value of −1 Hz to −2 Hz. This curve is shown in the figure as J_3. There is not a large change in J and the shape remains the same, as does the crossover point. In Figure 14B.5(c), we have changed A to +8.0 Hz from its initial value of +7.0 Hz. This curve is shown in the figure as J_4. Here we see that a small change in A eliminates the crossover of the curves, although again the general shape of the curve is similar.

Figure 14B.5(a)

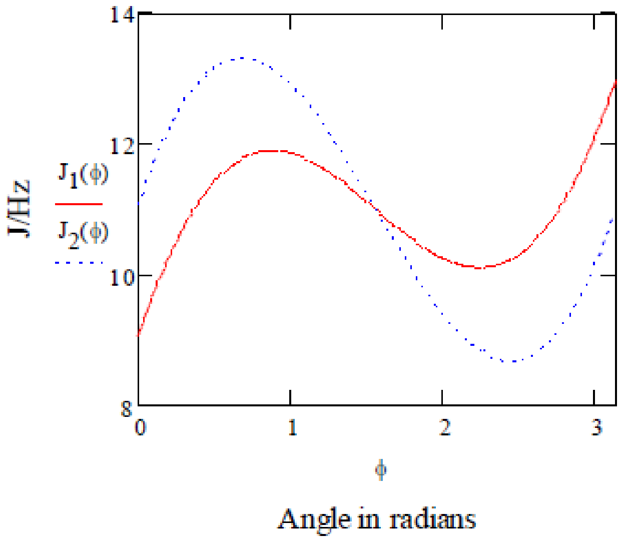


Figure 14B.5(b)

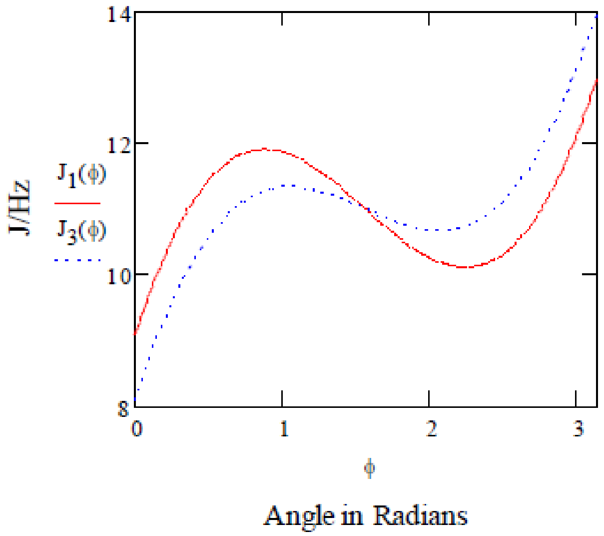
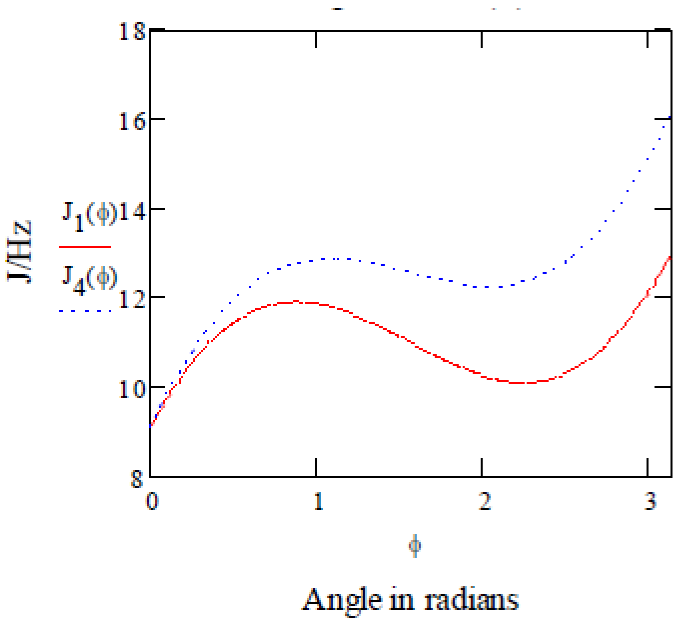


Figure 14B.5(c)



P14B.4 **(a)** The Karplus equation [14B.14] for ${}^3J_{\mathrm{HH}}$ is a linear equation in $\cos\phi$ and $\cos 2\phi$. The experimentally determined equation for ${}^3J_{\mathrm{SnSn}}$ is a linear equation in ${}^3J_{\mathrm{HH}}$. In general, if $F(f)$ is linear in f, and if $f(x)$ is linear in x, then $F(x)$ is linear. So we expect ${}^3J_{\mathrm{SnSn}}$ to be linear in $\cos\phi$ and $\cos 2\phi$. This is demonstrated in (**b**).

(b) $${}^3J_{\mathrm{SnSn}}/\mathrm{Hz} = 78.86({}^3J_{\mathrm{HH}}/\mathrm{Hz}) + 27.84$$

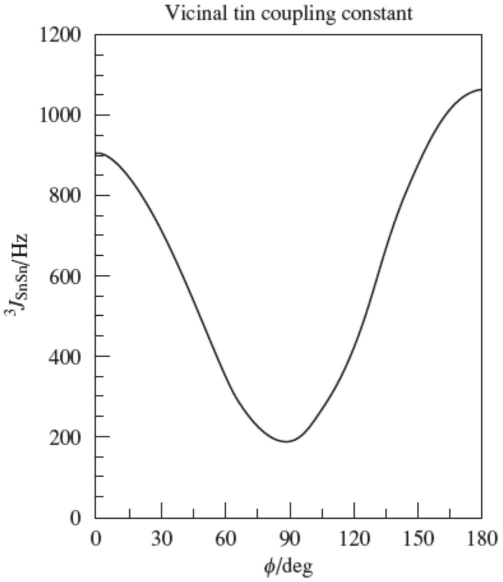
Inserting the Karplus equation for ${}^3J_{\mathrm{HH}}$ we obtain

${}^3J_{\mathrm{SnSn}}/\mathrm{Hz} = 78.86\{A + B\cos\phi + C\cos 2\phi\} + 27.84$. Using $A = 7$, $B = -1$, and $C = 5$, we obtain

$${}^3J_{\mathrm{SnSn}}/\mathrm{Hz} = \boxed{580 - 79\cos\phi + 395\cos 2\phi}$$

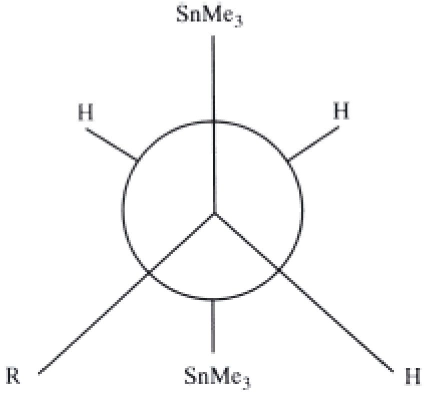
The plot of ${}^3J_{\mathrm{SnSn}}$ is shown in Fig.14B.6.

Figure 14B.6



(c) A staggered configuration (Fig.14B.7) with the $SnMe_3$ groups *trans* to each other is the preferred configuration. The $SnMe_3$ repulsions are then at a minimum.

Figure 14B.7



P14B.6 Equation 14B.15 may be written

$$\mathcal{B}_{\text{nuc}} = k(1-3\cos^2\theta)$$

where k is a constant independent of angle. Thus

$$\begin{aligned}(\mathcal{B}_{\text{nuc}}) &\propto \int_0^{\pi}(1-3\cos^2\theta)\sin\theta\,\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\phi \\ &\propto \int_1^{-1}(1-3x^2)\,\mathrm{d}x\times 2\pi\ [x=\cos\theta, \mathrm{d}x=-\sin\theta\,\mathrm{d}\theta] \\ &\propto (x-x^3)\Big|_1^{-1} = 0\end{aligned}$$

14C Pulse techniques in NMR

Answers to discussion questions

D14C.2 Both spin–lattice and spin–spin relaxation are caused by fluctuating magnetic and electric fields at the nucleus in question and these fields result from the random thermal motions present in the solution or other form of matter. These random motions can be a result of a number of processes and it is hard to summarize all that could be important. In theory every known nuclear interaction coupled with every type of motion can contribute to relaxation and detailed treatments can be exceedingly complex. However, they all depend on the magnetogyric ratio of the atom in question and the magnetogyric ratio of the proton is much larger than that of ^{13}C. Hence the interaction of the proton with fluctuating local magnetic fields caused by the presence of neighboring magnetic nuclei will be greater, and the relaxation will be quicker, corresponding to a shorter relaxation time for protons. Another consideration is the structure of compounds containing carbon and hydrogen. Typically the C atoms are in the interior of the molecule bonded to other C atoms, 99% of which are nonmagnetic, so the primary relaxation effects are due to bonded protons. Protons are on the outside of the molecule and are subject to many more interactions and hence faster relaxation.

D14C.4 In the nuclear Overhauser effect (NOE) in NMR, spin relaxation processes are used to transfer the population difference typical of one species of nucleus X to another nucleus A, thereby enhancing the intensity of the signal produced by A. Eqns. 14C.8 and 14C.9 show that the signal enhancement is given by

$$\frac{I_\mathrm{A}}{I_\mathrm{A}^0} = 1+\eta = 1+\frac{\gamma_\mathrm{X}}{2\gamma_\mathrm{A}}$$

NOE can be used to determine interproton distances in biopolymers. This application makes use of the fact that when the dipole-dipole mechanism is not the only relaxation mechanism, the NOE is given by

$$\frac{I_\mathrm{A}}{I_\mathrm{A}^0} = 1+\eta = 1+\frac{\gamma_\mathrm{X}}{2\gamma_\mathrm{A}}\times\frac{T_1}{T_\mathrm{1,dip\text{-}dip}}$$

where T_1 is the total relaxation time and $T_\mathrm{1,dip\text{-}dip}$ is the relaxation time due to the dipole-dipole mechanism. Here A and X are both protons. The enhancement depends strongly on the separation, r, of the two spins, for the strength of the dipole-dipole interaction is proportional to $1/r^3$, and its effect depends on the square of that strength and therefore on $1/r^6$.This sharp dependence on separation is used to build up a picture of the conformation of the biopolymer by using NOE to identify which protons can be regarded as neighbors.

Solutions to exercises

E14C.1(b) Analogous to precession of the magnetization vector in the laboratory frame due to the presence of $\mathcal{B}_0$ that is

$$\nu_\mathrm{L} = \frac{\gamma_\mathrm{N}\mathcal{B}_0}{2\pi}[14\mathrm{A}.7],$$

there is a precession in the rotating frame, due to the presence of $\mathcal{B}_1$, namely

$$\nu_\mathrm{L} = \frac{\gamma_\mathrm{N}\mathcal{B}_1}{2\pi} \quad \text{or} \quad \omega_1 = \gamma_\mathrm{N}\mathcal{B}_1$$

Since ω is an angular frequency, the angle through which the magnetization vector rotates is

$$\theta = \gamma_N \mathcal{B}_1 t = \frac{g_I \mu_N}{\hbar} \mathcal{B}_1 t$$

So $\mathcal{B}_1 = \frac{\theta\hbar}{g_I \mu_N t} = \frac{(\pi/2)\times(1.0546\times10^{-34}\ \mathrm{J\,s})}{(5.586)\times(5.0508\times10^{-27}\ \mathrm{J\,T^{-1}})\times(5\times10^{-6}\ \mathrm{s})} = \boxed{1.08\times10^{-3}\ \mathrm{T}}$

a 180º pulse requires $2\times5\ \mu\mathrm{s} = \boxed{10\ \mu\mathrm{s}}$

E14C.2(b) The effective transverse relaxation time is given by

$$T_2^* = \frac{1}{\pi\Delta\nu_{1/2}}\ [14C.7] = \frac{1}{\pi\times12\ \mathrm{s}^{-1}} = \boxed{0.027\ \mathrm{s}}$$

E14C.3(b) The maximum enhancement is given by

$$\eta = \frac{\gamma_{^1\mathrm{H}}}{2\times\gamma_{^{19}\mathrm{F}}}[14C.9] = \frac{26.752\times10^{7}\ \mathrm{T^{-1}s^{-1}}}{2\times25.177\times10^{7}\ \mathrm{T^{-1}s^{-1}}}[\text{Table 14A.2}] = \boxed{0.5312}$$

E14C.4(b) See Fig. 14C.1. Only the H(N) and H(C_α) protons and the H(C_α) and H(C_β) protons are expected to show coupling. This results in a simple COSY spectrum with only two off-diagonals, one at (8.25 ppm, 4.35 ppm) and the other at (4.35 ppm, 1.39 ppm).

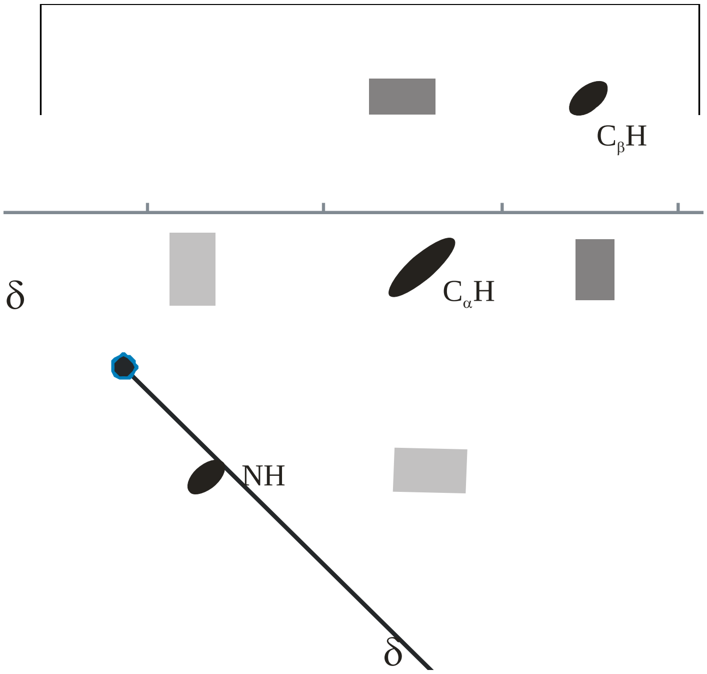


Figure 14C.1

P14C.2 The FID signals from the three nuclei are all of the form of eqn 14C.1 which we will write as $F(t) = \sum_j S_{0j}\cos(2\pi\nu_{\mathrm{L}j}t)\mathrm{e}^{-t/T_{2j}}$. 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

$$F(t) = S_0\sum_j \cos(2\pi\nu_{\mathrm{L}j}t)\mathrm{e}^{-t/T_2}$$

The solution is contained in the following MathCad® worksheet.

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: $\nu_0 := 800\cdot\mathrm{MHz}$

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: $F1_m := S_1\cdot\cos(2\cdot\pi\cdot\nu_1\cdot t_m)\cdot e^{\frac{-t_m}{T_2}}$

FID of signal 2: $F2_m := S_2\cdot\cos(2\cdot\pi\cdot\nu_2\cdot t_m)\cdot e^{\frac{-t_m}{T_2}}$

FID of signal 3: $F3_m := S_3\cdot\cos(2\cdot\pi\cdot\nu_3\cdot t_m)\cdot e^{\frac{-t_m}{T_2}}$

Total FID signal: $F := F1 + F2 + F3$

Figure 14C.2(a)

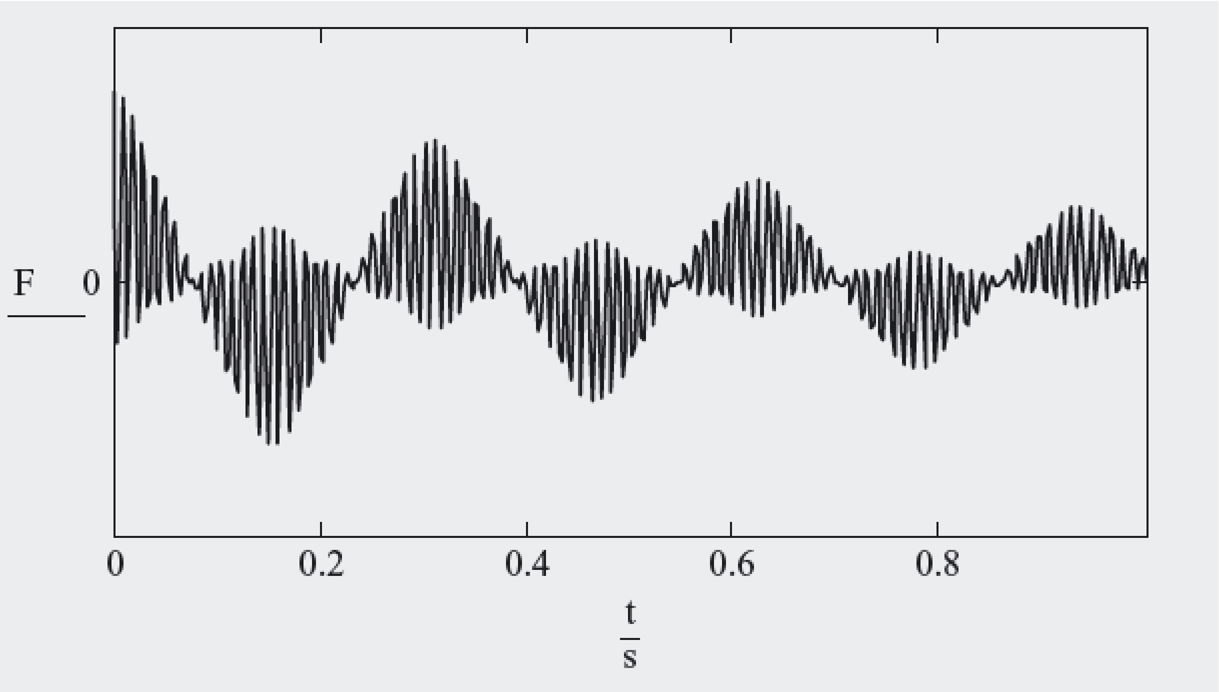
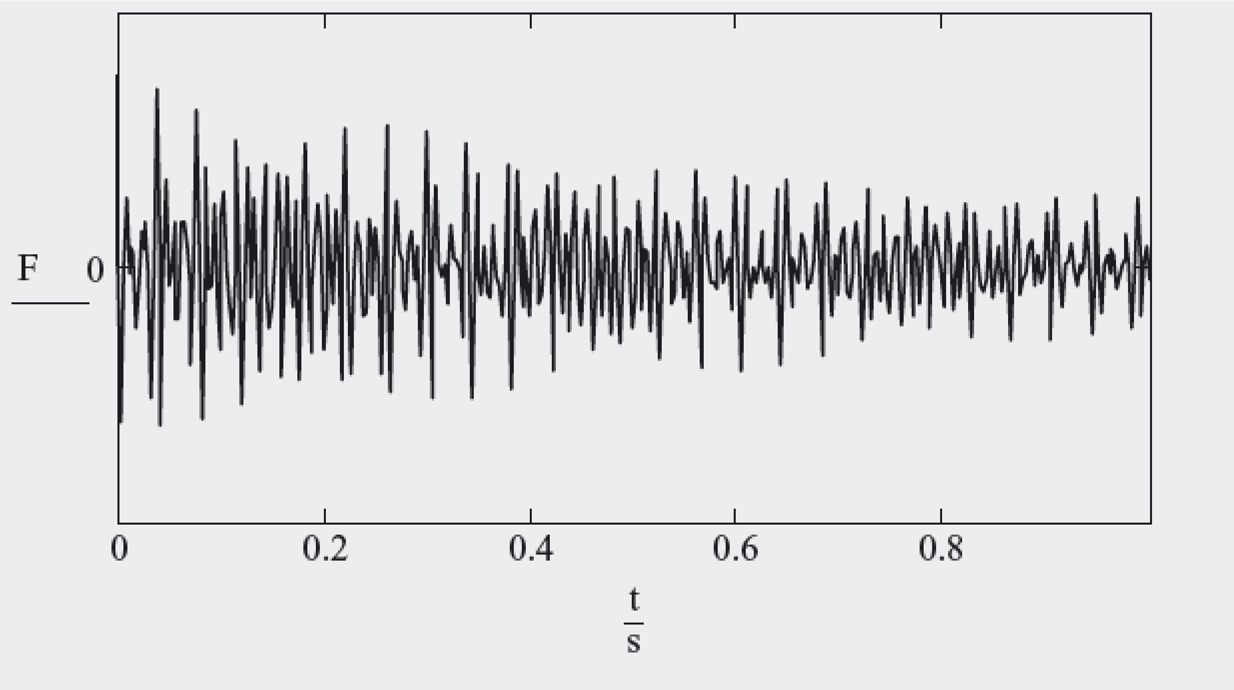


Figure 14C.2(b)



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 14C.7 and 14B.2 of the text

P14C.4 **(a)** The *Lorentzian function* in terms of angular frequencies is

$$I_L(\omega) = \frac{S_0T_2}{1+T_2^2(\omega-\omega_0)^2}$$

The maximum in this function occurs when $\omega = \omega_0$. Hence $I_{L,max} = S_0T_2$ and

$$I_L(\Delta\omega_{1/2}) = \frac{I_{L,max}}{2} = \frac{S_0T_2}{2} = \frac{S_0T_2}{1+T_2^2(\omega_{1/2}-\omega_0)^2} = \frac{S_0T_2}{1+T_2^2(\Delta\omega)^2}$$

where $\Delta\omega = \frac{1}{2}\Delta\omega_{½}$; hence $2 = 1+T_2^2(\Delta\omega)^2$ and $\Delta\omega = 1/T_2$. Therefore $\boxed{\Delta\omega_{½} = \dfrac{2}{T_2}}$

(b) The *Gaussian function* in terms of angular frequencies is

$$I_G(\omega) = S_0T_2\mathrm{e}^{-T_2^2(\omega-\omega_0)^2}$$

The maximum in this function occurs when $\omega = \omega_0$. Hence $I_{G,max} = S_0T_2$ and

$$I_G(\Delta\omega_{1/2}) = \frac{I_{G,max}}{2} = \frac{S_0T_2}{2} = S_0T_2\mathrm{e}^{-T_2^2(\omega_{½}-\omega_0)^2} = S_0T_2\mathrm{e}^{-T_2^2(\Delta\omega)^2}$$

where $\Delta\omega = \frac{1}{2}\Delta\omega_{½}$; hence $\ln 2 = T_2^2(\Delta\omega)^2$ and $\Delta\omega = (\ln 2)^{½}/T_2$

Therefore $\boxed{\Delta\omega_{½} = \dfrac{2(\ln 2)^{½}}{T_2}}$

(c) If we choose the same values of S_0, T_2, and ω_0 for both functions we may rewrite them as

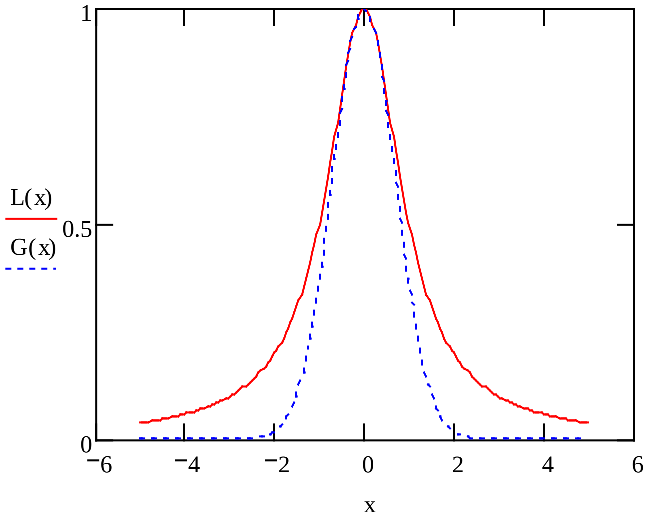
$$I_L(\omega) = L(x) \propto \frac{1}{1+x^2} \text{ and } I_G(\omega) = G(x) \propto \mathrm{e}^{-x^2} \text{ where } x = T_2(\omega-\omega_0)$$

These functions are plotted against x in the following Mathcad worksheet. Note that the Lorentzian function is slightly sharper in the center, although this is difficult to discern with the scale of x used in the figure, and decreases much more slowly in the wings beyond the half amplitude points. Also note that the functions plotted in the figure are not normalized but are matched at their peak amplitude in order to more clearly display the differences in their shapes. If the curves had been normalized the areas under the two curves would be equal, but the peak height in the Lorentzian would be lower than the Gaussian peak height.

Figure 14C.3

$$x := -5, -4.95 .. 5$$

$$L(x) := \frac{1}{1 + x^2} \qquad G(x) := e^{-x^2}$$



P14C.6 We have seen (Problem 14C.5) that if $G \propto \cos \omega_0 t$, then $I(\omega) \propto \frac{1}{\left[1+(\omega_0-\omega)^2 \tau^2\right]}$ which peaks at $\omega \approx \omega_0$.

Therefore, if

$$G(t) \propto a \cos \omega_1 t + b \cos \omega_2 t$$

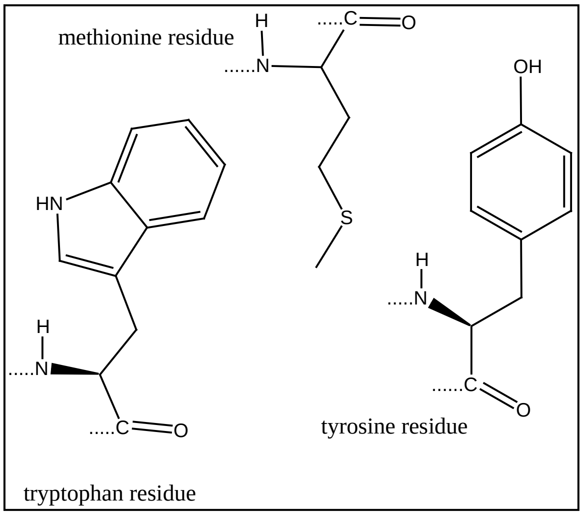
we can anticipate that

$$I(\omega) \propto \frac{a}{1+(\omega_1-\omega)^2 \tau^2} + \frac{b}{1+(\omega_2-\omega)^2 \tau^2}$$

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 $\omega \approx \omega_2$.

P14C.8 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 lay between them as represented in figure 14C.4

Figure 14C.4



14D Electron paramagnetic resonance

Answers to discussion questions

D14D.2 The hyperfine parameter *a* due to a nucleus in an aromatic radical, which is easily measured from the splittings of the lines in the EPR spectrum of the radical, as illustrated in Fig. 14D.3 of the textbook, for the benzene anion radical, can be related to the spin density ρ of the unpaired electron on the nuclei in the aromatic radical. For the hyperfine splitting due to protons in aromatic systems, the relationship required is the McConnell equation, eqn. 14D.5. The process of obtaining ρ from the McConnell equation is illustrated in *Brief Illustration* 14D.3 following eqn. 14D.5 in the text. For nuclei other than protons in aromatic radicals similar, although more complicated equations arise; but in all cases the spin densities can be related to the coefficients of the basis functions used to describe the molecular orbital of the unpaired electron.

Solutions to exercises

E14D.1(b) The *g* factor is given by

$$g = \frac{h\nu}{\mu_B \mathcal{B}_0}; \quad \frac{h}{\mu_B} = \frac{6.62608\times10^{-34}\,\text{J s}}{9.2740\times10^{-24}\,\text{J T}^{-1}} = 7.1448\times10^{-11}\,\text{T Hz}^{-1} = 71.448\ \text{mT GHz}^{-1}$$

$$g = \frac{71.448\ \text{mT GHz}^{-1}\times 9.2482\,\text{GHz}}{330.02\ \text{mT}} = \boxed{2.0022}$$

E14D.2(b) The hyperfine coupling constant for each proton is $\boxed{2.2\,\text{mT}}$, the difference between adjacent lines in the spectrum. The *g* value is given by

$$g = \frac{h\nu}{\mu_B \mathcal{B}_0} = \frac{(71.448\,\text{mT}\,\text{GHz}^{-1}) \times (9.332\,\text{GHz})}{334.7\,\text{mT}} = \boxed{1.992}$$

E14D.3(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

$$\boxed{328.865,\ 330.975,\ 331.735,\ 331.755,\ 333.845,\ 333.865,\ 334.625 \text{ and } 336.735\,\text{mT}}$$

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.

E14D.4(b) **(i)** 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.

(ii) 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.

E14D.5(b) The g value is given by

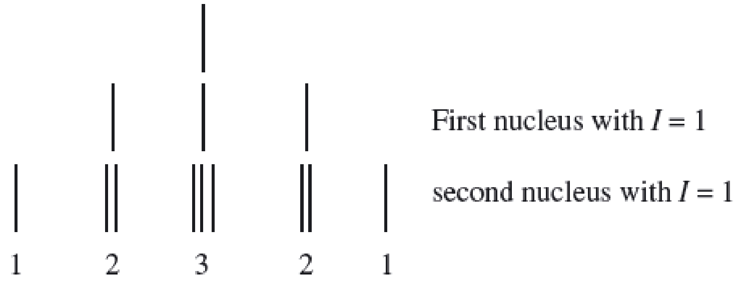
$$g = \frac{h\nu}{\mu_B \mathcal{B}_0} \text{ so } \mathcal{B}_0 = \frac{h\nu}{\mu_B g}, \quad \frac{h}{\mu_B} = 71.448\ \text{mT}\,\text{GHz}^{-1}$$

(i) $$\mathcal{B}_0 = \frac{(71.448\ \text{mT}\,\text{GHz}^{-1}) \times (9.501\,\text{GHz})}{2.0024} = \boxed{339.0\ \text{mT}}$$

(ii) $$\mathcal{B}_0 = \frac{(71.448\ \text{mT}\,\text{GHz}^{-1}) \times (34.77\,\text{GHz})}{2.0024} = \boxed{1241\,\text{mT}}$$

E14D.6(b) Two nuclei of spin $\boxed{I = 1}$ give five lines in the intensity ratio 1:2:3:2:1 (Fig. 14D.1).

Figure 10D.1



E14D.7(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 14D.4(a). (see Fig. 14D.2.)

Figure 10D.2

Solutions to problems

P14D.2

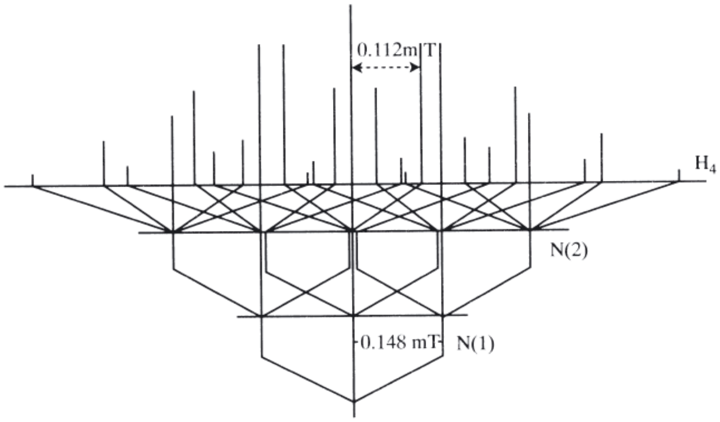
$$g = \frac{h\nu}{\mu_{\rm B}\mathcal{B}_0}\ [14D.2] = \frac{(7.14478\times10^{-11}\,{\rm T})\times(\nu/{\rm Hz})}{\mathcal{B}_0}$$

$$= \frac{(7.14478\times10^{-11}\,{\rm T})\times(9.302\times10^{9})}{\mathcal{B}_0} = \frac{0.6646\overline{1}}{\mathcal{B}_0/T}$$

$$g_{\parallel} = \frac{0.6646\overline{1}}{0.33364} = \boxed{1.992} \qquad g_{\perp} = \frac{0.6646\overline{1}}{0.33194} = \boxed{2.002}$$

P14D.4 Construct the spectrum by taking into account first the two equivalent $^{14}\mathrm{N}$ 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 Fig.14D.3. Note that Pascal's triangle does not apply to the intensities of the quintet due to $^{14}\mathrm{N}$, but does apply to the quintet due to the protons.

Figure 10D.3



P14D.6 Write $P(\mathrm{N2}s)=\dfrac{5.7\,\mathrm{mT}}{55.2\,\mathrm{mT}}=\boxed{0.10}$ $(10$ percent of its time$)$

$$P(\mathrm{N2}p_z)=\frac{1.3\,\mathrm{mT}}{3.4\,\mathrm{mT}}=\boxed{0.38}\ \ (38\text{ percent of its time})$$

The total probability is

(a) $P(\mathrm{N})=0.10+0.38=\boxed{0.48}$ $(48$ percent of its time$)$.

(b) $P(\mathrm{O})=1-P(\mathrm{N})=\boxed{0.52}$ $(52$ percent of its time$)$.

The hybridization ratio is

$$\frac{P(\mathrm{N2}p)}{P(\mathrm{N2}s)}=\frac{0.38}{0.10}=\boxed{3.8}$$

The unpaired electron therefore occupies an orbital that resembles an sp^3 hybrid on N, in accord with the radical's nonlinear shape.

From the discussion in Section 10A we can write

$$a^2=\frac{1+\cos\phi}{1-\cos\phi}$$

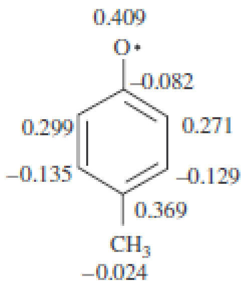
$$b^2=1-a^2=\frac{-2\cos\phi}{1-\cos\phi}$$

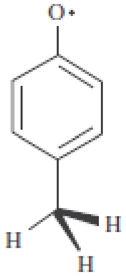
$$\lambda=\frac{b'^2}{a'^2}=\frac{-1\cos\phi}{1+\cos\phi},\ \text{implying that}\cos\phi=\frac{\lambda}{2+\ell}$$

Then, since $\lambda=3.8$, $\cos\phi=-0.66$, so $\phi=\boxed{131°}$

Integrated activities

I14.2 **(a)** The first figure displays spin densities computed by molecular modeling software (*ab initio*, density functional theory, Gaussian 98^{TM}).





(b) First, note that the software assigned slightly different values to the two protons *ortho* to the oxygen and to the two protons *meta* to the oxygen. This is undoubtedly a computational artifact, a result of the minimum-energy structure having one methyl proton in the plane of the ring, which makes the right and left side of the ring slightly non-equivalent. (See second figure.) In fact, fast internal rotation makes the two halves of the ring equivalent. We will take the spin density at the *ortho* carbons to be 0.285 and those of the *meta* carbons to be –0.132. Predict the form of the spectrum by using the McConnell equation (14D.5) for the splittings. The two *ortho* protons give rise to a 1:2:1 triplets with splitting $0.285\times 2.25\ \text{mT} = 0.64\ \text{mT}$; these will in turn be split by the two *meta* protons into 1:2:1 triplets with splitting

$$0.132\times 2.25\ \text{mT} = 0.297\ \text{mT} = 0.297\ \text{mT}$$

And finally, these lines will be seen to be further split by the three methyl protons into 1:3:3:1 quartets with splittings 1.045 mT. Note that the McConnell relation cannot be applied to calculate these latter splittings, but the software generates them directly from calculated spin densities on the methyl hydrogens. The computed splittings agree well with experiment at the *ortho* positions (0.60 mT) and at the methyl hydrogens (1.19 mT) but less well at the *meta* positions (0.145 mT).

I14.4 The desired result is the linear equation:

$$[\text{I}]_0 = \frac{[E]_0\Delta\nu}{\delta\nu} - K,$$ [Note: the intercept turns out to be –*K*, not *K* as *K* is defined in the problem statement.]

Our first task is to express quantities in terms of $[\text{I}]_0$, $[\text{E}]_0$, $\Delta\nu$, $\delta\nu$, and K, eliminating terms such as [I], [EI], [E], ν_1, ν_{EI}, and ν. [Note: symbolic mathematical software is helpful here.] Begin with ν:

$$\nu = \frac{[\text{I}]}{[\text{I}]+[\text{EI}]}\nu_{\text{I}} + \frac{[\text{EI}]}{[\text{I}]+[\text{EI}]}\nu_{\text{EI}} = \frac{[\text{I}]_0-[\text{EI}]}{[\text{I}]_0}\nu_{\text{I}} + \frac{[\text{EI}]}{[\text{I}]_0}\nu_{\text{EI}},$$

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]:

$$[\text{EI}] = \frac{[\text{I}]_0\left(\nu-\nu_{\text{I}}\right)}{\nu_{\text{EI}}-\nu_{\text{I}}} = \frac{[\text{I}]_0\delta\nu}{\Delta\nu},$$

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:

$$K = \frac{[\text{E}][\text{I}]}{[\text{EI}]} = \frac{\left([\text{E}]_0-[\text{EI}]\right)\left([\text{I}]_0-[\text{EI}]\right)}{[\text{EI}]} \approx \frac{\left([\text{E}]_0-[\text{EI}]\right)[\text{I}]_0}{[\text{EI}]}.$$

We have used the fact that total I is much greater than total E (from the condition that $[\text{I}]_0 \gg [\text{E}]_0$), so it must also be much greater than $[\text{EI}]$, even if all E binds I. Now solve this for $[\text{E}]_0$:

$$[\text{E}]_0 = \frac{K+[\text{I}]_0}{[\text{I}]_0}[\text{EI}] = \left(\frac{K+[\text{I}]_0}{[\text{I}]_0}\right)\left(\frac{[\text{I}]_0\delta\nu}{\Delta\nu}\right) = \frac{(K+[\text{I}]_0)\delta\nu}{\Delta\nu}.$$

The expression contains the desired terms and only those terms. Solving for $[\text{I}]_0$ yields:

$$\boxed{[\mathrm{I}]_0 = \frac{[\mathrm{E}]_0 \Delta v}{\delta v} - K}$$

which would result in a straight line with slope $[\mathrm{E}]_0\Delta v$ and y-intercept $-K$ if one plots $[\mathrm{I}]_0$ against $1/\delta v$.

15 Statistical thermodynamics

15A The Boltzmann distribution

Answers to discussion questions

15A.2 The principle of equal *a priori* probabilities is the assumption that the population of any physical state depends only on its energy and not how that energy is distributed. For example, a state in which the molecule's energy ε is all in translational motion is just as likely as a state where all its energy is in rotational motion or in vibrational motion or in any combination of these modes of motion—provided, of course, that the distribution is consistent with the molecule's quantized energy levels.

15A.4 Because the Boltzmann distribution gives the ratio of populations of states of different energy as a function of temperature, it accounts for the temperature dependence of many physical and chemical phenomena. In this chapter, reference was made to the intensities of spectral transitions (Topics 12A and 14A) as one phenomenon governed by the Boltzmann distribution. Chemical equilibrium is governed by the Boltzmann distribution: the equilibrium distribution of reactant and product species is determined by a single Boltzmann distribution of states of the system regardless of whether those states belong to reactant or product species (Topi 15F.2). The Maxwell-Boltzmann distribution of molecular speeds in the kinetic model of gases is an application of the Boltzmann distribution to translational motion (Topic 1B). Collision theory explains the temperature dependence of reaction rates through the Boltzmann distribution (Topic 21A).

Solutions to exercises

15A.1(b) The weight is given by

$$\mathcal{W} = \frac{N!}{N_0!N_1!N_2!\cdots} = \frac{21!}{6!0!5!0!4!0!3!0!2!0!0!1!} = \boxed{2.04\times10^{12}}$$

15A.2(b) **(i)** $10! = 10\times9\times8\times7\times6\times5\times4\times3\times2\times1 = \boxed{3628800}$ exactly.

(ii) According to Stirling's simple approximation [15A.2b],

$$\ln x! \approx x\ln x - x$$

so $\ln 10! \approx 10\ln 10 - 10 = 13.026$ and $10! \approx \mathrm{e}^{13.026} = \boxed{4.54\times10^{5}}$

(iii) According to Stirling's better approximation [15A.2a],

$$x! \approx (2\pi)^{1/2}x^{x+1/2}\mathrm{e}^{-x} \qquad \text{so} \qquad 10! \approx (2\pi)^{1/2}10^{10.5}\mathrm{e}^{-10} = \boxed{3.60\times10^{6}}$$

15A.3(b) For two non-degenerate levels,

$$\frac{N_2}{N_1} = \frac{\mathrm{e}^{-\beta\varepsilon_2}}{\mathrm{e}^{-\beta\varepsilon_1}} = \mathrm{e}^{-\beta(\varepsilon_2-\varepsilon_1)} = \mathrm{e}^{-\beta\Delta\varepsilon} = \mathrm{e}^{-\Delta\varepsilon/kT} \qquad \left[\text{15A.7a with } \beta = \frac{1}{kT}\right]$$

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.

15A.4(b) For two non-degenerate levels,

$$\frac{N_2}{N_1} = \frac{\mathrm{e}^{-\beta\varepsilon_2}}{\mathrm{e}^{-\beta\varepsilon_1}} = \mathrm{e}^{-\beta(\varepsilon_2-\varepsilon_1)} = \mathrm{e}^{-\beta\Delta\varepsilon} = \mathrm{e}^{-\Delta\varepsilon/kT} \qquad \left[\text{15A.7a with } \beta = \frac{1}{kT}\right]$$

so $\ln\frac{N_2}{N_1} = -\frac{\Delta\varepsilon}{kT}$ and $T = -\frac{\Delta\varepsilon}{k\ln\frac{N_2}{N_1}}$

Thus $T = -\frac{6.626\times10^{-34}\ \mathrm{J\ s}\times2.998\times10^{10}\ \mathrm{cm\ s^{-1}}\times300\ \mathrm{cm^{-1}}}{1.381\times10^{-23}\ \mathrm{J\ K^{-1}}\times\ln(1/2)} = \boxed{623\ \mathrm{K}}$

15A.5(b) See Example 15A.1. The ratio of populations of a particular *state* at the $J = 5$ level to the population of the non-degenerate $J = 0$ level is

$$\frac{N_2}{N_1} = \frac{\mathrm{e}^{-\beta\varepsilon_2}}{\mathrm{e}^{-\beta\varepsilon_1}} = \mathrm{e}^{-\beta(\varepsilon_2-\varepsilon_1)} = \mathrm{e}^{-\beta\Delta\varepsilon} = \mathrm{e}^{-\Delta\varepsilon/kT} \qquad \left[15\text{A.7a with } \beta = \frac{1}{kT}\right]$$

Because all of the states of a degenerate level are equally likely, the ratio of populations of a particular *level* is

$$\frac{N_5}{N_0} = \frac{g_5\mathrm{e}^{-\beta\varepsilon_5}}{g_0\mathrm{e}^{-\beta\varepsilon_0}} = \frac{g_5}{g_0}\mathrm{e}^{-(\varepsilon_5-\varepsilon_0)/kT}$$

The degeneracy of spherical rotor energy levels are

$g_J = (2J+1)^2$,

and its energy levels are [12B.8]

$$\varepsilon_J = hc\tilde{B}J(J+1)$$

Thus, using $kT/hc = 207.224\ \mathrm{cm^{-1}}$ at 298.15 K,

$$\frac{N_5}{N_0} = \frac{g_5}{g_0}\mathrm{e}^{-5(5+1)hc\tilde{B}/kT} = \frac{(2\times5+1)^2}{(2\times0+1)^2}\mathrm{e}^{-5(5+1)\times2.71\ \mathrm{cm^{-1}}/207.224\ \mathrm{cm^{-1}}}$$

$$= \boxed{81.7}\ .$$

15A.6(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

$$\frac{N_2}{N_1} = \frac{\mathrm{e}^{-\beta\varepsilon_2}}{\mathrm{e}^{-\beta\varepsilon_1}} = \mathrm{e}^{-\beta(\varepsilon_2-\varepsilon_1)} = \mathrm{e}^{-\beta\Delta\varepsilon} = \mathrm{e}^{-\Delta\varepsilon/kT} \qquad \left[15\text{A.7a with } \beta = \frac{1}{kT}\right]$$

Because each state at a given level is equally likely, the population ratio of the *levels* is

$$\frac{N_2}{N_1} = \frac{g_2\mathrm{e}^{-\beta\varepsilon_2}}{g_1\mathrm{e}^{-\beta\varepsilon_1}}[15\text{A.7b}] = \frac{g_2}{g_1}\mathrm{e}^{-\Delta\varepsilon/kT}$$

Assuming that other states (if any) are negligibly populated,

$$\ln\frac{N_2}{N_1} = \ln\frac{g_2}{g_1} - \frac{\Delta\varepsilon}{kT} \qquad \text{and} \qquad T = -\frac{\Delta\varepsilon}{k\ln\dfrac{N_2g_1}{g_2N_1}}$$

Thus $$T = -\frac{6.626\times10^{-34}\ \mathrm{J\ s}\times2.998\times10^{10}\ \mathrm{cm\ s^{-1}}\times360\ \mathrm{cm^{-1}}}{1.381\times10^{-23}\ \mathrm{J\ K^{-1}}\times\ln\left(\dfrac{15\times1}{(100-15)\times2}\right)} = \boxed{21\bar{3}\ \mathrm{K}}$$

Solutions to problems

15A.2 For a configuration to resemble an exponential decay, populations of successively higher states must be no greater than the previous state. In this entire list, the only configuration that meets this criterion is $\boxed{\{4,2,2,1,0,0,0,0,0,0\}}$. This is the configuration we anticipate will be most likely.

We draw up the following table:

0	ε	2ε	3ε	4ε	5ε	6ε	7ε	8ε	9ε	$\mathcal{W}$
8	0	0	0	0	0	0	0	0	1	9
7	1	0	0	0	0	0	0	1	0	72
7	0	1	0	0	0	0	1	0	0	72
7	0	0	1	0	0	1	0	0	0	72
7	0	0	0	1	1	0	0	0	0	72
6	2	0	0	0	0	0	1	0	0	252
6	0	2	0	0	1	0	0	0	0	252

6	0	0	3	0	0	0	0	0	0	84
6	1	0	0	2	0	0	0	0	0	252
6	1	1	0	0	0	1	0	0	0	504
6	1	0	1	0	1	0	0	0	0	504
6	0	1	1	1	0	0	0	0	0	504
5	3	0	0	0	0	1	0	0	0	504
5	0	3	1	0	0	0	0	0	0	504
5	2	1	0	0	1	0	0	0	0	1512
5	2	0	1	1	0	0	0	0	0	1512
5	1	2	0	1	0	0	0	0	0	1512
5	1	1	2	0	0	0	0	0	0	1512
4	4	0	0	0	1	0	0	0	0	630
4	3	1	0	1	0	0	0	0	0	2520
4	3	0	2	0	0	0	0	0	0	1260
4	2	2	1	0	0	0	0	0	0	3780
3	5	0	0	1	0	0	0	0	0	504
3	4	1	1	0	0	0	0	0	0	2520
2	6	0	1	0	0	0	0	0	0	252
2	5	2	0	0	0	0	0	0	0	756
1	7	1	0	0	0	0	0	0	0	72
0	9	0	0	0	0	0	0	0	0	1

Indeed, the “most exponential” distribution, {4,2,2,1,0,0,0,0,0,0}, is the most likely:

$$\mathcal{W} = \frac{N!}{N_0!N_1!N_2!\ \cdots}[15\text{A}.1] = \frac{9!}{4!2!2!1!} = \boxed{3780}$$

15A.4 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

$$\frac{N_1}{N_0} = \frac{g_1\mathrm{e}^{-\varepsilon_1/kT}}{g_0\mathrm{e}^{-\varepsilon_0/kT}}[15\text{A}.7\text{b}] = \frac{4}{2}\times\mathrm{e}^{-\Delta\varepsilon/kT} = 2\mathrm{e}^{-hc\tilde{\nu}/kT} = 2\mathrm{e}^{-\{(1.4388\times450)/300\}} = 0.23$$

The observed ratio is $\dfrac{0.30}{0.70} = 0.43$. Hence the populations are $\boxed{\text{not at equilibrium}}$.

15A.6 **(a)** The probability of finding a molecule in state j is

$$p_j = \frac{N_j}{N} = \frac{\mathrm{e}^{-\beta\varepsilon_j}}{q}[15\text{A}.6]$$

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

$$-j\beta\varepsilon = \ln N_j - \ln N + \ln q \qquad \text{and} \qquad \ln N_j = \ln N - \ln q - j\beta\varepsilon = \boxed{\ln\frac{N}{q} - \frac{j\varepsilon}{kT}}$$

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 15A.2

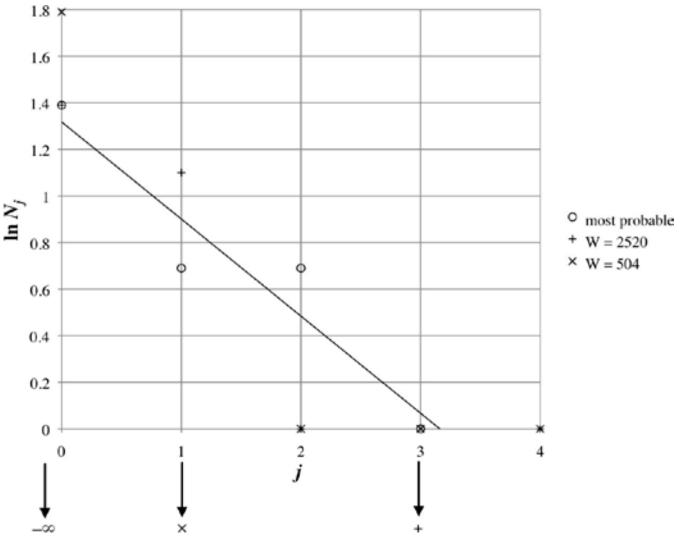
j	0	1	2	3
N_j	4	2	2	1
$\ln N_j$	1.39	0.69	0.69	0

[most probable configuration]

These are points plotted in Figure 15A.1 (full line). The slope is –0.416, and since $\frac{\varepsilon}{hc} = 50\,\text{cm}^{-1}$, the slope corresponds to a temperature

$$T = \frac{(50\,\text{cm}^{-1}) \times (2.998 \times 10^{10}\ \text{cm s}^{-1}) \times (6.626 \times 10^{-34}\ \text{J s})}{(0.416) \times (1.381 \times 10^{-23}\ \text{J K}^{-1})} = \boxed{163\ \text{K}}$$

Figure 15A.1



(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—even without considering the points represented by the unoccupied states.

15A.8 If the atmosphere were at equilibrium, then the Boltzmann distribution would apply, so the relative populations per unit volume would be

$$\frac{N_i}{N_j} = \frac{e^{-\beta\varepsilon_i}}{e^{-\beta\varepsilon_j}} = e^{-(\varepsilon_j-\varepsilon_i)/kT} \qquad \left[15\text{A.7a with } \beta = \frac{1}{kT}\right]$$

What distinguishes the states and energies of molecules in a planet's gravitational field is the distance r from the center of the planet. The energy is gravitational, measured from the ground-state energy

$$\varepsilon(r) = V(r) - V(r_0) = -GMm\left(\frac{1}{r} - \frac{1}{r_0}\right)$$

Note that the ground-state energy is literally the energy at the ground—or more precisely at the lowest point of the atmosphere, r_0 .

so $$\frac{N(r)}{N(r_0)} = \mathrm{e}^{-\{V(r)-V(r_0)\}/kT}$$

Far from the planet, we have

$$\lim_{r\to\infty} \varepsilon(r) = -GMm\left(0 - \frac{1}{r_0}\right) = \frac{GMm}{r_0}$$

and $$\lim_{r\to\infty} \frac{N(r)}{N(r_0)} = \mathrm{e}^{-GMm/r_0kT}$$

Hence, if the atmosphere were at equilibrium, the farther one ventured from the planet, the concentration of molecules would tend toward a non-zero fraction of the concentration at the surface. This is obviously not the current distribution for planetary atmospheres where the corresponding limit is zero. Consequently, we may conclude that no planet's atmosphere, including Earth's, is at equilibrium.

15B Molecular partition functions

Answers to discussion questions

15B.2 For two non-degenerate levels, see *Brief Illustration* 53.1. The mean energy is

$$\langle \varepsilon \rangle = \frac{\varepsilon}{1+\mathrm{e}^{\beta\varepsilon}}$$

where ε is the energy of the upper level (and zero the energy of the lower level). At low temperatures, the $\mathrm{e}^{\beta\varepsilon}$ in the denominator makes the denominator very large and the average energy close to zero. At high temperatures, the average energy levels off at a value of $\varepsilon/2$ as the $\mathrm{e}^{\beta\varepsilon}$ term comes down to approach 1.

15B.4 The symmetry number, σ, of a molecule is the number of its indistinguishable orientations. See Table 15B.2, *Justification* 15B.4, and *Brief illustration* 15B.4. We can think of including the symmetry number in the calculation of partition functions as a way of avoiding "double counting" or "multiple counting," because one divides by σ. But double counting is not, strictly speaking, what is prevented. Indistinguishable configurations rule out certain rotational states because of the Pauli principle. (See Topic 12C.3.) The symmetry number need not be included in calculation of the rotational partition function by direct summation over states, as long as only allowed states are included in the sum; furthermore, using the symmetry number to correct a direct sum that includes forbidden states is not exact. If the high-temperature expression for the partition function is a good approximation, though, the inclusion of the symmetry number in that expression is also a good approximation.

Solutions to exercises

15B.1(b) **(i)** The thermal wavelength is [15B.7b]

$$\Lambda = \frac{h}{(2\pi mkT)^{1/2}}$$

We need the molecular mass, not the molar mass:

$$m = \frac{20.18\times10^{-3}\ \mathrm{kg\ mol^{-1}}}{6.022\times10^{23}\ \mathrm{mol^{-1}}} = 3.351\times10^{-26}\ \mathrm{kg}$$

So $$\Lambda = \frac{6.626\times10^{-34}\ \mathrm{J\,s}}{(2\pi\times3.351\times10^{-26}\ \mathrm{kg}\times1.381\times10^{-23}\ \mathrm{J\,K^{-1}}\times T)^{1/2}} = \frac{3.886\times10^{-10}\ \mathrm{m}}{(T/\mathrm{K})^{1/2}}$$

T = 300 K: $$\Lambda = \frac{3.886\times10^{-10}\ \mathrm{m}}{(300)^{1/2}} = \boxed{2.243\times10^{-11}\ \mathrm{m}} = \boxed{22.43\ \mathrm{pm}}$$

$T = 3000\ \text{K}$: $\quad \Lambda = \dfrac{3.886 \times 10^{-10}\ \text{m}}{(3000)^{1/2}} = \boxed{7.094 \times 10^{-12}\ \text{m}} = \boxed{7.094\ \text{pm}}$

(ii) The translational partition function is

$$q^{\text{T}} = \frac{V}{\Lambda^3}\ [15\text{B}.10\text{b}]$$

$T = 300\ \text{K}$: $\quad q^{\text{T}} = \dfrac{(1.00 \times 10^{-2}\ \text{m})^3}{(2.243 \times 10^{-11}\ \text{m})^3} = \boxed{8.86 \times 10^{25}}$

$T = 3000\ \text{K}$: $\quad q^{\text{T}} = \dfrac{(1.00 \times 10^{-2}\ \text{m})^3}{(7.094 \times 10^{-12}\ \text{m})^3} = \boxed{2.80 \times 10^{27}}$

15B.2(b) $\quad q^{\text{T}} = \dfrac{V}{\Lambda^3}$ [15B.10b], implying that $\dfrac{q}{q'} = \left(\dfrac{\Lambda'}{\Lambda}\right)^3$

However, $\Lambda = \dfrac{h}{(2\pi mkT)^{1/2}}[52.7\text{b}] \propto \dfrac{1}{m^{1/2}}$ so $\quad \dfrac{q}{q'} = \left(\dfrac{m}{m'}\right)^{3/2}$

Therefore, $\dfrac{q_{\text{Ar}}}{q_{\text{Ne}}} = \left(\dfrac{39.95}{20.18}\right)^{3/2} = \boxed{2.785}$

15B.3(b) The high-temperature expression for the rotational partition function of a linear molecule is

$$q^{\text{R}} = \frac{kT}{\sigma hc\tilde{B}}[15\text{B}.13\text{b}], \quad \tilde{B} = \frac{\hbar}{4\pi cI}\ [12\text{B}.7], \quad I = \mu R^2\ [\text{Table 12B.1}]$$

Hence $q = \dfrac{8\pi^2 kTI}{\sigma h^2} = \dfrac{8\pi^2 kT\mu R^2}{\sigma h^2}$

For N$_2$, $\mu = \frac{1}{2}m(\text{N}) = \frac{1}{2} \times 14.007\ m_{\text{u}} = 7.00\ m_{\text{u}}$, and $\sigma = 2$; therefore

$$q = \frac{(8\pi^2)\times(1.381\times10^{-23}\,\text{J K}^{-1})\times(300\,\text{K})\times(7.00\times1.6605\times10^{-27}\ \text{kg})\times(1.0975\times10^{-10}\ \text{m})^2}{(2)\times(6.626\times10^{-34}\,\text{J s})^2}$$

$$= \boxed{52.2}$$

15B.4(b) The high-temperature expression for the rotational partition function of a non-linear molecule is [15B.14]

$$q^{\text{R}} = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2}$$

$$= \left(\frac{1.381\times10^{-23}\ \text{J K}^{-1}\times T}{6.626\times10^{-34}\ \text{J s}\times2.998\times10^{10}\ \text{cm s}^{-1}}\right)^{3/2}\left(\frac{\pi}{27.877\times14.512\times9.285\ \text{cm}^{-3}}\right)^{1/2}$$

$$= 0.01676\times(T/\text{K})^{3/2}$$

(i) At 25°C, $\quad q^{\text{R}} = 0.01676 \times (298)^{3/2} = \boxed{86.2}$

(ii) At 100°C, $\quad q^{\text{R}} = 0.01676 \times (373)^{3/2} = \boxed{121}$

15B.5(b) The rotational partition function of a nonsymmetrical linear molecule is

$$q^{\text{R}} = \sum_J (2J+1)\text{e}^{-hc\tilde{B}J(J+1)/kT} \qquad \left[15\text{B}.11 \text{ with } \beta = \frac{1}{kT}\right]$$

Use $\quad \dfrac{hc\tilde{B}}{k} = \dfrac{6.626\times10^{-34}\ \text{J s}\times2.998\times10^{10}\ \text{cm s}^{-1}\times6.511\ \text{cm}^{-1}}{1.381\times10^{-23}\ \text{J K}^{-1}} = 9.366\ \text{K}$

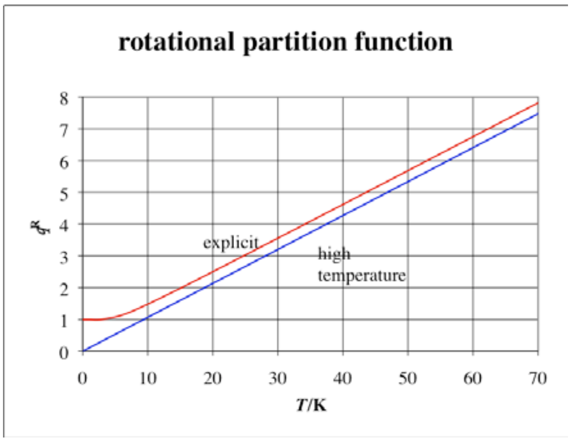
so $\quad q^{\text{R}} = \displaystyle\sum_J (2J+1)\text{e}^{-9.366\ \text{K}\times J(J+1)/T}$

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

$$q^{\text{R}} = \frac{kT}{hc\tilde{B}} = \frac{T}{9.366\ \text{K}}$$

The explicit and high-temperature expressions are compared in Figure 15B.1. The high-temperature expression reaches 95% of the explicit sum at $\boxed{62\ \mathrm{K}}$.

Figure 15B.1



15B.6(b) The rotational partition function of a spherical rotor molecule, ignoring nuclear statistics, is

$$q^{\mathrm{R}} = \sum_J g_J \mathrm{e}^{-\varepsilon_J^{\mathrm{R}}/kT}[15\mathrm{B}.1\mathrm{b}] = \sum_J (2J+1)^2 \mathrm{e}^{-hc\tilde{B}J(J+1)/kT}[12\mathrm{B}.8]$$

Use $\dfrac{hc\tilde{B}}{k} = \dfrac{6.626\times10^{-34}\ \mathrm{J\ s}\times 2.998\times10^{10}\ \mathrm{cm\ s^{-1}}\times 0.0572\ \mathrm{cm^{-1}}}{1.381\times10^{-23}\ \mathrm{J\ K^{-1}}} = 0.0823\ \mathrm{K}$

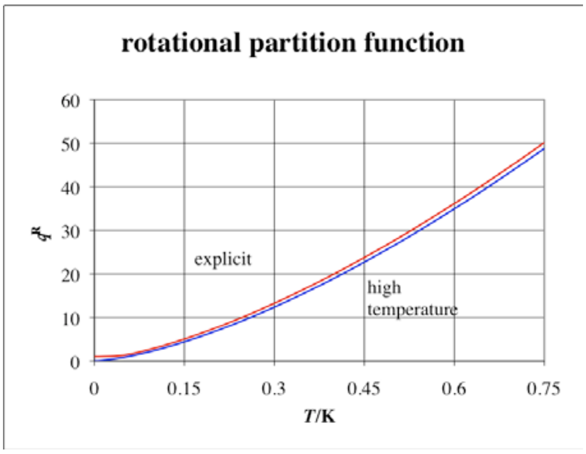
so $q^{\mathrm{R}} = \sum_J (2J+1)^2 \mathrm{e}^{-0.0823\ \mathrm{K}\times J(J+1)/T}$

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. 15B.14, with $\tilde{A} = \tilde{B} = \tilde{C}$:

$$q^{\mathrm{R}} = \pi^{1/2}\left(\frac{kT}{hc\tilde{B}}\right)^{3/2} = \pi^{1/2}\left(\frac{T}{0.0823\ \mathrm{K}}\right)^{3/2}$$

The explicit and high-temperature expressions are compared in Figure 15B.2. The high-temperature expression reaches 95% of the explicit sum at $\boxed{0.4\ \mathrm{K}}$.

Figure 15B.2



15B.7(b) The rotational partition function of a symmetric rotor molecule, ignoring nuclear statistics, is

$$q^{\mathrm{R}} = \sum_{J,K} g_{J,K} \mathrm{e}^{-\varepsilon_{J,K}^{\mathrm{R}}/kT}[15\mathrm{B}.1\mathrm{b}] = \sum_{J=0} (2J+1)\mathrm{e}^{-hc\tilde{B}J(J+1)/kT}\left(1+2\sum_{K=1}^{J}\mathrm{e}^{-hc(\tilde{A}-\tilde{B})K^2/kT}\right)[12\mathrm{B}.13]$$

Use $\frac{hc\tilde{B}}{k} = \frac{6.626\times10^{-34}\ \text{J s}\times2.998\times10^{10}\ \text{cm s}^{-1}\times9.444\ \text{cm}^{-1}}{1.381\times10^{-23}\ \text{J K}^{-1}} = 13.585\ \text{K}$, and

$$\frac{hc(\tilde{A}-\tilde{B})}{k} = \frac{6.626\times10^{-34}\ \text{J s}\times2.998\times10^{10}\ \text{cm s}^{-1}\times(6.196-9.444)\ \text{cm}^{-1}}{1.381\times10^{-23}\ \text{J K}^{-1}} = -4.672\ \text{K}$$

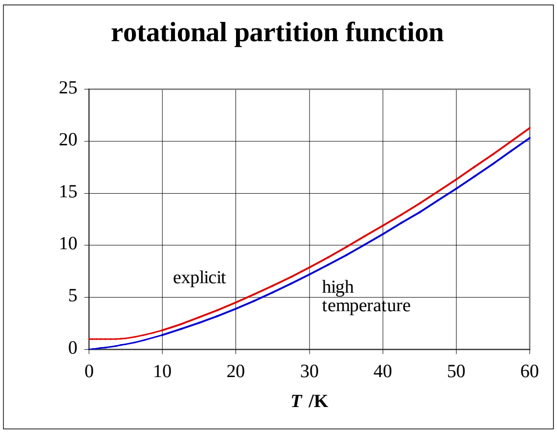
so $$q^{\text{R}} = \sum_{J=0}(2J+1)\text{e}^{-13.585\ \text{K}\times J(J+1)/T}\left(1+2\sum_{K=1}^{J}\text{e}^{+4.672\ \text{K}\times K^2/T}\right)$$

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 spreadsheets are more unwieldy. Compare the results of the direct sum with the high-temperature expression, eqn. 15B.14, with $\tilde{B} = \tilde{C}$:

$$q^{\text{R}} = \left(\frac{\pi}{\tilde{A}}\right)^{1/2}\left(\frac{kT}{hc}\right)^{3/2}\frac{1}{\tilde{B}}$$

The explicit and high-temperature expressions are compared in Figure 15B.3. The high-temperature expression reaches 95% of the explicit sum at $\boxed{55\ \text{K}}$.

Figure 15B.3



15B.8(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 σ = 2 if the molecule has inversion symmetry and 1 otherwise). The rotational subgroup contains only rotational operations and the identity. See Problem 15B.9.

(i) CO_2: Full group $D_{\infty h}$; subgroup C_2; hence $\sigma = \boxed{2}$

(ii) O_3: Full group C_{2v}; subgroup C_2; $\sigma = \boxed{2}$

(iii) SO_3: Full group D_{3h}; subgroup $\{E, C_3, C_3^{\,2}, 3C_2\}$; $\sigma = \boxed{6}$

(iv) SF_6: Full group O_h; subgroup O; $\sigma = \boxed{24}$

(v) Al_2Cl_6: Full group D_{2d}; subgroup D_2; $\sigma = \boxed{4}$

15B.9(b) Pyridine belongs to the C_{2v} group, the same as water, so σ = 2. The high-temperature expression for the rotational partition function of a non-linear molecule is [15B.14]

$$q^{\text{R}} = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2}$$

$$= \frac{1}{2}\left(\frac{1.381\times10^{-23}\ \text{J K}^{-1}\times298.15\ \text{K}}{6.626\times10^{-34}\ \text{J s}\times2.998\times10^{10}\ \text{cm s}^{-1}}\right)^{3/2}\left(\frac{\pi}{0.2014\times0.1936\times0.0987\ \text{cm}^{-3}}\right)^{1/2}$$

$$= \boxed{4.26\times10^{4}}$$

15B.10(b) The partition function for a mode of molecular vibration is

$$q^{\text{V}} = \sum_{v}\text{e}^{-vhc\tilde{\nu}/kT} = \frac{1}{1-\text{e}^{-hc\tilde{\nu}/kT}} \quad [\text{15B.15 with } \beta = 1/kT]$$

Use $$\frac{hc\tilde{\nu}}{k} = \frac{6.626\times10^{-34}\text{ J s}\times 2.998\times10^{10}\text{ cm s}^{-1}\times 214.5\text{ cm}^{-1}}{1.381\times10^{-23}\text{ J K}^{-1}} = 308.5\text{ K}$$

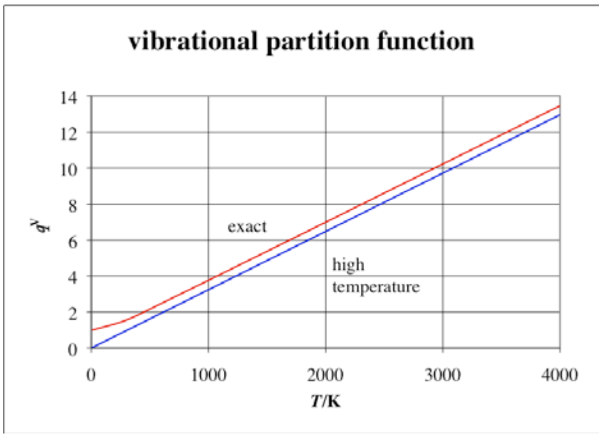
so $$q^{\mathrm{V}} = \sum_{v} \mathrm{e}^{-vhc\tilde{\nu}/kT} = \frac{1}{1-\mathrm{e}^{-308.5\text{ K}/T}}$$

The high-temperature expression is

$$q^{\mathrm{V}} = \frac{kT}{hc\tilde{\nu}} = \frac{T}{464.9\text{ K}} \quad [15\mathrm{B}.16]$$

The explicit and high-temperature expressions are compared in Figure 15B.4. The high-temperature expression reaches 95% of the explicit sum at $\boxed{3000\text{ K}}$.

Figure 15B.4



15B.11(b) The partition function for a mode of molecular vibration is

$$q^{\mathrm{V}} = \frac{1}{1-\mathrm{e}^{-hc\tilde{\nu}/kT}} \quad [15\mathrm{B}.15 \text{ with } \beta = 1/kT]$$

and the overall vibrational partition function is the product of the partition functions of the individual modes. (See Example 15B.2.) We draw up the following table:

mode	1	2	3	4
$\tilde{\nu}$ / cm^{-1}	3311	712	712	2097
$hc\tilde{\nu}/kT$	5.292	1.138	1.138	3.352
$q^{\mathrm{V}}{}_{\text{mode}}$	1.005	1.472	1.472	1.036

The overall vibrational partition function is

$$q^{\mathrm{V}} = 1.005 \times 1.472 \times 1.472 \times 1.036 = \boxed{2.256}$$

15B.12(b) The partition function for a mode of molecular vibration is

$$q^{\mathrm{V}} = \frac{1}{1-\mathrm{e}^{-hc\tilde{\nu}/kT}} \quad [15\mathrm{B}.15 \text{ with } \beta = 1/kT]$$

and the overall vibrational partition function is the product of the partition functions of the individual modes. (See Example 15B.2.) We draw up the following table, including the degeneracy of each level:

mode	1	2	3	4
$\tilde{\nu}$ / cm^{-1}	178	90	555	125
g_{mode}	1	2	3	3
$hc\tilde{\nu}/kT$	0.512	0.259	1.597	0.360
$q^{\mathrm{V}}{}_{\text{mode}}$	2.50	4.38	1.254	3.31

The overall vibrational partition function is

$$q^{\mathrm{V}}{}_{\text{mode}} = 2.50 \times 4.38^2 \times 1.254^3 \times 3.31^3 = \boxed{3.43\times10^3}$$

15B.13(b) $q=\sum_{\text{levels}} g_j \mathrm{e}^{-\beta\varepsilon_j}[15\mathrm{B.1b}]=\sum_{\text{levels}} g_j \mathrm{e}^{-hc\tilde{\nu}_j/kT} = 4+\mathrm{e}^{-hc\tilde{\nu}_1/kT}+2\mathrm{e}^{-hc\tilde{\nu}_2/kT}$

where $\dfrac{hc\tilde{\nu}_j}{kT}=\dfrac{6.626\times10^{-34}\ \mathrm{J\ s}\times2.998\times10^{10}\ \mathrm{cm\ s^{-1}}\times\tilde{\nu}_j}{1.381\times10^{-23}\ \mathrm{J\ K^{-1}}\times2000\ \mathrm{K}}=7.192\times10^{-4}\times(\tilde{\nu}_j/\mathrm{cm^{-1}})$

Therefore,

$$q=3+\mathrm{e}^{-7.192\times10^{-4}\times850}+5\mathrm{e}^{-7.192\times10^{-4}\times1100}=3+0.543+5\times0.453=\boxed{5.809}$$

The individual terms in the last expression are the relative populations of the levels, namely 5×0.453 to 0.543 to 3 (second excited level to first to ground) or $\boxed{0.756{:}0.181{:}1}$.

Solutions to problems

15B.2 According to the "integral" approximation

$$q^{\mathrm{T}}=\frac{X}{\Lambda}=\frac{(2\pi mkT)^{1/2}X}{h}\ [15\mathrm{B.10b}],$$

and hence, for an H atom in a one-dimensional 100-nm box, when $q^{\mathrm{T}}=10$,

$$T=\left(\frac{1}{2\pi mk}\right)\times\left(\frac{q^{\mathrm{T}}h}{X}\right)^2$$

$$=\left(\frac{1}{2\pi\times1.008\times1.6605\times10^{-27}\,\mathrm{kg}\times1.381\times10^{-23}\,\mathrm{J\ K^{-1}}}\right)\times\left(\frac{10\times6.626\times10^{-34}\ \mathrm{J\ s}}{100\times10^{-9}\ \mathrm{m}}\right)^2$$

$$=\boxed{0.030\ \mathrm{K}}$$

The exact partition function in one dimension is

$$q^{\mathrm{T}}=\sum_{n=1}^{\infty}\mathrm{e}^{-(n^2-1)h^2\beta/8mL^2}=\mathrm{e}^{h^2\beta/8mL^2}\sum_{n=1}^{\infty}(\mathrm{e}^{-h^2\beta/8mL^2})^{n^2}\ [15\mathrm{B.1a}]$$

For our H atom,

$$\frac{h^2\beta}{8mL^2}=\frac{(6.626\times10^{-34}\,\mathrm{J\ s})^2}{8\times1.008\times1.6605\times10^{-27}\,\mathrm{kg}\times1.381\times10^{-23}\,\mathrm{J\ K^{-1}}\times0.030\ \mathrm{K}\times(100\times10^{-9}\,\mathrm{m})^2}$$

$$=7.9\times10^{-3}$$

and $\quad \mathrm{e}^{h^2\beta/8mL^2}=\mathrm{e}^{7.9\times10^{-3}}=1.008\ ,\quad \mathrm{e}^{-h^2\beta/8mL^2}=\mathrm{e}^{-7.9\times10^{-3}}=0.992$

Then $\quad q^{\mathrm{T}}=1.008\times\sum_{n=1}^{\infty}(0.992)^{n^2}=1.008\times(0.992+0.969+0.932+\ldots)=\boxed{9.57}$

Comment. Even under these conditions, the integral approximation is less than 5% from the explicit sum.

15B.4 **(a)** First, evaluate the partition function

$$q=\sum_j g_j\mathrm{e}^{-\beta\varepsilon_j}[15\mathrm{B.1b}]=\sum_j g_j\mathrm{e}^{-hc\beta\tilde{\nu}_j}$$

At 3287°C = 3560 K, $hc\beta=hc\beta=\dfrac{6.626\times10^{-34}\ \mathrm{J\ s}\times2.998\times10^{10}\ \mathrm{cm\ s^{-1}}}{1.381\times10^{-23}\ \mathrm{J\ K^{-1}}\times3560\,\mathrm{K}}=4.041\times10^{-4}\ \mathrm{cm}$

$$q=5+7\mathrm{e}^{-\{(4.041\times10^{-4}\,\mathrm{cm})\times(170\,\mathrm{cm^{-1}})\}}+9\mathrm{e}^{-\{(4.041\times10^{-4}\,\mathrm{cm})\times(387\,\mathrm{cm^{-1}})\}}+3\mathrm{e}^{-\{(4.041\times10^{-4}\,\mathrm{cm})\times(6557\,\mathrm{cm^{-1}})\}}$$

$$=5+7\times(0.934)+9\times(0.855)+3\times(0.0707)=19.444$$

The fractions of molecules in the various energy levels are [15A.6, with degeneracy g_j included]

$$\frac{N_j}{N}=\frac{g_j\mathrm{e}^{-\beta\varepsilon_j}}{q}=\frac{g_j\mathrm{e}^{-hc\beta\tilde{\nu}_j}}{q}$$

$$\frac{N({}^3\mathrm{F}_2)}{N}=\frac{5}{19.444}=\boxed{0.257}\qquad\frac{N({}^3\mathrm{F}_3)}{N}=\frac{7\times(0.934)}{19.444}=\boxed{0.336}$$

$$\frac{N({}^3\mathrm{F}_4)}{N}=\frac{9\times(0.855)}{19.444}=\boxed{0.396}\qquad\frac{N({}^4\mathrm{F}_1)}{N}=\frac{3\times(0.0707)}{19.444}=\boxed{0.011}$$

Comment. $\sum_j \frac{N_j}{N} = 1$. Note that the most highly populated level is not the lowest level.

15B.6 The absorption lines are the values of differences in adjacent rotational terms. The wavenumbers of the lines are [42.8a]

$$\tilde{\nu}(J+1 \leftarrow J) = \tilde{F}(J+1) - \tilde{F}(J) = 2\tilde{B}(J+1)$$

for J = 0, 1, ... Therefore, we can find the rotational constant and reconstruct the energy levels from the data. To make use of all of the data, one would plot the wavenumbers, which represent $\tilde{\nu}(J+1 \leftarrow J)$ vs. J; from the above equation, the slope of that linear plot is $2\tilde{B}$. Inspection of the data show that the lines in the spectrum are equally spaced with a separation of 21.19 cm^{-1}, so that is the slope:

$$\text{slope} = 21.19\ \text{cm}^{-1} = 2\tilde{B} \quad \text{so} \quad \tilde{B} = 10.59\overline{5}\ \text{cm}^{-1}$$

The partition function is

$$q = \sum_J g_J \mathrm{e}^{-\beta\varepsilon_J} = \sum_{J=0}^{\infty}(2J+1)\mathrm{e}^{-\beta E(J)}\ [15\text{B}.1\text{b}] \text{ where } \quad E(J) = hc\tilde{B}J(J+1)\ [41.15]$$

and the factor of $2J+1$ is the degeneracy of the energy levels.

At 25°C, $hc\tilde{B}\beta = \frac{hc\tilde{B}}{kT} = \frac{6.626\times10^{-34}\ \text{J s}\times2.998\times10^{10}\ \text{cm s}^{-1}\times10.59\overline{5}\,\text{cm}^{-1}}{1.381\times10^{-23}\ \text{J K}^{-1}\times298.15\ \text{K}} = 0.05112$

$$q = \sum_{J=0}^{\infty}(2J+1)\mathrm{e}^{-0.05112J(J+1)}$$

$$= 1 + 3\mathrm{e}^{-0.05112\times1\times2} + 5\mathrm{e}^{-0.05112\times2\times3} + 7\mathrm{e}^{-0.05112\times3\times4} + \cdots$$

$$= 1 + 2.708 + 3.679 + 3.791 + 3.238 + \cdots = \boxed{19.90}$$

15B.8 **(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:

$$E_n = \left(1 - \frac{1}{n^2}\right)hc\tilde{R}_{\mathrm{H}}, \qquad n = 1, 2, 3, ..., \infty$$

which is given by eqn. 9A.14 with the zero of energy redefined as the energy of the n = 1 state. (The usual zero is taken to be the electrostatic energy of a proton and electron at infinite separation). 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.

$$q^{\mathrm{E}} = \sum_{n=1}^{\infty} g_n \mathrm{e}^{-E_n/kT} = 2\sum_{n=1}^{\infty} n^2 \mathrm{e}^{-\left(1-\frac{1}{n^2}\right)C}\ [15\text{B}.1\text{b}]$$

where $C = hc\tilde{R}_{\mathrm{H}} / kT_{\text{photosphere}} = 27.301$. q^{E}, when written as an infinite sum, is infinitely large because $\lim_{n\to\infty} n^2 e^{-\left(1-\frac{1}{n^2}\right)C} = \lim_{n\to\infty} n^2 e^{-C} = e^{-C}\lim_{n\to\infty} n^2 = \infty$

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

$$\delta E_n = \frac{\hbar}{\tau} = z_n\hbar\ \text{[Topic 12A.2(b)]}$$

where the last equality employs the collision frequency (derived in Topic 1B). The collision frequency of the nth state of an atomic perfect gas is given by

$$z_n = \frac{\sigma_n v_{\text{rel}} p}{kT}[1\text{B}.11\text{b}] = \frac{2^{1/2}\sigma_n v_{\text{mean}} p}{kT}[1\text{B}.10\text{a}] = \frac{2^{1/2}\sigma_n v_{\text{mean}}\rho N_{\mathrm{A}}}{M_{\mathrm{H}}}$$

The mean speed is [1B.8]

$$v_{\text{mean}} = \left(\frac{8RT}{\pi M}\right)^{1/2} = 1.106\times10^4\ \text{m s}^{-1}$$

The collision cross-section is

$$\sigma_n = \pi d^2[\text{Topic 1B.2(a)}] = \pi(r_n + a_0)^2$$

From Example 9A.2, the mean radius of a hydrogen atom with principal quantum number *n* might be surmised to be

$$r_n = \frac{3n^2 a_0}{2}$$

In fact, this is true of *n*s orbitals, which is good enough for this problem. So the collision cross-section is

$$\sigma_n = \pi a_0^2\left(\frac{3n^2+2}{2}\right)^2$$

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

$$E_{n_{\max}} = E_\infty - \delta E_{n_{\max}}$$

$$\left(1-\frac{1}{n_{\max}^2}\right)hc\tilde{R}_{\text{H}} = hc\tilde{R}_{\text{H}} - \frac{2^{1/2}\pi a_0^2\left(\dfrac{3n_{\max}^2+2}{2}\right)^2 v_{\text{mean}}\rho N_{\text{A}}\hbar}{M_{\text{H}}}$$

with $\rho = 1.99\times10^{-4}$ kg m^{-3} and $M_{\text{H}} = 1.01\times10^{-3}$ kg mol^{-1} .

The root function of a calculator or mathematical software may be used to solve this equation for $n_{\max}$:

$\boxed{n_{\max} = 28}$ for atomic hydrogen of the photosphere

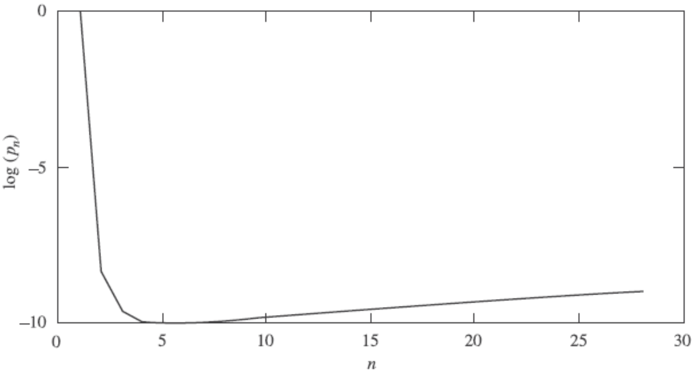
Furthermore, examination of the partition function terms $n = 2, 3, \ldots, n_{\max}$ indicates that they are negligibly small and may be discarded. The point is that very large *n* values should not be included in q^{E} because they do not reflect reality.

(c) The equilibrium probability of finding a hydrogen atom in energy level *n* is [15A.6 with degeneracy]

$$p_n = \frac{N_n}{N} = \frac{g_n \text{e}^{-\beta\varepsilon_v}}{q} = \frac{2n^2\text{e}^{-E_n/kT}}{q^{\text{E}}}$$

where $T = 5780$ K. (Note: the probability for each distinct **state** omits the factor of $2n^2$.) This function is plotted in Figure 15B.5.

Figure 15B.5



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).

15C Molecular energies

Solutions to exercises

15C.1(b) The mean energy is

$$\langle \varepsilon \rangle = \frac{1}{q}\sum_i \varepsilon_i \mathrm{e}^{-\beta\varepsilon_i}[15\mathrm{C}.2] = \frac{\sum_i \varepsilon_i \mathrm{e}^{-\beta\varepsilon_i}}{\sum_i \mathrm{e}^{-\beta\varepsilon_i}} = \frac{\varepsilon \mathrm{e}^{-\beta\varepsilon}}{1+\mathrm{e}^{-\beta\varepsilon}} = \frac{\varepsilon}{1+\mathrm{e}^{\beta\varepsilon}},$$

where the last expression specializes to two non-degenerate levels. Substitute

$$\varepsilon = hc\tilde{\nu} = 6.626\times10^{-34}\ \mathrm{J\,s}\times 2.998\times10^{10}\ \mathrm{cm\,s^{-1}}\times 600\ \mathrm{cm^{-1}} = 1.192\times10^{-20}\ \mathrm{J}$$

and $$\beta\varepsilon = \frac{\varepsilon}{kT} = \frac{1.192\times10^{-20}\ \mathrm{J}}{1.381\times10^{-23}\ \mathrm{J\,K^{-1}}\times 400\ \mathrm{K}} = 2.158$$

so $$\langle \varepsilon \rangle = \frac{1.192\times10^{-20}\ \mathrm{J}}{1+\mathrm{e}^{2.158}} = \boxed{1.235\times10^{-21}\ \mathrm{J}}$$

15C.2(b) The mean energy is

$$\langle \varepsilon \rangle = \frac{1}{q}\sum_{\text{states}} \varepsilon_i \mathrm{e}^{-\beta\varepsilon_i}[15\mathrm{C}.2] = \frac{1}{q}\sum_{\text{levels}} g_i\varepsilon_i \mathrm{e}^{-\beta\varepsilon_i} = \frac{1}{q}\sum_J (2J+1)\varepsilon_J \mathrm{e}^{-\varepsilon_J/kT}$$

$$\varepsilon_J = hc\tilde{B}J(J+1) = 6.626\times10^{-34}\ \mathrm{J\,s}\times 2.998\times10^{10}\ \mathrm{cm\,s^{-1}}\times 6.511\ \mathrm{cm^{-1}}\times J(J+1)$$

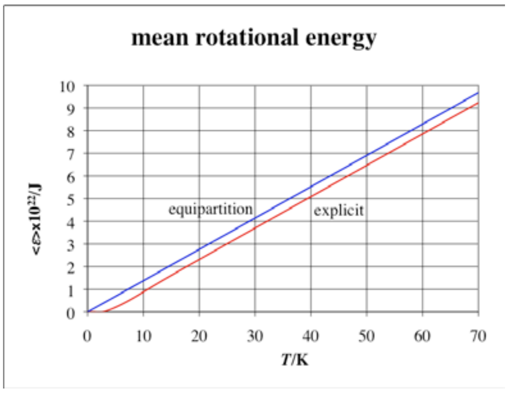
$$= J(J+1)\times 1.293\times10^{-22}\ \mathrm{J}$$

and $$\frac{\varepsilon_J}{k} = \frac{J(J+1)\times 1.293\times10^{-22}\ \mathrm{J}}{1.381\times10^{-23}\ \mathrm{J\,K^{-1}}} = J(J+1)\times 9.366\ \mathrm{K}$$

so $$\langle \varepsilon \rangle = \frac{1}{q}\sum_J J(J+1)(2J+1)\times 1.293\times10^{-22}\ \mathrm{J}\times \mathrm{e}^{-J(J+1)\times 9.366\ \mathrm{K}/T}$$

Use a spreadsheet or other mathematical software to evaluate the terms of the sum and to sum the terms until they converge. For the partition function, see Exercise 15B.5(b). The equipartition value is simply kT (*i.e.*, $kT/2$ for each rotational degree of freedom). The explicit and equipartition expressions are compared in Figure 15C.1. The explicit sum reaches 95% of the equipartition value at about $\boxed{63\ \mathrm{K}}$.

Figure 15C.1



15C.3(b) The mean energy is

$$\langle \varepsilon \rangle = \frac{1}{q}\sum_{\text{states}} \varepsilon_i \mathrm{e}^{-\beta\varepsilon_i}[15\mathrm{C}.2] = \frac{1}{q}\sum_{\text{levels}} g_i\varepsilon_i \mathrm{e}^{-\beta\varepsilon_i} = \frac{1}{\sigma q}\sum_J (2J+1)^2\varepsilon_J \mathrm{e}^{-\varepsilon_J/kT}\ [\text{Topic 12B.2(b)}]$$

Note that the sum over levels is restricted by nuclear statistics; in order to avoid multiple counting, we sum over all J without restriction and divide the result by the symmetry number σ.

$$\varepsilon_J = hc\tilde{B}J(J+1) = 6.626\times10^{-34}\ \text{J s}\times2.998\times10^{10}\ \text{cm s}^{-1}\times0.0572\ \text{cm}^{-1}\times J(J+1)$$

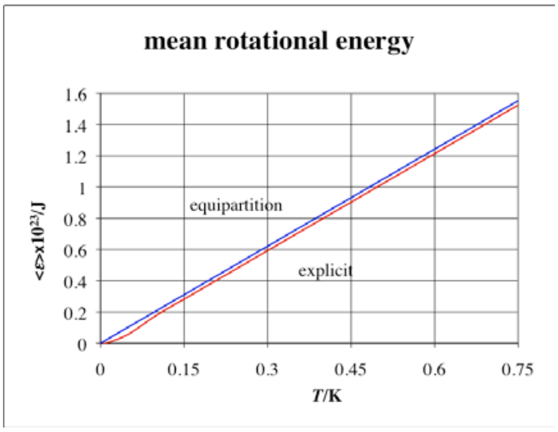
$$= J(J+1)\times1.136\times10^{-24}\ \text{J}$$

and $$\frac{\varepsilon_J}{k} = \frac{J(J+1)\times1.136\times10^{-24}\ \text{J}}{1.381\times10^{-23}\ \text{J K}^{-1}} = J(J+1)\times0.0823\ \text{K}$$

so $$\langle\varepsilon\rangle = \frac{1}{\sigma q}\sum_J J(J+1)(2J+1)^2\times1.136\times10^{-24}\ \text{J}\times \mathrm{e}^{-J(J+1)\times0.0823\ \text{K}/T}$$

Use a spreadsheet or other mathematical software to evaluate the terms of the sum and to sum the terms until they converge. For σq, see Exercise 15B.6(b). The quantity evaluated explicitly in that exercise is σq, for there we computed the partition function without taking the symmetry number into account; in effect, the sum evaluated here **and** the sum evaluated in the earlier exercise contain factors of σ, which cancel. The equipartition value is simply $3kT/2$ (*i.e.*, $kT/2$ for each rotational degree of freedom). The explicit and equipartition expressions are compared in Figure 15C.2. The explicit sum reaches 95% of the equipartition value at about $\boxed{0.27\ \text{K}}$.

Figure 15C.2



15C.4(b) The mean energy is

$$\langle\varepsilon\rangle = \frac{1}{q}\sum_{\text{states}}\varepsilon_i \mathrm{e}^{-\beta\varepsilon_i}\ [15\text{C}.2] = \frac{1}{q}\sum_{\text{levels}} g_i\varepsilon_i \mathrm{e}^{-\beta\varepsilon_i}$$

$$= \frac{1}{\sigma q}\sum_{J=0}(2J+1)\mathrm{e}^{-hc\tilde{B}J(J+1)/kT}\left(\sum_{K=-J}^{J}\varepsilon_{J,K}\mathrm{e}^{-hc(\tilde{A}-\tilde{B})K^2/kT}\right)\ [12\text{B}.13]$$

Note that the sum over levels is restricted by nuclear statistics; in order to avoid multiple counting, we sum over all J without restriction and divide the result by the symmetry number σ. (See Exercise 15C.3(b).)

$$\varepsilon_{J,K} = hc\left\{\tilde{B}J(J+1)+\left(\tilde{A}-\tilde{B}\right)K^2\right\}\ .$$

Use $$hc\tilde{B} = 6.626\times10^{-34}\ \text{J s}\times2.998\times10^{10}\ \text{cm s}^{-1}\times9.444\ \text{cm}^{-1} = 1.8760\times10^{-22}\ \text{J}$$

$$\frac{hc\tilde{B}}{k} = \frac{1.8760\times10^{-22}\ \text{J}}{1.381\times10^{-23}\ \text{J K}^{-1}} = 13.585\ \text{K}$$

$$hc\left(\tilde{A}-\tilde{B}\right) = 6.626\times10^{-34}\ \text{J s}\times2.998\times10^{10}\ \text{cm s}^{-1}\times(6.196-9.444)\ \text{cm}^{-1}$$

$$= -6.452\times10^{-23}\ \text{J}\ ,$$

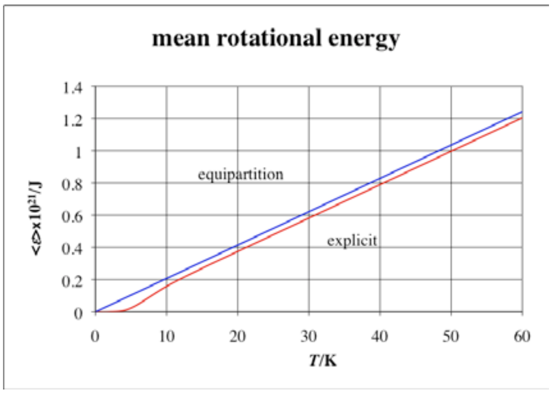
and $$\frac{hc\left(\tilde{A}-\tilde{B}\right)}{k} = \frac{-6.452\times10^{-23}\ \text{J}}{1.381\times10^{-23}\ \text{J K}^{-1}} = -4.672\ \text{K}$$

so $$\langle\varepsilon\rangle = \frac{1}{\sigma q}\sum_{J=0}(2J+1)\mathrm{e}^{-13.585\ \mathrm{K}\times J(J+1)/T}$$

$$\times\sum_{K=-J}^{J}\{J(J+1)\times 1.8760\times 10^{-22}\ \mathrm{J} - K^2\times 6.452\times 10^{-23}\ \mathrm{J}\}\mathrm{e}^{+4.672\ \mathrm{K}\times K^2/T}.$$

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 spreadsheets are more unwieldy. For σq, see Exercise 15B.7(b). The quantity evaluated explicitly in that exercise is σq, for there we computed the partition function without taking the symmetry number into account; in effect, the sum evaluated here **and** the sum evaluated in the earlier exercise contain factors of σ, which cancel. Compare the results of the direct sum with the equipartition value, namely $3kT/2$. The explicit and equipartition expressions are compared in Figure 15C.3. The explicit sum reaches 95% of the equipartition value at about $\boxed{38\ \mathrm{K}}$.

Figure 15C.3



15C.5(b) The mean vibrational energy is

$$\langle\varepsilon^{\mathrm{V}}\rangle = \frac{hc\tilde{\nu}}{\mathrm{e}^{hc\tilde{\nu}/kT}-1}\quad [15\mathrm{C}.8 \text{ with } \beta = 1/kT].$$

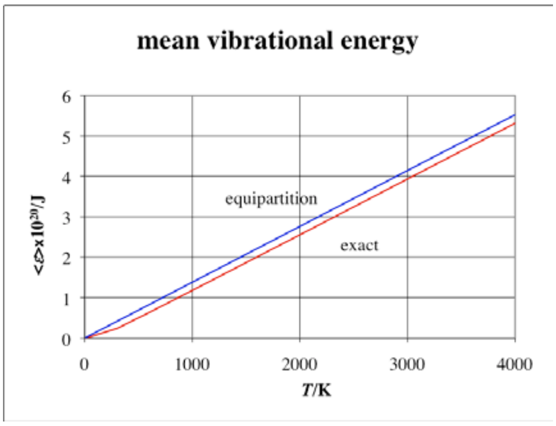
Use $hc\tilde{\nu} = 6.626\times10^{-34}\ \mathrm{J\ s}\times 2.998\times10^{10}\ \mathrm{cm\ s^{-1}}\times 214.5\ \mathrm{cm^{-1}} = 4.261\times10^{-21}\ \mathrm{J}$

and $$\frac{hc\tilde{\nu}}{k} = \frac{4.261\times10^{-21}\ \mathrm{J}}{1.381\times10^{-23}\ \mathrm{J\ K^{-1}}} = 308.5\ \mathrm{K}$$

so $$\langle\varepsilon^{\mathrm{V}}\rangle = \frac{4.261\times10^{-21}\ \mathrm{J}}{\mathrm{e}^{308.5\ \mathrm{K}/T}-1}$$

The equipartition value is simply kT for a single vibrational mode. The explicit and equipartition values are compared in Figure 15C.4. The explicit expression reaches 95% of the equipartition value at $\boxed{3000\ \mathrm{K}}$.

Figure 15C.4



15C.6(b) The mean vibrational energy per mode is

$$\langle \varepsilon^{\rm V} \rangle = \frac{hc\tilde{\nu}}{e^{hc\tilde{\nu}/kT}-1} \quad [15C.8 \text{ with } \beta = 1/kT].$$

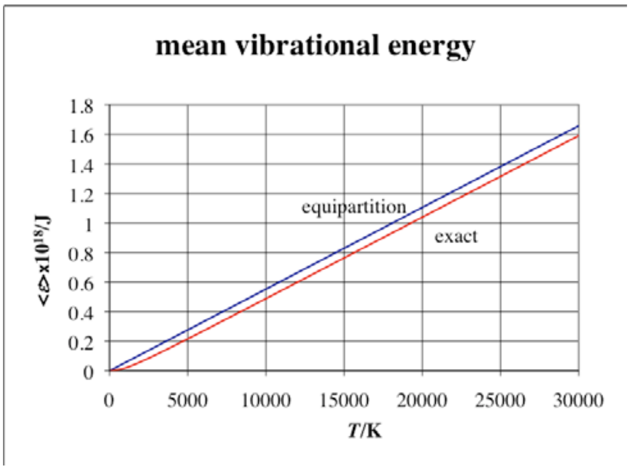
We draw up the following table:

mode	1	2	3	4
$\tilde{\nu}/\text{cm}^{-1}$	3311	712	712	2097
$hc\tilde{\nu}/(10^{-20}\text{ J})$	6.577	1.414	1.414	4.166
$(hc\tilde{\nu}/k)/\text{K}$	4763	1024	1024	3016

So $$\langle \varepsilon^{\rm V} \rangle = \frac{6.577\times10^{-20}\text{ J}}{e^{4763\text{ K}/T}-1} + 2\times\frac{1.414\times10^{-20}\text{ J}}{e^{1024\text{ K}/T}-1} + \frac{4.166\times10^{-20}\text{ J}}{e^{3016\text{ K}/T}-1}$$

The equipartition value is simply 4*kT*, that is, *kT* per vibrational mode. The explicit and equipartition values are compared in Figure 15C.5. The explicit expression reaches 95% of the equipartition value at $\boxed{24000\text{ K}}$.

Figure 15C.5



15C.7(b) The mean vibrational energy per mode is

$$\langle \varepsilon^{\rm V} \rangle = \frac{hc\tilde{\nu}}{e^{hc\tilde{\nu}/kT}-1} \quad [15C.8 \text{ with } \beta = 1/kT].$$

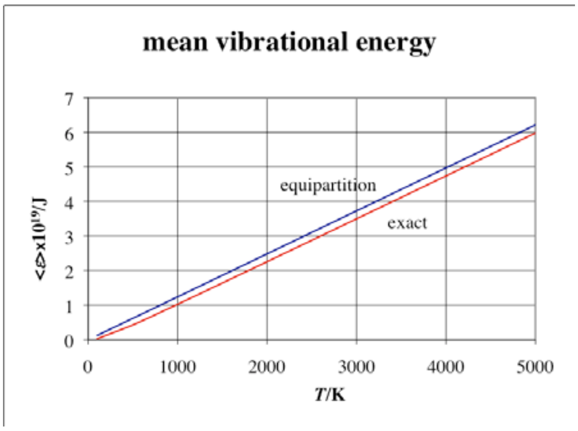
We draw up the following table:

mode	1	2	3	4
$\tilde{\nu}/\text{cm}^{-1}$	178	90	555	125
degeneracy	1	2	3	3
$hc\tilde{\nu}/(10^{-21}\text{ J})$	3.54	1.79	11.03	2.48
$(hc\tilde{\nu}/k)/\text{K}$	256	129	798	180

So $$\langle \varepsilon^{\rm V} \rangle = \frac{3.54\times10^{-21}\text{ J}}{e^{256\text{ K}/T}-1} + 2\times\frac{1.79\times10^{-21}\text{ J}}{e^{129\text{ K}/T}-1} + 3\times\frac{1.103\times10^{-20}\text{ J}}{e^{798\text{ K}/T}-1} + 3\times\frac{2.48\times10^{-21}\text{ J}}{e^{180\text{ K}/T}-1}$$

The equipartition value is simply 9*kT*, that is, *kT* per vibrational mode. The explicit and equipartition values are compared in Figure 15C.6. The explicit expression reaches 95% of the equipartition value at $\boxed{3700\text{ K}}$.

Figure 15C.6



15C.8(b) $$\langle\varepsilon\rangle = -\frac{1}{q}\frac{\partial q}{\partial\beta}[\text{15C.3}] = -\frac{1}{q}\frac{\partial}{\partial\beta}\left(3+\mathrm{e}^{-\beta\varepsilon_1}+5\mathrm{e}^{-\beta\varepsilon_2}\right) = -\frac{1}{q}\left(-\varepsilon_1\mathrm{e}^{-\beta\varepsilon_1}-5\varepsilon_2\mathrm{e}^{-\beta\varepsilon_2}\right)$$

$$= \frac{hc}{q}\left(\tilde{\nu}_1\mathrm{e}^{-\beta hc\tilde{\nu}_1}+5\tilde{\nu}_2\mathrm{e}^{-\beta hc\tilde{\nu}_2}\right) = \frac{hc}{q}\left(\tilde{\nu}_1\mathrm{e}^{-hc\tilde{\nu}_1/kT}+5\tilde{\nu}_2\mathrm{e}^{-hc\tilde{\nu}_2/kT}\right)$$

Use $\dfrac{hc\tilde{\nu}_j}{kT} = 7.192\times10^{-4}\times(\tilde{\nu}_j\,/\,\mathrm{cm}^{-1})$ and $q = 5.809$ [Exercise 15B.13b]

Thus $$\langle\varepsilon\rangle = \frac{6.626\times10^{-34}\ \mathrm{J\,s}\times2.998\times10^{10}\ \mathrm{cm\,s^{-1}}}{5.809}$$

$$\times\left(850\ \mathrm{cm^{-1}}\times\mathrm{e}^{-7.192\times10^{-4}\times850}+5\times1100\ \mathrm{cm^{-1}}\times\mathrm{e}^{-7.192\times10^{-4}\times1100}\right)$$

$$= \boxed{1.010\times10^{-20}\ \mathrm{J}}$$

Solutions to problems

15C.2 $$q = \sum_j g_j\,\mathrm{e}^{-\beta\varepsilon_j}[\text{15B.1b}] = \sum_j g_j\,\mathrm{e}^{-hc\beta\tilde{\nu}_j}$$

$$\frac{N_j}{N} = \frac{g_j\mathrm{e}^{-\beta\varepsilon_j}}{q}\ [\text{15A.6 with degeneracy included}] = \frac{g_j\mathrm{e}^{-hc\beta\tilde{\nu}_j}}{q}$$

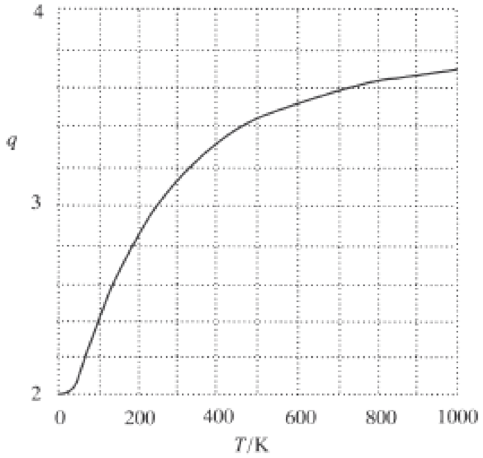
Here $$hc\beta\tilde{\nu} = \frac{hc\tilde{\nu}}{kT} = \frac{6.626\times10^{-34}\ \mathrm{J\,s}\times2.998\times10^{10}\ \mathrm{cm\,s^{-1}}\times121.1\ \mathrm{cm^{-1}}}{1.381\times10^{-23}\ \mathrm{J\,K^{-1}}\times(T/\mathrm{K})} = \frac{174.2}{T/\mathrm{K}}$$

We measure energies from the lower states and write

$$q = 2+2\mathrm{e}^{-hc\beta\tilde{\nu}} = 2+2\mathrm{e}^{-174.2/(T/\mathrm{K})}$$

This function is plotted in Figure 15C.7.

Figure 15C.7



(a) At 300 K

$$\frac{N_0}{N}=\frac{2}{q}=\frac{1}{1+\mathrm{e}^{-174.2/300}}=\boxed{0.641}$$

and $\frac{N_1}{N}=1-\frac{N_0}{N}=\boxed{0.359}$

(b) The electronic contribution to the mean molecular energy is

$$\langle\varepsilon\rangle=-\frac{1}{q}\frac{\partial q}{\partial\beta}\ [15\mathrm{C}.4\mathrm{a}]=\frac{2hc\tilde{\nu}\mathrm{e}^{-hc\beta\tilde{\nu}}}{q}$$

$$=\frac{6.626\times10^{-34}\ \mathrm{J\ s}\times2.998\times10^{10}\ \mathrm{cm\ s^{-1}}\times121.1\ \mathrm{cm^{-1}}\times\mathrm{e}^{-174.2/300}}{1+\mathrm{e}^{-174.2/300}}$$

$$=\boxed{8.63\times10^{-22}\ \mathrm{J}}$$

which corresponds to $\boxed{0.520\ \mathrm{kJ\ mol^{-1}}}$

15C.4 Mean values of any variable can be found by weighting possible values of that variable by the probability of that value. Thus, the mean of the square of energy is

$$\langle\varepsilon^2\rangle=\sum_j p_j\varepsilon_j{}^2=\sum_j\frac{\mathrm{e}^{-\beta\varepsilon_j}}{q}\varepsilon_j{}^2$$

Note that

$$-\frac{\partial}{\partial\beta}\mathrm{e}^{-\beta\varepsilon_j}=\varepsilon_j\mathrm{e}^{-\beta\varepsilon_j}\quad\text{so}\quad\frac{\partial^2}{\partial\beta^2}\mathrm{e}^{-\beta\varepsilon_j}=\varepsilon_j^2\mathrm{e}^{-\beta\varepsilon_j},$$

so $$\langle\varepsilon^2\rangle=\frac{1}{q}\sum_j\frac{\partial^2}{\partial\beta^2}\mathrm{e}^{-\beta\varepsilon_j}=\frac{1}{q}\frac{\partial^2}{\partial\beta^2}\sum_j\mathrm{e}^{-\beta\varepsilon_j}=\frac{1}{q}\frac{\partial^2 q}{\partial\beta^2}$$

Thus $$\langle\varepsilon^2\rangle^{1/2}=\boxed{\left(\frac{1}{q}\frac{\partial^2 q}{\partial\beta^2}\right)^{1/2}}\ \text{and}\ \Delta\varepsilon=\left(\langle\varepsilon^2\rangle-\langle\varepsilon\rangle^2\right)^{1/2}=\boxed{\left\{\frac{1}{q}\frac{\partial^2 q}{\partial\beta^2}-\left(\frac{1}{q}\frac{\partial q}{\partial\beta}\right)^2\right\}^{1/2}}.$$

For a harmonic oscillator, we have a closed form expression for the partition function:

$$q=\frac{1}{1-\mathrm{e}^{-\beta hc\tilde{\nu}}}\ [15\mathrm{B}.15]$$

so $$\frac{\partial q}{\partial\beta}=\frac{-hc\tilde{\nu}\mathrm{e}^{-\beta hc\tilde{\nu}}}{\left(1-\mathrm{e}^{-\beta hc\tilde{\nu}}\right)^2}\qquad\text{and}\qquad\frac{\partial^2 q}{\partial\beta^2}=\frac{(hc\tilde{\nu})^2\,\mathrm{e}^{-\beta hc\tilde{\nu}}\left(1+\mathrm{e}^{-\beta hc\tilde{\nu}}\right)}{\left(1-\mathrm{e}^{-\beta hc\tilde{\nu}}\right)^3}$$

$$\Delta\varepsilon=\left\{\frac{(hc\tilde{\nu})^2\,\mathrm{e}^{-\beta hc\tilde{\nu}}\left(1+\mathrm{e}^{-\beta hc\tilde{\nu}}\right)}{\left(1-\mathrm{e}^{-\beta hc\tilde{\nu}}\right)^2}-\left(\frac{-hc\tilde{\nu}\mathrm{e}^{-\beta hc\tilde{\nu}}}{1-\mathrm{e}^{-\beta hc\tilde{\nu}}}\right)^2\right\}^{1/2}$$

After some algebra, the expression becomes

$$\Delta\varepsilon = \boxed{\frac{hc\tilde{\nu}\mathrm{e}^{-\beta hc\tilde{\nu}/2}}{1-\mathrm{e}^{-\beta hc\tilde{\nu}}}} = \boxed{\frac{hc\tilde{\nu}}{2\sinh(\beta hc\tilde{\nu}/2)}}$$

15D The canonical ensemble

Answers to discussion questions

15D.2 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 they 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 the (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. This principle is connected to a famous assumption of Boltzmann's called the ergodic hypothesis.

15D.4 In the context of ensembles, the thermodynamic limit is the limit as the number of replications, $\tilde{N}$, approaches infinity. In that limit, the dominating configuration is overwhelmingly the most probable configuration, and its properties are essentially the same as those of the system. Note, however, that some authors use the phrase to refer to a limit of large numbers of *particles*.

Solution to exercise

15D.1(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. Solids are collections of particles that are distinguishable by their positions. The factor must be included in calculations on **(i)** $\boxed{\mathrm{CO_2\ gas}}$, but not **(ii)** graphite, **(iii)** diamond, or **(iv)** ice.

15E The internal energy and the entropy

Answers to discussion questions

15E.2 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 which indicates that $\beta \propto 1/T$ is a more natural variable than T.

15E.4 Given the statistical definition of entropy in terms of the number of configurations (microstates) consistent with a given energy [15E.7], the entropy for a collection of distinguishable particles must be greater than that of otherwise similar indistinguishable particles. If the particles are distinguishable, then exchanging, say, a pair of them would result in a different (albeit highly similar) microstate with the same energy as the original arrangement. Exchanging a pair of indistinguishable particles, however, results in not just a similar microstate, but **the same state**. That is part of what it means for particles to be indistinguishable. As a result, the number of microstates available to distinguishable particles is greater by a factor of $N!$ than the number available to indistinguishable ones, as reflected in eqns 15E.8a and 15E.8b, because $N!$ is the number of permutations of N

particles that would result in different microstates for distinguishable particles but the same microstate for indistinguishable particles.

15E.6 Residual entropy is due to the presence of some disorder in the system even at $T = 0$. It is observed in systems where there is very little energy difference—or none—between alternative arrangements of the molecules at very low temperatures. Consequently, the molecules cannot lock into a preferred orderly arrangement and some disorder persists. More precisely, more than one microstate is accessible even at the lowest temperature.

Solutions to exercises

15E.1(b) $C_{V,\mathrm{m}} = \frac{1}{2}(3 + \nu^{\mathrm{R}*} + 2\nu^{\mathrm{V}*})R$ [15E.6]

with a mode active if $T > \theta^{\mathrm{M}}$.

(i) O_3: $\nu^{\mathrm{R}*} = 3$, $\nu^{\mathrm{V}*} \approx 0$; hence $C_{V,\mathrm{m}} = \frac{1}{2}(3+3+0)R = 3R$ [experimental = $3.7R$]

(ii) C_2H_6: $\nu^{\mathrm{R}*} = 2$, $\nu^{\mathrm{V}*} \approx 1$; hence $C_{V,\mathrm{m}} = \frac{1}{2}(3+3+2\times 1)R = 4R$ [experimental = $6.3R$]

(iii) CO_2: $\nu^{\mathrm{R}*} = 2$, $\nu^{\mathrm{V}*} \approx 0$; hence $C_{V,\mathrm{m}} = \frac{1}{2}(3+2+0)R = \frac{5}{2}R$ [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.

15E.2(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 $C_{V,\mathrm{m}}/R = 3\left(\frac{1}{2}\right) + 2\left(\frac{1}{2}\right) + (3\times 3 - 6) = 5.5$ and $\gamma = \dfrac{6.5}{5.5} = \boxed{1.18}$

Without vibrations $C_{V,\mathrm{m}}/R = 3\left(\frac{1}{2}\right) + 2\left(\frac{1}{2}\right) = 2.5$ and $\gamma = \dfrac{3.5}{2.5} = \boxed{1.40}$

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.

15E.3(b) $q = \sum_j g_j \mathrm{e}^{-\beta\varepsilon_j}$, where $g = (2S+1) \times \begin{cases} 1 \text{ for } \Sigma \text{ states} \\ 2 \text{ for } \Pi,\ \Delta,\ \ldots \text{ states} \end{cases}$

At 400 K, $\beta\varepsilon = \dfrac{hc \times (7918.1\,\mathrm{cm^{-1}})}{kT} = \dfrac{(1.4388\ \mathrm{cm\ K}) \times (7918.1\,\mathrm{cm^{-1}})}{500\,\mathrm{K}} = 22.78$

The $^3\Sigma$ term is triply degenerate (from spin), and the $^1\Delta$ term is doubly (orbitally) degenerate. Hence

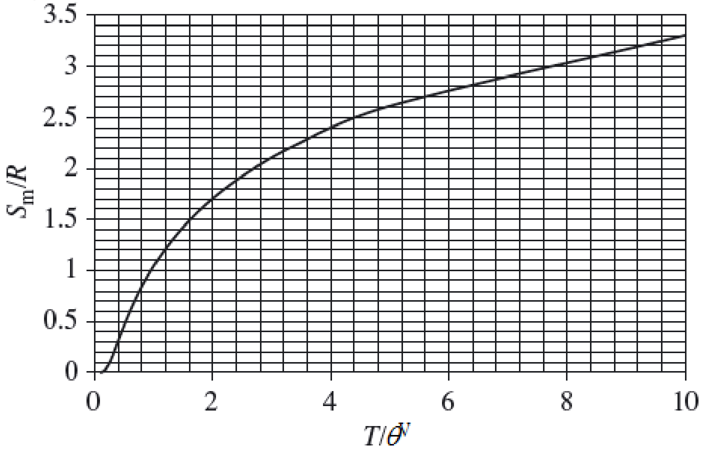
$q = 3 + 2\mathrm{e}^{-\beta\varepsilon} = 3 + 2\mathrm{e}^{-22.78} = \boxed{3.000}$

15E.4(b) The molar entropy of a collection of oscillators is given by

$$S_{\mathrm{m}} = \frac{U_{\mathrm{m}} - U_{\mathrm{m}}(0)}{T} + k\ln Q\ [\text{15E.8c}] = \frac{R(\theta^{\mathrm{V}}/T)}{\mathrm{e}^{\theta^{\mathrm{V}}/T} - 1} - R\ln(1 - \mathrm{e}^{-\theta^{\mathrm{V}}/T})\ [\text{15E.14b}]$$

where $\theta^{\mathrm{V}} = hc\tilde{\nu}/k$ is the vibrational temperature. A plot of S_{m}/R versus T/θ_{V} is shown in Figure 15E.1.

Figure 15E.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).

(i) At 298 K, $S_m = 0.708R = \boxed{5.88 \text{ J K}^{-1} \text{ mol}^{-1}}$

(ii) At 500 K, $S_m = 1.982R = \boxed{16.48 \text{ J K}^{-1} \text{ mol}^{-1}}$

15.5(b) The translational contribution to the total entropy of a polyatomic molecule is determined in the same manner as the translational entropy of a monatomic molecule.

$$S_m^{\ominus} = R\ln\left(\frac{e^{5/2}kT}{p^{\ominus}\Lambda^3}\right) \quad [15\text{E}.11\text{b with } p = p^{\ominus}]$$

(i)
$$\Lambda = \frac{h}{(2\pi mkT)^{1/2}} = \frac{6.626\times10^{-34}\text{ J s}}{\{(2\pi)(18.02)(1.6605\times10^{-27}\text{ kg})(1.381\times10^{-23}\text{ J K}^{-1})T\}^{1/2}}$$
$$= \frac{4.113\times10^{-10}\text{ m}}{(T/\text{K})^{1/2}}$$

$$S_m^{\ominus} = R\ln\left(\frac{(e^{5/2})\times(1.381\times10^{-23}\text{ J K}^{-1}T)}{(1.013\times10^{5}\text{ Pa})\times(4.113\times10^{-10}\text{m})^3}\right)\times\left(\frac{T}{\text{K}}\right)^{3/2}$$
$$= R\ln\{5.302\times(T/\text{K})^{5/2}\} = (8.3145\text{ J K}^{-1}\text{ mol}^{-1})\ln\{5.302\times(298)^{5/2}\}$$
$$= \boxed{132\text{ J K}^{-1}\text{ mol}^{-1}}$$

(ii)
$$\Lambda = \frac{h}{(2\pi mkT)^{1/2}} = \frac{6.626\times10^{-34}\text{ J s}}{\{(2\pi)(44.01)(1.6605\times10^{-27}\text{ kg})(1.381\times10^{-23}\text{ J K}^{-1})T\}^{1/2}}$$
$$= \frac{2.632\times10^{-10}\text{ m}}{(T/\text{K})^{1/2}}$$

$$S_{\mathrm{m}}^{\ominus} = R\ln\left(\frac{(\mathrm{e}^{5/2})\times(1.381\times10^{-23}\ \mathrm{J\,K^{-1}}T)}{(1.013\times10^{5}\ \mathrm{Pa})\times(2.632\times10^{-10}\mathrm{m})^{3}}\right)\times\left(\frac{T}{\mathrm{K}}\right)^{3/2}$$

$$= R\ln\{271.6\times(T/\mathrm{K})^{5/2}\} = (8.3145\ \mathrm{J\,K^{-1}\ mol^{-1}})\ln\{271.6\times(298)^{5/2}\}$$

$$= \boxed{165\ \mathrm{J\,K^{-1}\ mol^{-1}}}$$

15E.6(b) From the solution to Exercise 15E.5(b) we have, for translational contributions,

$$S_{\mathrm{m}}^{\ominus} = R\ln\{271.6\times(T/\mathrm{K})^{5/2}\}\ \text{ for } \mathrm{CO_2}$$

and $S_{\mathrm{m}}^{\ominus} = 132\ \mathrm{J\,K^{-1}\ mol^{-1}}$ for H_2O at 298 K

We solve for T:

$$T = \left\{\frac{1}{271.6}\times\exp\left(\frac{S_{\mathrm{m}}^{\ominus}}{R}\right)\right\}^{2/5}\mathrm{K} = \left\{\frac{1}{271.6}\times\exp\left(\frac{132\ \mathrm{J\,K^{-1}\ mol^{-1}}}{8.3145\ \mathrm{J\,K^{-1}\ mol^{-1}}}\right)\right\}^{2/5}\mathrm{K}$$

$$= \boxed{60.9\ \mathrm{K}}$$

15E.7(b) The high-temperature approximation to the rotational partition function of a non-linear molecule is (after substituting the numerical values of the constants in eqn 15B.14)

$$q^{\mathrm{R}} = \frac{1.0270}{\sigma}\frac{(T/\mathrm{K})^{3/2}}{(\tilde{A}\tilde{B}\tilde{C}/\mathrm{cm^{-3}})^{1/2}} = \frac{1.0270\times298^{3/2}}{(2)\times(2.02736\times0.34417\times0.293535)^{1/2}} = \boxed{5837}$$

The high-temperature approximation is valid if $T > \theta^{\mathrm{R}}$

and $$\theta^{\mathrm{R}} = \frac{hc(\tilde{A}\tilde{B}\tilde{C})^{1/3}}{k}$$

$$= \frac{(6.626\times10^{-34}\ \mathrm{J\,s})(2.998\times10^{10}\ \mathrm{cm\,s^{-1}})\{(2.02736)(0.34417)(0.293535)\ \mathrm{cm^{-3}}\}^{1/3}}{1.381\times10^{-23}\ \mathrm{J\,K^{-1}}}$$

$$= \boxed{0.8479\ \mathrm{K}}$$

so it is valid in this case. All the rotational modes of water are fully active at 25°C; therefore

$$U_{\mathrm{m}}^{\mathrm{R}} - U_{\mathrm{m}}^{\mathrm{R}}(0) = E^{\mathrm{R}} = \frac{3}{2}RT\text{ , the equipartition value}$$

$$S_{\mathrm{m}}^{\mathrm{R}} = \frac{E^{\mathrm{R}}}{T} + R\ln q^{\mathrm{R}} = \frac{3}{2}R + R\ln 5837 = \boxed{84.57\ \mathrm{J\,K^{-1}\ mol^{-1}}}$$

Comment. Division of q^{R} by $N_{\mathrm{A}}!$ is not required for the internal contributions; internal motions may be thought of as localized (distinguishable). It is the overall canonical partition function, which is a product of internal and external contributions, that is divided by $N_{\mathrm{A}}!$

15E.8(b) The degeneracy of a species with $S = \frac{5}{2}$ is 6. The electronic contribution to molar entropy is

$$S_{\mathrm{m}} = \frac{U_{\mathrm{m}} - U_{\mathrm{m}}(0)}{T} + R\ln q = R\ln q$$

(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.)

$$S_{\mathrm{m}} = (8.3145\ \mathrm{J\,mol^{-1}\ K^{-1}})\ln 6 = \boxed{14.9\ \mathrm{J\,mol^{-1}\ K^{-1}}}$$

15E.9(b) The molar entropy of a collection of oscillators is given by

$$S_{\mathrm{m}} = \frac{U_{\mathrm{m}} - U_{\mathrm{m}}(0)}{T} + k\ln Q\ [\text{15E.8c}] = \frac{R(\theta^{\mathrm{V}}/T)}{\mathrm{e}^{\theta^{\mathrm{V}}/T} - 1} - R\ln(1 - \mathrm{e}^{-\theta^{\mathrm{V}}/T})\ [\text{15E.14b}]$$

where $\theta^{\mathrm{V}} = hc\tilde{\nu}/k$ is the vibrational temperature. 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).

(i) At 298 K, $S_{\mathrm{m}} = 0.708R = \boxed{5.88\ \mathrm{J\ K^{-1}\ mol^{-1}}}$

(ii) At 500 K, $S_{\mathrm{m}} = 1.982R = \boxed{16.48\ \mathrm{J\ K^{-1}\ mol^{-1}}}$

Comment. These calculated values are the vibrational contributions to the standard molar entropy. The total molar entropy would also include translational and rotational contributions, but without knowledge of the rotational constants the total molar entropy cannot be calculated.

Solutions to problems

15E.2 $\Delta\varepsilon = \varepsilon = g_{\mathrm{e}}\mu_{\mathrm{B}}\mathcal{B}_0$ [14A.12a] so $q = 1 + \mathrm{e}^{-\beta\varepsilon}$

$$C_{V,\mathrm{m}} = -k\beta^2\left(\frac{\partial U_{\mathrm{m}}}{\partial \beta}\right)_V \quad [15\mathrm{E}.5]$$

The molar internal energy is [15E.2a]

$$U_{\mathrm{m}} - U_{\mathrm{m}}(0) = -\frac{N_{\mathrm{A}}}{q^{\mathrm{E}}}\left(\frac{\partial q^{\mathrm{E}}}{\partial \beta}\right)_V = \frac{N_{\mathrm{A}}\varepsilon \mathrm{e}^{-\beta\varepsilon}}{q^{\mathrm{E}}}$$

Let $x = \beta\varepsilon = 2\mu_{\mathrm{B}}\mathcal{B}_0\beta$ [$g_{\mathrm{e}} = 2$], then $\mathrm{d}\beta = \frac{1}{\varepsilon}\mathrm{d}x$

Therefore, if $\mathcal{B}_0 = 5.0$ T,

$$x = \frac{(2)\times(9.274\times10^{-24}\,\mathrm{J\,T^{-1}})\times(5.0\ \mathrm{T})}{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times T} = \frac{6.72}{T/\mathrm{K}}$$

and

$$C_{V,\mathrm{m}} = -k\left(\frac{x}{\varepsilon}\right)^2 \varepsilon\frac{\partial}{\partial x}\left(\frac{N_{\mathrm{A}}\varepsilon \mathrm{e}^{-x}}{1+\mathrm{e}^{-x}}\right) = -N_{\mathrm{A}}kx^2\times\frac{\partial}{\partial x}\left(\frac{\mathrm{e}^{-x}}{1+\mathrm{e}^{-x}}\right) = R\left(\frac{x^2\mathrm{e}^{-x}}{(1+\mathrm{e}^{-x})^2}\right)$$

(a) $T = 50$ K, $x = 0.134$, $C_{V,\mathrm{m}} = 4.47\times10^{-3}R$, implying that $C_{V,\mathrm{m}} = 3.7\times10^{-2}\ \mathrm{J\ K^{-1}\ mol^{-1}}$. Since the equipartition value is about $3R$ [$\nu^{\mathrm{R}*} = 3$, $\nu^{\mathrm{V}*} \approx 0$], the field brings about a change of about $\boxed{0.1\ \text{per cent}}$.

(b) $T = 298$ K, $x = 2.26\times10^{-2}$, $C_{V,\mathrm{m}} = 1.3\times10^{-4}R$, implying that $C_{V,\mathrm{m}} = 1.1\ \mathrm{mJ\ K^{-1}\ mol^{-1}}$, a change of about 4×10^{-3} per cent.

Question. What percentage change would a magnetic field of 1 kT cause?

15E.4 $q = 1 + 5\mathrm{e}^{-\beta\varepsilon}$ [$g_J = 2J + 1$]

$$\varepsilon = E(J=2) - E(J=0) = 6hc\tilde{B} \quad [E = hc\tilde{B}J(J+1)]$$

$$\frac{U - U(0)}{N} = -\frac{1}{q}\frac{\partial q}{\partial \beta} = \frac{5\varepsilon \mathrm{e}^{-\beta\varepsilon}}{1+5\mathrm{e}^{-\beta\varepsilon}}$$

$$C_{V,\mathrm{m}} = -k\beta^2\left(\frac{\partial U_{\mathrm{m}}}{\partial \beta}\right)_V \quad [15\mathrm{E}.5]$$

$$C_{V,\mathrm{m}}/R = \frac{5\varepsilon^2\beta^2\mathrm{e}^{-\beta\varepsilon}}{(1+5\mathrm{e}^{-\beta\varepsilon})^2} = \frac{180(hc\tilde{B}\beta)^2\mathrm{e}^{-6hc\tilde{B}\beta}}{(1+5\mathrm{e}^{-6hc\tilde{B}\beta})^2}$$

$$\frac{hc\tilde{B}}{k} = \frac{(6.626\times10^{-34}\ \mathrm{J\ s})(2.998\times10^{10}\ \mathrm{cm\ s^{-1}})(60.864\ \mathrm{cm^{-1}})}{1.381\times10^{-23}\ \mathrm{J\ K^{-1}}} = 87.571\ \mathrm{K}$$

Hence,

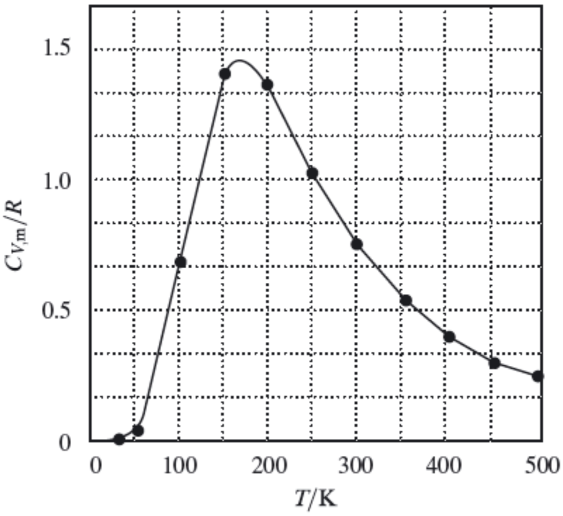
$$C_{V,\mathrm{m}}\big/R = \frac{1.380\times 10^{6}\,\mathrm{e}^{-525.4\mathrm{K}/T}}{(1+5\mathrm{e}^{-525.4\mathrm{K}/T})^{2}\times (T/\mathrm{K})^{2}}$$

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 15E.2.

Figure 15E.2



15E.6 The contribution to the heat capacity from this system of states is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = -k\beta^2\left(\frac{\partial U}{\partial \beta}\right)_V \quad [15\mathrm{E}.5]$$

where $U - U(0) = -N\left(\dfrac{\partial \ln q}{\partial \beta}\right)_V = -\dfrac{N}{q}\left(\dfrac{\partial q}{\partial \beta}\right)_V$ [15E.2a] $= \dfrac{NkT^2}{q}\left(\dfrac{\partial q}{\partial T}\right)_V$

We need to evaluate q for the energy levels of the Morse potential given in Problem 15B.1.

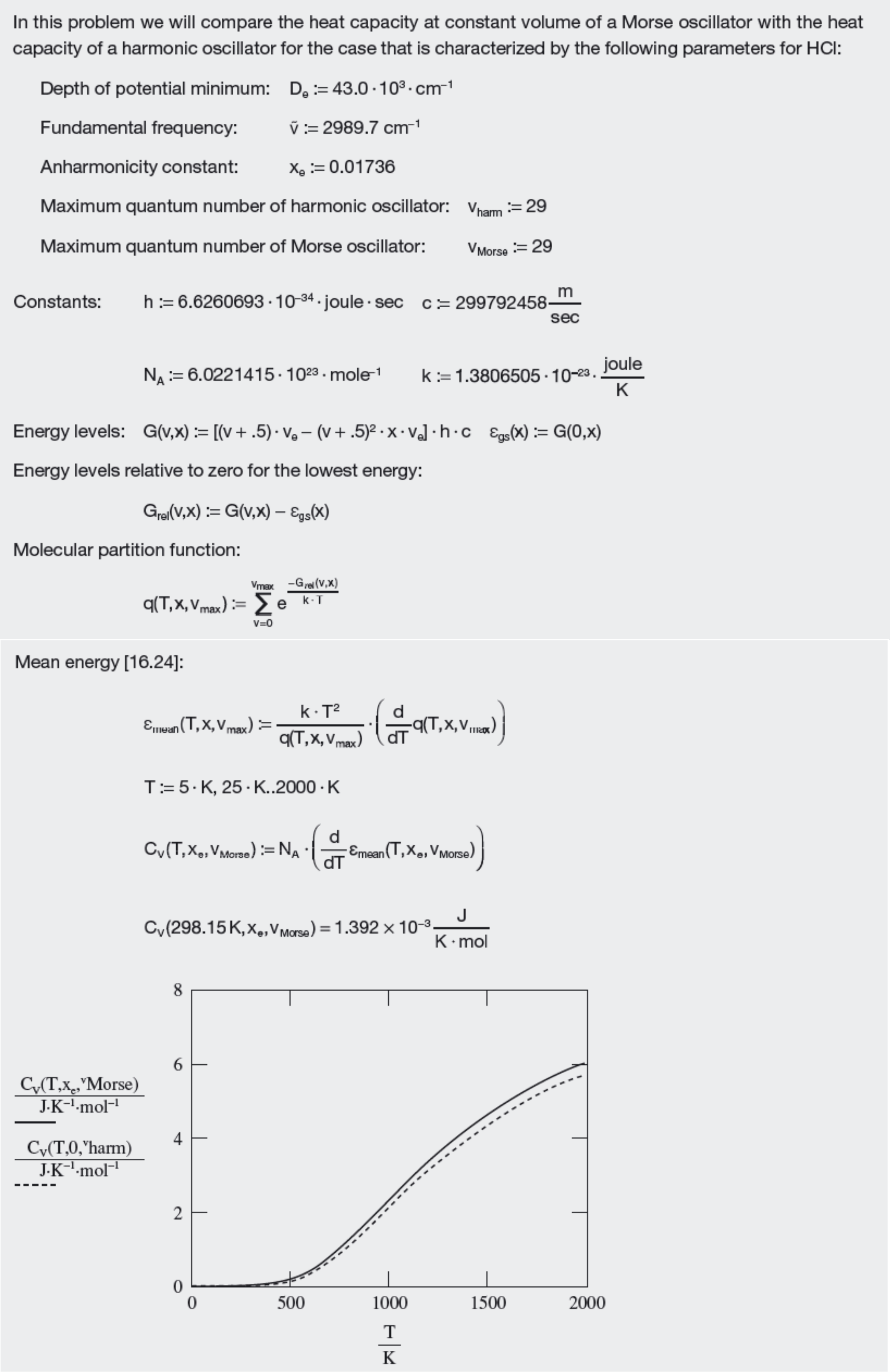
$$E_v = (v+\tfrac{1}{2})hc\tilde{\nu} - (v+\tfrac{1}{2})^2 hc\tilde{\nu}x_\mathrm{e}$$

Relative to $E_0 = 0$ the energy expression can be written as $E_v = vhc\tilde{\nu}\{1-(v+1)x_\mathrm{e}\}$.

Let $hc\tilde{\nu} \equiv u$. Then $E_v = v\{1 - (v+1)x_\mathrm{e}\}$. The partition function becomes

$$q = \sum_{v=0}^{v_{\max}} \mathrm{e}^{-\beta E_v} = \sum_{v=0}^{v_{\max}} \mathrm{e}^{-\beta u v\{1-(v+1)x_\mathrm{e}\}} = \sum_{v=0}^{v_{\max}} \mathrm{e}^{-uv\{1-(v+1)x_\mathrm{e}\}/kT}$$

$v_{\max}$ is the maximum value of v for the Morse oscillator before dissociation occurs. It can be calculated from $v_{\max} = \dfrac{2\tilde{D}_\mathrm{e}}{\tilde{\nu}} - \dfrac{1}{2}$. See the solution to Problem 12D.7 for a derivation of this formula. Since specific values of x_e, $\tilde{\nu}$, and $\tilde{D}_\mathrm{e}$ are required to solve this problem we will choose the case of HCl(g). Values of x_e, $\tilde{\nu}$, and $\tilde{D}_\mathrm{e}$ may be obtained from Table 12D.1 and Problem 12D.4. The value of x_e can also be calculated from $x_\mathrm{e} = \dfrac{\tilde{\nu}}{4\tilde{D}_\mathrm{e}}$ [12D.12]. The heat capacity is calculated in the following MathCad worksheet and Figure 15E.3.



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: $\tilde{v} := 2989.7\ \text{cm}^{-1}$

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:

$$G_{\text{rel}}(v,x) := G(v,x) - \varepsilon_{gs}(x)$$

Molecular partition function:

$$q(T,x,v_{\max}) := \sum_{v=0}^{v_{\max}} e^{\frac{-G_{\text{rel}}(v,x)}{k \cdot T}}$$

Mean energy [16.24]:

$$\varepsilon_{\text{mean}}(T,x,v_{\max}) := \frac{k \cdot T^2}{q(T,x,v_{\max})} \cdot \left(\frac{d}{dT} q(T,x,v_{\max})\right)$$

$$T := 5 \cdot K, 25 \cdot K..2000 \cdot K$$

$$C_V(T,x_e,v_{\text{Morse}}) := N_A \cdot \left(\frac{d}{dT} \varepsilon_{\text{mean}}(T,x_e,v_{\text{Morse}})\right)$$

$$C_V(298.15\,K,x_e,v_{\text{Morse}}) = 1.392 \times 10^{-3} \frac{J}{K \cdot \text{mol}}$$

Figure 15E.3

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

15E.8 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

$$C_V = -k\beta^2\left(\frac{\partial U}{\partial\beta}\right)_V \quad [15E.5]$$

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

$$\frac{C_V}{-k\beta^2} = \left(\frac{\partial U}{\partial\beta}\right)_V = \frac{N}{q}\left(-\sum_J g(J)\varepsilon^2(J)\mathrm{e}^{-\beta\varepsilon(J)}\right) - \frac{N}{q^2}\sum_J g(J)\varepsilon(J)\mathrm{e}^{-\beta\varepsilon(J)}\left(\frac{\partial q}{\partial\beta}\right) \qquad (1)$$

$$= -\frac{N}{q}\sum_J g(J)\varepsilon^2(J)\mathrm{e}^{-\beta\varepsilon(J)} + \frac{N}{q^2}\sum_J g(J)\varepsilon(J)\mathrm{e}^{-\beta\varepsilon(J)}\sum_{J'} g(J')\varepsilon(J')\mathrm{e}^{-\beta\varepsilon(J')}$$

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

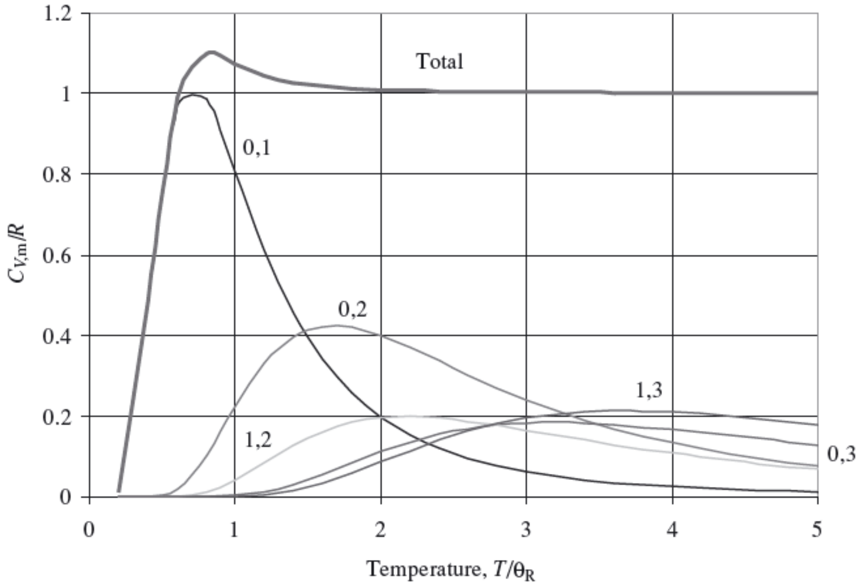
$$\varepsilon(J) = hc\tilde{B}J(J+1) = \theta^{\mathrm{R}}kJ(J+1)$$

so $\beta\varepsilon(J) = \theta^{\mathrm{R}}J(J+1)/T$.

The total heat capacity and the contributions of several transitions are plotted in Figure 15E.4. One can evaluate $C_{V,\mathrm{m}}/R$ 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 15E.4



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 value in $\zeta(\beta)$. In the plot, though, 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 1/2 in C_V would have to be removed.

15E.10 The absorption lines are the values of differences in adjacent rotational terms. Using eqns. 12B.15, and 12B.10, we have

$$\tilde{F}(J+1)-\tilde{F}(J)=\frac{E(J+1)-E(J)}{hc}=2\tilde{B}(J+1)$$

for J = 0, 1, ... Therefore, we can find the rotational constant and reconstruct the energy levels from the data of Problem 15B.6. To make use of all of the data, one would plot the wavenumbers, which represent $\tilde{F}(J+1)-\tilde{F}(J)$, vs. J; the slope of that linear plot is $2\tilde{B}$. However, in this case, plotting the data is not necessary because inspection of the data shows that the lines in the spectrum are equally spaced with a separation of 21.19 cm^{-1}, so that is the slope:

$$\text{slope}=21.19\ \text{cm}^{-1}=2\tilde{B} \quad \text{and hence} \quad \tilde{B}=10.59\bar{5}\ \text{cm}^{-1}$$

The partition function is

$$q=\sum_{J=0}^{\infty}(2J+1)\mathrm{e}^{-\beta hc\tilde{B}J(J+1)}\ [15\text{B}.11]=\sum_{J=0}^{\infty}(2J+1)\mathrm{e}^{-J(J+1)\theta^\mathrm{R}/T}\ [\theta^\mathrm{R}=hc\tilde{B}/k]$$

and the factor (2J + 1) is the degeneracy of the energy levels. For HCl, θ^R = 15.244 K. Defining $x\equiv\dfrac{T}{\theta^\mathrm{R}}$, q^R may be rewritten

$$q^\mathrm{R}=\sum_J(2J+1)\mathrm{e}^{-J(J+1)/x}$$

At temperatures above about 30 K the high temperature approximation for q^R would be adequate to calculate the molar entropy, but at lower temperatures the summation needs to be performed.

The molar entropy is calculated from

$$S_\mathrm{m}=\frac{U_\mathrm{m}-U_\mathrm{m}(0)}{T}+R\ln q^\mathrm{R}\ [15\text{E}.8\text{a}]$$

and the molar energy from

$$U_\mathrm{m}-U_\mathrm{m}(0)=N_\mathrm{A}\langle\varepsilon^\mathrm{R}\rangle=-\frac{N_\mathrm{A}}{q^\mathrm{R}}\left(\frac{\partial q^\mathrm{R}}{\partial\beta}\right)_V\ [15\text{E}.2\text{a}]$$

$$U_{\mathrm{m}}-U_{\mathrm{m}}(0)=\frac{1}{q^{\mathrm{R}}}N_{\mathrm{A}}hc\tilde{B}\sum_{J=1}(2J+1)\{J(J+1)\}\mathrm{e}^{-J(J+1)/x}$$
$$=\frac{1}{q^{\mathrm{R}}}R\theta^{\mathrm{R}}\sum_{J=1}(2J+1)\{J(J+1)\}\mathrm{e}^{-J(J+1)/x}$$

Substituting into the expression for the entropy we obtain

$$S_{\mathrm{m}}=\frac{1}{q^{\mathrm{R}}}R\frac{1}{x}\sum_{J=1}(2J+1)\{J(J+1)\}\mathrm{e}^{-J(J+1)/x}+R\ln q^{\mathrm{R}}$$

S_{m} and q^{R} are best evaluated with a spreadsheet program such as Excel® or a analytical mathematical software as Mathcad®. Here we have used Mathcad®. See the Mathcad® worksheet below. S_{m}/R is plotted as a function of $x\equiv\frac{T}{\theta^{\mathrm{R}}}$ in Figure 15E.5.

Figure 15E.5

$$i := 0\ldots 47$$

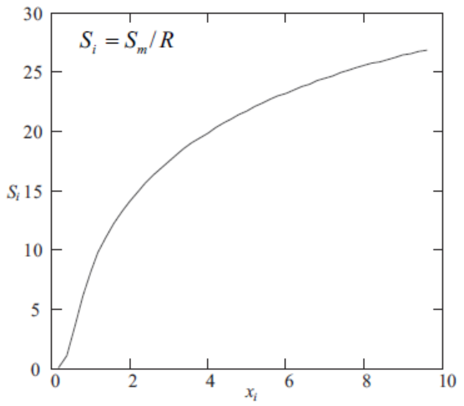
$$x_{\text{start}} := 0.2 \qquad x_{\text{end}} := 9.6$$

$$x_1 := x_{\text{start}}+(x_{\text{end}}-x_{\text{start}})\cdot\frac{\mathrm{i}}{47} \qquad x_i = \mathrm{T}/\Theta$$

$$q_i := \sum_{J=0}^{6}\left[(2\cdot\mathrm{J}+1)\cdot\mathrm{e}^{-\mathrm{J}\frac{\mathrm{J}+1}{\mathrm{X}_i}}\right] \qquad q_i = q^R$$

$$\mathrm{U}_{\mathrm{i}} := \left(\frac{1}{\mathrm{q}_{\mathrm{i}}}\right)\left[\frac{1}{\mathrm{x}_{\mathrm{i}}}\sum_{j=0}^{6}\left[(2\cdot\mathrm{J}+1)\cdot\mathrm{J}\cdot(\mathrm{J}+1)\cdot\mathrm{e}^{-\left(\mathrm{J}\frac{\mathrm{J}+1}{\mathrm{X}_i}\right)}\right]\right] \qquad \mathrm{U}_{\mathrm{i}} = \mathrm{U}_{\mathrm{m}}/\mathrm{R}T$$

$$S_i := 8.314\,(\mathrm{U}_{\mathrm{i}}+\ln(q_1)) \qquad S_i = S_{\mathrm{m}}\,R/R$$



$$x_i = T/\Theta$$

15E.12 The translational contribution to the entropy is given by the Sackur-Tetrode equation [15E.11a]:

$$S_{\mathrm{m}}^{\mathrm{T}\ominus}=R\ln\left(\frac{V_{\mathrm{m}}\mathrm{e}^{5/2}}{N_{\mathrm{A}}\Lambda^3}\right) \qquad \text{where} \qquad \Lambda=\frac{h}{(2\pi mkT)^{1/2}} \quad [15\mathrm{B}.7\mathrm{b}]$$

After substituting values for the constants we obtain

$$\Lambda=\frac{h}{(2\pi mkT)^{1/2}}=\frac{6.626\times10^{-34}\ \mathrm{J\ s}}{\{2\pi(38.00\times1.6605\times10^{-27}\ \mathrm{kg})(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})(298\ \mathrm{K})\}^{1/2}}$$
$$=1.64\times10^{-11}\ \mathrm{m}$$

and $$S_{\mathrm{m}}^{\mathrm{T}\ominus}=(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\ln\left(\frac{(2.479\times10^{-2}\ \mathrm{m^3})\mathrm{e}^{5/2}}{(6.022\times10^{23}\ \mathrm{mol^{-1}})(1.64\times10^{-11}\ \mathrm{m})^3}\right)$$
$$=154\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

The rotational contribution is [15E.13a]

$$S_{\mathrm{m}}^{\mathrm{R}}=R\left(1+\ln\frac{kT}{\sigma hc\tilde{B}}\right)$$

The rotational constant is

$$\tilde{B}=\frac{\hbar}{4\pi cI}=\frac{\hbar}{4\pi c\mu R^2}$$

$$=\frac{(1.0546\times10^{-34}\,\mathrm{J\,s})\times(6.022\times10^{23}\,\mathrm{mol^{-1}})}{4\pi(2.998\times10^{10}\,\mathrm{cm\,s^{-1}})\times(\frac{1}{2}\times19.00\times10^{-3}\,\mathrm{kg\,mol^{-1}})\times(190.0\times10^{-12}\,\mathrm{m})^2}$$

$$=0.4915\ \mathrm{cm^{-1}}$$

It will be useful to note that $\dfrac{kT}{hc}=\dfrac{(1.381\times10^{-23}\ \mathrm{J\,K^{-1}})(298\ \mathrm{K})}{(6.626\times10^{-34}\ \mathrm{J\,s})(2.998\times10^{10}\ \mathrm{cm\,s^{-1}})}=207.2\ \mathrm{cm^{-1}}$

Thus $S_{\mathrm{m}}^{\mathrm{R}}=(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\left(1+\ln\dfrac{207.2\ \mathrm{cm^{-1}}}{(2)(0.4915\ \mathrm{cm^{-1}})}\right)=52.8\ \mathrm{J\,K^{-1}\,mol^{-1}}$

The vibrational contribution is [15E.13a]

$$S_{\mathrm{m}}^{\mathrm{V}}=R\left(\frac{\theta^{\mathrm{V}}/T}{\mathrm{e}^{\theta^{\mathrm{V}}/T}-1}-\ln\left(1-\mathrm{e}^{-\theta^{\mathrm{V}}/T}\right)\right)\quad\text{with}\quad\frac{\theta^{\mathrm{V}}}{T}=\frac{hc\tilde{\nu}}{kT}=\frac{450.0\ \mathrm{cm^{-1}}}{207.2\ \mathrm{cm^{-1}}}=2.172$$

$$S_{\mathrm{m}}^{\mathrm{V}}=(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\left(\frac{2.172}{\mathrm{e}^{2.172}-1}-\ln\left(1-\mathrm{e}^{-2.172}\right)\right)=3.33\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

The Boltzmann factor for the lowest-lying excited electronic state is

$$\exp\left(\frac{-(1.609\,\mathrm{eV})\times(1.602\times10^{-19}\,\mathrm{J\,eV^{-1}})}{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}\right)=6\times10^{-28}$$

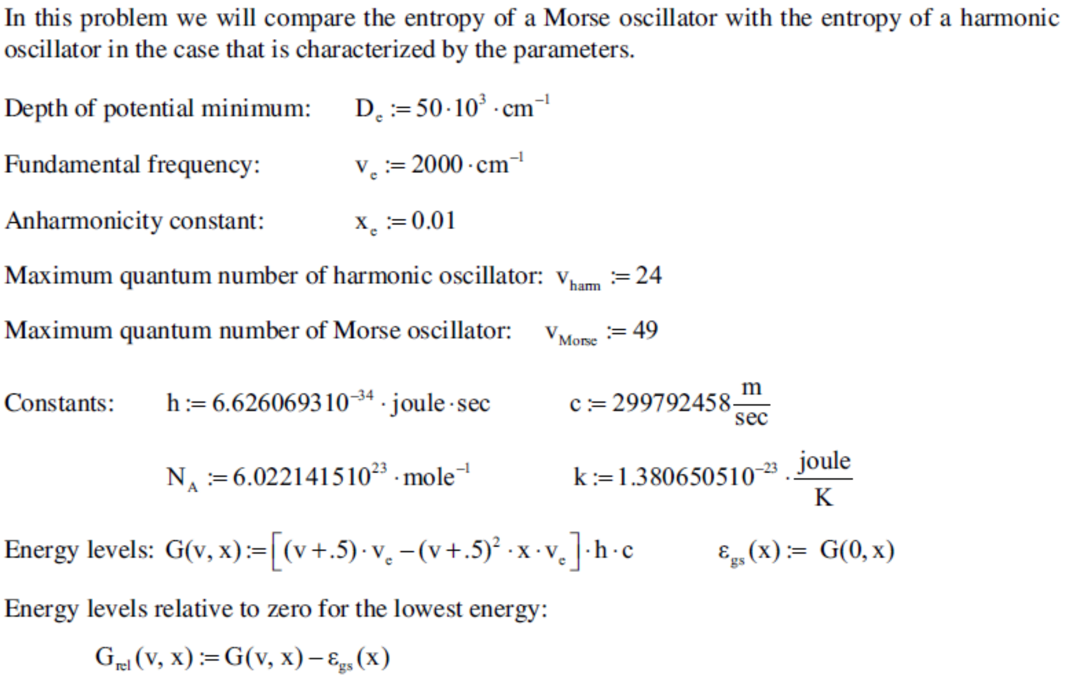
so we may take q^{E} to equal the degeneracy of the ground state, namely 2 and $U^{\mathrm{E}}-U^{\mathrm{E}}(0)$ to be zero. So the electronic contribution is

$$S^{\mathrm{E}}=\frac{U^{\mathrm{E}}-U^{\mathrm{E}}(0)}{T}+R\ln q^{\mathrm{E}}=0+(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\ln2=5.76\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

Putting it all together yields

$$S_{\mathrm{m}}^{\ominus}=S_{\mathrm{m}}^{\mathrm{T}\ominus}+S_{\mathrm{m}}^{\mathrm{R}}+S_{\mathrm{m}}^{\mathrm{V}}+S_{\mathrm{m}}^{\mathrm{E}}=\boxed{216\ \mathrm{J\,K^{-1}\,mol^{-1}}}$$

15E.14 The solution is provided in the MathCad® worksheet which is inserted below.



In this problem we will compare the entropy of a Morse oscillator with the entropy of a harmonic oscillator in the case that is characterized by the parameters.

Depth of potential minimum: $D_e := 50\cdot10^3\cdot\mathrm{cm}^{-1}$

Fundamental frequency: $v_e := 2000\cdot\mathrm{cm}^{-1}$

Anharmonicity constant: $x_e := 0.01$

Maximum quantum number of harmonic oscillator: $v_{harm} := 24$

Maximum quantum number of Morse oscillator: $v_{Morse} := 49$

Constants: $h := 6.626069310^{-34}\cdot\mathrm{joule}\cdot\mathrm{sec}$ $\quad c := 299792458\dfrac{\mathrm{m}}{\mathrm{sec}}$

$N_A := 6.022141510^{23}\cdot\mathrm{mole}^{-1}$ $\quad k := 1.380650510^{-23}\cdot\dfrac{\mathrm{joule}}{\mathrm{K}}$

Energy levels: $G(v,x) := \left[(v+.5)\cdot v_e-(v+.5)^2\cdot x\cdot v_e\right]\cdot h\cdot c$ $\qquad \varepsilon_{gs}(x) := G(0,x)$

Energy levels relative to zero for the lowest energy:

$$G_{rel}(v,x) := G(v,x)-\varepsilon_{gs}(x)$$

Molecular partition function:

$$q(T, x, v_{max}) := \sum_{v=0}^{v_{max}} e^{\frac{-G_{vd}(v,x)}{k \cdot T}}$$

Mean energy **[15C.4a]** :

$$\varepsilon_{mean}(T, x, v_{max}) := \frac{k \cdot T^2}{q(T, x, v_{max})} \cdot \left(\frac{d}{dt} q(T, x, v_{max})\right)$$

Entropy for distinguishable oscillators **[15E.8a]**:

$$s_m(T, x, v_{max}) := \frac{N_A \cdot \varepsilon_{mean}(T, x, v_{max})}{T} + N_A \cdot k \cdot \ln(q(T, x, v_{max}))$$

Molar entropy harmonic oscillator: $s_{harm}(T) := s_m(T, 0, v_{harm})$

Molar entropy Morse oscillator: $s_{Morse}(T) := s_m(T, x_e, v_{Morse})$

$T := 5 \cdot K, 25 \cdot K .. 2000 \cdot K$

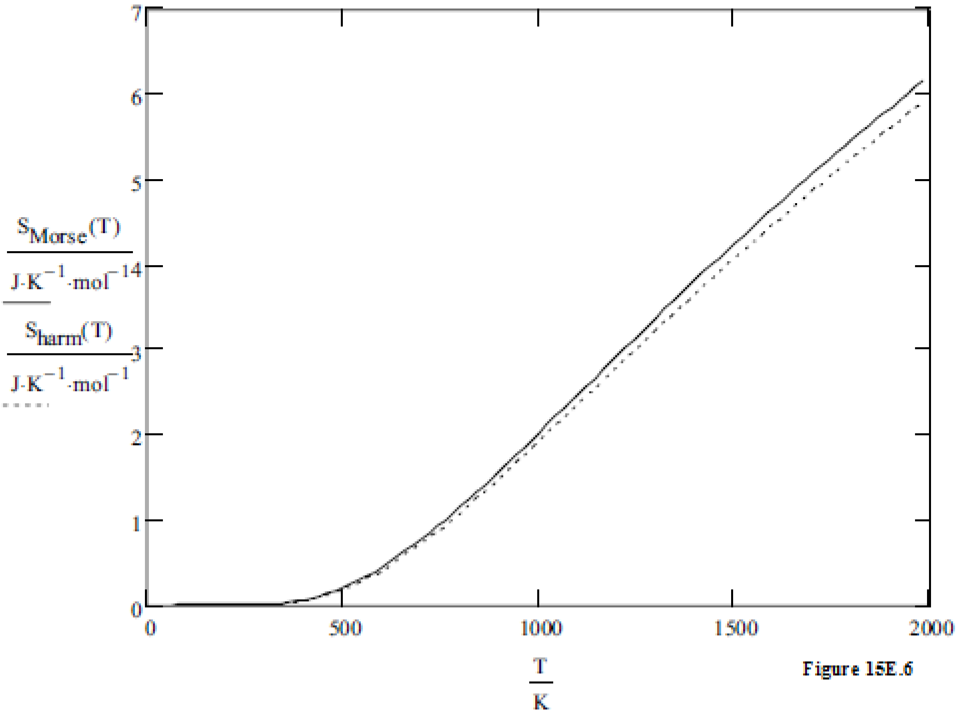


Figure 15E.6

The plot of the Morse oscillator entropy against temperature, when compared to a similar plot for the harmonic oscillator, shows that the Morse oscillator has the greater entropy (Figure 15E.6). This happens because the Morse oscillator has the greater number of available energy states at any temperature. However, the difference is remarkably small.

15E.16 A Sackur-Tetrode type of equation describes the translational entropy of the gas. Here

$$q^{\mathrm{T}} = q_x^{\mathrm{T}} q_y^{\mathrm{T}} \quad \text{with } q_x^{\mathrm{T}} = \left(\frac{2\pi m}{\beta h^2}\right)^{1/2} X \quad [15\text{B}.7\text{a}]$$

where X is the length of the surface. Therefore,

$$q^{\mathrm{T}} = \left(\frac{2\pi m}{\beta h^2}\right)XY = \frac{2\pi m\sigma}{\beta h^2}, \quad \sigma = XY$$

$$U_{\mathrm{m}} - U_{\mathrm{m}}(0) = -\frac{N_{\mathrm{A}}}{q}\left(\frac{\partial q}{\partial \beta}\right) = RT \text{ [or by equipartition]}$$

$$S_{\mathrm{m}} = \frac{U_{\mathrm{m}} - U_{\mathrm{m}}(0)}{T} + R(\ln q_{\mathrm{m}} - \ln N_{\mathrm{A}} + 1)\left[q_{\mathrm{m}} = \frac{q}{n}\right]$$

$$= R + R\ln\left(\frac{\mathrm{e}q_{\mathrm{m}}}{N_{\mathrm{A}}}\right) = R\ln\left(\frac{\mathrm{e}^2 q_{\mathrm{m}}}{N_{\mathrm{A}}}\right)$$

$$= \boxed{R\ln\left(\frac{2\pi \mathrm{e}^2 m\sigma_{\mathrm{m}}}{h^2 N_{\mathrm{A}}\beta}\right)}\left[\sigma_{\mathrm{m}} = \frac{\sigma}{n}\right]$$

Call this molar entropy of the mobile two-dimensional film S_{m2}. The molar entropy of condensation is the difference between this entropy and that of a (three-dimensional) gas:

$$\Delta S_{\mathrm{m}} = S_{\mathrm{m2}} - S_{\mathrm{m3}} .$$

The three-dimensional value is given by the Sackur-Tetrode equation

$$S_{\mathrm{m}} = R\ln\left\{\mathrm{e}^{5/2}\left(\frac{2\pi m}{h^2\beta}\right)^{3/2}\frac{V_{\mathrm{m}}}{N_{\mathrm{A}}}\right\} \text{ [15E.11a]}$$

So $$\Delta S_{\mathrm{m}} = R\ln\frac{\mathrm{e}^2(2\pi m/h^2\beta)\times(\sigma_{\mathrm{m}}/N_{\mathrm{A}})}{\mathrm{e}^{5/2}(2\pi m/h^2\beta)^{3/2}\times(V_{\mathrm{m}}/N_{\mathrm{A}})} = \boxed{R\ln\left\{\left(\frac{\sigma_{\mathrm{m}}}{V_{\mathrm{m}}}\right)\times\left(\frac{h^2\beta}{2\pi m\mathrm{e}}\right)^{1/2}\right\}}$$

15E.18 $$c_{\mathrm{s}} = \left(\frac{\gamma RT}{M}\right)^{1/2}, \quad \gamma = \frac{C_{p,\mathrm{m}}}{C_{V,\mathrm{m}}}, \qquad C_{p,\mathrm{m}} = C_{V,\mathrm{m}} + R$$

(a) $$C_{V,\mathrm{m}} = \tfrac{1}{2}R(3 + \nu^{\mathrm{R}*} + 2\nu^{\mathrm{V}*}) = \tfrac{1}{2}R(3+2) = \tfrac{5}{2}R$$

$$C_{p,\mathrm{m}} = \tfrac{5}{2}R + R = \tfrac{7}{2}R$$

$$\gamma = \frac{7}{5} = 1.40; \quad \text{hence} \quad \boxed{c_{\mathrm{s}} = \left(\frac{1.40RT}{M}\right)^{1/2}}$$

(b) Nothing significant changes upon going from a diatomic to a linear triatomic. There are no more rotational modes. There are additional vibrational modes, but we assume none is active.

$$\boxed{c_{\mathrm{s}} = \left(\frac{1.40RT}{M}\right)^{1/2}}$$

(c) $$C_{V,\mathrm{m}} = \tfrac{1}{2}R(3+3) = 3R$$

$$C_{p,\mathrm{m}} = 3R + R = 4R, \qquad \gamma = \frac{4}{3}, \qquad \boxed{c_{\mathrm{s}} = \left(\frac{4RT}{3M}\right)^{1/2}}$$

For air,

$$c_{\mathrm{s}} = \left(\frac{(1.40)\times(2.48\,\mathrm{kJ\,mol^{-1}})}{29\times10^{-3}\,\mathrm{kg\,mol^{-1}}}\right)^{1/2} = \boxed{350\,\mathrm{m\,s^{-1}}}$$

15E.20 **(a)** The heat capacity is

$$C_V = -k\beta^2\left(\frac{\partial U}{\partial \beta}\right)_V \text{ [15E.5]}$$

First express U as a function of β:

$$U = U(0) + \frac{N\varepsilon \mathrm{e}^{-\beta\varepsilon}}{1 + \mathrm{e}^{-\beta\varepsilon}}$$

Hence $\dfrac{C_V}{-k\beta^2} = \left(\dfrac{\partial U}{\partial \beta}\right)_V = \dfrac{1}{1+\mathrm{e}^{-\beta\varepsilon}} \times (-N\varepsilon^2 \mathrm{e}^{-\beta\varepsilon}) - \dfrac{N\varepsilon}{(1+\mathrm{e}^{-\beta\varepsilon})^2} \times (-\varepsilon \mathrm{e}^{-\beta\varepsilon})$

Collecting terms over a common denominator yields

$$C_V = \frac{kN\beta^2\varepsilon^2\mathrm{e}^{-\beta\varepsilon}}{(1+\mathrm{e}^{-\beta\varepsilon})^2}(1+\mathrm{e}^{-\beta\varepsilon}-1) = \frac{kN\beta^2\varepsilon^2\mathrm{e}^{-2\beta\varepsilon}}{(1+\mathrm{e}^{-\beta\varepsilon})^2} = \frac{kN(1/kT)^2\varepsilon^2\mathrm{e}^{-2\varepsilon/kT}}{(1+\mathrm{e}^{-\varepsilon/kT})^2}$$

Change the expression to molar rather than molecular quantities:

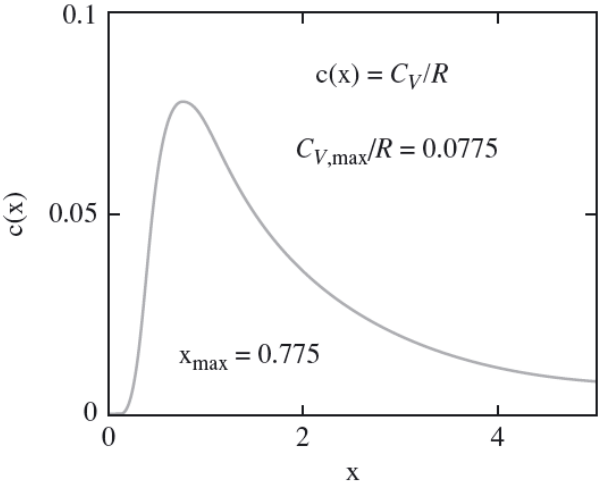
$N = N_\mathrm{A}$, $R = N_\mathrm{A}k$, and $\varepsilon/k = \varepsilon_\mathrm{m}/R$

so $C_{V,\mathrm{m}} = \dfrac{R(\varepsilon_\mathrm{m}/RT)^2\mathrm{e}^{-2\varepsilon_\mathrm{m}/RT}}{(1+\mathrm{e}^{-\varepsilon_\mathrm{m}/RT})^2}$

(b) It is convenient to plot $C_{V,\mathrm{m}}$ (in units of R) as a function of x where $x = kT/\varepsilon = RT/\varepsilon_\mathrm{m}$. See Figure 15C.7.

$$C_{V,\mathrm{m}} = \frac{R\mathrm{e}^{-2/x}}{x^2(1+\mathrm{e}^{-1/x})^2} \qquad c(x) \equiv \frac{C_{V,\mathrm{m}}}{R}$$

Figure 15C.7



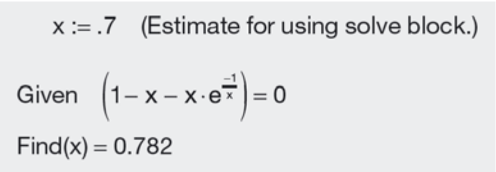
(c) Figure 15.20 shows a maximum heat capacity at about 0.08 R at a value for x of about 0.8. The *X-Y* Trace feature of mathematical software may be used to find a more accurate value for $x_{\max}$ of 0.775 and for $c(x_{\max})$ of 0.0775. A formula for the maximum is determined by the criterion that $\mathrm{d}C_{V,\mathrm{m}}/\mathrm{d}x = 0$ at the maximum.

$$\frac{\mathrm{d}(C_{V,\mathrm{m}}/R)}{\mathrm{d}x} = \frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\mathrm{e}^{-2/x}}{x^2(1+\mathrm{e}^{-1/x})^2}\right) = \frac{2\mathrm{e}^{-2/x}(1-x-x\mathrm{e}^{-1/x})}{x^4(1+\mathrm{e}^{-1/x})^3}$$

Thus, $C_{V,\mathrm{m}}$ is a maximum when $x = x_{\max}$ satisfies the equation

$$1 - x_{\max} - x_{\max}\mathrm{e}^{-1/x_{\max}} = 0$$

This is a transcendental equation so it is necessary to solve for $x_{\max}$ with a numerical method. $x_{\max}$ may be numerically determined with the Numeric Solver application of the modern scientific calculator. The Given/Find solve block of Mathcad can also be used and the following presents a Mathcad solution.



x := .7 (Estimate for using solve block.)

Given $\left(1 - x - x\cdot e^{\frac{-1}{x}}\right) = 0$

Find(x) = 0.782

This represents the best value of $x_{\max}$. $T_{\max} = \boxed{\dfrac{\varepsilon_\mathrm{m} x_{\max}}{R}}$ with $x_{\max}$ determined as above.

15F Derived functions

Answer to discussion question

15F.2 The relationship between the equilibrium constant and the standard molar partition functions of the species involved is [15F.10b]

$$K = \left\{ \prod_{\mathrm{J}} \left(\frac{q^{\ominus}_{\mathrm{J,m}}}{N_{\mathrm{A}}} \right)^{\nu_{\mathrm{J}}} \right\} \mathrm{e}^{-\Delta_{\mathrm{r}} E_0 / RT}$$

The equilibrium constant, of course, is related to the Gibbs functions of reactants and products, as discussed in Topic 6A. The Gibbs function itself is often interpreted as balancing energetic and entropic tendencies of the system (even if the energetic tendencies themselves can be interpreted as reflecting the entropy of the surroundings). We can clearly identify an energetic portion in the above expression, the exponential involving $\Delta_{\mathrm{r}}E_0$, with which we are not concerned at the moment. The remaining portion, the continued product (quotient) is highly reminiscent of the equilibrium constant expression [6A.13] in terms of species activities:

$$K = \left(\prod_{\mathrm{J}} a_{\mathrm{J}}{}^{\nu_{\mathrm{J}}} \right)_{\text{equilibrium}}$$

Thus, to the extent permitted by energetic considerations, the activities of reactants and products in a mixture at equilibrium are directly proportional to the number of accessible states they have. Indeed, recalling that activities are approximately proportional to concentrations, we can interpret 15F.10b as saying that species concentrations in an equilibrium mixture are directly proportional to the number of accessible states of that species.

Finally, recall that each species' partition function is measured with respect to the ground state of that species. If we computed the partition functions of all the species involved with respect to a **common** zero of energy, then the partition functions would absorb the energetic factor involving $\Delta_{\mathrm{r}}E_0$. (Note that that energetic term has the same functional form as a Boltzmann factor.) So we conclude by saying that species activities in an equilibrium mixture are directly proportional to the number of accessible states they have—period.

Solutions to exercises

15F.1(b) In each case the contribution to G is given by

$$G - G(0) = -nRT \ln q \quad \text{[15F.9 for non-tranlational modes]}$$

Therefore, we first evaluate q^{R} and q^{V}.

$$q^{\mathrm{R}} = \frac{1}{\sigma} \left(\frac{kT}{hc} \right)^{3/2} \left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}} \right)^{1/2}$$

$$= \frac{1}{2} \left(\frac{kT}{hc} \right)^{3/2} \left(\frac{1}{(3.553) \times (0.4452) \times (0.3948)} \right)^{1/2} = 3.35 \times 10^3$$

So $\quad G^{\mathrm{R}}_{\mathrm{m}} - G^{\mathrm{R}}_{\mathrm{m}}(0) = -(8.3145\,\mathrm{J\,mol^{-1}K^{-1}}) \times (298\,\mathrm{K}) \ln 3.35 \times 10^3$

$$= -20.1 \times 10^3\,\mathrm{J\,mol^{-1}} = \boxed{-20.1\,\mathrm{kJ\,mol^{-1}}}$$

The vibrational partition function for each vibrational mode is given by [15B.15]

$$q^{\mathrm{V}} = \frac{1}{1 - \mathrm{e}^{-\theta^{\mathrm{V}}/T}} \quad \text{where} \quad \theta^{\mathrm{V}} = \frac{hc\tilde{\nu}}{k} = 1.4388\ \mathrm{K} \times (\tilde{\nu} / \mathrm{cm^{-1}})$$

The vibrational partition functions are so small that we are better off taking

$$\ln q^{\mathrm{V}} = -\ln(1 - \mathrm{e}^{-\theta^{\mathrm{V}}/T}) \approx \mathrm{e}^{-\theta^{\mathrm{V}}/T}$$

so $\quad \ln q^{\mathrm{V}}_1 \approx \mathrm{e}^{-\{1.4388(1110)/298\}} = 4.70 \times 10^{-3} \qquad \ln q^{\mathrm{V}}_2 \approx \mathrm{e}^{-\{1.4388(705)/298\}} = 3.32 \times 10^{-2}$

and $\quad \ln q^{\mathrm{V}}_3 \approx \mathrm{e}^{-\{1.4388(1042)/298\}} = 6.53 \times 10^{-3}$

$$G_m^V - G_m^V(0) = -(8.3145\ \text{J mol}^{-1}\text{K}^{-1}) \times (298\,\text{K})$$
$$\times(4.70\times10^{-3} + 3.32\times10^{-2} + 6.53\times10^{-3})$$
$$= -110\ \text{J mol}^{-1} = \boxed{-0.110\ \text{kJ mol}^{-1}}$$

15F.2(b) See the solution to Exercise 15E.3(b). At 400 K

At 400 K, $$\beta\varepsilon = \frac{hc\times(7918.1\text{cm}^{-1})}{kT} = \frac{(1.4388\ \text{cm K})\times(7918.1\text{cm}^{-1})}{500\,\text{K}} = 22.78$$

Therefore, the contribution to G_m is

$$G_m - G_m(0) = -RT\ln q \quad [\text{15F.9 for non-tranlational modes}]$$

$$G_m - G_m(0) = -(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(400\,\text{K})\times\ln(3+2\times e^{-28.48}) = \boxed{-3.65\text{kJ mol}^{-1}}$$

Comment. The contribution of the excited state is negligible at this temperature.

15F.3(b) We need to calculate

$$K = \prod_J \left(\frac{q_{J,m}^{\ominus}}{N_A}\right)^{\nu_J} \times e^{-\Delta_r E_0/RT}\ [\text{15F.10b}] = \frac{q_m^{\ominus}(^{79}\text{Br}_2)q_m^{\ominus}(^{81}\text{Br}_2)}{q_m^{\ominus}(^{79}\text{Br}^{81}\text{Br})^2} e^{-\Delta_r E_0/RT}$$

Each of these partition functions is a product

$$q_m^{\ominus} = q_m^T q^R q^V q^E \text{ with all } q^E = 1.$$

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

$$\frac{q^R(^{79}\text{Br}_2)q^R(^{81}\text{Br}_2)}{q^R(^{79}\text{Br}^{81}\text{Br})^2} = 0.25$$

The value of $\Delta_r E_0$ is also very small compared with RT, so

$$K \approx \boxed{0.25}$$

Solutions to problems

15F.2 $$H_2O + DCl \rightleftharpoons HDO + HCl \quad \text{(all in gas phase)}$$

The equilibrium constant is [15F.10, with $\Delta_r E_0$ here defined as the molecular, not molar, energy difference; N_A factors cancel]

$$K = \frac{q_m^{\ominus}(\text{CHD}_3)q_m^{\ominus}(\text{DCl})}{q_m^{\ominus}(\text{CD}_4)q_m^{\ominus}(\text{HCl})} e^{-\beta\Delta_r E_0}$$

Use partition function expressions from Topic 15B.
The ratio of translational partition functions is

$$\frac{q_m^T(\text{HDO})q_m^T(\text{HCl})}{q_m^T(\text{H}_2\text{O})q_m^T(\text{DCl})} = \left(\frac{M(\text{HDO})M(\text{HCl})}{M(\text{H}_2\text{O})M(\text{DCl})}\right)^{3/2} = \left(\frac{19.02\times36.46}{18.02\times37.46}\right)^{3/2} = 1.041$$

The ratio of rotational partition functions is, with $\sigma = 2$ for H_2O and $\sigma = 1$ for the others.

$$\frac{q^R(\text{HDO})q^R(\text{HCl})}{q^R(\text{H}_2\text{O})q^R(\text{DCl})} = \frac{\sigma(\text{H}_2\text{O})}{1}\frac{(\tilde{A}(\text{H}_2\text{O})\tilde{B}(\text{H}_2\text{O})\tilde{C}(\text{H}_2\text{O}))^{1/2}\tilde{B}(\text{DCl})}{(\tilde{A}(\text{HDO})\tilde{B}(\text{HDO})\tilde{C}(\text{HDO}))^{1/2}\tilde{B}(\text{HCl})}$$

$$= 2\times\frac{(27.88\times14.51\times9.29)^{1/2}\times5.449}{(23.38\times9.102\times6.417)^{1/2}\times10.59} = 1.707$$

The ratio of vibrational partition functions (call it f_V) is

$$f_V = \frac{q^V(\text{HDO})q^V(\text{HCl})}{q^V(\text{H}_2\text{O})q^V(\text{DCl})} = \frac{q(2726.7)q(1402.2)q(3707.5)q(2991)}{q(3656.7)q(1594.8)q(3755.8)q(2145)}$$

where $$q(x) = \frac{1}{1-e^{-hc\tilde{\nu}/kT}} = \frac{1}{1-e^{-1.4388x/(T/\text{K})}}$$

$$\begin{aligned}\frac{\Delta_{\mathrm{r}}E_0}{hc} &= \frac{1}{2}\{(2726.7+1402.2+3707.5+2991)\\ &\quad -(3656.7+1594.8+3755.8+2145)\}\,\mathrm{cm}^{-1}\\ &\quad = -162\,\mathrm{cm}^{-1}\end{aligned}$$

So the exponent in the energy term is

$$-\beta\Delta_{\mathrm{r}}E_0 = -\frac{\Delta_{\mathrm{r}}E_0}{kT} = -\frac{hc}{k}\times\frac{\Delta_{\mathrm{r}}E_0}{hc}\times\frac{1}{T} = -\frac{1.4388\times(-162)}{T/\mathrm{K}} = +\frac{233}{T/\mathrm{K}}$$

Therefore, $K = 1.041\times 1.707\times f_{\mathrm{V}}\times \mathrm{e}^{233/(T/\mathrm{K})} = 1.777\, f_{\mathrm{V}}\mathrm{e}^{233/(T/\mathrm{K})}$

We then draw up the following table

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 (a) $K = \boxed{3.89}$ at 298 K and (b) $K = \boxed{2.41}$ at 800 K.

15F.4 The standard molar Gibbs energy is given by

$$G_{\mathrm{m}}^{\ominus} - G_{\mathrm{m}}^{\ominus}(0) = RT\ln\frac{q_{\mathrm{m}}^{\ominus}}{N_{\mathrm{A}}} \quad \text{where}\ \frac{q_{\mathrm{m}}^{\ominus}}{N_{\mathrm{A}}} = \frac{q_{\mathrm{m}}^{\mathrm{T}\ominus}}{N_{\mathrm{A}}}q^{\mathrm{R}}q^{\mathrm{V}}q^{\mathrm{E}} \quad [15\mathrm{F}.9]$$

Translation:

$$\frac{q_{\mathrm{m}}^{\mathrm{T}\ominus}}{N_{\mathrm{A}}} = \frac{kT}{p^{\ominus}\Lambda^3} \qquad \Lambda = \frac{h}{(2\pi mkT)^{1/2}}$$

After substituting the values of the constants, we obtain

$$\begin{aligned}\frac{q_{\mathrm{m}}^{\mathrm{T}\ominus}}{N_{\mathrm{A}}} &= 2.561\times10^{-2}(T/\mathrm{K})^{5/2}\times(M/\mathrm{g\,mol^{-1}})^{3/2}\\ &= (2.561\times10^{-2})\times(2000)^{5/2}\times(38.90)^{3/2} = 1.111\times10^{9}\end{aligned}$$

Rotation of a linear molecule:

$$q^{\mathrm{R}} = \frac{kT}{\sigma hc\tilde{B}}$$

The rotational constant is

$$\tilde{B} = \frac{\hbar}{4\pi cI} = \frac{\hbar}{4\pi c\mu R^2}$$

where $$\mu = \frac{m_{\mathrm{B}}m_{\mathrm{Si}}}{m_{\mathrm{B}}+m_{\mathrm{Si}}} = \frac{(10.81)\times(28.09)}{10.81+28.09}\times\frac{10^{-3}\mathrm{kg\ mol^{-1}}}{6.022\times10^{23}\mathrm{mol^{-1}}} = 1.296\times10^{-26}\mathrm{kg}$$

so $$\tilde{B} = \frac{1.0546\times10^{-34}\,\mathrm{J\,s}}{4\pi(2.998\times10^{10}\mathrm{cm\,s^{-1}})\times(1.296\times10^{-26}\mathrm{kg})\times(190.5\times10^{-12}\mathrm{m})^2} = 0.5952\ \mathrm{cm}^{-1}$$

and $$q^{\mathrm{R}} = \frac{k}{hc}\times\frac{2000\ \mathrm{K}}{2(0.5952\ \mathrm{cm}^{-1})} = 2335$$

Vibration:

$$\begin{aligned}q^{\mathrm{V}} &= \frac{1}{1-\mathrm{e}^{-hc\tilde{\nu}/kT}} = \frac{1}{1-\exp\left(\frac{-1.4388(\tilde{\nu}/\mathrm{cm}^{-1})}{T/\mathrm{K}}\right)} = \frac{1}{1-\exp\left(\frac{-1.4388(772)}{2000}\right)} =\\ &= 2.467\end{aligned}$$

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

$$q^{\mathrm{E}} = 4(1+3.2\times10^{-3}) = 4.013$$

Putting it all together yields

$$G_{\mathrm{m}}^{\ominus}-G_{\mathrm{m}}^{\ominus}(0)=(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(2000\ \mathrm{K})$$

$$\times\ln[(1.111\times10^{9})\times(2335)\times(2.467)\times(4.013)]$$

$$=5.135\times10^{5}\ \mathrm{J\ mol^{-1}}=\boxed{513.5\ \mathrm{kJ\ mol^{-1}}}$$

15F.6 The standard molar Gibbs energy is given by

$$G_{\mathrm{m}}^{\ominus}-G_{\mathrm{m}}^{\ominus}(0)=RT\ln\frac{q_{\mathrm{m}}^{\ominus}}{N_{\mathrm{A}}}\ \text{ where }\frac{q_{\mathrm{m}}^{\ominus}}{N_{\mathrm{A}}}=\frac{q_{\mathrm{m}}^{\mathrm{T}\ominus}}{N_{\mathrm{A}}}q^{\mathrm{R}}q^{\mathrm{V}}q^{\mathrm{E}}\quad[15\mathrm{F}.9]$$

Translation:

$$\frac{q_{\mathrm{m}}^{\mathrm{T}\ominus}}{N_{\mathrm{A}}}=\frac{kT}{p^{\ominus}\Lambda^{3}}\qquad\Lambda=\frac{h}{(2\pi mkT)^{1/2}}$$

After substituting the values of the constants, we obtain

$$\frac{q_{\mathrm{m}}^{\mathrm{T}\ominus}}{N_{\mathrm{A}}}=2.561\times10^{-2}(T/\mathrm{K})^{5/2}(M/\mathrm{g\ mol^{-1}})^{3/2}$$

First, at 10.00 K: $\dfrac{q_{\mathrm{m}}^{\mathrm{T}\ominus}}{N_{\mathrm{A}}}=(2.561\times10^{-2})\times(10.00)^{5/2}\times(36.033)^{3/2}=1752$

Rotation of a nonlinear 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

$$\tilde{B}=\frac{\hbar}{4\pi cI}\ \text{ so }\ \tilde{A}\tilde{B}\tilde{C}=\left(\frac{\hbar}{4\pi c}\right)^{3}\frac{1}{I_{\mathrm{A}}I_{\mathrm{B}}I_{\mathrm{C}}},$$

$$\tilde{A}\tilde{B}\tilde{C}=\left(\frac{1.0546\times10^{-34}\ \mathrm{J\ s}}{4\pi(2.998\times10^{10}\ \mathrm{cm\ s^{-1}})}\right)^{3}$$

$$\times\frac{(10^{10}\ \square\ \mathrm{m^{-1}})^{6}}{(39.340)\times(39.032)\times(0.3082)\times(m_{\mathrm{u}}\ \square^{2})^{3}\times(1.66054\times10^{-27}\ \mathrm{kg}\ m_{\mathrm{u}}^{-1})^{3}}$$

$$=101.2\ \mathrm{cm^{-3}}$$

so $$q^{\mathrm{R}}=\frac{1.0270}{2}\times\frac{(10.00)^{3/2}}{(101.2)^{1/2}}=1.614$$

Vibration:

$$q^{\mathrm{V}}=\frac{1}{1-\mathrm{e}^{-hc\tilde{\nu}/kT}}=\frac{1}{1-\exp\left(\frac{-1.4388(\tilde{\nu}/\mathrm{cm^{-1}})}{T/\mathrm{K}}\right)}=\frac{1}{1-\exp\left(\frac{-1.4388(63.4)}{10.00}\right)}=1.0001$$

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^{E} = 1. Putting it all together yields

$$G_{\mathrm{m}}^{\ominus}(10\ \mathrm{K})-G_{\mathrm{m}}^{\ominus}(0)=(8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}})\times(10.00\ \mathrm{K})\ln[(1752)\times(1.614)\times(1)\times(1)]$$

$$=\boxed{660.8\ \mathrm{J\ mol^{-1}}}$$

Now at 1000 K

Translation: $\dfrac{q_{\mathrm{m}}^{\mathrm{T}\ominus}}{N_{\mathrm{A}}}=(2.561\times10^{-2})\times(1000)^{5/2}\times(36.033)^{3/2}=1.752\times10^{8}$

Rotation: $q^{\mathrm{R}}=\dfrac{1.0270}{2}\times\dfrac{(1000)^{3/2}}{(101.2)^{1/2}}=1614$

Vibration: $q_{1}^{\mathrm{V}}=\dfrac{1}{1-\exp\left(-\frac{(1.4388)\times(63.4)}{1000}\right)}=11.47\quad q_{2}^{\mathrm{V}}=\dfrac{1}{1-\exp\left(-\frac{(1.4388)\times(1224.5)}{1000}\right)}=1.207$

$$q_3^{\mathrm{V}} = \frac{1}{1-\exp\left(-\frac{(1.4388)\times(2040)}{1000}\right)} = 1.056$$

$$q^{\mathrm{V}} = (11.47)\times(1.207)\times(1.056) = 14.62$$

Putting it all together yields

$$G_{\mathrm{m}}^{\ominus}(1000\ \mathrm{K}) - G_{\mathrm{m}}^{\ominus}(0) = (8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}})\times(1000\ \mathrm{K})$$
$$\times\ln[(1.752\times10^{8})\times(1614)\times(14.62)\times(1)]$$
$$= 2.415\times10^{5}\ \mathrm{J\ mol^{-1}} = \boxed{241.5\ \mathrm{kJ\ mol^{-1}}}$$

16 Molecular interactions

16A Electric properties of molecules

Answers to discussion questions

16A.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 16A.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**.

Solutions to exercises

16A.1(b) A molecule with a centre of symmetry may not be polar but molecules belonging to the groups C_n, C_{nv}, and C_s may be polar (Topic 11A). 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.

16A.2(b) $\mu_{\text{res}} = (\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta)^{1/2}$ [16A.3a]

$$= [(2.5)^2 + (0.50)^2 + (2)\times(2.5)\times(0.50)\times(\cos 120^\circ)]^{1/2}\,\text{D} = \boxed{2.3\ \text{D}}$$

16A.3(b) $\mu = \sum_i Q_i \boldsymbol{r}_i = 4e(0) - 2e\boldsymbol{r}_2 - 2e\boldsymbol{r}_3$ where $r_2 = \mathbf{i}x_2$ and $\boldsymbol{r}_3 = \mathbf{i}x_3 + \mathbf{j}y_3$

$$x_2 = +162\ \text{pm}$$

$$x_3 = r_3\cos 30^\circ = (+143\ \text{pm})\times(0.86\overline{6}) = 12\overline{4}\ \text{pm}$$

$$y_3 = r_3\sin 30^\circ = (143\ \text{pm})\times(0.50\overline{0}) = 71.5\ \text{pm}$$

The components of the vector sum are the sums of the components.

$$\mu_x = -2ex_2 - 2ex_3 = -2e\times\{(162)+(12\overline{4})\}\ \text{pm} = -e\times(57\overline{2}\ \text{nm})$$

$$\mu_y = -2ey_3 = -2e\times(71.5\ \text{pm}) = -e\times(143\ \text{pm})$$

$$\mu = \left(\mu_x^2 + \mu_y^2\right)^{1/2} \quad [16\text{A}.4\text{b}]$$

$$= e\times\left\{\left(57\overline{2}\ \text{pm}\right)^2 + \left(143\ \text{pm}\right)^2\right\}^{1/2} = \left(1.602\times10^{-19}\ \text{C}\right)\times\left(59\overline{0}\times10^{-12}\ \text{m}\right)$$

$$= \left(9.4\overline{5}\times10^{-29}\ \text{C m}\right)\times\left(\frac{1\ \text{D}}{3.33564\times10^{-30}\ \text{C m}}\right) = \boxed{28\ \text{D}}$$

The angle that μ makes with x-axis is given by

$$\cos\theta = \frac{|\mu_x|}{\mu} = \frac{57\overline{2}}{59\overline{0}} \qquad \text{so} \qquad \theta = \cos^{-1}\left(\frac{57\overline{2}}{59\overline{0}}\right) = \boxed{14.\overline{2}°}$$

16A.4(b) Polarizability α, dipole moment μ, and molar polarization P_m are related by

$$P_\text{m} = \left(\frac{N_\text{A}}{3\varepsilon_0}\right)\times\left(\alpha + \frac{\mu^2}{3kT}\right) \quad [16\text{A}.12]$$

In order to solve for α, it is first necessary to obtain μ from the temperature variation of P_m.

$$\alpha + \frac{\mu^2}{3kT} = \frac{3\varepsilon_0 P_\text{m}}{N_\text{A}}$$

Therefore, $\left(\frac{\mu^2}{3k}\right)\times\left(\frac{1}{T} - \frac{1}{T'}\right) = \left(\frac{3\varepsilon_0}{N_\text{A}}\right)\times\left(P_\text{m} - P'_\text{m}\right) \quad [P_\text{m}\ \text{at}\ T,\ P'_\text{m}\ \text{at}\ T']$

and hence

$$\mu^2 = \frac{9\varepsilon_0 k\times(P_\text{m} - P'_\text{m})}{N_\text{A}\times\left(\frac{1}{T} - \frac{1}{T'}\right)}$$

$$= \frac{9\times(8.854\times10^{-12}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^{-1})\times(1.381\times10^{-23}\ \text{J K}^{-1})\times(75.74 - 71.43)\times10^{-6}\ \text{m}^3\ \text{mol}^{-1}}{(6.022\times10^{23}\ \text{mol}^{-1})\times\left(\frac{1}{320.0\ \text{K}} - \frac{1}{421.7\ \text{K}}\right)}$$

$$= 1.04\overline{5}\times10^{-59}\ \text{C}^2\ \text{m}^2$$

$$\mu = 3.23\times10^{-30}\ \text{C m}\times\left(\frac{1\ \text{D}}{3.33564\times10^{-30}\ \text{C m}}\right) = \boxed{0.968\ \text{D}}$$

$$\alpha = \frac{3\varepsilon_0 P_\text{m}}{N_\text{A}} - \frac{\mu^2}{3kT}$$

$$= \frac{3\times\left(8.854\times10^{-12}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^{-1}\right)\times\left(75.74\times10^{-6}\ \text{m}^3\ \text{mol}^{-1}\right)}{6.022\times10^{23}\ \text{mol}^{-1}} - \frac{1.04\overline{5}\times10^{-59}\ \text{C}^2\ \text{m}^2}{3\times\left(1.381\times10^{-23}\ \text{J K}^{-1}\right)\times\left(320.0\ \text{K}\right)}$$

$$= \boxed{2.56\times10^{-39}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^2}$$

Corresponding to $\alpha' = \frac{\alpha}{4\pi\varepsilon_0}\ [16\text{A}.6] = \boxed{2.29\times10^{-29}\ \text{m}^3}$

16A.5(b) $M = 85.0\ \text{g mol}^{-1}$

$$\varepsilon_\text{r} - 1 = \frac{\rho P_\text{m}}{M}\times\left(\varepsilon_\text{r} + 2\right) \quad [16\text{A}.11]$$

$$\left(1 - \frac{\rho P_\text{m}}{M}\right)\varepsilon_\text{r} = 1 + \frac{2\rho P_\text{m}}{M}$$

$$\varepsilon_\text{r} = \frac{M + 2\rho P_\text{m}}{M - \rho P_\text{m}}$$

$$= \frac{85.0\ \text{g mol}^{-1} + 2\times\left(1.92\ \text{g cm}^{-3}\right)\times\left(32.16\ \text{cm}^3\ \text{mol}^{-1}\right)}{85.0\ \text{g mol}^{-1} - \left(1.92\ \text{g cm}^{-3}\right)\times\left(32.16\ \text{cm}^3\ \text{mol}^{-1}\right)}$$

$$= \boxed{8.97}$$

16A.6(b) $n_{\mathrm{r}} = (\varepsilon_{\mathrm{r}})^{1/2}$ [16A.14] and $\dfrac{\varepsilon_{\mathrm{r}}-1}{\varepsilon_{\mathrm{r}}+2} = \dfrac{\rho N_{\mathrm{A}}\alpha}{3M\varepsilon_0}$ [16A.13]

Therefore,

$$\begin{aligned}
\alpha &= \frac{3M\varepsilon_0}{\rho N_{\mathrm{A}}}\left(\frac{n_{\mathrm{r}}^2-1}{n_{\mathrm{r}}^2+2}\right) \\
&= \frac{3\times\left(65.5\ \mathrm{g\ mol^{-1}}\right)\times\left(8.854\times10^{-12}\ \mathrm{J^{-1}\ C^2\ m^{-1}}\right)}{\left(2.99\times10^{6}\ \mathrm{g\ m^{-3}}\right)\times\left(6.022\times10^{23}\ \mathrm{mol^{-1}}\right)}\times\left(\frac{1.622^2-1}{1.622^2+2}\right) \\
&= \boxed{3.40\times10^{-40}\ \mathrm{J^{-1}\ C^2\ m^2}}
\end{aligned}$$

16A.7(b) $\alpha' = \dfrac{\alpha}{4\pi\varepsilon_0}$ [16A.6]

$$\alpha = 4\pi\varepsilon_0\alpha' = \left(1.11265\times10^{-10}\ \mathrm{J^{-1}\ C^2\ m^{-1}}\right)\times\left(2.2\times10^{-30}\ \mathrm{m^3}\right) = 2.4\overline{5}\times10^{-40}\ \mathrm{J^{-1}\ C^2\ m^2}$$

Let

$$C = \frac{\rho N_{\mathrm{A}}\alpha}{3M\varepsilon_0} = \frac{\left(865\times10^{3}\ \mathrm{g\ m^{-3}}\right)\times\left(6.022\times10^{23}\ \mathrm{mol^{-1}}\right)\times\left(2.4\overline{5}\times10^{-40}\ \mathrm{J^{-1}\ C^2\ m^2}\right)}{3\times\left(72.3\ \mathrm{g\ mol^{-1}}\right)\times\left(8.85419\times10^{-12}\ \mathrm{J^{-1}\ C^2\ m^{-1}}\right)} = 0.066\overline{5}$$

and solve the Clausius−Mossotti eqn [17A.13] for ε_{r} with which we calculate the refractive index.

$$\frac{\varepsilon_{\mathrm{r}}-1}{\varepsilon_{\mathrm{r}}+2} = C \quad \text{[16A.13, the Clausius – Mossotti eqn]}$$

$$\begin{aligned}
\varepsilon_{\mathrm{r}} &= \frac{1+2C}{1-C} \\
&= \frac{1+2\times\left(0.066\overline{5}\right)}{1-0.066\overline{5}} \\
&= 1.2137
\end{aligned}$$

$$n_{\mathrm{r}} = \varepsilon_{\mathrm{r}}^{1/2}\ [17.17] = \left(1.2137\right)^{1/2} = \boxed{1.10}$$

16A.8(b) $\mu = 5.17\times10^{-30}\ \mathrm{C\ m}$ for bromobenzene (157.00 g mol^{-1})

$$\alpha = 4\pi\varepsilon_0\alpha'\ [16\mathrm{A}.6] = \left(1.11265\times10^{-10}\ \mathrm{J^{-1}\ C^2\ m^{-1}}\right)\times\left(1.5\times10^{-29}\ \mathrm{m^3}\right) = 1.6\overline{7}\times10^{-39}\ \mathrm{J^{-1}\ C^2\ m^2}$$

$$\begin{aligned}
P_{\mathrm{m}} &= \frac{N_{\mathrm{A}}}{3\varepsilon_0}\left(\alpha+\frac{\mu^2}{3kT}\right) \quad [16\mathrm{A}.12] \\
&= \frac{6.022\times10^{23}\ \mathrm{mol^{-1}}}{3\times\left(8.85419\times10^{-12}\ \mathrm{J^{-1}\ C^2\ m^{-1}}\right)}\left(\begin{array}{l}\left(1.6\overline{7}\times10^{-39}\ \mathrm{J^{-1}\ C^2\ m^2}\right) \\ +\dfrac{\left(5.17\times10^{-30}\ \mathrm{C\ m}\right)^2}{3\times\left(1.3807\times10^{-23}\ \mathrm{J\ K^{-1}}\right)\times\left(298.15\ \mathrm{K}\right)}\end{array}\right) \\
&= 8.6\overline{9}\times10^{-5}\ \mathrm{m^3\ mol^{-1}}
\end{aligned}$$

Let

$$C = \frac{\rho P_{\mathrm{m}}}{M} = \frac{\left(1.491\times10^{6}\ \mathrm{g\ m^{-3}}\right)\times\left(8.6\overline{9}\times10^{-5}\ \mathrm{m^3\ mol^{-1}}\right)}{157.00\ \mathrm{g\ mol^{-1}}} = 0.82\overline{5}$$

and solve the Debye eqn [16A.11] for ε_{r}.

$$\frac{\varepsilon_{\mathrm{r}}-1}{\varepsilon_{\mathrm{r}}+2} = C \quad \text{[16A.11, the Debye eqn]}$$

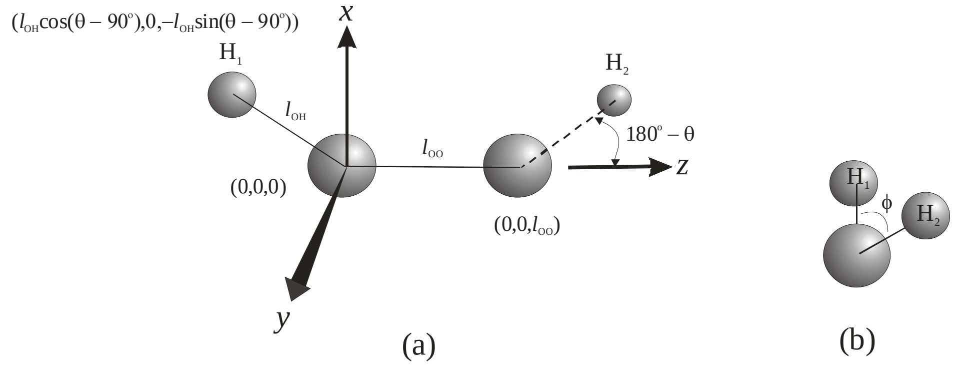
$$\begin{aligned}
\varepsilon_{\mathrm{r}} &= \frac{1+2C}{1-C} \\
&= \frac{1+2\times\left(0.82\overline{5}\right)}{1-0.82\overline{5}} \\
&= \boxed{15}
\end{aligned}$$

Solutions to problems

16A.2 The point charge model can be used to estimate the magnitude of the electric dipole moment of hydrogen peroxide as a function of ϕ (defined in Fig. 16A.1b as a view down the *z* axis of the O–O bond). Each hydrogen atom has a partial charge of δ; each oxygen atom has a partial charge of $-\delta$. The dipole moment magnitude is

$$\mu = (\mu \cdot \mu)^{1/2} = (\mu_x{}^2 + \mu_y{}^2 + \mu_z{}^2)^{1/2} \text{ where } \mu_x = \sum_J Q_J x_J = \delta \times \{x_{H_1} - x_{O_1} - x_{O_2} + x_{H_2}\} \text{ [16A.4a,b], etc.}$$

We will use the Cartesian coordinate system defined in Fig. 16A.1a. The bond lengths are l_{OH} = 97 pm and l_{OO} = 149 pm. We also use the ratio $l_{ratio} = l_{OO} / l_{OH} = 1.54$ and calculate μ in units of δl_{OH} so that it is unnecessary to estimate the magnitude of δ. The O–O–H bond angle, θ, may be estimated as 90° but we will use the experimental value of 100°. The computations of μ_x, μ_y, and μ_z require the coordinates of each atom; those of H_1 and the oxygen atoms are shown in Fig. 16A.1a.



(a) (b)

Figure 16A.1

The coordinates of H_2 can be determined by analogy to the relationships between Cartesian coordinates and spherical polar coordinates. They are:

$$x = l_{OH} \sin(180° - \theta)\cos\phi$$
$$y = l_{OH} \sin(180° - \theta)\sin\phi$$
$$z = l_{OO} + l_{OH} \cos(180° - \theta)$$

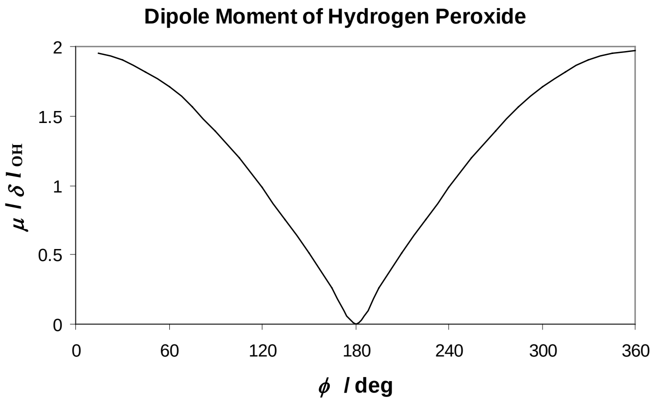
Substitution of variables into eqn. 16A.4b, yields

$$(\mu/\delta l_{OH})^2 = (\mu_x/\delta l_{OH})^2 + (\mu_y/\delta l_{OH})^2 + (\mu_z/\delta l_{OH})^2$$
$$= \{\cos(10°) + \sin(80°)\cos\phi\}^2 + \{\sin(80°)\sin\phi\}^2 + \{-\sin(10°) - l_{ratio} + l_{ratio} + \cos(80°)\}^2$$
$$= \{\cos(10°) + \sin(80°)\cos\phi\}^2 + \{\sin(80°)\sin\phi\}^2 + \{-\sin(10°) + \cos(80°)\}^2$$

We now draw a table to calculate $(\mu/\delta l_{OH})^2$ in ϕ increments of 15° and, subsequently, calculate $\mu/\delta l_{OH}$ values at each ϕ. Fig. 16A.2 is a plot of the variation. As expected, there the dipole is a maximum of almost twice the single O–H bond dipole when the hydrogen atoms are eclipsed and it is zero when they have a gauche conformation.

ϕ / deg	ϕ / radians	sq(μ / δl)	μ / δl
0	0	3.879385	1.969616
15	0.261799	3.813292	1.952765
30	0.523599	3.619516	1.902502
45	0.785398	3.311262	1.819687
60	1.047198	2.909539	1.705737

Figure 16A.2



16A.4[‡] Let the partial charge on the carbon atom equal δe and the N-to-C distance equal l. Then,

$$\mu = \delta el \text{ [16A.4a]} \quad \text{or} \quad \delta = \frac{\mu}{el}$$

$$\delta = \frac{(1.77 \text{ D}) \times (3.3356 \times 10^{-30} \text{ C m D}^{-1})}{(1.602 \times 10^{-19} \text{ C}) \times (299 \times 10^{-12} \text{ m})} = \boxed{0.123}$$

16A.6 The induced dipole moment μ^* is given by

$$\mu^* = \alpha \mathcal{E} \text{ [16A.5a]} = 4\pi\varepsilon_0 \alpha' \mathcal{E} \text{ [16A.6]} = \frac{4\pi\varepsilon_0 \alpha' e}{4\pi\varepsilon_0 r^2} = \frac{\alpha' e}{r^2}$$

Consequently, the dipole-proton distance needed to induce a particular dipole is

$$r = \left(\frac{\alpha' e}{\mu^*} \right)^{1/2}$$

$$= \left(\frac{(1.48 \times 10^{-30} \text{ m}^3) \times (1.602 \times 10^{-19} \text{ C})}{(1.85 \text{ D}) \times (3.336 \times 10^{-30} \text{ C m D}^{-1})} \right)^{1/2} = \boxed{196 \text{ pm}}$$

16A.8 $P_m = \frac{M}{\rho} \times \left(\frac{\varepsilon_r - 1}{\varepsilon_r + 2} \right)$ [16A.11] and $P_m = \frac{4\pi}{3} N_A \alpha' + \frac{N_A \mu^2}{9\varepsilon_0 kT}$ [16A.12, with $\alpha = 4\pi\varepsilon_0 \alpha'$]

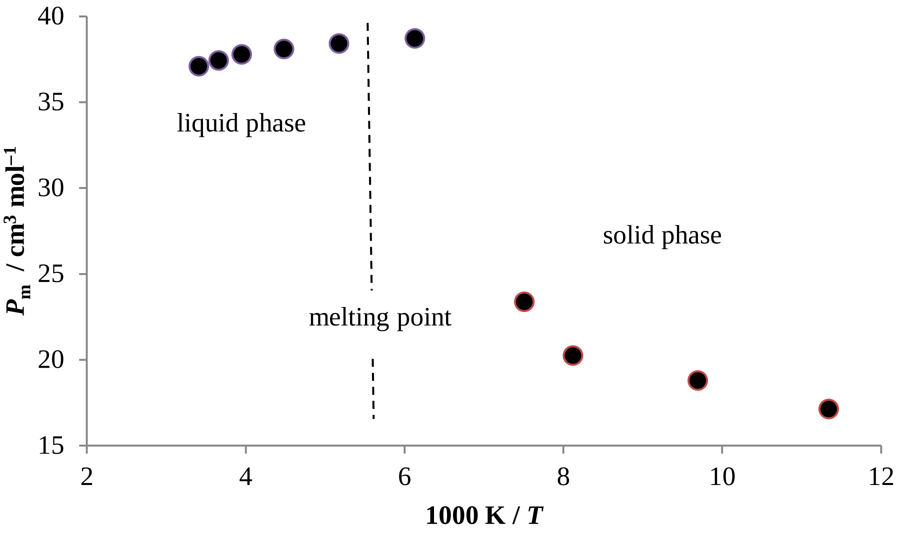
Eqn 16A.12 indicates that, when the permanent dipole moment μ contributes to the molar polarization in a manner that is consistent with thermal averaging of the electric dipole moment in the presence of the applied field (i.e., free rotation), a plot of P_m against $1/T$ should be linear with an intercept at $1/T = 0$ equal to $\frac{4\pi}{3} N_A \alpha'$ and a constant slope for which $\frac{dP_m}{d(1/T)}$ equals $\frac{N_A \mu^2}{9\varepsilon_0 k}$. Eqn 16A.12 is replaced by the Clausius−Mossotti expression, $P_m = \frac{4\pi}{3} N_A \alpha'$ [16A.13], 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 16A.11 or eqn 16A.13, we draw up the following table and prepare the Figure 16A.3 plot of P_m against $1/T$. The molar polarization P_m is calculated with eqn 16A.11 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 $M = 32.0 \text{ g mol}^{-1}$.

[‡] These problems were supplied by Charles Trapp and Carmen Giunta

θ / °C	−185	−170	−150	−140	−110	−80	−50	−20	0	20
T / K	88	103	123	133	163	193	223	253	273	293
$\dfrac{1000}{T/\text{K}}$	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
$\dfrac{\varepsilon_r - 1}{\varepsilon_r + 2}$	0.42	0.46	0.50	0.58	0.957	0.949	0.941	0.933	0.925	0.917
P_m / (cm^3 mol^{-1})	17.1	18.8	20.2	23.4	38.7	38.4	38.1	37.7	37.4	37.1

Figure 16A.3



Inspection of Figure 16A.3 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 16A.12 and 16A.13 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 does provide valuable conceptual information about molecular motion in the condensed phases.

Figure 16A.3 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 $\theta \le -110°\text{C}$ reflects this significant non-linearity:

$$P_m / \text{cm}^3\,\text{mol}^{-1} = 31.246 + 2.3788 \times (10^3\,\text{K} / T) - 0.1904 \times (10^3\,\text{K} / T)^2 \quad \text{with} \quad R^2 = 0.9914$$

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 −110ºC data point exhibiting liquid-like, hindered rotation. The large decline of P_m below −110ºC 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.

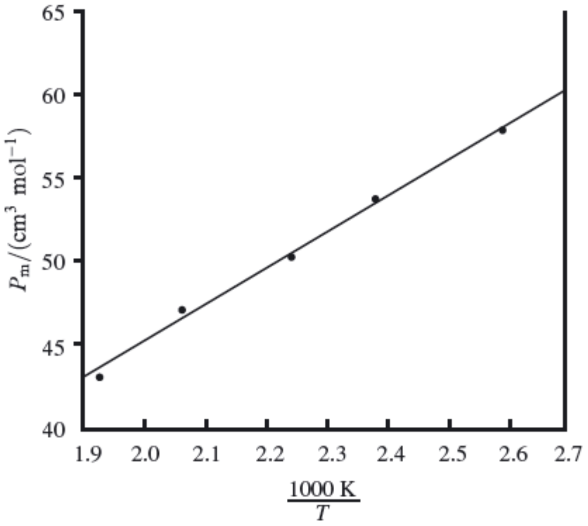
16A.10 Calculate the dipole moment of H_2O and its polarizability volume.

$$P_m = \frac{4\pi}{3} N_A \alpha' + \frac{N_A \mu^2}{9\varepsilon_0 kT} \quad [16\text{A}.12, \text{with } \alpha = 4\pi\varepsilon_0\alpha']$$

Eqn 16A.12 indicates that a plot of P_m against $1/T$ should be linear with a slope, $\dfrac{dP_m}{d(1/T)}$, equal to $\dfrac{N_A \mu^2}{9\varepsilon_0 k}$ and a $1/T = 0$ intercept that equals $\dfrac{4\pi}{3} N_A \alpha'$. 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 16A.4.

T/K	384.3	420.1	444.7	484.1	522.0
$\dfrac{1000}{T/\mathrm{K}}$	2.602	2.380	2.249	2.066	1.916
$P_\mathrm{m}/(\mathrm{cm^3\ mol^{-1}})$	57.4	53.5	50.1	46.8	43.1

Figure 16A.4



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 $\mathrm{d}P_\mathrm{m}/\mathrm{d}(1/T) = 2.08 \times 10^4\ \mathrm{cm^3\ mol^{-1}\ K}$. It follows that

$$\alpha' = \frac{3P_\mathrm{m}\,(\text{at intercept})}{4\pi N_\mathrm{A}} = \frac{3\times(3.44\ \mathrm{cm^3\ mol^{-1}})}{4\pi\times(6.022\times10^{23}\ \mathrm{mol^{-1}})} = \boxed{1.36\times10^{-24}\ \mathrm{cm^3}}$$

$$\mu^2 = \frac{9\varepsilon_0 k}{N_\mathrm{A}}\frac{\mathrm{d}P_\mathrm{m}}{\mathrm{d}(1/T)}$$

$$= \left\{\frac{9\times(8.85419\times10^{-12}\ \mathrm{J^{-1}\ C^2\ m^{-1}})\times(1.3807\times10^{-23}\ \mathrm{J\ K^{-1}})}{6.022\times10^{23}\ \mathrm{mol^{-1}}}\right\}\times(2.08\times10^{-2}\ \mathrm{m^3\ mol^{-1}\ K})$$

$$= 3.80\times10^{-59}\ \mathrm{C^2\ m^2}$$

$$\mu = (3.80\times10^{-59}\ \mathrm{C^2\ m^2})^{1/2}\times\left(\frac{1\ \mathrm{D}}{3.33564\times10^{-30}\ \mathrm{C\ m}}\right) = \boxed{1.85\ \mathrm{D}}$$

16A.12 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 $C \equiv \dfrac{\varepsilon_\mathrm{r}-1}{\varepsilon_\mathrm{r}+2}$ must be much less than 1 greatly simplifies mathematical manipulations.

$$\frac{\varepsilon_\mathrm{r}-1}{\varepsilon_\mathrm{r}+2} = \frac{\rho N_\mathrm{A}\alpha}{3M\varepsilon_0}\ [\text{16A.13, Clausius}-\text{Mossotti eqn}] = \frac{\alpha p}{3\varepsilon_0 kT}\ \ [\rho = Mp/RT,\ \text{perfect gas}] \equiv C$$

Solving the Clausius–Mossotti eqn for ε_r gives

$$\varepsilon_\mathrm{r} = \frac{1+2C}{1-C} \quad \text{where} \quad C = \frac{\alpha p}{3\varepsilon_0 kT}$$

$$= (1+2C)\times(1-C+C^2-C^3+\cdots)\ \ [\text{Taylor series expansion of } (1-C)^{-1} \text{ for } C \ll 1]$$

$$= 1+C\ \ [\text{Second order and higher powers are insignificantly small and may be discarded.}]$$

$$\begin{aligned} n_\mathrm{r} &= (1+C)^{1/2} \quad [16A.14] \\ &= 1 + \tfrac{1}{2}C \quad \text{[Taylor expansion, discard higher order terms]} \\ &= 1 + \frac{\alpha}{6\varepsilon_0 kT}\,p \end{aligned}$$

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 (~$10^{-4}$ 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:

$$\alpha = 6\varepsilon_0 kT \times \left(n_\mathrm{r} - 1\right)/p$$

The polarizability volume is calculated with

$$\alpha' = \alpha / 4\pi\varepsilon_0 \quad [16A.6]$$

16B Interactions between molecules

Answers to discussion questions

16B.2 See Fig. 16A.2 of the text for typical charge arrays corresponding to electric multipoles. As a generality we may write $V \propto 1/r^{n+m-1}$ [16B.6] for the potential energy of interaction between an n-pole and an m-pole. More specifically, the interaction potential between a point charge Q_2 (monopole, n = 1) and any of the multipoles (m = 2 or 3 or ...) is given as $V \propto 1/r^m$ where r is the separation distance between Q_2 and the multipole. This is a steeper potential energy decrease with r than that observed for the Coulombic interaction between two point charges: $V \propto 1/r$. The steeper decline originates in the case for which $r \gg l$, where l is the separation of charge within the multipole, because, as r becomes relatively large, the array of charges in the multipole appears to blend together into neutrality causing lower order interaction terms to cancel. For example, the dipole terms within the monopole-quadrupole (m = 3) interaction potential cancel leaving only a $1/r^3$ term when $r \gg l$.

We use the linear quadrupole charge arrangement shown in Fig. 16B.1 to show this cancellation of lower order terms. Since we are interested in the case $x = l/r << 1$, the following Taylor series expansions are useful substitutions:

$$(1+x)^{-1} = 1 - x + x^2 - x^3 + \cdots \qquad \text{and} \qquad (1-x)^{-1} = 1 + x + x^2 + x^3 + \cdots$$

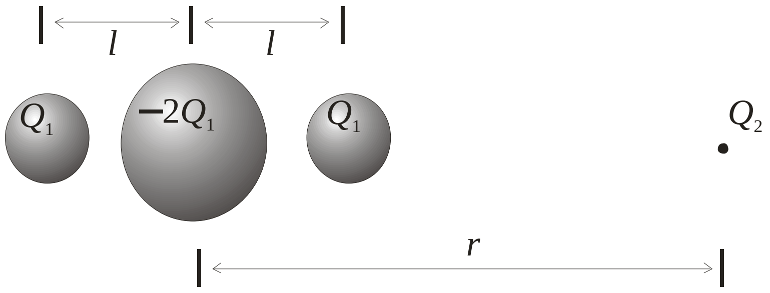
Begin by adding the terms for the Coulomb potential interaction between the charge array of the quadrupole and the monopole Q_2, substitute $x = l/r$, and perform Taylor series expansions on the functions of x.

$$\begin{aligned} 4\pi\varepsilon_0 V &= \frac{Q_1Q_2}{r+l} - \frac{2Q_1Q_2}{r} + \frac{Q_1Q_2}{r-l} \\ &= \frac{Q_1Q_2}{r}\left\{\frac{1}{1+x} - 2 + \frac{1}{1-x}\right\} \\ &= \frac{Q_1Q_2}{r}\left\{\cancel{1}\ \cancel{-x} + x^2 - x^3 + x^4 + \cdots \cancel{-2}\ \cancel{+1}\ \cancel{+x} + x^2 + x^3 + x^4 \cdots\right\} \\ &= \frac{2x^2Q_1Q_2}{r}\left\{1 + x^2 + x^4 + \cdots\right\} \end{aligned}$$

The higher order terms within the polynomial are negligibly small compared to 1 in the case for which $x = l/r <<$ 1, thereby, leaving the simple expression:

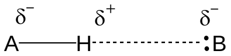
$$V = \frac{2x^2Q_1Q_2}{4\pi\varepsilon_0 r} = \frac{l^2Q_1Q_2}{2\pi\varepsilon_0 r^3} \qquad \text{or} \qquad V \propto \frac{1}{r^3}.$$

Figure 16B.1



16B.4 A **hydrogen bond** ($\cdots$) is an attractive interaction between two species that arises from a link of the form $\mathrm{A-H\cdots B}$, where A and B are highly electronegative elements (usually nitrogen, oxygen, or fluorine) and B possesses a lone pair of electrons. It is a contact-like attraction that requires AH to touch B. Experimental evidences supports a linear or near-linear structural arrangement and a bond strength of about 20 kJ mol^{-1}. The hydrogen bond strength is considerably weaker than a covalent bond but it is larger than, and dominates, other intermolecular attractions such as dipole-dipole attractions. Its formation can be understood in terms of either the (a) electrostatic interaction model or with (b) molecular orbital calculations.

(a) A and B, being highly electronegative, are viewed as having partial negative charges (δ^-) in the electrostatic interaction model of the hydrogen bond. Hydrogen, being less electronegative than A, is viewed as having a partial positive (δ^+). The linear structure maximizes the electrostatic attraction between H and B:

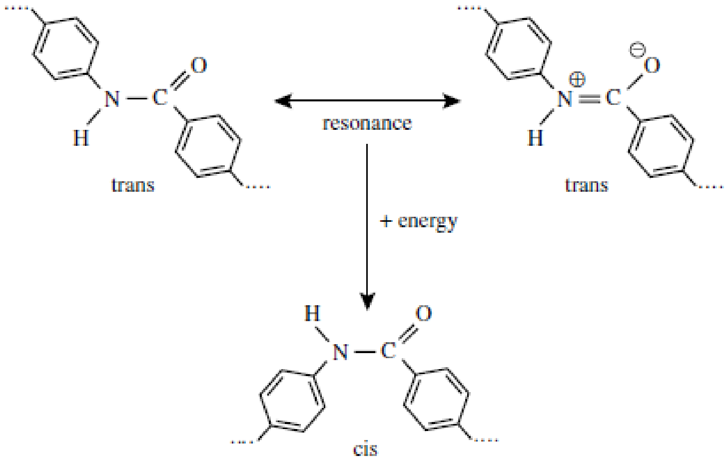


$$\overset{\delta^-}{\mathrm{A}}\text{—}\overset{\delta^+}{\mathrm{H}}\cdots\cdots\overset{\delta^-}{\mathrm{:B}}$$

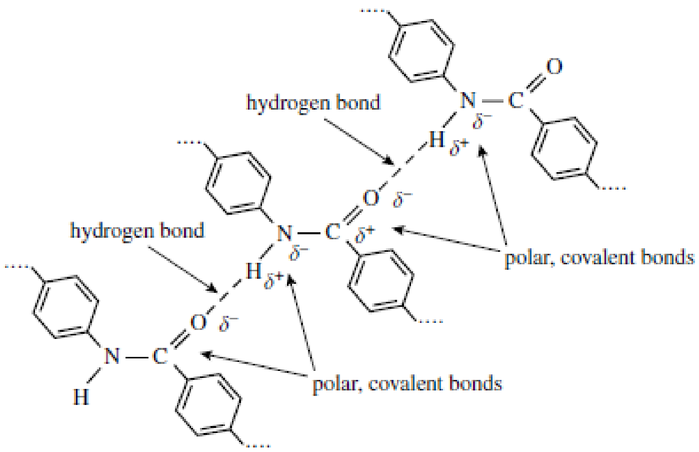
This model is conceptually very useful. However, it is impossible to exactly calculate the interaction strength with this model because the partial atomic charges cannot be precisely defined. There is no way to define which fraction of the electrons of the AB covalent bond should be assigned to one or the other nucleus.

(b) *Ab initio* quantum calculations are needed in order to explore questions about the linear structure, the role of the lone pair, the shape of the potential energy surface, and the extent to which the hydrogen bond has covalent sigma bond character. Yes, the hydrogen bond appears to have some sigma bond character. This was initially suggested by Linus Pauling in the 1930's and more recent experiments with Compton scattering of x-rays and NMR techniques indicate that the covalent character may provide as much as 20% of the hydrogen bond strength. A three-center molecular orbital model provides a degree of insight. A linear combination of an appropriate sigma orbital on A, the 1*s* hydrogen orbital, and an appropriate orbital for the lone pair on B yields a total of three molecular orbitals. One of the MOs is bonding, one is almost nonbonding, and the third is antibonding. Both bonding MO and the almost nonbonding orbital are occupied by two electrons (the sigma bonding electrons of A–H and the lone pair of B). The antibonding MO is empty. Thus, depending on the precise location of the almost nonbonding orbital, the nonbonding orbital may lower the total energy and account for the hydrogen bond.

16B.6 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.



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.



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.

Solutions to exercises

16B.1(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 center. 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.

$$V_{\text{min}} \sim -\frac{\mu_{\text{HCl}} Q_{\text{Mg}^{2+}}}{4\pi\varepsilon_0 r^2}\ [16\text{B}.2] = -\frac{2\mu_{\text{HCl}} e}{4\pi\varepsilon_0 r^2}$$

$$\sim -\frac{2\times(1.08\ \text{D})\times(3.336\times10^{-30}\ \text{C m D}^{-1})\times(1.602\times10^{-19}\ \text{C})}{(1.113\times10^{-10}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^{-1})\times(300\times10^{-12}\ \text{m})^2}$$

$$\sim -1.15\times10^{-19}\ \text{J}$$

The interaction potential becomes a maximum upon flipping the dipole. This effectively changes the sign of the dipole in the previous calculation giving

$$V_{\text{max}} \sim 1.15\times10^{-19}\ \text{J}$$

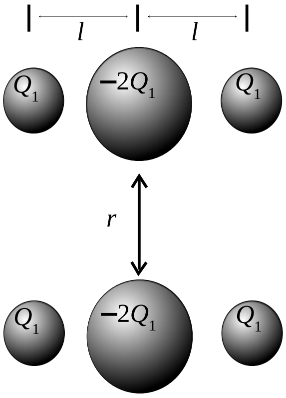
The work w required to flip the dipole is the difference $V_{\text{max}} - V_{\text{min}}$.

$$w \sim V_{\text{max}} - V_{\text{min}} = 2.30\times10^{-18}\ \text{J}$$

$$w_{\text{m}} = wN_{\text{A}} \sim \boxed{1.39\times10^{3}\ \text{kJ mol}^{-1}}$$

16B.2(b) The two linear quadrupoles are shown in Fig. 16B.2 with a parallel configuration.

Figure 16B.2



In addition to the distance r between some of the point charges in one quadrupole and point charges in the other, the Pythagorean theorem provides the distances $(r^2 + l^2)^{1/2}$ and $(r^2 + 4l^2)^{1/2}$. The total potential energy of the interaction between the quadrupoles is:

$$4\pi\varepsilon_0 V = \frac{Q_1^{\,2}}{r} - \frac{2Q_1^{\,2}}{\left(r^2+l^2\right)^{1/2}} + \frac{Q_1^{\,2}}{\left(r^2+4l^2\right)^{1/2}} - \frac{2Q_1^{\,2}}{\left(r^2+l^2\right)^{1/2}} + \frac{4Q_1^{\,2}}{r}$$

$$- \frac{2Q_1^{\,2}}{\left(r^2+l^2\right)^{1/2}} + \frac{Q_1^{\,2}}{\left(r^2+4l^2\right)^{1/2}} - \frac{2Q_1^{\,2}}{\left(r^2+l^2\right)^{1/2}} + \frac{Q_1^{\,2}}{r}$$

$$\frac{2\pi\varepsilon_0 rV}{Q_1^{\,2}} = 3 - \frac{4}{\left(1+x^2\right)^{1/2}} + \frac{1}{\left(1+4x^2\right)^{1/2}} \qquad \text{where} \qquad x = \frac{l}{r}$$

With the point quadrupole condition that $x \ll 1$ the last two terms in the above expression can be expanded with the Taylor series:

$$(1+z)^{-1/2} = 1 - \tfrac{1}{2}z + \tfrac{1}{2}\tfrac{3}{4}z^2 - \tfrac{1}{2}\tfrac{3}{4}\tfrac{5}{6}z^3 + \tfrac{1}{2}\tfrac{3}{4}\tfrac{5}{6}\tfrac{7}{8}z^4 - \cdots$$

$$= 1 - \tfrac{1}{2}z + \tfrac{3}{8}z^2 - \tfrac{15}{48}z^3 + \tfrac{105}{384}z^4 - \cdots$$

where z is either x^2 or $4x^2$.

$$\frac{2\pi\varepsilon_0 rV}{Q_1^{\,2}} = 3 - 4\left\{1 - \tfrac{1}{2}x^2 + \tfrac{3}{8}x^4 - \tfrac{15}{48}x^6 + \tfrac{105}{384}x^8 - \cdots\right\} + \left\{1 - 2x^2 + 6x^4 - 20x^6 + 70x^8 - \cdots\right\}$$

$$= -\tfrac{9}{2}x^4 + \text{higher order terms}$$

In the limit of small x values the higher order terms are negligibly small, thereby, leaving

$$V = -\frac{9x^4Q_1^{\,2}}{4\pi\varepsilon_0 r} = \boxed{-\frac{9l^4Q_1^{\,2}}{4\pi\varepsilon_0 r^5}}$$

Thus, $V \propto \dfrac{1}{r^5}$ for the quadrupole-quadrupole interaction. See Discussion question 16B.2 and note that a quadrupole is n-pole array of charges with $n = 3$. So the above derivation demonstrates the general potential energy relation between an n-pole array and an m-pole array: $V \propto \dfrac{1}{r^{n+m-1}} = \dfrac{1}{r^{3+3-1}} = \dfrac{1}{r^5}$.

16B.3(b) $V_{\text{London}} = -\dfrac{3\left(\alpha'_{\text{Ar}}I_{\text{Ar}}\right)^2}{2\left(I_{\text{Ar}}+I_{\text{Ar}}\right)r^6}\ [16\text{B}.8] = -\dfrac{3\left(\alpha'_{\text{Ar}}\right)^2 I_{\text{Ar}}}{4r^6}$

$$= -\frac{3\times\left(1.66\times10^{-30}\ \text{m}^3\right)^2\times\left(1520.4\ \text{kJ mol}^{-1}\right)}{4\times\left(1.0\times10^{-9}\ \text{m}\right)^6}$$

$$= \boxed{3.1\ \text{J mol}^{-1}}$$

16B.4(b) Using the partial charge presented in the table to the right, we estimate the partial charge on each hydrogen atom of a water molecule to be $Q_H = \delta e$ where $\delta = 0.42$. The electroneutrality of an H_2O molecule implies that the estimated partial charge on the oxygen atom is $Q_O = -2\delta e$. 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

Partial charges in polypeptides
(from Physical Chemistry;
Atkins and de Paula,OUP, 9th ed. 2010)

Atom	Partial charge / *e*
C(=O)	+0.45
C(–CO)	+0.06
H(–C)	+0.02
H(–N)	+0.18
H(–O)	+0.42
N	–0.36
O	–0.38

$$V = \frac{Q_HQ_O}{4\pi\varepsilon r} = -\frac{2(\delta e)^2}{4\pi\varepsilon_r\varepsilon_0 r}\ [16B.1]$$

$$= -\frac{2\left(0.42\times1.60\times10^{-19}\ \text{C}\right)^2}{4\pi(80)\times\left(8.85\times10^{-12}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^{-1}\right)\times\left(170\times10^{-12}\ \text{m}\right)} = -6.0\times10^{-21}\ \text{J}$$

The molar energy required to break these bonds is

$$E_m = -N_AV = -\left(6.022\times10^{23}\ \text{mol}^{-1}\right)\times\left(-6.0\times10^{-21}\ \text{J}\right) = \boxed{3.6\ \text{kJ mol}^{-1}}$$

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.

Solutions to problems

16B.2 The positive end of the dipole will lie closer to the (negative) anion in the most energetically favourable orientation for which the anion will be on line with the dipole. Let the positive end of the dipole have a charge δe while the charge on the other end is $-\delta e$ and the water dipole is defined by $\mu = \delta el$. The electric field generated by a dipole at the distance r where $r \gg l$ is sum of the fields generated by these two charges.

$$\mathcal{E} = \frac{\delta e}{4\pi\varepsilon_0\left(r - l/2\right)^2} - \frac{\delta e}{4\pi\varepsilon_0\left(r + l/2\right)^2}$$

$$= \frac{\delta e}{4\pi\varepsilon_0 r^2}\left\{\frac{1}{\left(1 - l/2r\right)^2} - \frac{1}{\left(1 + l/2r\right)^2}\right\}$$

$$= \frac{\delta e}{4\pi\varepsilon_0 r^2}\left\{\left(1 + l/r\right) - \left(1 - l/r\right)\right\}\quad \text{[Taylor series expansion with } l/2r \ll 1.]$$

$$= \frac{\delta el}{2\pi\varepsilon_0 r^3}$$

$$= \frac{\mu}{2\pi\varepsilon_0 r^3}\quad \text{[Electric field generated by a point dipole.]}$$

$$= \frac{(1.85\ \text{D})\times(3.34\times10^{-30}\ \text{C m D}^{-1})}{2\pi\times(8.854\times10^{-12}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^{-1})\times r^3} = \frac{1.11\times10^{-19}\ \text{V m}^{-1}}{(r/\text{m})^3} = \frac{1.11\times10^{8}\ \text{Vm}^{-1}}{(r/\text{nm})^3}$$

(a) $\mathcal{E} = \boxed{1.1\times10^8\ \text{V m}^{-1}}$ when $r = 1.0\,\text{nm}$

(b) $$\mathcal{E}=\frac{1.11\times10^{8}\ \mathrm{V\,m^{-1}}}{0.3^{3}}=\boxed{4\times10^{9}\ \mathrm{V\,m^{-1}}}\quad \text{for } r=0.3\,\mathrm{nm}$$

(c) $$\mathcal{E}=\frac{1.11\times10^{8}\ \mathrm{V\,m^{-1}}}{30^{3}}=\boxed{4\ \mathrm{kV\,m^{-1}}}\quad \text{for } r=30\,\mathrm{nm}.$$

16B.4 (a) The energy of induced-dipole–induced-dipole interactions can be approximated by the London formula (eqn. 16B.8):

$$V=-\frac{C}{r^{6}}=-\frac{3\alpha_1'\alpha_2'}{2r^{6}}\frac{I_1I_2}{I_1+I_2}=-\frac{3\alpha'^2 I}{4r^{6}}$$

where the second equality uses the fact that the interaction is between two of the same molecule. For two phenyl groups, we have:

$$V=-\frac{3(1.04\times10^{-29}\,\mathrm{m^{3}})^{2}\times(5.0\ \mathrm{eV})\times(1.602\times10^{-19}\,\mathrm{J\,eV^{-1}})}{4\times(4.0\times10^{-9}\,\mathrm{m})^{6}}=-1.8\times10^{-26}\ \mathrm{J}\ \text{or}\ \boxed{-0.0096\ \mathrm{J\,mol^{-1}}}$$

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.)

16B.6 By the law of cosines $r_{\mathrm{O\cdot\cdot H}}^{2}=r_{\mathrm{O-H}}^{2}+r_{\mathrm{O-O}}^{2}-2r_{\mathrm{O-H}}r_{\mathrm{O-O}}\cos\theta$. Therefore,

$$r_{\mathrm{O\cdot\cdot H}}=f(\theta)=\left(r_{\mathrm{O-H}}^{2}+r_{\mathrm{O-O}}^{2}-2r_{\mathrm{O-H}}r_{\mathrm{O-O}}\cos\theta\right)^{1/2}$$

$$V_{\mathrm{m}}=\frac{N_{\mathrm{A}}e^{2}}{4\pi\varepsilon_0}\left\{\frac{\delta_{\mathrm{O}}\delta_{\mathrm{H}}}{r_{\mathrm{O-H}}}+\frac{\delta_{\mathrm{O}}\delta_{\mathrm{H}}}{r_{\mathrm{O\cdot\cdot H}}}+\frac{\delta_{\mathrm{O-O}}^{2}}{r_{\mathrm{O-O}}}\right\}=\frac{N_{\mathrm{A}}e^{2}}{4\pi\varepsilon_0}\left\{\delta_{\mathrm{O}}\delta_{\mathrm{H}}\left(\frac{1}{r_{\mathrm{O-H}}}+\frac{1}{f(\theta)}\right)+\frac{\delta_{\mathrm{O-O}}^{2}}{r_{\mathrm{O-O}}}\right\}$$

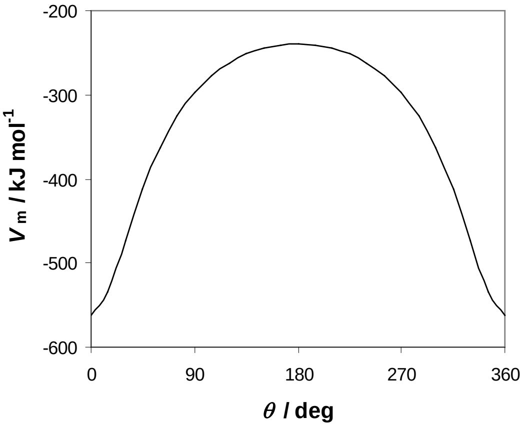
$$=\frac{N_{\mathrm{A}}e^{2}}{4\pi\varepsilon_0\times\left(10^{-12}\ \mathrm{m}\right)}\left\{\delta_{\mathrm{O}}\delta_{\mathrm{H}}\left(\frac{1}{r_{\mathrm{O-H}}/\mathrm{pm}}+\frac{1}{f(\theta)/\mathrm{pm}}\right)+\frac{\delta_{\mathrm{O-O}}^{2}}{r_{\mathrm{O-O}}/\mathrm{pm}}\right\}$$

$$=\left(139\ \mathrm{MJ\,mol^{-1}}\right)\times\left\{\delta_{\mathrm{O}}\delta_{\mathrm{H}}\left(\frac{1}{r_{\mathrm{O-H}}/\mathrm{pm}}+\frac{1}{f(\theta)/\mathrm{pm}}\right)+\frac{\delta_{\mathrm{O-O}}^{2}}{r_{\mathrm{O-O}}/\mathrm{pm}}\right\}$$

With $\delta_{\mathrm{O}} = -0.83$, $\delta_{\mathrm{H}} = 0.45$, $r_{\mathrm{O-H}} = 95.7$ pm, and $r_{\mathrm{O-O}} = 200$ pm we draw up a tabular computation of $f(\theta)$ and $V_{\mathrm{m}}(\theta)$ over the range $0 \le \theta \le 2\pi$ and plot $V_{\mathrm{m}}(\theta)$ in Fig. 16B.3. As expected, the potential is a minimum when θ = 0 because at that angle the hydrogen lies directly between the two oxygen atoms, which repel.

θ / deg	θ / radian	$f(\theta)$	V / kJ/mol
0	0	104.30	-561
15	0.261799	110.38	-534
30	0.523599	126.52	-474
45	0.785398	148.63	-413
60	1.047198	173.26	-363
75	1.308997	198.12	-326
90	1.570796	221.72	-298
105	1.832596	243.04	-277
120	2.094395	261.34	-262
135	2.356194	276.09	-252
150	2.617994	286.90	-245
165	2.879793	293.49	-241
180	3.141593	295.70	-239

Figure 16B.3



16B.8 The number of molecules in a volume element dτ is $\dfrac{N\,\mathrm{d}\tau}{V} = \mathcal{N}\mathrm{d}\tau$. The energy of interaction of these molecules with one at a distance *R* is $V(R)\mathcal{N}\,\mathrm{d}\tau$. The total interaction energy, taking into account the entire sample volume, is therefore

$$u = \int V(R)\mathcal{N}\,\mathrm{d}\tau = \mathcal{N}\int V(R)\,\mathrm{d}\tau \quad [V(R)\text{is the interaction energy, not the volume}]$$

The total interaction energy of a sample of *N* molecules is ½*Nu* (the ½ is included to avoid double counting), and so the cohesive energy density is

$$\mathcal{U} = -\frac{U}{V} = \frac{-\tfrac{1}{2}Nu}{V} = -\frac{1}{2}\mathcal{N}u = -\frac{1}{2}\mathcal{N}^2\int V(R)\,\mathrm{d}\tau$$

For $V(R) = -\dfrac{C_6}{R^6}$ and $\mathrm{d}\tau = 4\pi R^2\,\mathrm{d}R$

$$-\frac{U}{V} = 2\pi\mathcal{N}^2 C_6\int_d^\infty \frac{\mathrm{d}R}{R^4} = \frac{2\pi}{3}\times\frac{\mathcal{N}^2 C_6}{d^3}$$

However, $\mathcal{N} = \dfrac{N_\mathrm{A}\rho}{M}$, where *M* is the molar mass; therefore

$$\mathcal{U} = \boxed{\left(\frac{2\pi}{3}\right)\times\left(\frac{N_\mathrm{A}\rho}{M}\right)^2\times\left(\frac{C_6}{d^3}\right)}$$

16C Liquids

Solutions to exercises

16C.1(b) Calculate the vapour pressure of a spherical droplet of water of radius 20.0 nm at 35.0 °C. The vapour pressure of bulk water at that temperature is 5.623 kPa and its density is 994.0 kg m^{-3}.

$$V_\mathrm{m} = \frac{M}{\rho} = \frac{18.02\text{ g mol}^{-1}}{0.9940\text{ g cm}^{-3}} = 18.13\text{ cm}^3$$

$$p = p^*\mathrm{e}^{2\gamma V_\mathrm{m}(\mathrm{l})/rRT} \quad [\text{16C.20, the Kelvin eqn}]$$

$$= (5.623\text{ kPa})\times\exp\left\{\frac{2\times(72.75\times10^{-3}\text{ N m}^{-1})\times(18.13\times10^{-6}\text{ m}^3\text{ mol}^{-1})}{(20.0\times10^{-9}\text{ m})\times(8.3145\text{ J K}^{-1}\text{ mol}^{-1})\times(308.15\text{ K})}\right\}$$

$$= \boxed{5.92\text{ kPa}}$$

16C.2(b) The contact angle for water on clean glass is close to zero. Calculate the surface tension of water at 30 °C given that at that temperature water climbs to a height of 9.11 cm in a clean glass capillary tube of internal diameter 0.320 mm. The density of water at 30 °C is 0.9956 g cm^{-3}.

$$\gamma = \tfrac{1}{2}\rho grh \quad [\text{16C.9}]$$

$$= \tfrac{1}{2}\times\left(995.6\ \mathrm{kg\ m^{-3}}\right)\times\left(9.80665\ \mathrm{m\ s^{-2}}\right)\times\left(0.320\times10^{-3}\ \mathrm{m}\right)\times\left(9.11\times10^{-2}\ \mathrm{m}\right)$$
$$= 0.142\bar{3}\ \mathrm{kg\ s^{-2}} = \boxed{142\ \mathrm{mN\ m^{-1}}}$$

16C.3(b) Calculate the pressure differential of ethanol across the surface of a spherical droplet of radius 220 nm at 20 °C. The surface tension of ethanol at that temperature is 22.39 mN m^{-1}.

$$p_{\mathrm{in}} - p_{\mathrm{out}} = \frac{2\gamma}{r}\ \text{[16C.7, the Laplace eqn]}$$
$$= \frac{2\times\left(22.39\times10^{-3}\ \mathrm{N\ m^{-1}}\right)}{220\times10^{-9}\ \mathrm{m}}$$
$$= 2.04\times10^{5}\ \mathrm{N\ m^{-2}} = \boxed{204\ \mathrm{kPa}}$$

Pressure differentials for small droplets are quite large.

Integrated activities

16.2 (a) $V = 4\varepsilon\left\{\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6}\right\}$ [16B.14, Lennard – Jones potential]

The depth of the well in Joules is $\varepsilon = hc\tilde{D}_{\mathrm{e}} = \boxed{1.51\times10^{-23}\ \mathrm{J}}$.

The distance at which the potential is zero is given by

$$r_{\mathrm{e}} = 2^{1/6}r_0 \quad \text{so} \quad r_0 = r_{\mathrm{e}}2^{-1/6} = 2^{-1/6}\times\left(297\ \mathrm{pm}\right) = \boxed{265\ \mathrm{pm}}.$$

A plot of the Lennard-Jones potential is shown in Figure I16.1.

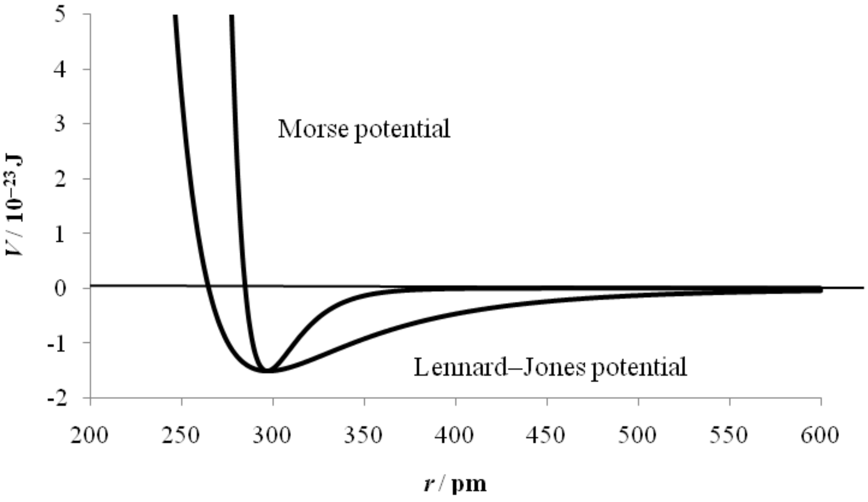


Figure I16.1

(b) $V = hc\tilde{D}_{\mathrm{e}}\left\{1 - \mathrm{e}^{-a\times(r-r_{\mathrm{e}})}\right\}^2 - hc\tilde{D}_{\mathrm{e}}$ [12D.11, Morse potential energy]

The constant $-hc\tilde{D}_{\mathrm{e}}$ has been added to the above expression for the Morse potential so that it has a minimum of $-hc\tilde{D}_{\mathrm{e}}$ at $r = r_{\mathrm{e}}$. This makes it easy to compare the Morse potential with the Lennard–Jones potential of part (a), which also has a minimum of $-hc\tilde{D}_{\mathrm{e}}$ at $r = r_{\mathrm{e}}$. Plots of both potentials are shown in Figure I16.1 with a = 0.0579 pm^{-1} for the Morse potential. The Morse potential has a much steeper repulsive component at separations lower than r_{e} while the Lennard–Jones potential shows a longer-range attractive component.

16.4 (a) Figure I16.2 displays electrostatic charges on the atoms of trans-*N*-methylacetamide as calculated with the DF/B3LYP/6-31G* method using Spartan '10 software. The dipole moment vector is shown in the figure and it approximates points from the positive H atom at the C–H bond to the negative O atom. The calculated dipole moment is $\boxed{\mu = 3.64\ \text{D}}$. This agrees well with the experimental dipole moments at 25° of both acetamide (3.6 D, Handbook of Chemistry and Physics, 1991) and trans-*N*-methylacetamide in benzene solution (3.74 D, V.S. Rangra et al, *Z. Naturforsch*, 61a, 197, 2006).

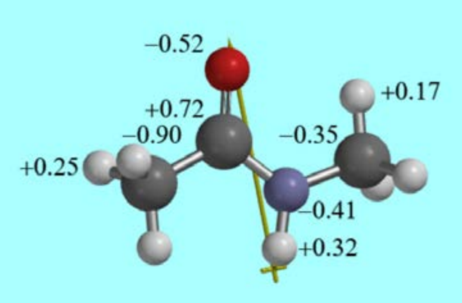


Figure I16.2

The interaction energy of two parallel dipoles is given by eqn. 16B.4:

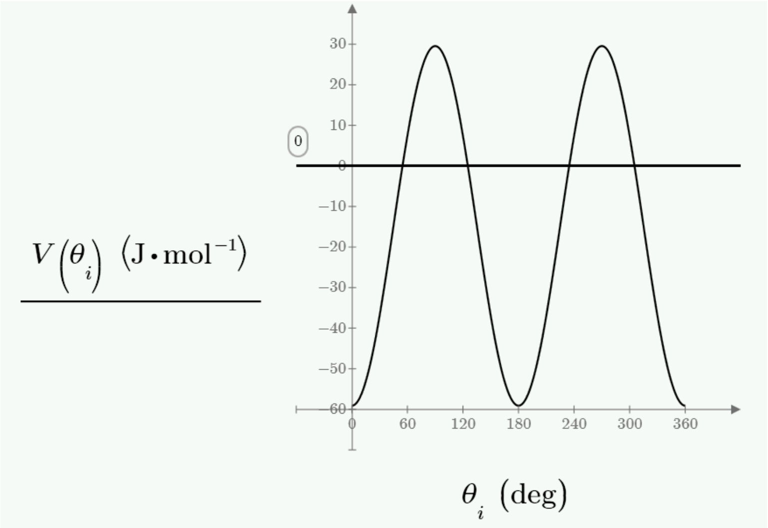
$$V = \frac{\mu_1\mu_2 f(\theta)}{4\pi\varepsilon_0 r^3} \quad \text{where } f(\theta) = 1 - 3\cos^2\theta$$

where r is the distance between the dipoles and θ the angle between the direction of the dipoles and the line that joins them. A plot of the interaction angular dependence is shown in the following Mathcad Prime 2 worksheet. Note that $V(\theta)$ is at a minimum for $\theta = 0°$ and 180° while it is at a maximum for 90° and 270°. Furthermore the interaction is positive and repulsive both when $54.74° < \theta < 125.26°$ and when $234.74° < \theta < 305.26°$. Outside these ranges the potential is negative and attractive.

$$\mu := 3.64 \cdot 3.33564 \cdot 10^{-30} \cdot \text{C} \cdot \text{m} \qquad r := 3.0 \cdot 10^{-9} \cdot \text{m} \qquad \varepsilon_0 := 8.85419 \cdot 10^{-12} \cdot \text{J}^{-1} \cdot \text{C}^2 \cdot \text{m}^{-1}$$

$$f(\theta) := 1 - 3 \cdot \cos(\theta)^2 \qquad i := 0 \,..\, 360 \qquad \theta_i := i \cdot \text{deg} \qquad N_A := 6.02214 \cdot 10^{23} \cdot \text{mol}^{-1}$$

$$V(\theta) := \frac{\mu^2 \cdot f(\theta)}{4 \cdot \pi \cdot \varepsilon_0 \cdot r^3} \cdot N_A$$



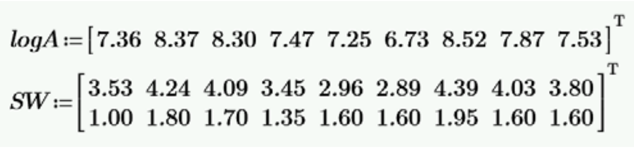
(b)

$$V_{max\_repulsion} := V(90 \cdot \text{deg}) \qquad V_{max\_attraction} := V(180 \cdot \text{deg})$$

$$V_{max\_repulsion} = 0.0296\ \text{kJ} \cdot \text{mol}^{-1} \qquad V_{max\_attraction} = -0.0591\ \text{kJ} \cdot \text{mol}^{-1}$$

The maximum of both the dipole-dipole repulsion and attraction at 3.0 nm are $\boxed{\text{dwarfed by a hydrogen bond attraction}}$ that is typically 20 kJ mol^{-1} at about 200 pm. However, the typical hydrogen bond length is much shorter, so this may not be a fair comparison.

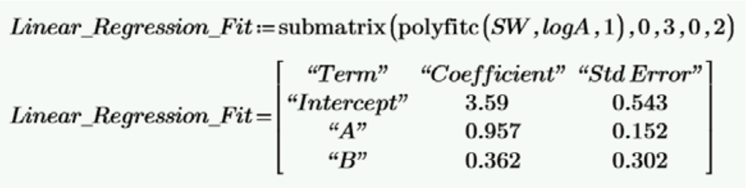
16.6 (a) Here’s a solution using MathCad Prime 2 to perform the bivariable linear model regression fit.
Data:



$$logA := \begin{bmatrix} 7.36 & 8.37 & 8.30 & 7.47 & 7.25 & 6.73 & 8.52 & 7.87 & 7.53 \end{bmatrix}^T$$

$$SW := \begin{bmatrix} 3.53 & 4.24 & 4.09 & 3.45 & 2.96 & 2.89 & 4.39 & 4.03 & 3.80 \\ 1.00 & 1.80 & 1.70 & 1.35 & 1.60 & 1.60 & 1.95 & 1.60 & 1.60 \end{bmatrix}^T$$

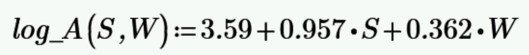
The function polyfitc with n = 1 performs the linear fit. The function submatrix takes rows 0-3 and columns 0-2 of polyfitc.



$$Linear\_Regression\_Fit := \mathrm{submatrix}(\mathrm{polyfitc}(SW, logA, 1), 0, 3, 0, 2)$$

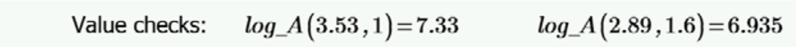
$$Linear\_Regression\_Fit = \begin{bmatrix} \text{“Term”} & \text{“Coefficient”} & \text{“Std Error”} \\ \text{“Intercept”} & 3.59 & 0.543 \\ \text{“A”} & 0.957 & 0.152 \\ \text{“B”} & 0.362 & 0.302 \end{bmatrix}$$

Thus, the linear fit is:



$$log\_A(S, W) := 3.59 + 0.957 \cdot S + 0.362 \cdot W$$

Value checks give reasonable agreement with the data:

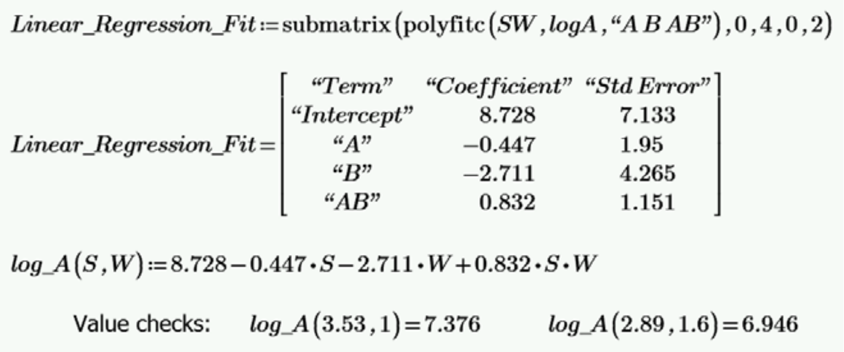


Value checks: $log\_A(3.53, 1) = 7.33$ $log\_A(2.89, 1.6) = 6.935$

(b) For a group having the properties S = 4.84 and log A = 7.60, the linear structure-activity model of part (a) requires the following value of W if the group is to belong to the set of the data.

$$W = \frac{7.60 - (3.59 + 0.957 \times 4.84)}{0.362}$$
$$= \boxed{-1.72}$$

Clearly, the value S = 4.84 is very much out of the S data range as is the computed value of W (−1.72) so we expect that a group X, which has these structure values, does not linearly correlate with this data set. So the question becomes “Can we modify the model so that it meaningfully includes the new group?” Let’s try by adding the cross-term $S \times W$ to the linear model. Here’s the Prime 2 worksheet:



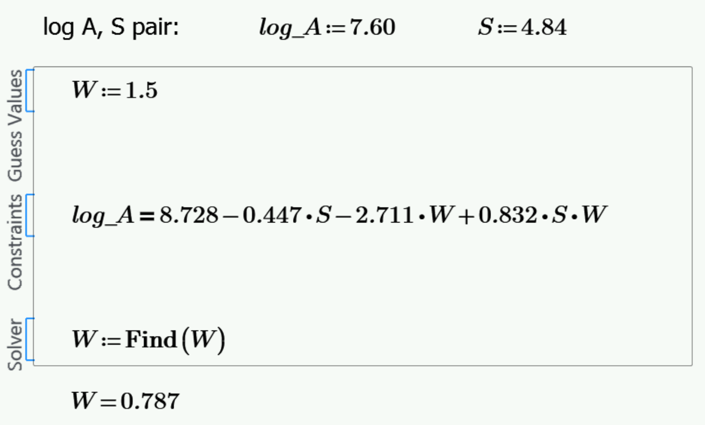
$$Linear\_Regression\_Fit := \mathrm{submatrix}(\mathrm{polyfitc}(SW, logA, \text{“A B AB”}), 0, 4, 0, 2)$$

$$Linear\_Regression\_Fit = \begin{bmatrix} \text{“Term”} & \text{“Coefficient”} & \text{“Std Error”} \\ \text{“Intercept”} & 8.728 & 7.133 \\ \text{“A”} & -0.447 & 1.95 \\ \text{“B”} & -2.711 & 4.265 \\ \text{“AB”} & 0.832 & 1.151 \end{bmatrix}$$

$$log\_A(S, W) := 8.728 - 0.447 \cdot S - 2.711 \cdot W + 0.832 \cdot S \cdot W$$

Value checks: $log\_A(3.53, 1) = 7.376$ $log\_A(2.89, 1.6) = 6.946$

This non-linear structure-activity model seems to adequately describe the groups of part (a) so we now calculate the W value, using a Mathcad Solve block, for what is an outlier group in the linear model.



log A, S pair: $log\_A := 7.60$ $S := 4.84$

$W := 1.5$

$log\_A = 8.728 - 0.447 \cdot S - 2.711 \cdot W + 0.832 \cdot S \cdot W$

$W := \mathbf{Find}(W)$

$W = 0.787$

This is close to the other W values and it is possible that the cross-term has extended the applicability of the model.

17 Macromolecules and self-assembly

17A The structures of macromolecules

Answers to discussion questions

17A.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 Figs. 17A.4 and 17A.5). 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 $n << N$. This model is obviously an oversimplification because a bond is actually constrained to a cone of angles around a direction defined by its neighbor 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_{rms} and R_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 neighbor. This **constrained chain** reduces R_{rms} and R_g values of a freely jointed random coil by a factor of F:

$$F=\left(\frac{1-\cos\theta}{1+\cos\theta}\right)^{1/2} \quad [17\text{A}.7]$$

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.

17A.4 The **Corey–Pauling rules** for the secondary structures of proteins describe the arrangement of atoms at each peptide link (see test Fig. 17A.10). They are:

1. The four atoms of the peptide link lie in a relatively rigid plane. The planarity of the link is due to delocalization of π electrons over the O, C, and N atoms and the maintenance of maximum overlap of their p orbitals.

2. The N, H, and O atoms of a hydrogen bond lie in a straight line (with displacements of H tolerated up to not more than 30° from the N–O direction).

3. All NH and CO groups of the peptide links are engaged in hydrogen bonding.

The rules are satisfied by both helical and sheet structures, for which hydrogen bonding link peptide groups located at separate positions in the primary chain of amino acid residues.

Solutions to exercises

17A.1(b) $R_{\text{rms}} = N^{1/2}l \quad [17\text{A}.4] = (1200)^{1/2}\times(1.125\text{ nm}) = \boxed{38.97\text{ nm}}$

17A.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

$$N=\frac{M_{\text{polymer}}}{M_{\text{monomer}}}=\frac{174\text{ kg mol}^{-1}}{42.1\times10^{-3}\text{ kg mol}^{-1}}=4.13\times10^{3}$$

$l = 2R(\text{C}-\text{C})$ [Add half a bond-length on either side of monomer.]

$$R_c = Nl\ [17\text{A}.3] = 2\times\left(4.13\times10^{3}\right)\times\left(1.54\times10^{-10}\text{ m}\right)=\boxed{1.27\ \mu\text{m}}$$

$$R_{\mathrm{rms}} = N^{1/2}l\ [17\mathrm{A}.4] = 2\times\left(4.13\times10^{3}\right)^{1/2}\times\left(1.54\times10^{-10}\ \mathrm{m}\right) = \boxed{19.8\ \mathrm{nm}}$$

17A.3(b) For a one-dimensional random coil, the radius of gyration is

$$R_{\mathrm{g}} = N^{1/2}l\ [17\mathrm{A}.5] \quad \text{so is number of links is} \quad N = \left(\frac{R_{\mathrm{g}}}{l}\right)^{2} = \left(\frac{18.9\ \mathrm{nm}}{0.450\ \mathrm{nm}}\right)^{2} = \boxed{1.76\times10^{3}}$$

17A.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

$$N = \frac{M_{\mathrm{polymer}}}{M_{\mathrm{monomer}}} = \frac{85\,000\ \mathrm{g\ mol^{-1}}}{28\ \mathrm{g\ mol^{-1}}} = 3.0\overline{4}\times10^{3}$$

$l = 2R(\mathrm{C}$—$\mathrm{C}) = 2 \times 154$ pm = 308 pm [Add half a bond-length on either side of monomer.]

In units of l the polymer ends are separated by the distance

$$n = \frac{15\times10^{-9}\ \mathrm{m}}{l} = \frac{15\times10^{-9}\ \mathrm{m}}{308\times10^{-12}\ \mathrm{m}} = 48.\overline{7}$$

Thus,

$$P = \left(\frac{2}{\pi N}\right)^{1/2} \mathrm{e}^{-n^{2}/2N}\quad [17\mathrm{A}.1]$$

$$= \left(\frac{2}{\pi\times3.0\overline{4}\times10^{3}}\right)^{1/2} \mathrm{e}^{-\left(48.\overline{7}\right)^{2}/\left\{2\times\left(3.0\overline{4}\times10^{3}\right)\right\}} = \boxed{9.8\times10^{-3}}$$

17A.5(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

$$N = \frac{M_{\mathrm{polymer}}}{M_{\mathrm{monomer}}} = \frac{75\,000\ \mathrm{g\ mol^{-1}}}{28\ \mathrm{g\ mol^{-1}}} = 2.6\overline{8}\times10^{3}$$

$l = 2R(\mathrm{C}$—$\mathrm{C}) = 2 \times 154$ pm = 308 pm [Add half a bond-length on either side of monomer.]

Thus,

$$a = \left(\frac{3}{2Nl^{2}}\right)^{1/2}\quad [17\mathrm{A}.2]$$

$$= \left(\frac{3}{2\times\left(2.6\overline{8}\times10^{3}\right)\times\left(308\times10^{-12}\ \mathrm{m}\right)^{2}}\right)^{1/2} = 7.6\overline{8}\times10^{7}\ \mathrm{m}^{-1}$$

The 14.00 nm to 14.10 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 $f(r) = f(14.05\ \mathrm{nm})$. The probability that the polymer ends are in this range is

$$P = f\left(r\right)\Delta r = 4\pi\left(\frac{a}{\pi^{1/2}}\right)^{3} r^{2}\mathrm{e}^{-a^{2}r^{2}}\Delta r\quad [17\mathrm{A}.2]$$

$$= 4\pi\left(\frac{7.6\overline{8}\times10^{7}\ \mathrm{m}^{-1}}{\pi^{1/2}}\right)^{3}\times\left(14.05\times10^{-9}\ \mathrm{m}\right)^{2}\times\mathrm{e}^{-\left(7.6\overline{8}\times10^{7}\ \mathrm{m}^{-1}\right)^{2}\left(14.05\times10^{-9}\ \mathrm{m}\right)^{2}}\times\left(14.1-14.00\right)\times10^{-9}\ \mathrm{m}$$

$$= \boxed{6.3\times10^{-3}}$$

17A.6(b) The radius of gyration for a constrained chain that has successive individual bonds constrained to a single cone of angle θ = 120° (i.e., $\cos\theta = -½$) is

$$R_{\mathrm{g,constrained\ coil}} = R_{\mathrm{g,random\ coil}}F \quad \text{with} \quad F = \left(\frac{1-\cos\theta}{1+\cos\theta}\right)^{1/2}\ [17\mathrm{A}.7] = \left(\frac{1+\frac{1}{2}}{1-\frac{1}{2}}\right)^{1/2} = \sqrt{3}$$

The percentage change in the radius of gyration upon application of the constraint is

$$\left(\frac{R_{\text{g,constrained coil}}-R_{\text{g,random coil}}}{R_{\text{g,random coil}}}\right)\times100\% = \left(\frac{R_{\text{g,constrained coil}}}{R_{\text{g,random coil}}}-1\right)\times100\% = (F-1)\times100\%$$
$$= \left(\sqrt{3}-1\right)\times100\%$$
$$= \boxed{+73.21\%}$$

The percentage change in the volume upon application of the constraint is

$$\left(\frac{V_{\text{constrained coil}}-V_{\text{random coil}}}{V_{\text{random coil}}}\right)\times100\% = \left(\frac{R_{\text{g,constrained coil}}{}^3-R_{\text{g,random coil}}{}^3}{R_{\text{g,random coil}}{}^3}\right)\times100\%$$
$$= \left\{\left(\frac{R_{\text{g,constrained coil}}}{R_{\text{g,random coil}}}\right)^3-1\right\}\times100\% = \left(F^3-1\right)\times100\%$$
$$= \left(3^{3/2}-1\right)\times100\%$$
$$= \boxed{+419.6\%}$$

17A.7(b) $R_{\text{rms}} = R_{\text{rms,random coil}}F = N^{1/2}lF$ [17A.10] 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 $0.025R_c$ with constant contour length is given by the expression

$$\left(\frac{R_{\text{rms}}-R_{\text{rms,random coil}}}{R_{\text{rms,random coil}}}\right)\times100\% = \left(\frac{R_{\text{rms}}}{R_{\text{rms,random coil}}}-1\right)\times100\% = (F-1)\times100\%$$
$$= \left\{\left(\frac{2l_p}{l}-1\right)^{1/2}-1\right\}\times100\%$$
$$= \left\{\left(\frac{2\times(0.025R_c)}{l}-1\right)^{1/2}-1\right\}\times100\%$$
$$= \left\{\left(\frac{2\times(0.025\times Nl)}{l}-1\right)^{1/2}-1\right\}\times100\% \quad [17A.3]$$
$$= \left\{(0.050N-1)^{1/2}-1\right\}\times100\%$$
$$= \boxed{+600\ \%\text{ when }N=1000}$$

The percentage change in the volume as determined by the root-mean-square separation is

$$\left(\frac{V-V_{\text{rms,random coil}}}{V_{\text{rms,random coil}}}\right)\times100\% = \left(\frac{R_{\text{rms}}{}^3-R_{\text{rms,random coil}}{}^3}{R_{\text{rms,random coil}}{}^3}\right)\times100\% = \left(F^3-1\right)\times100\%$$
$$= \left\{\left(\frac{2l_p}{l}-1\right)^{3/2}-1\right\}\times100\%$$
$$= \left\{\left(\frac{2\times(0.025R_c)}{l}-1\right)^{3/2}-1\right\}\times100\%$$
$$= \left\{\left(\frac{2\times(0.025\times Nl)}{l}-1\right)^{3/2}-1\right\}\times100\% \quad [17A.3]$$
$$= \left\{(0.050N-1)^{3/2}-1\right\}\times100\%$$
$$= \boxed{+3.42\times10^4\ \%\text{ when }N=1000}$$

17A.8(b) In analogy to eqn 17A.10 we assume the following relation for a three-dimensional partially rigid polymer.

$$R_{\mathrm{g}} = R_{\mathrm{g,random\ coil}}F = \left(\frac{N}{6}\right)^{1/2} lF \quad \text{where} \quad F = \left(\frac{2l_p}{l}-1\right)^{1/2}$$

Solving for l_{p} gives

$$l_p = \frac{l}{2}\left\{\frac{6R_{\mathrm{g}}{}^2}{Nl^2}+1\right\}$$

$$= \frac{164\ \mathrm{pm}}{2}\left\{\frac{6\times(3000\ \mathrm{pm})^2}{1500\times(164\ \mathrm{pm})^2}+1\right\} = \boxed{1.9\times10^2\ \mathrm{pm}}$$

Solutions to problems

17A.2 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

$$f(r) = 4\pi\left(\frac{a}{\pi^{1/2}}\right)^3 r^2\mathrm{e}^{-a^2r^2} \qquad a = \left(\frac{3}{2Nl^2}\right)^{1/2} \quad [17\mathrm{A}.2]$$

The mean nth power of the end-to-end separation is

$$\langle r^n\rangle = \int_0^\infty r^n f(r)\mathrm{d}r$$

(a) The square of the root mean square separation of the chain ends is

$$R_{\mathrm{rms}}{}^2 = \langle r^2\rangle = \int_0^\infty r^2 f(r)\mathrm{d}r$$

$$= 4\pi\left(\frac{a}{\pi^{1/2}}\right)^3\int_0^\infty r^4\mathrm{e}^{-a^2r^2}\mathrm{d}r$$

$$= 4\pi\left(\frac{a}{\pi^{1/2}}\right)^3\frac{\Gamma\left(\tfrac{5}{2}\right)}{2a^5} \quad \text{where } \Gamma\left(\tfrac{5}{2}\right) = \tfrac{3}{4}\pi^{1/2} \quad [\text{standard integral}]$$

$$= \frac{3}{2a^2} = \frac{3}{2}\left(\frac{2Nl^2}{3}\right) = Nl^2$$

$$R_{\mathrm{rms}} = \langle r^2\rangle^{1/2} = \boxed{N^{1/2}l}$$

Note: The general form of the above standard integral is

$$\int_0^\infty r^m\mathrm{e}^{-a^2r^2}\mathrm{d}r = \frac{\Gamma\left[(m+1)/2\right]}{2a^{m+1}} \quad \text{where } \Gamma \text{ is the gamma function found in math handbooks}$$

When $N = 4000$ and $l = 154$ pm, $R_{\mathrm{rms}} = 4000^{1/2}\times154\ \mathrm{pm} = \boxed{9.74\ \mathrm{nm}}$

(b) The mean separation is

$$R_{\mathrm{mean}} = \langle r\rangle = \int_0^\infty rf(r)\mathrm{d}r$$

$$= 4\pi\left(\frac{a}{\pi^{1/2}}\right)^3\int_0^\infty r^3\mathrm{e}^{-a^2r^2}\mathrm{d}r$$

$$= 4\pi\left(\frac{a}{\pi^{1/2}}\right)^3\frac{\Gamma(2)}{2a^4} \quad \text{where } \Gamma(2) = 1 \quad [\text{standard integral}]$$

$$= \frac{2}{\pi^{1/2}a} = \boxed{\left(\frac{8N}{3\pi}\right)^{1/2} l}$$

When $N = 4000$ and $l = 154$ pm, $R_{\mathrm{mean}} = \left(\frac{8\times4000}{3\pi}\right)^{1/2} 154\ \mathrm{pm} = \boxed{8.98\ \mathrm{nm}}$

(c) The most probable separation, R^*, is the value of r for which f is a maximum, so set $\left.\dfrac{\mathrm{d}f}{\mathrm{d}r}\right]_{r=R^*}=0$ and solve for R^*.

$$\frac{\mathrm{d}f}{\mathrm{d}r}=4\pi\left(\frac{a}{\pi^{1/2}}\right)^3\left(2r-2a^2r^3\right)\mathrm{e}^{-a^2r^2}$$

Evaluation of the slope of f at $r = R^*$ shows that it is zero when

$$1-a^2R^{*2}=0$$

$$R^*=\frac{1}{a}=\boxed{\left(\tfrac{2}{3}N\right)^{1/2}l}$$

When $N = 4000$ and $l = 154$ pm, $R^*=\left(\tfrac{2}{3}\times 4000\right)^{1/2}\times 154\text{ pm}=\boxed{7.95\text{ nm}}$

17A.4 There are two standard sums found in math handbooks that are used in the following derivation. They are:

$$\sum_{j=1}^{i} j=\tfrac{1}{2}i(i+1)\quad\text{and}\quad\sum_{j=1}^{i} j^2=\tfrac{1}{6}i(i+1)(2i+1)$$

We begin with the following definition of the radius of gyration:

$$2N^2R_\mathrm{g}{}^2=\sum_{i=1}^{N}\sum_{j=1}^{N}\left\langle R_{ij}{}^2\right\rangle$$

where $\left\langle R_{ij}{}^2\right\rangle$ is the mean over all conformations of the separation between atoms i and j in a chain of identical atoms linked with the bond length l. In fact, $\left\langle R_{ij}{}^2\right\rangle$ is identical to the end separation of a chain of $|i-j|$ atoms and, consequently, $\left\langle R_{ij}{}^2\right\rangle=|i-j|\,l^2$.

$$2N^2R_\mathrm{g}{}^2/l^2=\sum_{i=1}^{N}\sum_{j=1}^{N}|i-j|$$

We now break the inner summation of absolute values into two separate summations of positive terms.

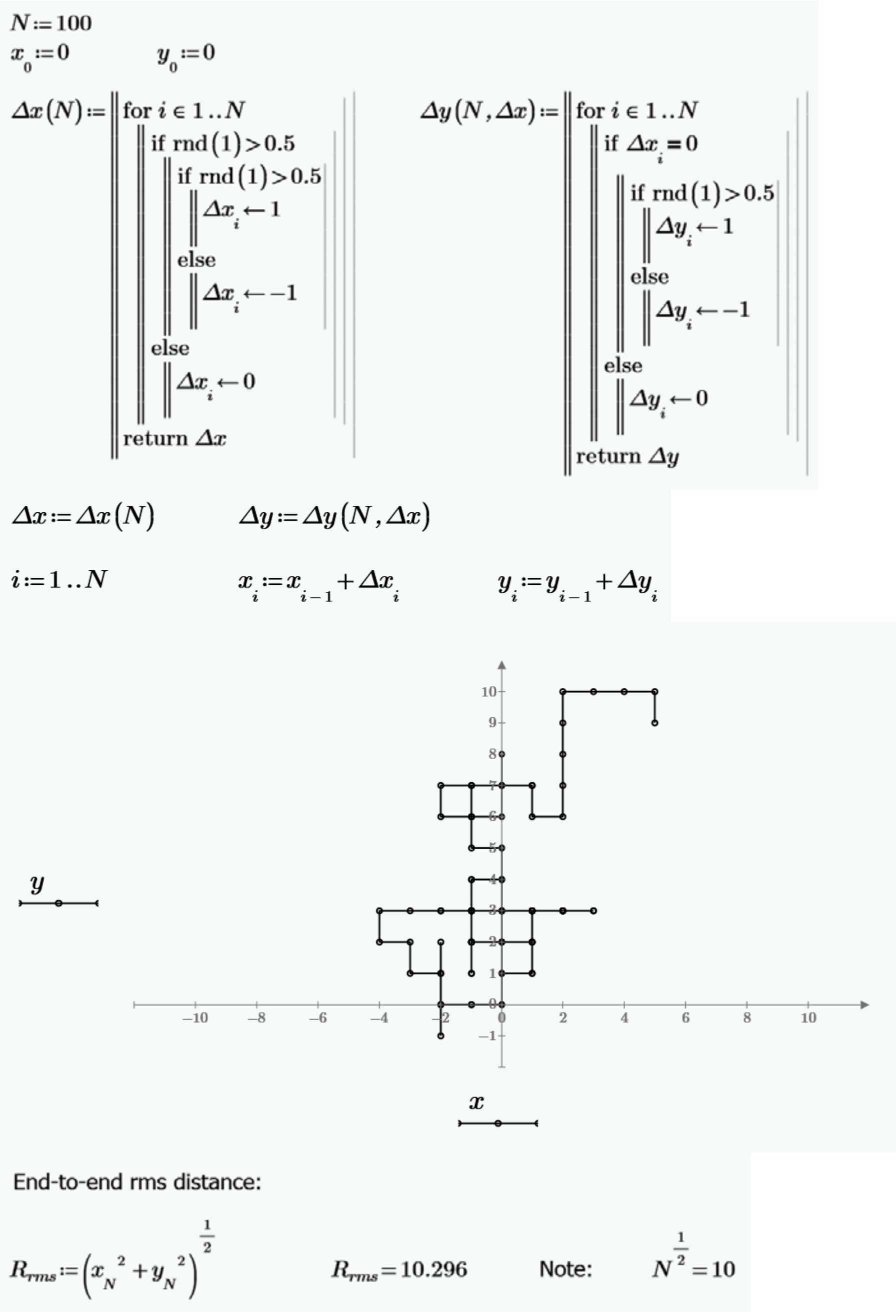
$$\begin{aligned}
2N^2R_\mathrm{g}{}^2/l^2&=\sum_{i=1}^{N}\left\{\sum_{j=1}^{i}(i-j)+\sum_{j=i+1}^{N}(j-i)\right\}\\
&=\sum_{i=1}^{N}\left\{i\sum_{j=1}^{i}1-\sum_{j=1}^{i}j+\sum_{j=i+1}^{N}j-i\sum_{j=i+1}^{N}1\right\}\\
&=\sum_{i=1}^{N}\left\{i^2-\tfrac{1}{2}i(i+1)+\sum_{j=1}^{N}j-\sum_{j=1}^{i}j-i(N-i)\right\}\\
&=\sum_{i=1}^{N}\left\{i^2-\tfrac{1}{2}i(i+1)+\tfrac{1}{2}N(N+1)-\tfrac{1}{2}i(i+1)-i(N-i)\right\}\\
&=\sum_{i=1}^{N}\left\{i^2-i(N+1)+\tfrac{1}{2}N(N+1)\right\}\\
&=\sum_{i=1}^{N}i^2-(N+1)\sum_{i=1}^{N}i+\tfrac{1}{2}N(N+1)\sum_{i=1}^{N}1\\
&=\tfrac{1}{6}N(N+1)(2N+1)-\tfrac{1}{2}N(N+1)^2+\tfrac{1}{2}N^2(N+1)
\end{aligned}$$

Since $N \gg 1$, $N + 1$ effectively equals N.

$$2N^2R_\mathrm{g}{}^2/l^2=\tfrac{1}{3}N^3-\tfrac{1}{2}N^3+\tfrac{1}{2}N^3=\tfrac{1}{3}N^3$$

$R_\mathrm{g}{}^2=\tfrac{1}{6}Nl^2$ or $\boxed{R_\mathrm{g}=\sqrt{N/6}\,l}$, which confirms eqn 17A.6

17A.6 A simple procedure is to generate numbers in the range 1 to 8, and to step north for a 1 or 2, east for 3 or 4, south for 5 or 6, and west for 7 or 8 on a uniform grid. Alternatively, the random number generator rnd(1), which gives a random number between 0 and 1, can be used to generate the random steps. Can you follow the following Mathcad Prime 2 program logic for constructing a two-dimensional walk? If you recreate the program notice that each recalculation produces a new path for the walk because of the use of random numbers; also, explore the effect of changing the value of N upon the plot. Notice that the random nature of the walk tends to severely restrict expansion of R_{rms} by favoring back and forth, up and down motions that pretty much keep the walker in the same local region for many steps. Roughly, the rms end-to-end separations would appear to vary as $N^{1/2}$. Can you rewrite the program so that each step occurs at a random angle to the *x*-axis at a constant length of 1?



```
N := 100
x_0 := 0          y_0 := 0

Δx(N) := | for i ∈ 1..N                    Δy(N, Δx) := | for i ∈ 1..N
         |   if rnd(1) > 0.5                            |   if Δx_i = 0
         |     if rnd(1) > 0.5                          |     if rnd(1) > 0.5
         |       Δx_i ← 1                               |       Δy_i ← 1
         |     else                                     |     else
         |       Δx_i ← −1                              |       Δy_i ← −1
         |   else                                       |   else
         |     Δx_i ← 0                                 |     Δy_i ← 0
         | return Δx                                    | return Δy

Δx := Δx(N)          Δy := Δy(N, Δx)

i := 1..N            x_i := x_(i−1) + Δx_i          y_i := y_(i−1) + Δy_i
```

End-to-end rms distance:

$$R_{rms} := \left(x_N{}^2 + y_N{}^2\right)^{\frac{1}{2}} \qquad R_{rms} = 10.296 \qquad \text{Note:} \quad N^{\frac{1}{2}} = 10$$

17A.8 The definition of radius of gyration is

$$R_{\text{g}} = \frac{1}{N}\left(\frac{1}{2}\sum_{ij}\boldsymbol{R}_{ij}{}^2\right)^{1/2}$$

So, $$2N^2R_{\text{g}}{}^2 = \sum_{ij}R_{ij}{}^2 = \sum_{i=1}^{N}\sum_{j=1}^{N}R_{ij}{}^2$$

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 center of mass), the interatomic vectors $\boldsymbol{R}_{ij}$ can be expressed in terms of vectors from the origin: $\boldsymbol{R}_{ij} = \boldsymbol{R}_j - \boldsymbol{R}_i$. Therefore,

$$R_g{}^2 = \frac{1}{2N^2}\sum_i\sum_j(\boldsymbol{R}_j-\boldsymbol{R}_i)\cdot(\boldsymbol{R}_j-\boldsymbol{R}_i)$$

$$= \frac{1}{2N^2}\sum_i\sum_j(\boldsymbol{R}_j\cdot\boldsymbol{R}_j+\boldsymbol{R}_j\cdot\boldsymbol{R}_j-2\boldsymbol{R}_i\cdot\boldsymbol{R}_j) = \frac{1}{2N^2}\sum_i\sum_j(R_j{}^2+R_i{}^2-2\boldsymbol{R}_i\cdot\boldsymbol{R}_j)$$

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 $R_g{}^2 = \frac{1}{N}\sum_j R_j{}^2 - \frac{1}{N^2}\sum_i\sum_j \boldsymbol{R}_i\cdot\boldsymbol{R}_j = \frac{1}{N}\sum_j R_j{}^2 - \frac{1}{N^2}\sum_i \boldsymbol{R}_i\cdot\sum_j\boldsymbol{R}_j$

If we choose the origin of our coordinate system to be the center of mass, then

$$\sum_i \boldsymbol{R}_i = \sum_j \boldsymbol{R}_j = 0 \qquad \text{and} \qquad R_g{}^2 = \frac{1}{N}\sum_j R_j{}^2$$

for the center of mass is the point in the center of the distribution such that all vectors from that point to identical individual masses sum to zero.

17B Properties of macromolecules

Answers to discussion questions

17B.2 As illustrated in the stress–strain curve of text Fig. 17B.2, the stress-strain region of **elastic deformation** is where the strain is proportional to the stress and is reversible: when the stress is removed, the sample returns to its initial shape. At the **yield point**, the reversible, linear deformation gives way to **plastic deformation**, where the strain is no longer linearly proportional to the stress and the initial shape of the sample is not recovered when the stress is removed.

17B.4 Conducting polymers have extensively conjugated double bond networks that permit electron conduction along the polymer chain. The delocalized π bonds contribute to electrical conductivity by allowing electrons can move up and down the polymer chain. One conducting polymer, polyacetylene, exhibits conductivity increases when it is partially oxidized by I_2 and other strong oxidants. The oxidation product is a **polaron**, a partially localized cation radical that travels virtually (by exchanging its identity with a neighbour) through the chain (see text Fig. 17B.7). Further oxidation of the polymer forms either **bipolarons**, a di-cation that moves virtually as a unit through the chain, or **solitons**, two separate cation radicals that move independently.

Solutions to exercises

17B.1(b) We obtain (see exercise 17A.4(b)) $N = 3.0\overline{4}\times10^3$ and l = 308 pm. In units of l the polymer ends are moved apart by the distance

$$n = \frac{2.0\times10^{-9}\ \text{m}}{l} = \frac{2.0\times10^{-9}\ \text{m}}{308\times10^{-12}\ \text{m}} = 6.4\overline{9}$$

Thus, the molar change in conformational entropy arising from the stretch is

$$\Delta S = -\tfrac{1}{2}RN\ln\{(1+\nu)^{1+\nu}(1-\nu)^{1-\nu}\}\ \ [17\text{B}.1] \quad \text{with} \quad \nu = n/N = 6.4\overline{9}/3.0\overline{4}\times10^3 = 2.1\overline{3}\times10^{-3}$$

$$= -\tfrac{1}{2}\times\left(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}\right)\times\left(3.0\overline{4}\times10^3\right)\times\ln\left\{\left(1.0021\overline{3}\right)^{1.0021\overline{3}}\times\left(0.99787\right)^{0.99787}\right\}$$

$$= \boxed{-57\ \text{mJ mol}^{-1}\ \text{K}^{-1}}$$

17B.2(b) Each polyethene chain bond has a length l = 154 pm = 0.154 nm and the number N chain bonds is the polymer molar mass divided by the molar mass of the repeating CH_2 unit.

$$N = \frac{M_{\text{polymer}}}{M_{\text{CH}_2}} = \frac{85\ 000\ \text{g mol}^{-1}}{14\ \text{g mol}^{-1}} = 6.0\overline{7} \times 10^3$$

The restore forcing of a freely jointed chain is

$$\mathcal{F} = \frac{kT}{2l} \ln\left(\frac{1+\nu}{1-\nu}\right) \qquad \nu = n/N \quad [17\text{B}.2\text{a}]$$

n is the displacement from equilibrium in units of l so

$$\nu = \frac{n}{N} = \frac{(2.0\ \text{nm})/(0.154\ \text{nm})}{6.0\overline{7} \times 10^3} = 2.1\overline{4} \times 10^{-3}$$

Since $\nu << 1$, we use the simplified form of eqn 17B.2a.

$$\mathcal{F} = \frac{nkT}{Nl} \quad [17\text{B}.2\text{b}]$$

$$= \frac{(2.1\overline{4} \times 10^{-3}) \times (1.381 \times 10^{-23}\ \text{J K}^{-1}) \times (298.15\ \text{K})}{154 \times 10^{-12}\ \text{m}} = \boxed{5.7 \times 10^{-14}\ \text{N}}$$

Solutions to problems

17B.2 On the assumption that the tension, *t*, required to keep a sample at a constant length is proportional to the temperature ($t = aT$, the analogue of $p \propto T$), show that the tension can be ascribed to the dependence of the entropy on the length of the sample. Account for this result in terms of the molecular nature of the sample. Consider the thermodynamic description of stretching rubber. The observables are the tension, *t*, and the sample length *l*. Because $\mathrm{d}w = t\mathrm{d}l$, the basic equation is $\mathrm{d}U = T\mathrm{d}S + t\mathrm{d}l$. This is analogous to the basic equation with *pV* work alone ($\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$) with the transformations $p \rightarrow -t$ and $V \rightarrow l$. This suggests that we apply the transformation to the Maxwell relation $\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$ [Table 3D.1] for *pV* work in order to acquire an expression that relates *l* and *S*. It is

$$-\left(\frac{\partial t}{\partial T}\right)_l = \left(\frac{\partial S}{\partial l}\right)_T$$

Since $\mathrm{d}U = T\mathrm{d}S + t\mathrm{d}l$, $t = aT$ (given), and $a = \left(\frac{\partial t}{\partial T}\right)_l$,

$$\left(\frac{\partial U}{\partial l}\right)_T = T\left(\frac{\partial S}{\partial l}\right)_T + t = -T\left(\frac{\partial t}{\partial T}\right)_l + t = -Ta + t = -t + t = 0$$

Thus, the internal energy is independent of the extension and

$$t = aT = T\left(\frac{\partial t}{\partial T}\right)_l = \boxed{-T\left(\frac{\partial S}{\partial l}\right)_T}$$

This shows that tension is a measure of the dependence of entropy on the length of the sample. Sample extension reduces the disorder of the chains, and they tend to revert to their disorderly (non-extended) state.

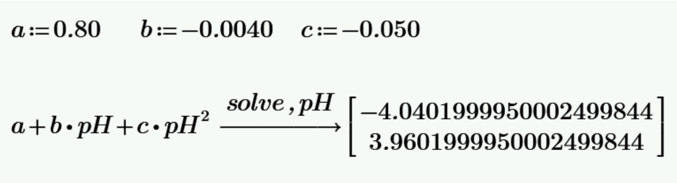
17C Self-assembly

Answers to discussion questions

17C.2 The formation of micelles is favored by the interaction between hydrocarbon tails and is opposed by charge repulsion of the polar groups which are placed close together at the micelle surface. As salt concentration is increased, the repulsion of head groups is reduced because their charges are partly shielded by the ions of the salt. This favors micelle formation causing the micelles to be larger and the critical micelle concentration to be smaller.

Solutions to exercises

17C.1(b) $v/(\mu\text{m s}^{-1}) = a + b(\text{pH}) + c(\text{pH})^2$ with $a = 0.80$, $b = -4.0 \times 10^{-3}$, and $c = -5.0 \times 10^{-2}$
At the **isoelectric point** the pH is such that there is no net charge on the macromolecule, thereby, eliminating the normal protein velocity caused by an electric field. The following Mathcad Prime 2 worksheet sets the above speed expression equal to zero and numerically solves for the pH.



$a := 0.80 \quad b := -0.0040 \quad c := -0.050$

$$a + b \cdot pH + c \cdot pH^2 \xrightarrow{solve,\,pH} \begin{bmatrix} -4.0401999950002499844 \\ 3.9601999950002499844 \end{bmatrix}$$

The negative value is non-physical so we conclude that the isoelectric point occurs at a pH of $\boxed{3.96}$.

17D Determination of size and shape

Answers to discussion questions

17D.2 Polymers are unlike small molecules in that all small molecules of the same species have nearly identical masses with variations caused by a distribution of isotopes. Polymers, however, vary widely in mass because they can vary in the number of monomeric units they contain. Depending on how a polymer mixture is synthesized and purified, it is entirely possible for one macromolecule to contain 1000 monomer units and another 1500. We call a polymer sample **polydisperse** if there is a large variation in mass among the molecules of the sample; conversely, a sample is **monodisperse** if its range of masses is narrow.

The various experimental methods for measuring the average molar mass of a polymer mixture (such as mass spectrometry, light scattering, osmometry, and viscosity) yield similar results for a monodisperse polymer solution. But the measurements can show great variation for a polydisperse polymer mixture. The differences in averages are in the weighting factors. The weighting factor for $\bar{M}_\text{n}$ is the number of molecules that have a particular mass and the weighting factor in $\bar{M}_\text{w}$ is the mass fraction of a sample that has a particular mass. Different measurement techniques yield different weighting factors because they are sensitive to different factors. The intensity of a mass spectrometry peak, for instance, is proportional to the number of molecules of a given mass. Some techniques, like light scattering, are more sensitive to the size (volume) and shape of particles, and some, like sedimentation, are more sensitive to the mass. Discussions in the text reveal, however, that the measurements capture a complicated function of size, shape, mass, and number. Osmometry, measuring a colligative property, is sensitive to the number of molecules N_i that have molar mass M_i . Consequently, average osmotic properties depend upon the number average molar mass. Light scattering depends upon molecular size and shape, which indirectly depend upon mass, so weight average molar mass becomes important. Other mass averages become important when the technique is sensitive to intermolecular attractions and repulsions, molecular entanglements, gravitational and centrifuge effects.

Solutions to exercises

17D.1(b) Equal amounts imply equal numbers of molecules. Hence the number-average is (eqn 17D.1)

$$\bar{M}_{\mathrm{n}} = \frac{N_1M_1 + N_2M_2}{N} = \frac{n_1M_1 + n_2M_2}{n}$$

$$= \tfrac{1}{5}(3\times 62 + 2\times 78)\ \mathrm{kg\ mol^{-1}} = \boxed{68\ \mathrm{kg\ mol^{-1}}}$$

and the weight-average is (eqns 17D.2a and b)

$$\bar{M}_{\mathrm{w}} = \frac{m_1M_1 + m_2M_2}{m} = \frac{n_1M_1^2 + n_2M_2^2}{n_1M_1 + n_2M_2}$$

$$= \frac{3\times 62^2 + 2\times 78^2}{3\times 62 + 2\times 78}\mathrm{kg\ mol^{-1}} = \boxed{69\ \mathrm{kg\ mol^{-1}}}$$

17D.2(b) (i) Osmometry gives the number-average molar mass, so

$$\bar{M}_{\mathrm{n}} = \frac{N_1M_1 + N_2M_2}{N_1 + N_2}\ [17\mathrm{D}.1] = \frac{n_1M_1 + n_2M_2}{n_1 + n_2} = \frac{\left(\frac{m_1}{M_1}\right)M_1 + \left(\frac{m_2}{M_2}\right)M_2}{\left(\frac{m_1}{M_1}\right) + \left(\frac{m_2}{M_2}\right)} = \frac{m_1 + m_2}{\left(\frac{m_1}{M_1}\right) + \left(\frac{m_2}{M_2}\right)}$$

$$= \frac{100\ \mathrm{g}}{\left(\frac{25\ \mathrm{g}}{22\ \mathrm{kg\ mol^{-1}}}\right) + \left(\frac{75\ \mathrm{g}}{7.3\bar{3}\ \mathrm{kg\ mol^{-1}}}\right)}[\text{assume 100 g of solution}] = \boxed{8.8\ \mathrm{kg\ mol^{-1}}}$$

(ii) Light-scattering gives the mass-average molar mass, so

$$\bar{M}_{\mathrm{w}} = \frac{m_1M_1\ +\ m_2M_2}{m_1 + m_2} = \frac{(25)\times(22)\ +\ (75)\times(7.33)}{100}\ \mathrm{kg\ mol^{-1}} = \boxed{11\ \mathrm{kg\ mol^{-1}}}$$

17D.3(b) Since the two spherical particles have different radii and different densities, their buoyancy b must be considered. The buoyancy is

$$b = 1 - \rho\upsilon_{\mathrm{s}}\ \ [17\mathrm{D}.8] = 1 - \rho/\rho_{\mathrm{s}}$$

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 $a^3\rho_{\mathrm{s}}$. Therefore,

$$m_{\mathrm{eff}} \propto ba^3\rho_{\mathrm{s}}$$

According to eqn 17D.12, the Stoke's frictional coefficient is proportional to a and eqn 17D.9 indicates that the sedimentation rate s is proportional to the effective mass and inversely proportional to the frictional coefficient. Thus,

$$s \propto \frac{ba^3\rho_{\mathrm{s}}}{a}$$

$$\propto ba^2\rho_{\mathrm{s}}$$

$$\propto (\rho_{\mathrm{s}} - \rho)a^2$$

The constant of proportionality cancels when taking ratios so the relative rates of sedimentation of the two different particles is

$$\frac{s_2}{s_1} = \left(\frac{\rho_2 - \rho}{\rho_1 - \rho}\right)\times\left(\frac{a_2}{a_1}\right)^2$$

$$= \left(\frac{1.10 - 0.794}{1.18 - 0.794}\right)\times(8.4)^2 = \boxed{56}$$

17D.4(b) $\bar{M}_{\mathrm{n}} = \dfrac{SfN_{\mathrm{A}}}{b}\ [17\mathrm{D}.11] = \dfrac{SfN_{\mathrm{A}}}{1 - \rho\upsilon_{\mathrm{s}}}\ [17\mathrm{D}.8]$

Assuming that the solution density equals that of water at 298 K (0.9969 g cm^{-3}) and substitution of the Stokes−Einstein relation, $f = kT/D$ [19B.19a], gives

$$\overline{M}_{\mathrm{n}} = \frac{SRT}{(1-\rho\upsilon_{\mathrm{s}})D}$$

$$= \frac{(7.46\ \mathrm{Sv})\times(10^{-13}\ \mathrm{s\ Sv^{-1}})(8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}})\times(298.15\ \mathrm{K})}{\{1-(996.9\ \mathrm{kg\ m^{-3}})\times(8.01\times10^{-4}\ \mathrm{m^3\ kg^{-1}})\}\times(7.72\times10^{-11}\ \mathrm{m^2\ s^{-1}})}$$

$$= \boxed{119\ \mathrm{kg\ mol^{-1}}}$$

17D.5(b) The net force acting upon the settling particle equals zero because of the balance between the gravitation pull, $m_{\mathrm{eff}}g$, and the frictional force, fs where s is the drift speed and the frictional coefficient is given by Stokes's relation $f = 6\pi a\eta$ [17D.12] for a particle of radius a. Thus,

$$fs = m_{\mathrm{eff}}\,g$$

$$s = \frac{m_{\mathrm{eff}}\,g}{f} = \frac{bmg}{f} = \frac{(1-\rho/\rho_{\mathrm{s}})\times\{(\tfrac{4}{3}\pi a^3)\times\rho_{\mathrm{s}}\}\,g}{6\pi a\eta} \quad [\text{17D.8 and 17D.12}]$$

$$= \frac{2(\rho_{\mathrm{s}}-\rho)a^2 g}{9\eta}$$

$$= \frac{2\times(1250\ \mathrm{kg\ m^{-3}} - 1000\ \mathrm{kg\ m^{-3}})\times(15.5\times10^{-6}\ \mathrm{m})^2\times(9.8067\ \mathrm{m\ s^{-2}})}{9\times(8.9\times10^{-4}\ \mathrm{kg\ m^{-1}\ s^{-1}})}$$

$$= \boxed{0.15\ \mathrm{mm\ s^{-1}}}$$

17D.6(b) $\overline{M}_{\mathrm{n}} = \dfrac{SfN_{\mathrm{A}}}{b}\ [17\mathrm{D}.11] = \dfrac{SfN_{\mathrm{A}}}{1-\rho\upsilon_{\mathrm{s}}}\ [17\mathrm{D}.8]$

Substitution of the Stokes–Einstein relation, $f = kT/D$ [19B.19a], gives

$$\overline{M}_{\mathrm{n}} = \frac{SRT}{(1-\rho\upsilon_{\mathrm{s}})D}$$

$$= \frac{(5.1\ \mathrm{Sv})\times(10^{-13}\ \mathrm{s\ Sv^{-1}})(8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}})\times(293.15\ \mathrm{K})}{\{1-(0.997\ \mathrm{g\ cm^{-3}})\times(0.721\ \mathrm{cm^3\ g^{-1}})\}\times(7.9\times10^{-11}\ \mathrm{m^2\ s^{-1}})}$$

$$= \boxed{56\ \mathrm{kg\ mol^{-1}}}$$

17D.7(b) The number of solute molecules with energy E is proportional to $\mathrm{e}^{-E/kT}$, hence

$$c \propto N \propto \mathrm{e}^{-E/kT} \quad \text{where} \quad E = \tfrac{1}{2}m_{\mathrm{eff}}r^2\omega^2$$

Therefore, $c \propto \mathrm{e}^{Mb\omega^2 r^2/2RT}$ $[m_{\mathrm{eff}} = bm, M = mN_{\mathrm{A}}]$ and

$$\ln c = \text{const.} + \frac{Mb\omega^2 r^2}{2RT} \qquad [b = 1-\rho\upsilon_{\mathrm{s}}]$$

This expression indicates that the slope of a plot of ln c against r^2 is equal to $Mb\omega^2/2RT$. Therefore

$$M = \frac{2RT\times\text{slope}}{b\omega^2} = \frac{2\times(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(293\ \mathrm{K})\times(821\times10^4\ \mathrm{m^{-2}})}{\{1-(997\ \mathrm{kg\ m^{-3}})\times(7.2\times10^{-4}\ \mathrm{m^3\ kg^{-1}})\}\times(2\pi\times1080\ \mathrm{s^{-1}})^2}$$

$$= \boxed{3.1\times10^3\ \mathrm{kg\ mol^{-1}}}$$

Solutions to problems

17D.2 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 $\mathrm{CH_2CH(C_6H_5)}$ (8 C atoms and 8 H atoms) has a molar mass of 8 × (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

$$M(\text{terminal}) = 2M(t\text{-butyl}) = 2(4\times12+9)\ \text{g mol}^{-1} = 114\ \text{g mol}^{-1}$$

and $$n = \frac{M(\text{peak}) - M(\text{Ag}^+) - M(\text{terminal})}{M(\text{repeat})} = \frac{25578-108-114}{104} = \boxed{244}$$

17D.4 $S = \dfrac{s}{r\omega^2}$ [17D.10]

Since $s = \dfrac{\mathrm{d}r}{\mathrm{d}t}$, $\dfrac{s}{r} = \dfrac{1}{r}\dfrac{\mathrm{d}r}{\mathrm{d}t} = \dfrac{\mathrm{d}\ln r}{\mathrm{d}t}$

Thus, if we plot ln *r* against *t*, the slope gives *S* through

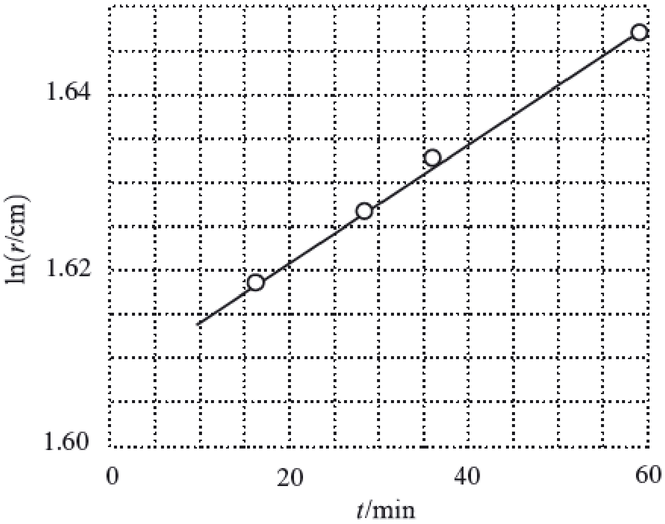
$$S = \frac{1}{\omega^2}\frac{\mathrm{d}\ln \mathrm{r}}{\mathrm{d}t}$$

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 Fig. 17D.1.

Figure 17D.1



The least-squares slope is 6.62 × 10^{-4} min^{-1}, so

$$S = \frac{6.62\times10^{-4}\ \text{min}^{-1}}{\omega^2} = \frac{(6.62\times10^{-4}\ \text{min}^{-1})\times\left(\dfrac{1\ \text{min}}{60\ \text{s}}\right)}{\left(2\pi\times\dfrac{4.5\times10^4}{60\ \text{s}}\right)^2} = 4.9\bar{7}\times10^{-13}\ \text{s or } \boxed{5.0\ \text{Sv}}$$

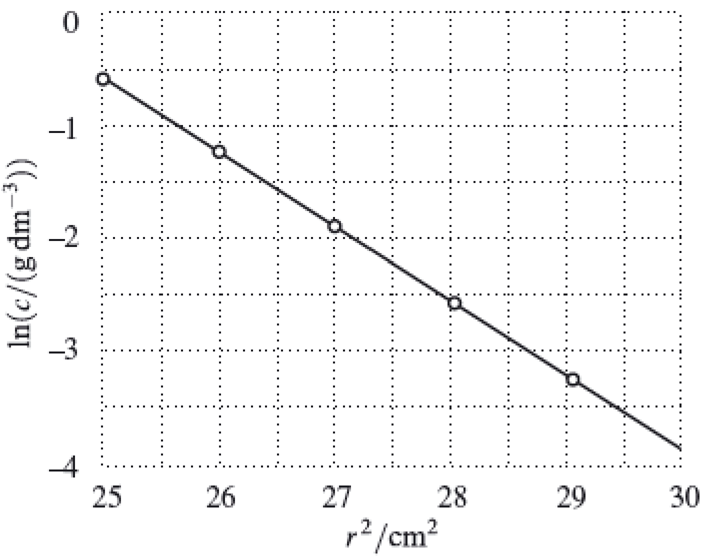
17D.6 Rearrange eqn 17D.14 to yield

$$\ln c = \text{const.} + \frac{\bar{M}_{\text{w}} b\omega^2 r^2}{2RT},$$

which shows that a plot of ln c against r^2 should be a straight line of slope $\bar{M}_{\text{w}} b\omega^2 / 2RT$ from which we find that $\bar{M}_{\text{w}} = \frac{2RT \times slope}{b\omega^2}$. We construct the following table and prepare the plot shown in Figure 17D.2.

r/cm	5.0	5.1	5.2	5.3	5.4
$c/(\text{mg cm}^{-3})$	0.536	0.284	0.148	0.077	0.039
$r^2/(\text{cm}^2)$	25.0	26.0	27.0	28.1	29.2
$\ln(c/\text{mg cm}^{-3})$	−0.624	−1.259	−1.911	−2.564	−3.244

Figure 17D.2



The plot of Figure 17D.2 is seen to be linear and a linear regression fit of the data gives a slope equal to −0.623 cm^{-2}. Therefore

$$\bar{M}_{\text{w}} = \frac{2RT \times slope}{b\omega^2} = \frac{2RT \times slope}{(1-\rho\upsilon_{\text{s}})\omega^2} \quad [17\text{D}.8]$$

$$= \frac{2 \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (293\ \text{K}) \times (-0.623 \times 10^4\ \text{m}^{-2})}{\{1-(1.001\ \text{g cm}^{-3}) \times (1.112\ \text{cm}^3\ \text{g}^{-1})\} \times (2\pi \times 322\ \text{s}^{-1})^2}$$

$$= \boxed{65.6\ \text{kg mol}^{-1}}$$

17D.8 $S = \frac{s}{r\omega^2}$ [17D.10]

Since $s = \frac{\mathrm{d}r}{\mathrm{d}t}$, $\frac{s}{r} = \frac{1}{r}\frac{\mathrm{d}r}{\mathrm{d}t} = \frac{\mathrm{d}\ln r}{\mathrm{d}t}$

and if we plot ln r against t, the slope gives S through

$$S = \frac{1}{\omega^2}\frac{\mathrm{d}\ln \mathrm{r}}{\mathrm{d}t}$$

We prepare the following table and plot the points as shown in Figure 17D.3.

t/s	0	300	600	900	1200	1500	1800
r/cm	6.127	6.153	6.179	6.206	6.232	6.258	6.284
ln(r/cm)	1.813	1.817	1.821	1.826	1.830	1.834	1.838

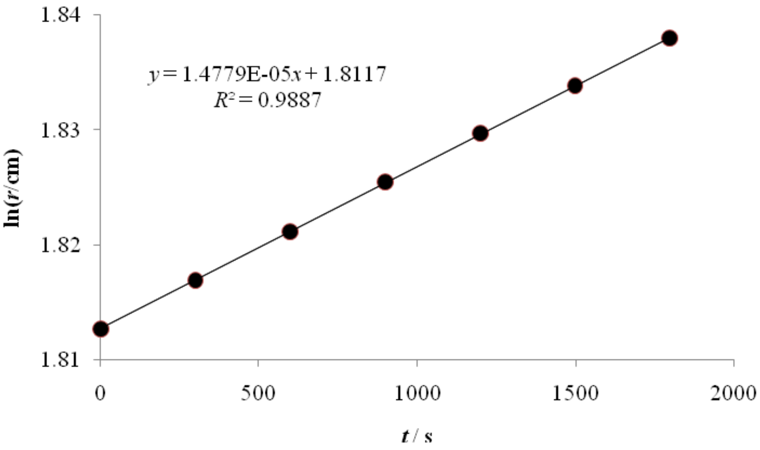


Figure 17D.3

Figure 17D.3 shows that the plot is linear with a regression slope of $1.48 \times 10^{-5}\ \mathrm{s^{-1}}$. Thus,

$$S = \frac{\left(1.48\times10^{-5}\ \mathrm{s^{-1}}\right)}{\left(2\pi\times\dfrac{50\times10^{3}}{60\ \mathrm{s}}\right)^{2}} = 5.40\times10^{-13}\ \mathrm{s} \quad \text{or} \quad \boxed{5.40\ \mathrm{Sv}}$$

$$\bar{M}_{\mathrm{n}} = \frac{SfN_{\mathrm{A}}}{b}\ [17\mathrm{D}.11] = \frac{SfN_{\mathrm{A}}}{1-\rho\upsilon_{\mathrm{s}}}\ [17\mathrm{D}.8]$$

Substitution of the Stokes–Einstein relation, $f = kT/D$ [19B.19a], gives

$$\begin{aligned}\bar{M}_{\mathrm{n}} &= \frac{SRT}{\left(1-\rho\upsilon_{\mathrm{s}}\right)D}\\ &= \frac{\left(5.40\ \mathrm{Sv}\right)\times\left(10^{-13}\ \mathrm{s\ Sv^{-1}}\right)\left(8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}}\right)\times\left(293.15\ \mathrm{K}\right)}{\left\{1-\left(998.1\ \mathrm{kg\ m^{-3}}\right)\times\left(0.728\times10^{-3}\ \mathrm{m^{3}\ kg^{-1}}\right)\right\}\times\left(7.62\times10^{-11}\ \mathrm{m^{2}\ s^{-1}}\right)}\\ &= \boxed{63.2\ \mathrm{kg\ mol^{-1}}}\end{aligned}$$

Information about the molecular geometry is inferred by calculation of the ratio of the actual frictional coefficient, f, of the macromolecule to that of the frictional coefficient, f_0, of a sphere of the same volume. Interpolation between ratios given in Table 17D.2 provides dimensions of the molecular ellipsoid.

$$f = \frac{kT}{D} = \frac{(1.381\times 10^{-23}\ \mathrm{J\ K^{-1}})\times(293\ \mathrm{K})}{7.62\times10^{-11}\ \mathrm{m^{2}\ s^{-1}}} = 5.31\times 10^{-11}\ \mathrm{kg\ s^{-1}}$$

$$V_{\mathrm{m}} = (0.728\ \mathrm{cm^3\ g^{-1}}) \times (63.2 \times 10^3\ \mathrm{g\ mol^{-1}}) = 46.0 \times 10^3\ \mathrm{cm^3\ mol^{-1}} = 4.60 \times 10^{-2}\ \mathrm{m^3\ mol^{-1}}$$

Then, the effective sphere radius is

$$a = \left(\frac{3V_{\mathrm{m}}}{4\pi N_{\mathrm{A}}}\right)^{1/3} = \left(\frac{3\times\left(4.60\times10^{-2}\ \mathrm{m^{3}\ mol^{-1}}\right)}{4\pi\times\left(6.022\times10^{23}\ \mathrm{mol^{-1}}\right)}\right)^{1/3} = 2.63\ \mathrm{nm}$$

$$f_0 = 6\pi a\eta = 6\pi \times (2.63 \times 10^{-9}\ \mathrm{m}) \times (1.00 \times 10^{-3}\ \mathrm{kg\ m^{-1}\ s^{-1}}) = 4.96 \times 10^{-11}\ \mathrm{kg\ s^{-1}}$$

Thus,

$$\frac{f}{f_0} = \frac{5.31}{4.96} = 1.07$$

Interpolation for the Table 17D.2 value of 1.07 reveals that the a/b ellipsoidal ratio of major-minor axes is about 2.3 for both the prolate and oblate ellipsoids. So it appears that the protein is an ellipsoid with $a/b = 2.3$. We cannot, however, determine whether it is a prolate or an oblate ellipsoid.

17D.10 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 17D.5. Then from the relation

$$[\eta] = K\bar{M}_{\mathrm{v}}^{\,a}\ [17\mathrm{D}.18] \quad \text{or} \quad \frac{[\eta]}{\mathrm{cm^{3}\ g^{-1}}} = \left(\frac{K}{\mathrm{cm^{3}\ g^{-1}}}\right)\times\left(\frac{\bar{M}_{\mathrm{v}}}{\mathrm{g\ mol^{-1}}}\right)^{a} \quad \text{in conventional units}$$

with K and a from Table 17D.3, 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 relation

$$\frac{\eta}{\eta_0}=\frac{t}{t_0}\times\frac{\rho}{\rho_0}\approx\frac{t}{t_0}\quad[17\mathrm{D}.17]$$

noting that in the limit as c approaches 0 the approximation becomes exact.

As explored in Self-test 178D.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 $\eta\cong\eta_0$,

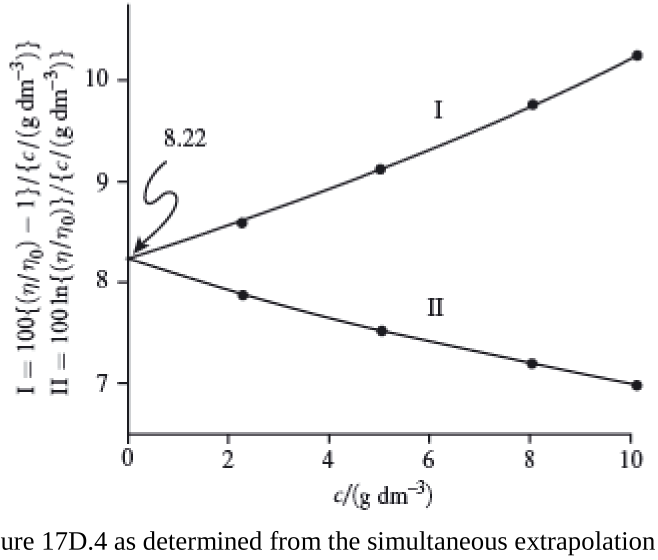
$$\ln\frac{\eta}{\eta_0}=\ln\left(1+\frac{\eta-\eta_0}{\eta_0}\right)=\frac{\eta-\eta_0}{\eta_0}=\frac{\eta}{\eta_0}-1$$

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, thereby, show that they give identical results.

We draw up the following table and plot the points as shown in Figure 17D.4.

$c\,/\,\mathrm{g\,dm^{-3}}$	0.000	2.22	5.00	8.00	10.00
$t\,/\,s$	208.2	248.1	303.4	371.8	421.3
$\eta\,/\,\eta_0$	—	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 17D.4



The intercept of Figure 17D.4 as determined from the simultaneous extrapolation of both plots is 8.22. Hence

$$[\eta]=8.22\times\left(0.01\ \mathrm{dm^3\ g^{-1}}\right)\times\left(10\ \mathrm{cm\ dm^{-1}}\right)^3=82.2\ \mathrm{cm^3\ g^{-1}}$$

$$\bar{M}_{\mathrm{v}}=\left(\frac{[\eta]}{K}\right)^{1/a}=\left(\frac{82.2\ \mathrm{cm^3\ g^{-1}}}{9.5\times10^{-3}\ \mathrm{cm^3\ g^{-1}}}\right)^{1/0.74}\mathrm{g\ mol^{-1}}=\boxed{2.1\times10^{5}\ \mathrm{g\ mol^{-1}}}$$

Integrated activities

17.2 Given that $G = U - TS - tl$ and $\mathrm{d}U = T\mathrm{d}S + t\mathrm{d}l$, we take the differential, obtaining

$$\mathrm{d}G = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T - l\mathrm{d}t - t\mathrm{d}l$$

$$= T\mathrm{d}S + t\mathrm{d}l - T\mathrm{d}S - S\mathrm{d}T - l\mathrm{d}t - t\mathrm{d}l = \boxed{-S\mathrm{d}T - l\mathrm{d}t}$$

Since $A = U - TS$, we have $A = G + tl$, so

$$\mathrm{d}A = \mathrm{d}G + t\mathrm{d}l + l\mathrm{d}t = -S\mathrm{d}T - l\mathrm{d}t + t\mathrm{d}l + l\mathrm{d}t = \boxed{-S\mathrm{d}T + t\mathrm{d}l}$$

Since dA and dG are both exact differentials, the above differential give use the Maxwell relations

$$\left(\frac{\partial S}{\partial l}\right)_T = -\left(\frac{\partial t}{\partial T}\right)_l \quad \text{and} \quad \left(\frac{\partial S}{\partial t}\right)_T = \left(\frac{\partial l}{\partial T}\right)_t$$

Since $\mathrm{d}U = T\mathrm{d}S + t\mathrm{d}l$ [given],

$$\left(\frac{\partial U}{\partial l}\right)_T = T\left(\frac{\partial S}{\partial l}\right)_T + t = \boxed{-T\left(\frac{\partial t}{\partial T}\right)_l + t} \text{ [Maxwell relation above]}$$

17.4 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 $v_{\text{mol}} = \tfrac{4}{3}\pi a^3$ but the excluded volume is determined by the smallest distance possible between centers of two molecules, which is 2a, so the excluded volume is $\tfrac{4}{3}\pi(2a)^3 = 8v_{\text{mol}}$ for a pair of molecules. The volume excluded per molecule is one-half this volume or $4v_{\text{mol}}$. Thus, for an effective radius of $a = \gamma R_{\text{g}} = 0.85R_{\text{g}}$ the osmotic virial coefficient is

$$B = 4N_{\text{A}}v_{\text{mol}} = \frac{16\pi}{3}N_{\text{A}}a^3 = \frac{16\pi}{3}N_{\text{A}}\gamma^3R_g^3$$

(a) For a freely jointed chain: $R_{\text{g}} = \left(\frac{N}{6}\right)^{1/2} l$ [17A.6]

$$B = \boxed{\frac{16\pi}{3}N_{\text{A}}(\gamma l)^3\left(\frac{N}{6}\right)^{3/2}}$$

$$= \frac{16\pi}{3}\times\left(6.022\times10^{23}\ \text{mol}^{-1}\right)\left\{0.85\times\left(154\times10^{-12}\ \text{m}\right)\right\}^3\times\left(\frac{4000}{6}\right)^{3/2}$$

$$= \boxed{0.38\ \text{m}^3\ \text{mol}^{-1}}$$

(b) For a chain with tetrahedral bond angles: $R_{\text{g}} = \left(\frac{N}{3}\right)^{1/2} l$ [17A.8]

$$B = \boxed{\frac{16\pi}{3}N_{\text{A}}(\gamma l)^3\left(\frac{N}{3}\right)^{3/2}}$$

$$= \frac{16\pi}{3}\times\left(6.022\times10^{23}\ \text{mol}^{-1}\right)\left\{0.85\times\left(154\times10^{-12}\ \text{m}\right)\right\}^3\times\left(\frac{4000}{3}\right)^{3/2}$$

$$= \boxed{1.1\ \text{m}^3\ \text{mol}^{-1}}$$

18 Solids

18A Crystal structure

Answers to discussion questions

18A.2 Lattice planes are labeled by their Miller indices *h*, *k*, and *l*, where *h*, *k*, and *l* refer respectively to the reciprocals of the smallest intersection distances (in units of the lengths of the unit cell, *a*, *b* and *c*) of the plane along the *a*, *b*, and *c* axes, which may be non-orthogonal.

18A.4 The atomic **scattering factor**, *f*, describes the dependence of the magnitude of an atom's scattering of X-rays upon the scattering angle θ: $f = 4\pi\int_0^\infty \rho(r)\frac{\sin kr}{kr}r^2\mathrm{d}r$ where $k = \frac{4\pi}{\lambda}\sin\theta$ [18A.3]

The dependence upon the electron 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 18A.2 that the scattering factor equals the total number of atomic, or ionic, electrons in the forward direction of scattering . It is smaller in non-forward directions. When comparing isoelectronic atoms and ions, the less diffuse species (greater $\rho(r)$) exhibits greater scattering.

18A.6 The **structure factor** F_{hkl} is the sum over all *j* atoms of terms each of which has a scattering factor f_j:

$$F_{hkl} = \sum_j f_j e^{i\phi_{hkl}(j)} \quad \text{where} \quad \phi_{hkl}(j) = 2\pi\left(hx_j + ky_j + lz_j\right) \quad [18A.4]$$

The importance of the structure factor to the X-ray crystallographic method of structure determination is its relationship to the electron density distribution, $\rho(r)$, within the crystal:

$$\rho(\boldsymbol{r}) = \frac{1}{V}\sum_{hkl} F_{hkl} e^{-2\pi i(hx+ky+lz)} \quad [18A.5]$$

Eqn 18A.5 reveals that if the structure factors for the lattice planes can be measured then the electron density distribution can be calculated by performing the indicated sum. Therein lays the **phase problem**. Measurement detectors yield only the intensity of scattered radiation, which is proportional to $|F_{hkl}|^2$, and give no direct information about F_{hkl}. To see this, consider the structure factor form $F_{hkl} = |F_{hkl}|e^{i\alpha_{hkl}}$ where α_{hkl} is the phase of the *hkl* reflection plane. Then,

$$|F_{hkl}|^2 = \left\{|F_{hkl}|e^{i\alpha_{hkl}}\right\}^* \left\{|F_{hkl}|e^{i\alpha_{hkl}}\right\} = |F_{hkl}| \times |F_{hkl}| e^{-i\alpha_{hkl}} e^{i\alpha_{hkl}} = |F_{hkl}| \times |F_{hkl}|$$

and we see that all information about the phase is lost in an intensity measurement. It seems impossible to perform the sum of eqn 18A.5 since we do not have the important factor $e^{i\alpha_{hkl}}$. Crystallographers have developed numerous methods to resolve the phase problem. In the **Patterson synthesis**, X-ray diffraction spot intensities are used to acquire separation and relative orientations of atom pairs. Another method uses the dominance of heavy atom scattering to deduce phase. **Heavy atom replacement** may be necessary for this type of application. **Direct methods** dominate modern X-ray diffraction analysis. These methods use statistical techniques, and the considerable computational capacity of the modern computer, to compute the probabilities that the phases have a particular value.

Solutions to exercises

18A.1(b) The volume of an orthorhombic unit cell is

$$V = abc = (589\,\mathrm{pm}) \times (822\,\mathrm{pm}) \times (798\,\mathrm{pm}) = \frac{3.86\times10^{8}\,\mathrm{pm}^3}{(10^{10}\,\mathrm{pm\,cm^{-1}})^3} = 3.86\times10^{-22}\,\mathrm{cm}^3$$

The mass per formula unit is

$$m = \frac{135.01\,\mathrm{g\,mol^{-1}}}{6.02214\times10^{23}\,\mathrm{mol^{-1}}} = 2.2419\times10^{-22}\,\mathrm{g}$$

The density 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

$$d = \frac{Nm}{V} \quad \text{so} \quad N = \frac{dV}{m} = \frac{(2.9\ \text{g cm}^{-3}) \times (3.86 \times 10^{-22}\ \text{cm}^3)}{2.24 \times 10^{-22}\ \text{g}} = \boxed{5}$$

A more accurate density, then, is

$$d = \frac{5(2.24 \times 10^{-22}\ \text{g})}{3.86 \times 10^{-22}\ \text{cm}^3} = \boxed{2.90\ \text{g cm}^{-3}}$$

18A.2(b) When the axes intersections are ($-a$,2b,$-c$) and (a,4b,$-4c$), the Miller indices of the planes are $\left(\bar{2}1\bar{2}\right)$ and $\left(41\bar{1}\right)$. Simply take the inverse of the intersection multiple and clear fractions to find these planes.

18A.3(b) For the cubic unit cell: $d_{hkl} = \dfrac{a}{\left(h^2+k^2+l^2\right)^{1/2}}$ [18A.1b]

$$d_{123} = \frac{a}{\left(1^2+2^2+3^2\right)^{1/2}} = \frac{712\ \text{pm}}{(14)^{1/2}} = \boxed{190\ \text{ppm}}$$

$$d_{222} = \frac{a}{\left(2^2+2^2+2^2\right)^{1/2}} = \frac{712\ \text{pm}}{(12)^{1/2}} = \boxed{206\ \text{ppm}}$$

$$d_{246} = \frac{a}{\left(2^2+4^2+6^2\right)^{1/2}} = \frac{712\ \text{pm}}{(56)^{1/2}} = \boxed{95.1\ \text{ppm}}$$

18A.4(b) $d_{hkl} = \left[\left(\dfrac{h}{a}\right)^2 + \left(\dfrac{k}{b}\right)^2 + \left(\dfrac{l}{c}\right)^2\right]^{-1/2}$ [18A.1c]

$$d_{312} = \left[\left(\frac{3}{769}\right)^2 + \left(\frac{1}{891}\right)^2 + \left(\frac{2}{690}\right)^2\right]^{-1/2} \text{pm} = \boxed{200\ \text{pm}}$$

18A.5(b) $\lambda = 2d\sin\theta$ [18A.2b] $= 2 \times (128.2\ \text{pm}) \times \sin 19.76° = \boxed{86.7\ \text{pm}}$

18A.6(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-centered cubic lattice, h, k, and l must be all odd or all even (see Fig. 18A.24 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

$$\frac{\lambda}{2a} = \frac{\lambda}{4\sqrt{2}R} = \frac{129\ \text{pm}}{4\sqrt{2}(144\ \text{pm})} = 0.158$$

We set up the following table:

hkl	$\sin\theta$	θ / °
111	0.274	15.9
200	0.316	18.4
220	0.447	26.6

18A.7(b) $\theta_{hkl} = \arcsin\dfrac{\lambda}{2d_{hkl}}$ [18A.2b] $= \arcsin\left\{\dfrac{\lambda}{2}\left[\left(\dfrac{h}{a}\right)^2 + \left(\dfrac{k}{b}\right)^2 + \left(\dfrac{l}{c}\right)^2\right]^{1/2}\right\}$ [18A.1c, $\arcsin \equiv \sin^{-1}$]

$$\theta_{100} = \arcsin\left\{\frac{83.42}{2}\times\left[\left(\frac{1}{574.1}\right)^2+\left(\frac{0}{796.8}\right)^2+\left(\frac{0}{495.9}\right)^2\right]^{1/2}\right\} = \boxed{4.166°}$$

$$\theta_{010} = \arcsin\left\{\frac{83.42}{2}\times\left[\left(\frac{0}{574.1}\right)^2+\left(\frac{1}{796.8}\right)^2+\left(\frac{0}{495.9}\right)^2\right]^{1/2}\right\} = \boxed{3.001°}$$

$$\theta_{111} = \arcsin\left\{\frac{83.42}{2}\times\left[\left(\frac{1}{574.1}\right)^2+\left(\frac{1}{796.8}\right)^2+\left(\frac{1}{495.9}\right)^2\right]^{1/2}\right\} = \boxed{7.057°}$$

18A.8(b) $\theta = \arcsin\dfrac{\lambda}{2d}$ [18A.2b, $\arcsin \equiv \sin^{-1}$]

$$\Delta\theta = \arcsin\frac{\lambda_2}{2d} - \arcsin\frac{\lambda_1}{2d} = \arcsin\left(\frac{95.123\text{ pm}}{(2)\times(82.3\text{ pm})}\right) - \arcsin\left(\frac{93.222\text{ pm}}{(2)\times(82.3\text{ pm})}\right)$$

$$= 0.807° = 0.0141\text{ rad}$$

Consequently, the difference in the glancing angles (2θ) is $\boxed{1.61°}$.

18A.9(b) Justification 18A.2 demonstrates that the scattering factor in the forward direction equals the number of electrons in the atom or simple ion. Consequently, $\boxed{f_{\text{Mg}^{2+}} = 10}$

18A.10(b) The structure factor is given by

$$F_{hkl} = \sum_i f_i e^{i\phi_i} \quad \text{where} \quad \phi_i = 2\pi(hx_i + ky_i + lz_i) \ \ [18\text{A}.4]$$

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-center point belongs exclusively to one unit cell, so its scattering factor is f. The phase is

$$\phi = 2\pi\left(\tfrac{1}{2}h + \tfrac{1}{2}k + \tfrac{1}{2}l\right) = \pi(h+k+l)$$

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

$$F_{hkl} = 8(f/8)(1) + f(-1)^{h+k+l}$$

$$= \boxed{2f \text{ for } h+k+l \text{ even} \quad \text{and} \quad 0 \text{ for } h+k+l \text{ odd}}$$

18A.11(b) The structure factor is given by

$$F_{hkl} = \sum_i f_i e^{i\phi_i} \quad \text{where} \quad \phi_i = 2\pi(hx_i + ky_i + lz_i) \ \ [18\text{A}.4]$$

All eight of the vertices of the cube are shared by eight cubes, so each vertex has a scattering factor of f/8 and their total contribution to the structure factor equals f (see exercise 18A.10(a)). The body-centered ion of the bcc(I) unit cell belongs entirely to the cell. In this problem it has a scattering factor of 2f and its coordinates are (½*a*, ½*a*, ½*a*). Thus, the contribution of the body-centered ion to the structure factor is

$$\sum_{i\text{(body-centred)}} f_i e^{i\phi_i} = 2f\ e^{2\pi i(h/2+k/2+l/2)} = 2f\ e^{\pi i(h+k+l)}$$

$$= 2f\left\{\cos\left(\pi\left(h+k+l\right)\right) + i\sin\left(\pi\left(h+k+l\right)\right)\right\} \quad \text{(Euler's identity)}$$

$$= 2f\cos\left(\pi\left(h+k+l\right)\right)$$

$$= 2f\left(-1\right)^{h+k+l}$$

With contributions from the vertices and body-centered ion, the structure factor becomes

$$F_{hkl} = \sum_{i\text{(vertices)}} f_i e^{i\phi_i} + \sum_{i\text{(body-centred)}} f_i e^{i\phi_i} = f + 2f\left(-1\right)^{h+k+l} = f\left\{1 + 2\left(-1\right)^{h+k+l}\right\}$$

$$F_{hkl} = \boxed{3f \text{ for } h+k+l \text{ even} \quad \text{and} \quad -f \text{ for } h+k+l \text{ odd}}$$

18A.12(b) The electron density is given by

$$\rho(r)=\frac{1}{V}\sum_{hkl}F_{hkl}\mathrm{e}^{-2\pi\mathrm{i}(hx+ky+lz)}\quad[18\text{A}.5]$$

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 computation of $\rho(x)$ and plot shown in Fig. 18A.1 shows high electron density at the ends of unit cell edge (i.e., at the vertices).

$$F := \begin{pmatrix}10\\10\\4\\4\\6\\6\\8\\8\\10\\10\end{pmatrix}\qquad \rho(x) := \sum_{h=-9}^{9}\left(F_{|h|}\cdot e^{-2\cdot\pi\cdot i\cdot h\cdot x}\right)$$

$$\rho(1.0) = 142$$

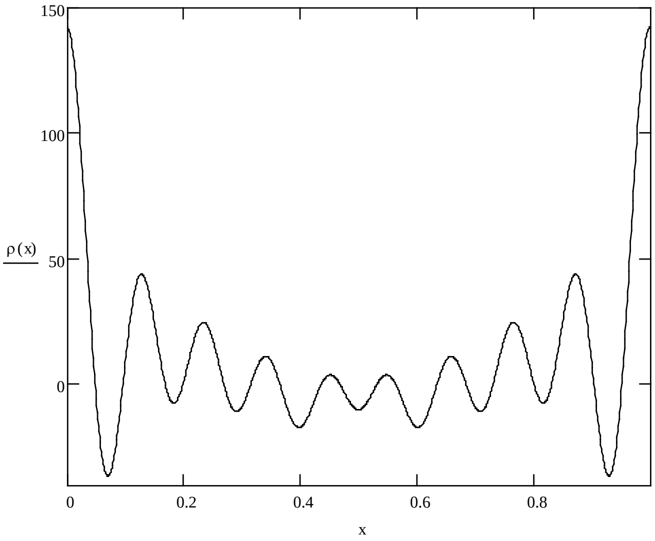


Figure 18A.1

18A.13(b) Using the information of exercise 18A.12(b), the Mathcad computation of $P(x)$ is performed with Equation 18A.6.

$$F := \begin{pmatrix}10\\10\\4\\4\\6\\6\\8\\8\\10\\10\end{pmatrix}\qquad P(x) := \sum_{h=-9}^{9}\left[\left(F_{|h|}\right)^{2}\cdot e^{-2\cdot\pi\cdot i\cdot h\cdot x}\right]$$

$$P(1.0) = 1.164\times 10^{3}$$

The Patterson synthesis $P(x)$ of Fig. 18A.2 shows that atoms represented by this data are separated by 1 *a* unit along the *x* axis.

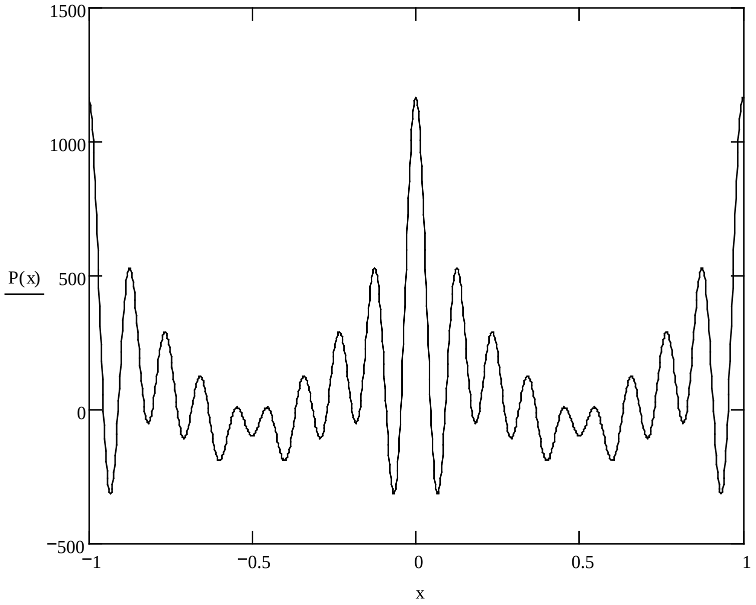
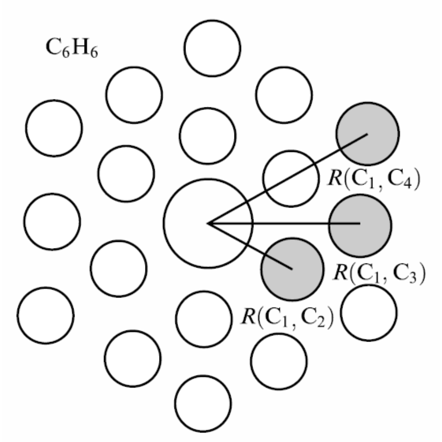


Figure 18A.2

18A.14(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 ($\overrightarrow{\mathrm{AB}}$ and $\overleftarrow{\mathrm{AB}}$); don't forget the AA zero vectors for the center point of the diagram. See Fig. 18A.3 for C_6H_6.

Figure 18A.3



18A.15(b) $\lambda = \dfrac{h}{p} = \dfrac{h}{mv}$

Hence, $v = \dfrac{h}{m\lambda} = \dfrac{6.626 \times 10^{-34}\ \mathrm{J\,s}}{(9.109 \times 10^{-31}\ \mathrm{kg}) \times (105 \times 10^{-12}\ \mathrm{m})} = \boxed{692\bar{8}\ \mathrm{km\ s^{-1}}}$

18A.16(b) $\lambda = \dfrac{h}{p} = \dfrac{h}{mv}$ Hence, $v = \dfrac{h}{m\lambda}$.

Combine $E = \frac{1}{2}kT$ and $E = \frac{1}{2}mv^2 = \dfrac{h^2}{2m\lambda^2}$, to obtain

$$\lambda = \frac{h}{(mkT)^{1/2}} = \frac{6.626\times10^{-34}\ \mathrm{J\ s}}{[(9.109\times10^{-31}\ \mathrm{kg})\times(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})\times(380\ \mathrm{K})]^{1/2}} = \boxed{958\ \mathrm{nm}}$$

Solutions to problems

18A.2 Examination of the monoclinic P unit cells shown in text Figure 18A.8 reveals that its volume V equals the length b multiplied by the area of the parallelogram of sides a and c separated by angle β. The parallelogram is replicated alone in Figure 18A.4 where it is seen that the object has the area $c\times x = c\times a \sin(180° - \beta)$. Using the trigonometric relation sin(A – B) = sin(A) cos(B) – cos(A) sin(B), the area formula becomes:

$$\begin{aligned}\text{area} &= c\times a \sin(180° - \beta) = ca\,\{\sin(180°)\cos(\beta) - \cos(180°)\sin(\beta)\}\\ &= ac\,\{0\times\cos(\beta) - (-1)\times\sin(\beta)\}\\ &= ac\sin(\beta)\end{aligned}$$

Thus, we conclude that $\boxed{V = abc\sin(\beta)}$.

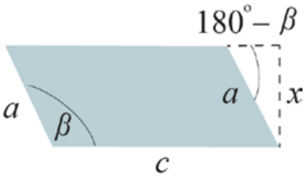


Figure 18A.4

18A.4 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

$$V^2 = \begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix}\begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix}$$

$$= \begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix}\begin{vmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{vmatrix}$$

[interchange rows and columns, no change in value]

$$= \begin{vmatrix} a_xa_x + a_ya_y + a_za_z & a_xb_x + a_yb_y + a_zb_z & a_xc_x + a_yc_y + a_zc_z \\ b_xa_x + b_ya_y + b_za_z & b_yb_x + b_yb_y + b_zb_z & b_xc_x + b_yc_y + b_zc_z \\ c_xa_x + c_ya_y + c_za_z & c_xb_x + c_yb_y + c_zb_z & c_xc_x + c_yc_y + c_zc_z \end{vmatrix}$$

$$= \begin{vmatrix} a^2 & \boldsymbol{a}\cdot\boldsymbol{b} & \boldsymbol{a}\cdot\boldsymbol{c} \\ \boldsymbol{b}\cdot\boldsymbol{a} & b^2 & \boldsymbol{b}\cdot\boldsymbol{c} \\ \boldsymbol{c}\cdot\boldsymbol{a} & \boldsymbol{c}\cdot\boldsymbol{b} & c^2 \end{vmatrix} = \begin{vmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ac\cos\beta & bc\cos\alpha & c^2 \end{vmatrix}$$

$$= a^2b^2c^2(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)$$

Hence $\boxed{V = abc(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)^{1/2}}$

For a monoclinic cell, $\alpha = \gamma = 90^\circ$

$$V = abc(1 - \cos^2\beta)^{1/2} = \boxed{abc\sin\beta}$$

For an orthorhombic cell, $\alpha = \beta = \gamma = 90^\circ$, and

$$V = \boxed{abc}$$

A tetragonal unit cell, as shown in Fig. 18A.8 of the text, has $a = b \neq c$. Therefore

$$V=(651\,\text{pm})\times(651\,\text{pm})\times(934\,\text{pm})=\boxed{3.96\times10^{-28}\,\text{m}^3}$$

18A.6 $$\rho=\frac{m\ (\text{unit cell})}{V\ (\text{unit cell})}=\frac{2\times M(\text{CH}_2\text{CH}_2)/N_\text{A}}{abc}$$

$$\rho=\frac{(2)\times(28.05\ \text{g mol}^{-1})}{(6.022\times10^{23}\,\text{mol}^{-1})\times[(740\times493\times253)\times10^{-36}]\ \text{m}^3}$$

$$=1.01\times10^{6}\ \text{g m}^{-3}=\boxed{1.01\,\text{g cm}^{-3}}$$

18A.8‡ The volume per unit cell is

$$V=abc=(3.6881\,\text{nm})\times(0.9402\,\text{nm})\times(1.7652\,\text{nm})=6.121\ \text{nm}^3=6.121\times10^{-21}\ \text{cm}^3$$

The mass per unit cell is 8 times the mass of the formula unit, $[\text{N(C}_4\text{H}_9)_4][\text{Ru(N)(S}_2\text{C}_6\text{H}_4)_2]$, for which the molar mass is

$$M=\{101.07+2(14.007)+28(12.011)+44(1.008)+4(32.066)\}\,\text{g mol}^{-1}=638.01\,\text{g mol}^{-1}$$

The density is

$$\rho=\frac{m}{V}=\frac{8M}{N_\text{A}V}=\frac{8(638.01\,\text{g mol}^{-1})}{(6.022\times10^{23}\,\text{mol}^{-1})\times(6.121\times10^{-21}\,\text{cm}^3)}=\boxed{1.385\,\text{g cm}^{-3}}$$

The osmium analogue has a molar mass of 727.1 g mol^{-1}. If the volume of the crystal changes negligibly with the substitution, then the densities of the complexes are in proportion to their molar masses

$$\rho_\text{Os}=\frac{727.1}{638.01}\left(1.385\ \text{g cm}^{-3}\right)=\boxed{1.578\ \text{g cm}^{-3}}$$

18A.10 $$\lambda=2d_{hkl}\sin\theta_{hkl}=\frac{2a\sin\theta_{hkl}}{(h^2+k^2+l^2)^{1/2}}\ [\text{18A.2b and 18A.1b}]=2a\sin6.0°=0.209a$$

In a NaCl unit cell (text Fig. 18A.23) the number of formula units is 4 (each corner ion is shared by 8 cells, each edge ion by 4, and each face ion by 2). Therefore,

$$\rho=\frac{NM}{VN_\text{A}}=\frac{4M}{a^3N_\text{A}},\quad \text{implying that}\quad a=\left(\frac{4M}{\rho N_\text{A}}\right)^{1/3}$$

$$a=\left(\frac{(4)\times(58.44\,\text{g mol}^{-1})}{(2.17\times10^{6}\,\text{g m}^{-3})\times(6.022\times10^{23}\,\text{mol}^{-1})}\right)^{1/3}=563.\bar{5}\,\text{pm}$$

and hence $\lambda=(0.209)\times(563.\bar{5}\,\text{pm})=\boxed{118\,\text{pm}}$

18A.12 For the three given reflections

$$\sin19.076°=0.32682\qquad \sin22.171°=0.37737\qquad \sin32.256°=0.53370$$

For cubic lattices $\sin\theta_{hkl}=\dfrac{\lambda\left(h^2+k^2+l^2\right)^{1/2}}{2a}$ [18A.2b with 18A.1b]

First, consider the possibility of simple cubic; the first three reflections are (100), (110), and (200). (See Discussion questions 18A.3 and 18A.5 above.)

$$\frac{\sin\theta_{100}}{\sin\theta_{110}}=\frac{1}{\sqrt2}\neq\frac{0.32682}{0.37737}\quad[\text{not simple cubic}]$$

Consider next the possibility of body-centred cubic; the first three reflections are (110), (200), and (211).

$$\frac{\sin\theta_{110}}{\sin\theta_{200}}=\frac{\sqrt2}{\sqrt4}=\frac{1}{\sqrt2}\neq\frac{0.32682}{0.37737}\quad(\text{not bcc})$$

Consider finally face-centred cubic; the first three reflections are (111), (200) and (220)

$$\frac{\sin\theta_{111}}{\sin\theta_{200}}=\frac{\sqrt3}{\sqrt4}=0.86603$$

which compares very favourably to $\dfrac{0.32682}{0.37737}=0.86605$. Therefore, the lattice is $\boxed{\text{face-centred cubic}}$.

This conclusion may easily be confirmed in the same manner using the second and third reflection.

$$a = \frac{\lambda}{2\sin\theta_{111}}(h^2+k^2+l^2)^{1/2} = \left(\frac{154.18\,\text{pm}}{(2)\times(0.32682)}\right)\times\sqrt{3} = \boxed{408.55\ \text{pm}}$$

$$\rho = \frac{N\,M}{N_\text{A}V}[\text{exercise 18A.1(a)}] = \frac{(4)\times(107.87\,\text{g mol}^{-1})}{(6.0221\times10^{23}\,\text{mol}^{-1})\times(4.0855\times10^{-8}\,\text{cm})^3}$$

$$= \boxed{10.507\,\text{g cm}^{-3}}$$

This compares favourably to the value listed in the text Resource section Table 0.1.

18A.14 The scattering factor is given by

$$f = 4\pi\int_0^\infty \rho(r)\frac{\sin kr}{kr}r^2\text{d}r\ [18\text{A}.3] \qquad \text{where} \qquad k = \frac{4\pi}{\lambda}\sin\theta$$

The integral may be divided into segments such as

$$f = 4\pi\int_0^R \rho(r)\frac{\sin kr}{kr}r^2\text{d}r + 4\pi\int_R^\infty \rho(r)\frac{\sin kr}{kr}r^2\text{d}r$$

In the case for which $\rho = 3Z/4\pi R^3$ when $0 \le r \le R$ and $\rho = 0$ when $r > R$, the second integral vanishes, leaving

$$f = \frac{3Z}{R^3}\int_0^R \frac{\sin kr}{kr}r^2\text{d}r = \frac{3Z}{R^3k}\int_0^R \sin(kr)\,r\text{d}r$$

$$= \frac{3Z}{R^3k}\left[\frac{\sin kr}{k^2} - \frac{r\cos kr}{k}\right]_{r=0}^{r=R}$$

$$= \frac{3Z}{(kR)^3}\left\{\frac{\sin kR}{kR} - \cos kR\right\}$$

This shows that the scattering factor is proportional to the atomic number Z, which is illustrated in a plot of f against $\sin(\theta)/\lambda$ in Fig. 18A.5. As expected, $f = Z$ in the forward direction.

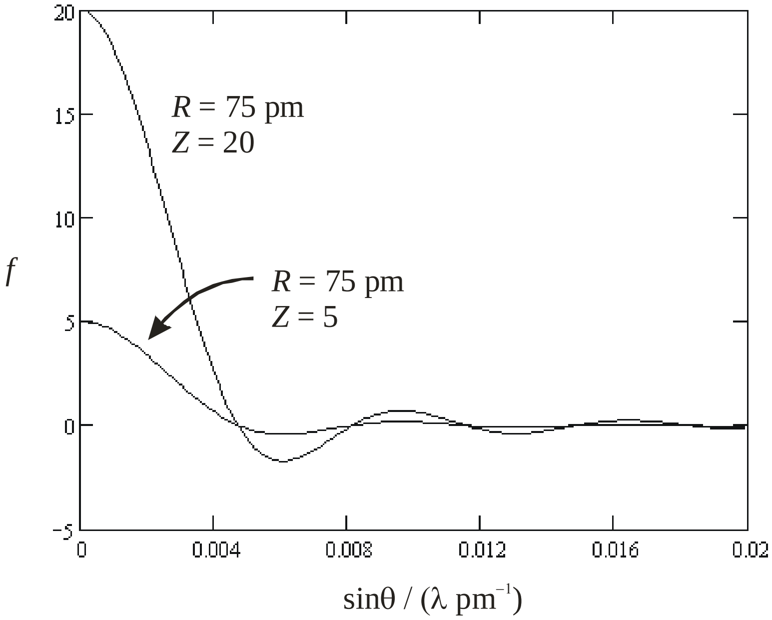


Figure 18A.5

Figure 18A.6 is a plot of the scattering factor for several R values at constant Z. As R increases, the scattering factor shifts to the forward direction.

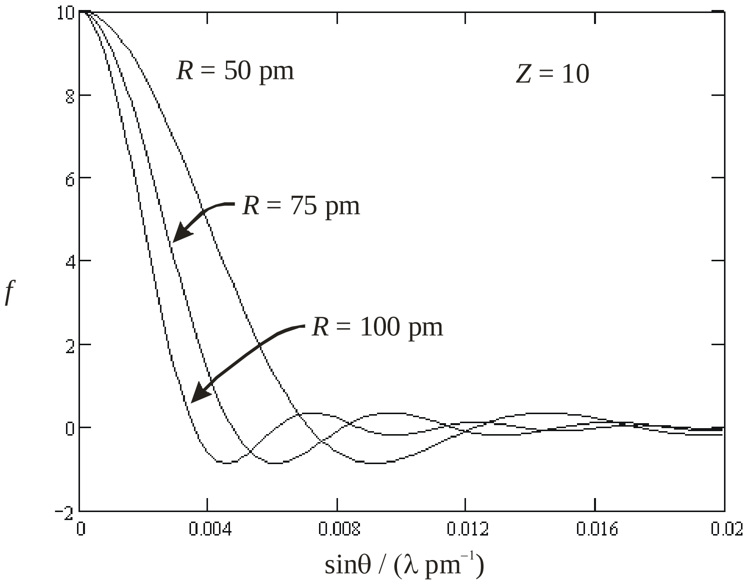


Figure 18A.6

18A.16 $F_{hkl}=\sum_i f_i e^{2\pi i(hx_i+ky_i+lz_i)}$ [18A.4]

For each A atom use $\frac{1}{8}f_{\rm A}$ (each A atom shared by eight cells) but use $f_{\rm B}$ for the central atom (since it contributes solely to the cell).

$$F_{hkl}=\tfrac{1}{8}f_{\rm A}\left\{1+{\rm e}^{2\pi ih}+{\rm e}^{2\pi ik}+{\rm e}^{2\pi il}+{\rm e}^{2\pi i(h+k)}+{\rm e}^{2\pi i(h+l)}+{\rm e}^{2\pi i(k+l)}+{\rm e}^{2\pi i(h+k+l)}\right\}+f_{\rm B}{\rm e}^{\pi i(h+k+l)}$$

$$=f_{\rm A}+(-1)^{(h+k+l)}f_{\rm B}\quad [h,k,l \text{ are all integers}, {\rm e}^{i\pi}=-1]$$

(a) $f_{\rm A}=f,\quad f_{\rm B}=0;\quad F_{hkl}=f$ $\boxed{\text{no systematic absences}}$

(b) $f_{\rm B}=\frac{1}{2}f_{\rm A};\quad F_{hkl}=f_{\rm A}\left[1+\frac{1}{2}(-1)^{(h+k+l)}\right]$

Therefore, when $h+k+l$ is odd, $F_{hkl}=f_{\rm A}\left(1-\frac{1}{2}\right)=\frac{1}{2}f_{\rm A}$, and when $h+k+l$ is even, $F_{hkl}=\frac{3}{2}f_{\rm A}$.

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) $f_{\rm A}=f_{\rm B}=f;\quad F_{hkl}=f\left\{1+(-1)^{h+k+l}\right\}$

Therefore, when $h+k+l$ is odd, $F_{hkl}=0$, and when $h+k+l$ is even, $F_{hkl}=2f$.

Thus, $\boxed{\text{all } h+k+l \text{ odd lines are missing}}$.

18B Bonding in solids

Answers to discussion questions

18B.2 In a face-centred cubic close-packed lattice, there is an octahedral hole in the centre. The rock-salt structure can be thought of as being derived from an fcc structure of $\mathrm{Cl^-}$ ions in which $\mathrm{Na^+}$ ions have filled the octahedral holes. The cesium-chloride structure can be considered to be derived from the ccp structure by having $\mathrm{Cl^-}$ ions occupy all the primitive lattice points and octahedral sites, with all tetrahedral sites occupied by $\mathrm{Cs^+}$ ions. This is exceedingly difficult to visualize and describe without carefully constructed figures or models. Refer to S.-M. Ho and B. E. Douglas, *J. Chem. Educ.* **46**, 208, 1969, for the appropriate diagrams.

Solutions to exercises

18B.1(b) There are two smaller (white) 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 $b = \frac{1}{2}B(\text{base})$ and $h = \frac{1}{2}H(\text{height})$, $a = \frac{1}{4}A$. The white space is then $2N\,A/4$, for N of the larger triangles. The total space is then $\left(NA + \frac{NA}{2}\right) = 3NA/2$. Therefore the fraction filled is $NA/(3NA/2) = \boxed{\frac{2}{3}}$

18B.2(b) The diagonal of the face that has a lattice point in its center 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 2 atoms. (Each of the 8 vertices is shared among 8 cells; each of the 2 face points is shared by 2 cells.) So the packing fraction is

$$\frac{2V_{\text{atom}}}{V_{\text{cell}}} = \frac{2(4/3)\pi r^3}{(2\sqrt{2}r)^3} = \frac{\pi}{3(2)^{3/2}} = \boxed{0.370}$$

18B.3(b) (a) It is shown in Exercise 18B.3(a) that for a six-fold coordination $\frac{r}{R} = 0.414$.

Thus, $r = 0.414R = (0.414)\times(149\text{ pm}) = \boxed{61.9\text{ pm}}$

(b) It is shown in Exercise 18B.3(a) that for an eight-fold coordination $\frac{r}{R} = 0.732$.

Thus, $r = 0.732R = (0.732)\times(149\text{ pm}) = \boxed{109\text{ pm}}$

18B.4(b) The volume of an atomic crystal is proportional to the cube of the atomic radius divided by the packing fraction. The packing fractions for hcp, a close-packed structure, is 0.740; for bcc, it is 0.680 (see Exercise 18B.2(a)). So for iron

$$\frac{V_{\text{bcc}}}{V_{\text{hcp}}} = \frac{0.740}{0.680}\left(\frac{122\,\text{pm}}{126\,\text{pm}}\right)^3 = 0.988$$

The bcc structure has a smaller volume, so the transition involves a $\boxed{\text{contraction}}$. (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.)

18B.5(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

$$\Delta_{\text{f}}H^{\ominus}(\text{MgBr}_2,\text{s}) = \Delta_{\text{sub}}H^{\ominus}(\text{Mg},\text{s}) + \Delta_{\text{ion}}H^{\ominus}(\text{Mg},\text{g}) + \Delta_{\text{vap}}H^{\ominus}(\text{Br}_2,\text{l})$$
$$+ \Delta_{\text{bond diss}}H^{\ominus}(\text{Br}_2,\text{g}) + 2\Delta_{\text{eg}}H^{\ominus}(\text{Br},\text{g}) - \Delta_{\text{L}}H^{\ominus}(\text{MgBr}_2,\text{s})$$

So the lattice enthalpy is

$$\Delta_{\text{L}}H^{\ominus}(\text{MgBr}_2,\text{s}) = \Delta_{\text{sub}}H^{\ominus}(\text{Mg},\text{s}) + \Delta_{\text{ion}}H^{\ominus}(\text{Mg},\text{g}) + \Delta_{\text{vap}}H^{\ominus}(\text{Br}_2,\text{l})$$
$$+ \Delta_{\text{bond diss}}H^{\ominus}(\text{Br}_2,\text{g}) + 2\Delta_{\text{eg}}H^{\ominus}(\text{Br},\text{g}) - \Delta_{\text{f}}H^{\ominus}(\text{MgBr}_2,\text{s})$$

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

Solutions to problems

18B.2 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 Fig. 18B.1(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

$$f=\frac{\pi abL}{LA_{\rm p}}=\frac{\pi ab}{A_{\rm p}} \quad \text{where } A_{\rm p} \text{ is the cross-section area of the unit cell.}$$

Fig. 18B.1(b) defines the parameters needed for the determination of $A_{\rm p}$. Examination of the center positions of a pair of stacked ellipses reveals that they have the relative coordinates (0,0) and (0,2b). The adjacent ellipse column is centered 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

$$h=2x=\sqrt{3}a$$

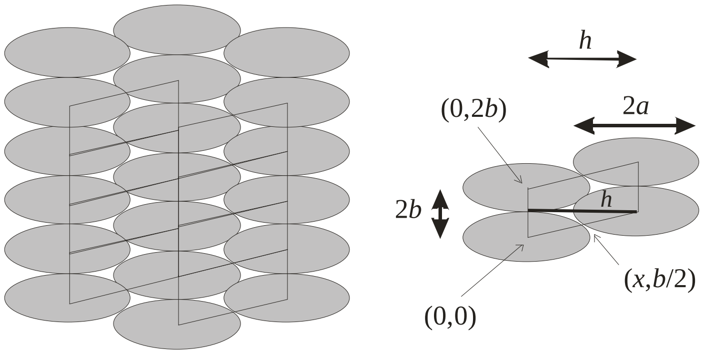
Thus,

$$A_{\rm p}=2bh=2\sqrt{3}ab$$

and

$$f=\frac{\pi \mathrm{ab}}{2\sqrt{3}ab}=\frac{\pi}{2\sqrt{3}}=\boxed{0.907}$$

The above formula for the packing fraction shows that it is independent of the ellipse eccentricity.



(a) (b)

Figure 18B.1

18B.4 (a) The density of energy levels is:

$$\rho(E)=\frac{\mathrm{d}k}{\mathrm{d}E}=\left(\frac{\mathrm{d}E}{\mathrm{d}k}\right)^{-1} \quad \text{where} \quad \frac{\mathrm{d}E}{\mathrm{d}k}=\frac{\mathrm{d}}{\mathrm{d}k}\left(\alpha+2\beta\cos\frac{k\pi}{N+1}\right)\ [38.1]=-\frac{2\pi\beta}{N+1}\sin\frac{k\pi}{N+1}$$

so $$\rho(E)=-\frac{N+1}{2\pi\beta}\left(\sin\frac{k\pi}{N+1}\right)^{-1}$$

Unlike the expression just derived, the relationship the problem asks us to derive has no trigonometric functions, and it contains E and α within a square root. This comparison suggests that the trigonometric identity $\sin^2\theta+\cos^2\theta=1$ will be of use here. Let $\theta=k\pi/(N+1)$; then $\sin\theta=(1-\cos^2\theta)^{1/2}$. However, $\cos\theta$ is related to the energy

$$E=\alpha+2\beta\cos\theta \quad \text{so} \quad \cos\theta=\frac{E-\alpha}{2\beta} \quad \text{and} \quad \sin\theta=\left[1-\left(\frac{E-\alpha}{2\beta}\right)^2\right]^{1/2}$$

Finally, $$\boxed{\rho(E)=-\frac{(N+1)/2\pi\beta}{\left[1-\left(\dfrac{E-\alpha}{2\beta}\right)^2\right]^{1/2}}}$$

(b) The denominator of this expression vanishes as the energy approaches $\alpha \pm 2\beta$. Near those limits, $E-\alpha$ becomes $\pm 2\beta$, making the quantity under the square root zero, and $\rho(E)$ approach infinity.

18B.6 As discussed in Topic 7B.2(c), the wavefunction must be continuous, have a continuous slope, be single-valued, be square-integrable. This means that, when a line of *N* tight-bonding identical atoms are wrapped into a ring, the wavefunction must satisfy the conditions: ψ(left end) = ψ(right end) and ψ'(left end) = ψ'(right end). These boundary conditions are more restrictive than those required for the line of atoms: ψ(left end) = $\pm\psi$(right end) and ψ'(left end) = $\pm\psi'$(right end). As the line is wrapped into a ring, the states for which ψ(left end) = $-\psi$(right end) become forbidden and only alternate quantum numbers for which ψ(left end) = ψ(right end) are allowed.

18B.8 The problem asks for an estimate of $\Delta_f H^\ominus(\text{CaCl,s})$. A Born–Haber cycle would envision formation of CaCl(s) from its elements as sublimation of Ca(s), ionization of Ca(g), atomization of $\text{Cl}_2(\text{g})$, electron gain of Cl(g), and formation of CaCl(s) from gaseous ions. Therefore

$$\Delta_f H^\ominus(\text{CaCl,s}) = \Delta_{\text{sub}}H^\ominus(\text{Ca,s}) + \Delta_{\text{ion}}H^\ominus(\text{Ca,g}) + \Delta_f H^\ominus(\text{Cl,g}) + \Delta_{\text{eg}}H^\ominus(\text{Cl,g}) - \Delta_L H^\ominus(\text{CaCl,s})$$

Before we can estimate the lattice enthalpy of CaCl, we select a lattice with the aid of the radius-ratio rule. The ionic radius for Cl^- is 181 pm (Table 18B.2); use the ionic radius of K^+ (138 pm) for Cs^+.

$$\gamma = \frac{138\,\text{pm}}{181\,\text{pm}} = 0.762$$

suggesting the CsCl structure (Madelung constant *A* = 1.763, Table 18B.3). We can interpret the Born–Mayer equation (eqn. 18B.6) as giving the negative of the lattice enthalpy.

$$\Delta_L H^\ominus \approx E_{\text{p,min}} = \frac{A|z_1z_2|N_A e^2}{4\pi\varepsilon_0 d}\left(1-\frac{d^*}{d}\right) \qquad \text{where } d^* \text{ is taken to be 34.5 pm (common choice).}$$

The distance d is $d = (138+181)\ \text{pm} = 319\ \text{pm}$.

$$\Delta_L H^\ominus \approx \frac{(1.763)\times|(1)(-1)|\times(6.022\times10^{23}\ \text{mol}^{-1})\times(1.602\times10^{-19}\ \text{C})^2}{4\pi(8.854\times10^{-12}\ \text{J}^{-1}\text{C}^2\ \text{m}^{-1})\times(319\times10^{-12}\ \text{m})}\left(1-\frac{34.5\,\text{pm}}{319\,\text{pm}}\right)$$

$$\approx 6.85\times10^5\ \text{J mol}^{-1} = 685\ \text{kJ mol}^{-1}$$

The enthalpy of formation, then, is

$$\Delta_f H^\ominus(\text{CaCl,s}) \approx [176+589.7+121.7-348.7-685]\ \text{kJ mol}^{-1} = \boxed{-146\ \text{kJ mol}^{-1}}\,.$$

Although formation of CaCl(s) from its elements is exothermic, formation of $\text{CaCl}_2(\text{s})$ is still more favoured energetically. Consider the disproportionation reaction 2 CaCl(s) → Ca(s) + CaCl_2(s) for which

$$\begin{aligned}\Delta H^\ominus &= \Delta_f H^\ominus(\text{Ca,s}) + \Delta_f H^\ominus(\text{CaCl}_2\text{,s}) - 2\Delta_f H^\ominus(\text{CaCl,s})\\ &\approx [0-795.8-2(-146)]\ \text{kJ mol}^{-1}\\ &\approx -504\ \text{kJ mol}^{-1}\end{aligned}$$

and the thermodynamic instability of CaCl(s) toward disproportionation to Ca(s) and CaCl_2(s) becomes apparent.

Note: Using the tabulated ionic radius of Ca (i.e., that of Ca^{2+}) would be less valid than using the atomic radius of a neighbouring monovalent ion, for the problem asks about a hypothetical compound of monovalent calcium. Predictions with the smaller Ca^{2+} radius (100 pm) differ from those listed above but the conclusion remains the same: the expected structure changes to rock-salt, the lattice enthalpy to $758\ \text{kJ mol}^{-1}$, $\Delta_f H^\ominus(\text{CaCl,s})$ to $-219\ \text{kJ mol}^{-1}$ and the disproportionation enthalpy to $-358\ \text{kJ mol}^{-1}$.

18B.10 A macroscopic two-dimensional crystal that has the ionic structure depicted in text Fig. 18.2 is unstable because it requires energy to hold the ions in position, thereby, preventing them from flying apart as small clumps of ions or shifting into a more stable lattice structure. To see this, consider one of the diagonals within the figure. This is a line of cations separated by the distance 2*r* where *r* is the radius of the smallest circle. Moving along this diagonal, away from the figure center, we find that rather quickly all cation or anions that are not on the line are so far away from the cations of this diagonal that electrostatic interaction with out-liners is negligibly small. The appreciable interaction is among the cations of the diagonal only and it is repulsive. To say that it is infinitely large, and positive, is a good approximation for a large array. This repulsive interaction overwhelms the small attractive interaction near the center of the figure. We conclude that there is $\boxed{\text{no Madelung constant to compute for a large array of this lattice}}$.

What about a small clump of atoms? To explore this question, consider a clump that consists only of the 5 ions found in the very center of the text figure. Their potential energy is

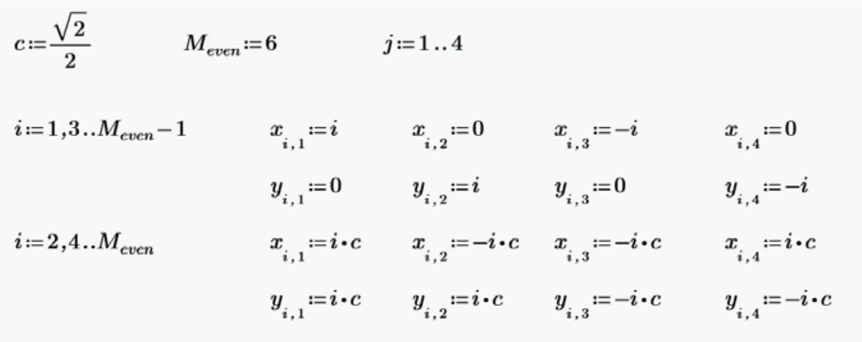
$$E_\mathrm{p} = \left(\frac{e^2}{4\pi\varepsilon_0}\right)\times\left\{4\times\left(\frac{-|z|^2}{r}\right)+\left(1+\frac{4}{\sqrt{2}}\right)\times\left(\frac{|z|^2}{r}\right)\right\}$$

$$= \left(-4+1+\frac{4}{\sqrt{2}}\right)\times\left(\frac{|z|^2 e^2}{4\pi\varepsilon_0 r}\right)$$

$$= -0.1716\times\left(\frac{|z|^2 e^2}{4\pi\varepsilon_0 r}\right)$$

The first term in the above expression accounts for the electrostatic attraction between the central cation (+|z|) and the 4 anions (−|z|) of the first ring. The second term accounts for the repulsive interaction between the anions of the first ring. Since $E_\mathrm{p} < 0$, the five-member clump is stable.

We expect that as additional rings are considered around the five-member clump the potential energy will become successively more stable. However, if too many rings are added, the repulsive interactions along one-dimensional lines of like ions will begin to dominate and the clump will become unstable. What is the maximum number of rings that can be placed around the central cation to form a stable clump of ions? In the following Mathcad Prime 2 worksheet, the potential energy in units of $|z|^2e^2/4\pi\varepsilon_0$ is calculated for the case in which an even number of rings surround the central cation. The worksheet begins by forming a matrix of *x* coordinates and a matrix of *y* coordinates for the ions of the clump. Each matrix row contains coordinates (*x*,*y*) for ions of a ring (ring 1, 2, 3,..., M_even). The 4 matrix columns provide locations for the coordinates of each of the identical ions of the ring.



$$c := \frac{\sqrt{2}}{2} \qquad M_{even} := 6 \qquad j := 1..4$$

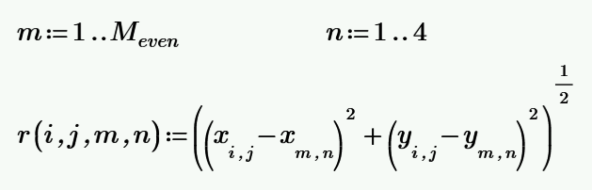
$$i := 1,3..M_{even}-1 \qquad x_{i,1} := i \quad x_{i,2} := 0 \quad x_{i,3} := -i \quad x_{i,4} := 0$$

$$y_{i,1} := 0 \quad y_{i,2} := i \quad y_{i,3} := 0 \quad y_{i,4} := -i$$

$$i := 2,4..M_{even} \qquad x_{i,1} := i\cdot c \quad x_{i,2} := -i\cdot c \quad x_{i,3} := -i\cdot c \quad x_{i,4} := i\cdot c$$

$$y_{i,1} := i\cdot c \quad y_{i,2} := i\cdot c \quad y_{i,3} := -i\cdot c \quad y_{i,4} := -i\cdot c$$

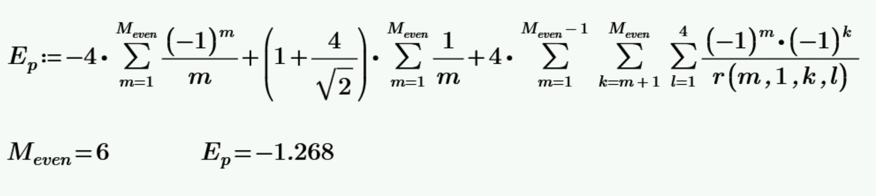
Next, the worksheet establishes a formula that can calculate the distance between the ion whose coordinates are at the matrix element *i,j* and the ion whose coordinates are at the matrix element *m,n*.



$$m := 1..M_{even} \qquad n := 1..4$$

$$r(i,j,m,n) := \left(\left(x_{i,j}-x_{m,n}\right)^2+\left(y_{i,j}-y_{m,n}\right)^2\right)^{\frac{1}{2}}$$

Now a formula for the reduced potential energy of the clump is setup. The first term of the expression accounts for the interaction between the central cation and all other ions of the clump. The second term accounts for the repulsive interactions between the 4 ions of a ring and sums over all rings. The last term accounts for interactions between the 4 ions of a ring and all ions in larger rings and sums over all rings. It uses the symmetry that the interaction of each of the 4 ions in the smaller ring experiences identical interactions with ions in larger rings. The terms of this expression have accounted for all interactions of the clump while avoiding self-interactions and avoiding the inclusion of any ion-ion interaction more than once.



$$E_p := -4\cdot\sum_{m=1}^{M_{even}}\frac{(-1)^m}{m}+\left(1+\frac{4}{\sqrt{2}}\right)\cdot\sum_{m=1}^{M_{even}}\frac{1}{m}+4\cdot\sum_{m=1}^{M_{even}-1}\ \sum_{k=m+1}^{M_{even}}\ \sum_{l=1}^{4}\frac{(-1)^m\cdot(-1)^k}{r(m,1,k,l)}$$

$$M_{even} = 6 \qquad E_p = -1.268$$

For 4, 6, 8, and 10 rings the worksheet gives reduced potential energies of −1.599, −1.268, +0.167, and +2.487 $|z|^2e^2/4\pi\varepsilon_0$, respectively. Interpolation indicates that 7 rings should be stable (about −0.7 $|z|^2e^2/4\pi\varepsilon_0$). We conclude that the largest stable clump of this two-dimensional lattice of ions consists of 7 rings around the central cation.

18C Mechanical, electrical, and magnetic properties of solids

Answers to discussion questions

18C.2 The most obvious difference is that there is no magnetic analog of electric charge; hence, there are no magnetic ‘ions.’ Both electric and magnetic moments exist and these can be either permanent or induced. Induced magnetic moments in the entire sample can be either parallel or antiparallel to the applied field producing them (paramagnetic or diamagnetic moments), whereas in the electric case they are always parallel. Magnetization, $\mathcal{M}$, is the analog of polarization, $\mathcal{P}$. Although both magnetization and induced dipole moment are proportional to the fields producing them, they are not analogous quantities, neither are volume magnetic susceptibility, χ, and electric polarizability, α. The magnetic quantities refer to the sample as a whole, the electric quantities to the molecules. Molar magnetic susceptibility is analogous to molar polarization as can be seen by comparing equations 18C.7 and 16A.5a and magnetizability is analogous to electric polarizability.

Solutions to exercises

18C.1(b) Poisson’s ratio: $\nu_{\mathrm{p}} = \dfrac{\text{transverse strain}}{\text{normal strain}}\ [18\text{C}.2] = 0.41$

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:

$$\left(\frac{\Delta L}{L}\right)_z = +0.020, \qquad \left(\frac{\Delta L}{L}\right)_x = \left(\frac{\Delta L}{L}\right)_y = -0.020\times 0.41 = -0.0082 \ \ [\text{a contraction of widths}]$$

Application of the stress to 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 $\boxed{3.3\times10^{-3}\ \text{dm}^3}$.

18C.2(b) Is gallium-doped germanium a p-type or n-type semiconductors?
p-type; the dopant, gallium, belongs to Group 13 whereas germanium belongs to Group 14.

18C.3(b) $m = g_{\mathrm{e}}\{S(S+1)\}^{1/2}\mu_{\mathrm{B}} \quad [18\text{C}.9, \text{with } S \text{ in place of } s]$

Therefore, since $m = 5.3\ \mu_{\mathrm{B}}$ and $g_{\mathrm{e}} \approx 2$,

$$S(S+1) = \left(\tfrac{1}{4}\right)\times(5.3)^2 = 7.0, \quad \text{implying that} \quad S = 2.2$$

Because $S \approx \frac{4.4}{2}$, the Mn^{2+} ions typically have 4-5 unpaired spins.

In actuality most Mn^{2+} compounds have 5 unpaired spins.

18C.4(b) $\chi_{\mathrm{m}} = \chi V_{\mathrm{m}}[18\text{C}.8] = \chi M/\rho = (-7.9\times10^{-6})\times(84.15\,\text{g mol}^{-1})/(0.811\,\text{g cm}^{-3})$

$$= \boxed{-8.2\times10^{-4}\ \text{cm}^3\,\text{mol}^{-1}} = \boxed{-8.2\times10^{-10}\ \text{m}^3\ \text{mol}^{-1}}$$

18C.5(b) The molar susceptibility is given by

$$\chi_{\mathrm{m}} = \frac{N_{\mathrm{A}}g_{\mathrm{e}}^2\mu_0\mu_{\mathrm{B}}^2 S(S+1)}{3kT}\ [18\text{C}.10\text{a}] \quad \text{so} \quad S(S+1) = \frac{3kT\chi_{\mathrm{m}}}{N_A g_{\mathrm{e}}^2\mu_0\mu_{\mathrm{B}}^2}$$

$$S(S+1)=\frac{3(1.381\times10^{-23}\ \mathrm{J\,K^{-1}})\times(298\ \mathrm{K})}{(6.022\times10^{23}\ \mathrm{mol^{-1}})\times(2.0023)^2}\times\frac{(6.00\times10^{-8}\ \mathrm{m^3\ mol^{-1}})}{(4\pi\times10^{-7}\ \mathrm{T^2\ J^{-1}\ m^3})\times(9.274\times10^{-24}\ \mathrm{J\,T^{-1}})^2}$$

$$=2.84 \quad \text{so} \quad S=\frac{-1+\sqrt{1+4(2.84)}}{2}=1.26$$

corresponding to $\boxed{2.52}$ 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.

18C.6(b) The molar susceptibility is given by

$$\chi_{\mathrm{m}}=\frac{N_{\mathrm{A}}g_{\mathrm{e}}^2\mu_0\mu_{\mathrm{B}}^2S(S+1)}{3kT} \quad [18\mathrm{C}.10\mathrm{a}]$$

Mn^{2+} has five unpaired spins, so $S = 2.5$ and

$$\chi_{\mathrm{m}}=\frac{(6.022\times10^{23}\ \mathrm{mol^{-1}})\times(2.0023)^2\times(4\pi\times10^{-7}\ \mathrm{T^2\ J^{-1}\ m^3})\times(9.274\times10^{-24}\ \mathrm{J\,T^{-1}})^2\times(2.5)\times(2.5+1)}{3(1.381\times10^{-23}\ \mathrm{J\,K^{-1}})\times(298\ \mathrm{K})}$$

$$=\boxed{1.85\times10^{-7}\ \mathrm{m^3\ mol^{-1}}}$$

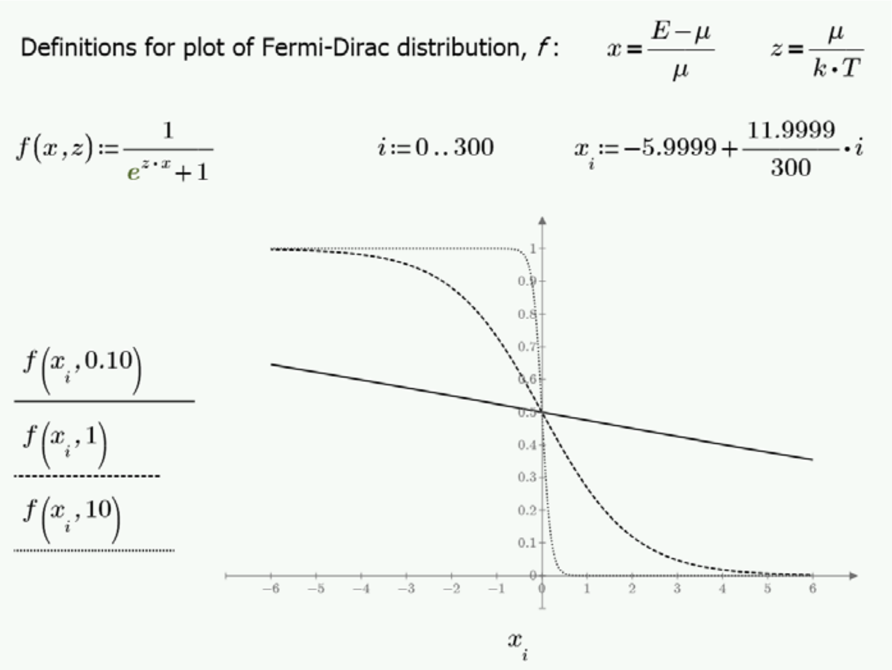
Solutions to problems

18C.2 The Fermi-Dirac distribution, *f*, can be transformed to the variables of text Figure 18C.6 as follows.

$$\frac{E-\mu}{kT}=\left(\frac{\mu}{kT}\right)\times\left(\frac{E-\mu}{\mu}\right)\equiv z\times x$$

$$f(x,z)=\frac{1}{e^{z\times x}+1}\ [39.2\mathrm{a}] \quad \text{where} \quad x\equiv\frac{E-\mu}{\mu} \quad \text{and} \quad z\equiv\frac{\mu}{kT}$$

Text Figure 18C.6 is replicated in the following Mathcad Prime 2 worksheet. The effect of changing values of *z*, the ratio of μ to *kT*, is readily explored by simply altering *z* values in the plot. Values *z* = 0.10, 1, and 10 are shown in the worksheet. It is seen that as $T\to\infty$, $z\to0$, and $f\to½$; that is all available energy states have an occupational probability of ½ (a state is filled with at most two electrons by the Pauli exclusion Principle). As $T\to0$, $z\to\infty$, and *f* becomes a step distribution for which $f = 1$ for $x < 0$ and $f = 0$ for $x > 0$ (see Brief illustration 18C.2 of the text for the significance of this distribution).



Definitions for plot of Fermi-Dirac distribution, *f*: $x=\dfrac{E-\mu}{\mu}$ $z=\dfrac{\mu}{k\cdot T}$

$f(x,z):=\dfrac{1}{e^{z\cdot x}+1}$ $i:=0\,..\,300$ $x_i:=-5.9999+\dfrac{11.9999}{300}\cdot i$

18C.4 $N_{\mathrm{e}} = \int_{E=0}^{E=\infty} \mathrm{d}N(E) = \int_0^\infty \rho(E)\times f(E)\mathrm{d}E = \int_0^\infty \frac{\rho(E)}{\mathrm{e}^{(E-\mu)/kT}+1}\mathrm{d}E$ [18C.5 and 18C.6a]

In order for N to remain a constant of this equation as the temperature is raised, the exponential term $\exp\{(E-\mu)/kT\}$ must remain constant. It is apparent that, when $\exp\{E/kT\}$ gets smaller as T grows larger for each value of E, it must be multiplied by a larger value of $\exp\{-\mu/kT\}$, so $\mu(T)$ must decrease.

18C.6 Tans and coworkers (S.J. Tans et al., *Nature*, **393**, 49 (1998)) have draped a semiconducting carbon nanotube (CNT) over metal (gold in Fig. 18C.1) electrodes that are 400 nm apart atop a silicon surface coated with silicon dioxide. A bias voltage between the electrodes provides the source and drain of the molecular field-effect transistor(FET). The silicon serves as a gate electrode and the thin silicon oxide layer (at least 100 nm thick) insulates the gate from the CNT circuit. By adjusting the magnitude of an electric field applied to the gate, current flow across the CNT may be turned on and off.

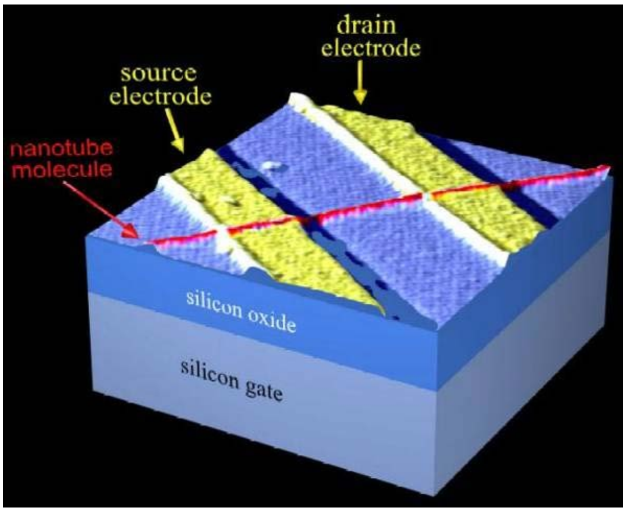


Figure 18C.1

Wind and coworkers (S.J. Wind et al., *Applied Physics Letters*, **80**(20, May 20), 3817 (2002)) have designed (Fig. 18C.2) a CNTFET of improved current carrying capability. The gate electrode is above the conduction channel and separated from the channel by a thin oxide dielectric. In this manner the CNT-to-air contact is eliminated, an arrangement that prevents the circuit from acting like a p-type transistor. This arrangement also reduces the gate oxide thickness to about 15 nm, allowing for much smaller gate voltages and a steeper subthreshold slope, which is a measure of how well a transistor turns on or off.

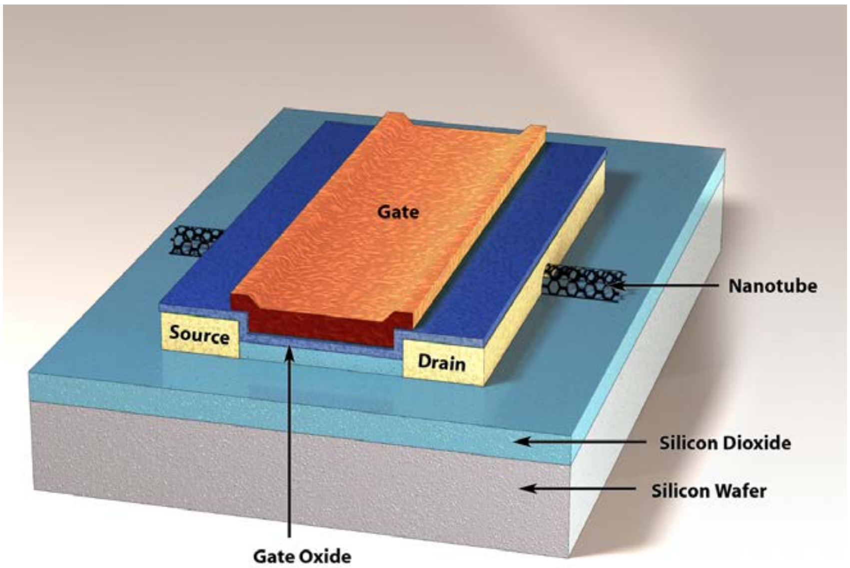


Figure 18C.2

A single-electron transistor (SET) has been prepared by Cees Dekker and coworkers (*Science*, **293**, 76, (2001)) with a CNT. The SET is prepared by putting two bends in a CNT with the tip of an AFM (Fig. 18C.3). Bending causes two buckles that, at a distance of 20 nm, serves as a conductance barrier. When an appropriate voltage is applied to the gate below the barrier, electrons tunnel one at a time across the barrier.

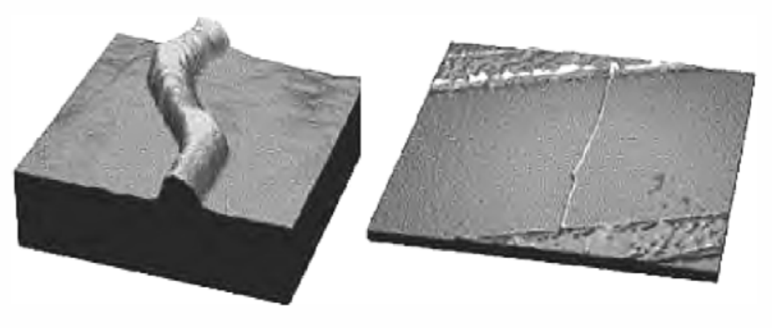


Figure 18C.3

Weitz et al.(Phys. Stat. Sol. (b) **243**, 13, 3394 (2006)) report on the construction of a single-wall CNT using a silane-based organic self-assembled monolayer (SAM) as a gate dielectric on top of a highly doped silicon wafer. The organic SAM is made of 18-phenoxyoctadecyltrichlorosilane. This ultrathin layer (Fig. 18C.4) ensures strong gate coupling and therefore low operation voltages. Single-electron transistors (SETs) were obtained from individual metallic SWCNTs. Field-effect transistors made from individual semiconducting SWCNTs operate with gate-source voltages of –2 V, show good saturation, small hysteresis (200 mV) as well as a low subthreshold swing (290 mV/dec).

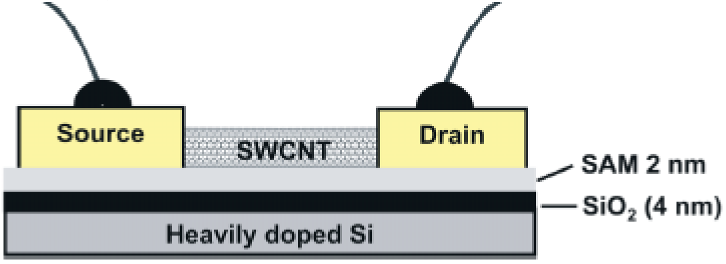


Figure 18C.4

John Rodgers and researchers at the University of Illinois have reported a technique for producing near perfect alignment of CNT transistors (Fig. 18C.5). The array is prepared by patterning thin strips of an iron catalyst on quartz crystals and then growing nanometer-wide CNTs along those strips using conventional carbon vapor deposition. The quartz crystal aligns the nanotubes. Transistor development then includes depositing source, drain, and gate electrodes using conventional photolithography. Transistors made with about 2,000 nanotubes can carry currents of one ampere. The research group also developed a technique for transferring the nanotube arrays onto any substrate, including silicon, plastic, and glass. See Coskun Kocabas, Seong Jun Kang, Taner Ozel, Moonsub Shim, and John A. Rogers, *J. Phys. Chem. C* **2007,** *111*, 17879, Improved Synthesis of Aligned Arrays of Single-Walled Carbon Nanotubes and Their Implementation in Thin Film Type Transistors.

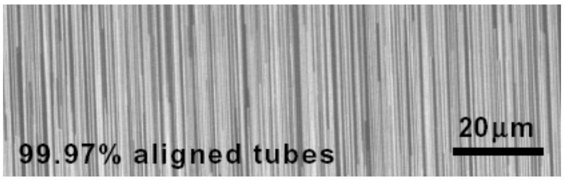


Figure 18C.5

Further background discussion of carbon nanotube field-effect transistors (CNTFET) can be found at wikipedia.org. For a review of the CNT catalytic growth technique, methods to grow oriented long CNTs with controlled diameters, and process steps for the fabrication of both back and top-grated CNTFET see K.C. Narasimhamurthy and R. Paily, *IETE Technical Review*, 2011, V 28, Issue 1, 57, Fabrication of Carbon Nanotube Field Effect Transistor.

18C.8 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 level

($p_{3/2}$) are given by the following equations, which are derived from the Boltzmann distribution in the note below.

$$p_{1/2}=\frac{1}{1+\mathrm{e}^{-\varepsilon/kT}} \quad \text{and} \quad p_{3/2}=\frac{\mathrm{e}^{-\varepsilon/kT}}{1+\mathrm{e}^{-\varepsilon/kT}}=\frac{1}{1+\mathrm{e}^{\varepsilon/kT}}$$

Since the ground state of nitric oxide exhibits no paramagnetism, only $p_{3/2}N_\mathrm{A}$ molecules contribute to the observed magnetic moment of a mole of nitric oxide molecules. Consequently, eqn 18C.10a for the molar paramagnetic susceptibility must be modified with the inclusion of a factor $p_{3/2}$.

$$\chi_\mathrm{m}=\frac{p_{3/2}N_\mathrm{A}g_\mathrm{e}^2\mu_0\mu_\mathrm{B}^2S(S+1)}{3kT} \text{ [18C.10a]}$$

Substitution of $S(S+1)=(m/g_\mathrm{e}\mu_\mathrm{B})^2$ [18C.9] where m is the magnetic moment into the above expression gives

$$\chi_\mathrm{m}=\frac{p_{3/2}N_\mathrm{A}\mu_0\mu_\mathrm{B}^2(m/\mu_\mathrm{B})^2}{3kT}$$

$$=\frac{N_\mathrm{A}\mu_0\mu_\mathrm{B}^2(m/\mu_\mathrm{B})^2}{3kT\times\left(1+\mathrm{e}^{\varepsilon/kT}\right)} \quad \text{where} \quad \varepsilon/k=hc\tilde{\nu}/k=hc\times\left(121.1\ \mathrm{cm}^{-1}\right)/k=174.2\ \mathrm{K}$$

Thus, with $m/\mu_\mathrm{B}=2$

$$\chi_\mathrm{m}=\frac{6.286\times10^{-6}\ \mathrm{m}^3\ \mathrm{mol}^{-1}}{(T/\mathrm{K})\times\left(1+\mathrm{e}^{174.2/(T/\mathrm{K})}\right)}$$

This relation gives the molar paramagnetic susceptibility of NO as a function of temperature. For example, χ_m at 90 K is

$$\chi_\mathrm{m}=\frac{6.286\times10^{-6}\ \mathrm{m}^3\ \mathrm{mol}^{-1}}{(90)\times\left(1+\mathrm{e}^{174.2/(90)}\right)}=\boxed{8.81\times10^{-9}\ \mathrm{m}^3\ \mathrm{mol}^{-1}}$$

The mass paramagnetic susceptibility is

$$\chi_\mathrm{mass}=\chi_\mathrm{m}/M=\left(8.81\times10^{-9}\ \mathrm{m}^3\ \mathrm{mol}^{-1}\right)/\left(0.03001\ \mathrm{kg\ mol}^{-1}\right)=2.94\times10^{-7}\ \mathrm{m}^3\ \mathrm{kg}^{-1}$$

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.

$$\chi_\mathrm{mass}\text{ in cgs}=\left(2.94\times10^{-4}\ \mathrm{cm}^3\ \mathrm{g}^{-1}\right)/4\pi=23.4\times10^{-6}\ \mathrm{cm}^3\ \mathrm{g}^{-1}$$

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. Fig. 18C.6 is a plot of the molar paramagnetic susceptibility, as modeled in this problem, against temperature below the normal fusion point (110 K) of nitric oxide. The curve is remarkably different than the $\chi_\mathrm{m}(T)$ behavior of most paramagnetic substances. Paramagnetism is normally a property of the ground electronic state and, consequently, there is an inverse relation between χ_m and T [18C.10b] so that χ_m decreases with increasing T. Effective angular momentums 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, $\chi_\mathrm{m}=0$. As T is increased from absolute zero, molecules are thermally promoted to the excited state and the observed paramagnetism increases as shown in Fig. 18C.6.

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 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 $p_1\propto g_1\mathrm{e}^{-\varepsilon/kT}$. 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 $1/(g_0+g_1\mathrm{e}^{-\varepsilon/kT})$ and the probabilities are

$$p_0=g_0/(g_0+g_1\mathrm{e}^{-\varepsilon/kT}) \quad \text{and} \quad p_1=g_1\mathrm{e}^{-\varepsilon/kT}/(g_0+g_1\mathrm{e}^{-\varepsilon/kT})$$

In the special case for which $g_0=g_1$ the probabilities simplify to those given at the top.

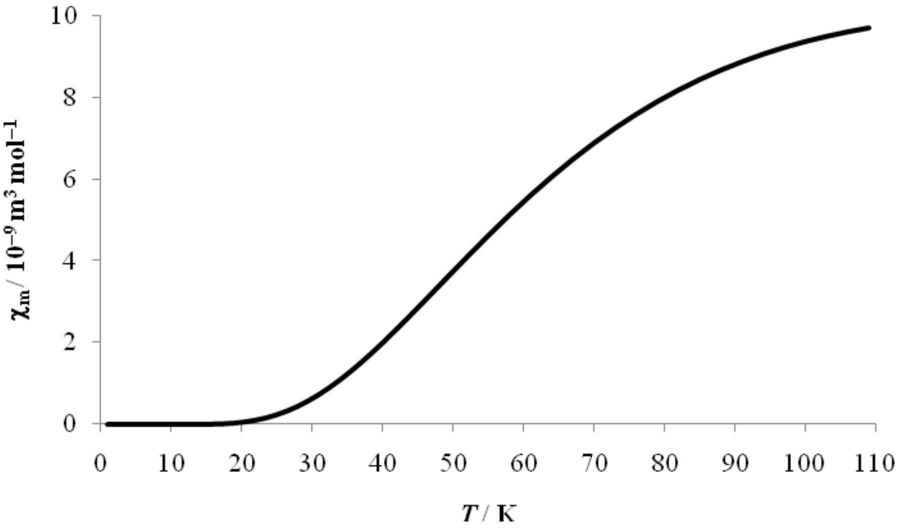


Figure 18C.6

18D The optical properties of solids

Answers to discussion questions

18D.2 Figure 18D.1 is a simplified schematic of a light-emitting diode. The upper portion of the figure shows the electric circuit symbol of the LED. The lower portion represents the electron motion and energy flows of the LED when, as shown, it is forward-biased (see text Fig. 18C.9 and associated discussion). Electrons are represent with solid circles while electron holes are white circles Here's a list of important features that you should label within the figure: the location of both the p−type and n−type semiconductors, the junction between semiconductors, the line representing the energy of the conduction band, the line representing the energy of the valence band, electron flow in the circuit, current direction in the circuit, flow of electrons and holes in the semiconductors, and light-emitting transitions. The intensity of radiative emissions depends upon the applied voltage but the wavelength depends upon the band gap energy.

In addition to having the basic features of the LED, the laser diode must have a resonant cavity, which can be formed by using the high refractive index of the semiconducting material and cleaving single crystals so that the light is trapped by the abrupt variation of refractive index.

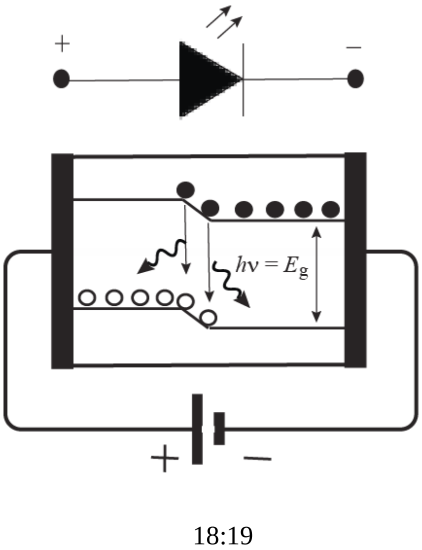


Figure 18D.1

Solutions to exercises

18D.1(b) $E_{\mathrm{g}} = h\nu_{\mathrm{min}}$

$$\nu_{\mathrm{min}} = \frac{h}{E_{\mathrm{g}}} = \frac{6.626\times10^{-34}\ \mathrm{J\ s}}{1.12\ \mathrm{eV}}\left(\frac{1\ \mathrm{eV}}{1.602\times10^{-19}\ \mathrm{J}}\right) = 3.69\times10^{-15}\ \mathrm{s}^{-1} = \boxed{3.69\ \mathrm{fHz}}$$

Solutions to problems

18D.2 (a) $\hat{H}\psi_{+\mathrm{or}-} = \tilde{\nu}_{+\mathrm{or}-}\psi_{+\mathrm{or}-}$ and $\left(\hat{H} - \tilde{\nu}_{+\mathrm{or}-}\right)\psi_{+\mathrm{or}-} = 0$

$$\begin{pmatrix} \tilde{\nu}_{\mathrm{mon}} - \tilde{\nu}_{+\mathrm{or}-} & \beta \\ \beta & \tilde{\nu}_{\mathrm{mon}} - \tilde{\nu}_{+\mathrm{or}-} \end{pmatrix}\psi_{+\mathrm{or}-} = 0 \quad \text{where} \quad \beta = \frac{\mu_{\mathrm{mon}}^2}{4\pi\varepsilon_0 hcr^3}\left(1-3\cos^2\theta\right) \ \text{[See Problem 18D.1]}$$

$$\begin{pmatrix} x_{+\mathrm{or}-} & 1 \\ 1 & x_{+\mathrm{or}-} \end{pmatrix}\psi_{+\mathrm{or}-} = 0 \quad \text{where} \quad x_{+\mathrm{or}-} = \left(\tilde{\nu}_{\mathrm{mon}} - \tilde{\nu}_{+\mathrm{or}-}\right)/\beta$$

$$\begin{vmatrix} x_{+\mathrm{or}-} & 1 \\ 1 & x_{+\mathrm{or}-} \end{vmatrix} = x_{+\mathrm{or}-}^2 - 1 = 0$$

$$x_{+\mathrm{or}-} = \left(\tilde{\nu}_{\mathrm{mon}} - \tilde{\nu}_{+\mathrm{or}-}\right)/\beta = \pm1 \quad \text{and} \quad \tilde{\nu}_{+\mathrm{or}-} = \tilde{\nu}_{\mathrm{mon}} \pm \beta$$

$$\tilde{\nu}_+ = \tilde{\nu}_{\mathrm{mon}} - \beta \quad \text{and} \quad \tilde{\nu}_- = \tilde{\nu}_{\mathrm{mon}} + \beta$$

$\tilde{\nu}_+$ and $\tilde{\nu}_-$ are plotted in Fig. 18D.2 as a function of θ using μ_{mon} = 4.00 D, $\tilde{\nu}_{\mathrm{mon}}$ = 25000 cm^{-1}, and r = 0.5 nm.

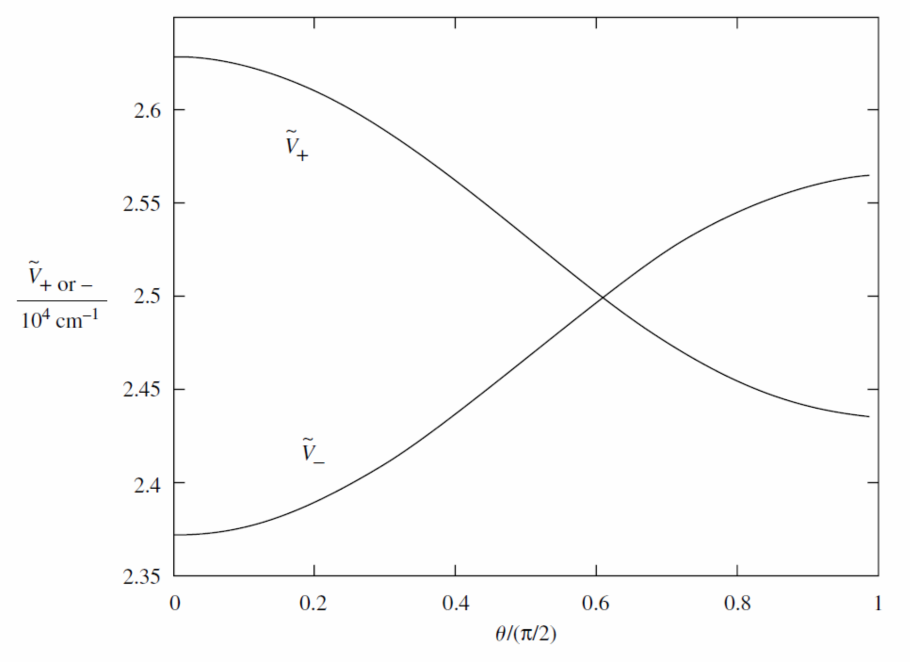


Figure 18D.2

The ratio of μ_+^2/μ_-^2 (and the relative intensities of the dimer transitions) doesn't depend upon β or θ because μ_+ = 0. To see this, we use the coefficients of the normalized wavefunctions for ψ_+ and ψ_- and the overlap integral $S = \langle\psi_1|\psi_2\rangle$.

$$\begin{pmatrix} x_{+\text{or}-} & 1 \\ 1 & x_{+\text{or}-} \end{pmatrix}\begin{pmatrix} c_{+\text{or}-,1} \\ c_{+\text{or}-,2} \end{pmatrix} = 0 \qquad \text{where} \qquad x_{+\text{or}-} = \pm 1$$

$$x_{+\text{or}-}c_{+\text{or}-,1} + c_{+\text{or}-,2} = 0$$

$$c_{+\text{or}-,2} = -x_{+\text{or}-}c_{+\text{or}-,1} \qquad \text{(i)}$$

The coefficients must also satisfy the normalization condition.

$$\begin{aligned}\left\langle \psi_{+\text{or}-} \mid \psi_{+\text{or}-} \right\rangle &= \left\langle c_{+\text{or}-,1}\psi_1 + c_{+\text{or}-,2}\psi_2 \mid c_{+\text{or}-,1}\psi_1 + c_{+\text{or}-,2}\psi_2 \right\rangle \\ &= c_{+\text{or}-,1}{}^2 + c_{+\text{or}-,2}{}^2 + 2c_{+\text{or}-,1}c_{+\text{or}-,2}S \\ &= c_{+\text{or}-,1}{}^2 + c_{+\text{or}-,1}{}^2 - 2x_{+\text{or}-}c_{+\text{or}-,1}{}^2S = 1 \qquad \text{(ii)}\end{aligned}$$

Thus,

$$c_{+,1} = \frac{1}{\left\{2\left(1-S\right)\right\}^{1/2}} \qquad c_{+,2} = -c_{+,1}$$

and

$$c_{-,1} = \frac{1}{\left\{2\left(1+S\right)\right\}^{1/2}} \qquad c_{-,2} = c_{-,1}$$

$$\frac{\mu_+^2}{\mu_-^2} = \left(\frac{\mu_+}{\mu_-}\right)^2 = \left(\frac{\left(c_{+,1}+c_{+,2}\right)\mu_{\text{mon}}}{\left(c_{-,1}+c_{-,2}\right)\mu_{\text{mon}}}\right)^2 \ [\text{See Problem 18D.1}] = \left(\frac{c_{+,1}-c_{+,1}}{c_{-,1}+c_{-,1}}\right)^2 = 0$$

(b) The secular determinant for N monomers has the dimension $N\times N$.

$$\begin{vmatrix} \tilde{\nu}_{\text{mon}} - \tilde{\nu}_{\text{dimer}} & V & 0 & \cdots \\ V & \tilde{\nu}_{\text{mon}} - \tilde{\nu}_{\text{dimer}} & V & \cdots \\ 0 & V & \tilde{\nu}_{\text{mon}} - \tilde{\nu}_{\text{dimer}} & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{vmatrix} = 0$$

$$\tilde{\nu}_{\text{dimer}} = \tilde{\nu}_{\text{mon}} + 2V\cos\left(\frac{k\pi}{N+1}\right) \qquad k = 1,\ 2,\ 3, ...,\ N \qquad [18\text{B}.1]$$

$$V = \beta(0) = \frac{\mu_{\text{mon}}^2}{4\pi\varepsilon_0 hcr^3}\left(1-3\cos^2 0\right) = \frac{-\mu_{\text{mon}}^2}{2\pi\varepsilon_0 hcr^3}$$

The following plot, Fig. 18D.3, 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 $25000\ \text{cm}^{-1} + 2V = 25000\ \text{cm}^{-1} + 2\times(-1289\ \text{cm}^{-1}) = 22422\ \text{cm}^{-1}$ as $N \to \infty$.

Since the model considers only nearest neighbor interactions, the transition dipole moment of the lowest energy transition doesn't depend upon the size of the chain.

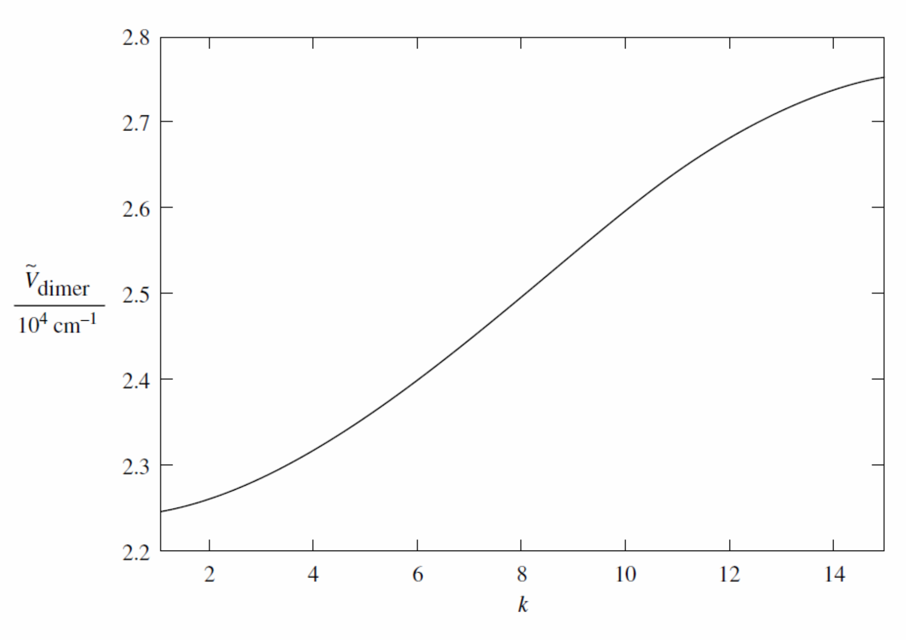


Figure 18D.3

Integrated activities

18.2 The electron density distribution in a hydrogenic atom, $\rho(r)$, is related to the radial wavefunction, $R(r)$, by

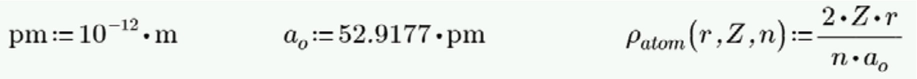
$$\rho(r)=\frac{P(r)}{4\pi r^2}\ [\text{given}]=\frac{r^2R(r)^2}{4\pi r^2}\ [9\text{A}.18\text{b}]=\frac{R(r)^2}{4\pi}$$

where the radial wavefunctions are found in Table 9A.1. Substitution into eqn. 18A.3 for the scattering factor f yields a computational feasible expression for scattering from 1s (n = 1) and 2s (n = 2) atomic orbitals.

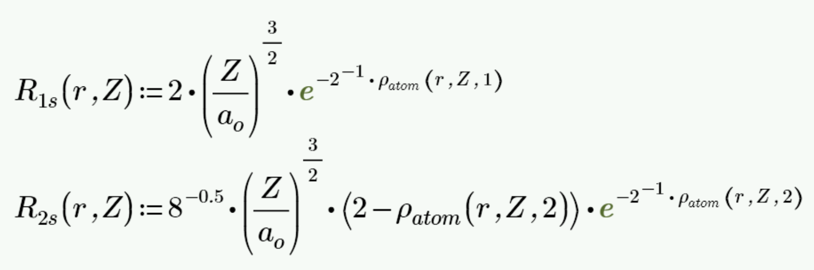
$$f\,(\xi,Z,n)=4\pi\int_0^\infty \rho(r,Z,n)\frac{\sin(4\pi\xi r)}{4\pi\xi r}\,r^2\mathrm{d}r\ [18\text{A}.3]\quad \text{where}\quad \xi=\frac{\sin\theta}{\lambda}$$

$$=\frac{1}{4\pi\xi}\int_0^\infty R(r,Z,n)^2\sin(4\pi\xi r)\,r\,\mathrm{d}r$$

Plots of f against ξ are prepared in a Mathcad Prime 2 worksheet.

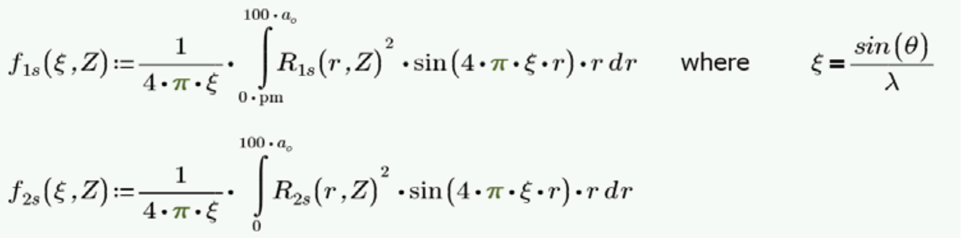


$$\text{pm}:=10^{-12}\cdot\text{m}\qquad a_o:=52.9177\cdot\text{pm}\qquad \rho_{atom}(r,Z,n):=\frac{2\cdot Z\cdot r}{n\cdot a_o}$$



$$R_{1s}(r,Z):=2\cdot\left(\frac{Z}{a_o}\right)^{\frac{3}{2}}\cdot e^{-2^{-1}\cdot\rho_{atom}(r,Z,1)}$$

$$R_{2s}(r,Z):=8^{-0.5}\cdot\left(\frac{Z}{a_o}\right)^{\frac{3}{2}}\cdot\left(2-\rho_{atom}(r,Z,2)\right)\cdot e^{-2^{-1}\cdot\rho_{atom}(r,Z,2)}$$

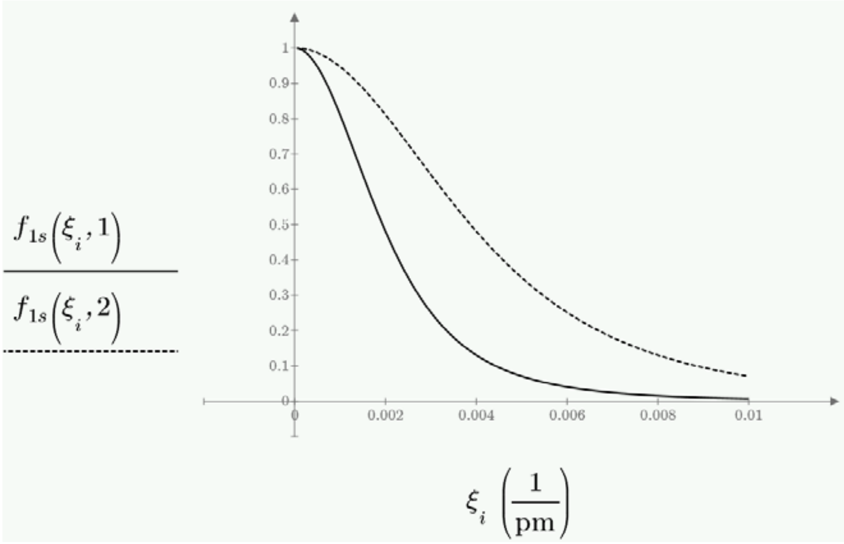


$$f_{1s}(\xi,Z):=\frac{1}{4\cdot\pi\cdot\xi}\cdot\int_{0\cdot\text{pm}}^{100\cdot a_o}R_{1s}(r,Z)^2\cdot\sin(4\cdot\pi\cdot\xi\cdot r)\cdot r\,dr\qquad\text{where}\qquad \xi=\frac{sin(\theta)}{\lambda}$$

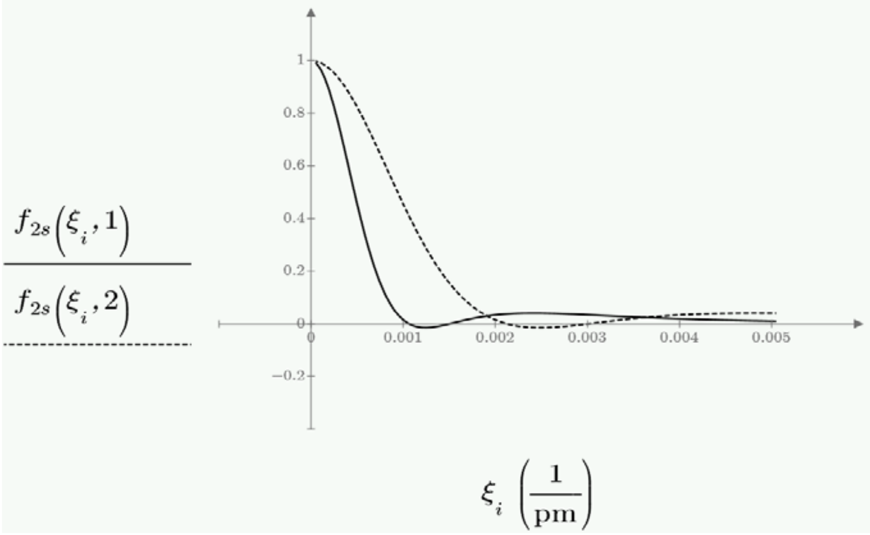
$$f_{2s}(\xi,Z):=\frac{1}{4\cdot\pi\cdot\xi}\cdot\int_{0}^{100\cdot a_o}R_{2s}(r,Z)^2\cdot\sin(4\cdot\pi\cdot\xi\cdot r)\cdot r\,dr$$

(a) Plot of scattering factor of a 1s hydrogen-like orbital against $\xi=\sin(\theta)/\lambda$ for Z = 1 and 2. Scattering in the forward direction corresponds to θ = 0 and ξ = 0. The plot shows us that the scattering factor is a maximum in the forward direction and it decreases as the reflection angle increases. The scattering factor decreases less rapidly for larger *Z* values.

$N := 200 \qquad \xi_{max} := 0.01 \cdot \text{pm}^{-1} \qquad i := 0..N \qquad \xi_i := \frac{i}{N} \cdot \xi_{max}$



(b) Plot of scattering factor of a 2s hydrogen-like orbital against $\xi = \sin(\theta)/\lambda$ for $Z = 1$ and 2. Scattering in the forward direction corresponds to $\theta = 0$ and $\xi = 0$. The plot shows us that the scattering factor is a maximum in the forward direction and it decreases as the reflection angle increases. The scattering factor decreases less rapidly for larger *Z* values. Also, the 2s scattering factor decreases far more rapidly with θ than that of the 1s scattering factor of part (a) so we say that 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.



19 Molecular motion

19A Transport properties of a perfect gas

Answers to discussion questions

19A.2 Simple molecular kinetic theory finds that the diffusion and viscosity coefficients are related to T, p, and the collision cross-section $\sigma = \pi d^2$ by the following expressions. It is important to recognize that these formulations are not applicable at either very low pressure where the mean free path becomes comparable to the container size or at very high densities where the mean free path becomes comparable to molecular size. Using L to represent container size, simple molecular kinetic theory approximately applies to the range $\sigma << \lambda << L$.

$$D = \tfrac{1}{3}\lambda v_{\text{mean}} \ [19\text{A}.10]$$

$$= \tfrac{1}{3}\left(\frac{v_{\text{rel}}}{z}\right)v_{\text{mean}} \ [1\text{B}.12] = \tfrac{1}{3}\left(\frac{v_{\text{rel}}}{\sigma v_{\text{rel}}\, p/kT}\right)v_{\text{mean}} \ [1\text{B}.11\text{b}]$$

$$= \left(\frac{kT}{3\sigma p}\right)\times\left(\frac{8RT}{\pi M}\right)^{1/2} \ [1\text{B}.8]$$

The diffusion coefficient is inversely proportional to p so an increase in pressure causes the gas molecules to diffuse more slowly. The coefficient is proportional to $T^{3/2}$ so increasing the temperature causes molecules to diffuse more rapidly. The inverse relation to σ means that large molecules diffuse more slowly. Finally, simple kinetic theory predicts that the diffusion coefficient is inversely proportional to $M^{1/2}$ which means that molecules of larger mass diffuse more slowly.

$$\eta = \frac{pMD}{RT} \ [19\text{A}.16\text{c}] = \left(\frac{pM}{RT}\right)\times\left(\frac{kT}{3\sigma p}\right)\times\left(\frac{8RT}{\pi M}\right)^{1/2}$$

$$= \left(\frac{k}{3\sigma}\right)\times\left(\frac{8MT}{\pi R}\right)^{1/2}$$

Thus, the viscosity coefficient decreases with increasing size but it increases with increasing temperature as it is proportional to $T^{1/2}$. The gas phase viscosity is independent of pressure. Finally, the viscosity coefficient is proportional to $M^{1/2}$ so molecules of larger mass have greater viscosity.

Solutions to exercises

19A.1(b) For a perfect dinitrogen gas: $\lambda = \dfrac{kT}{\sigma p} \ [1\text{B}.13] = \dfrac{RT}{\sigma N_{\text{A}} p} = \dfrac{1}{\sigma N_{\text{A}}[\text{N}_2]}$. Thus,

$$\kappa = \tfrac{1}{3}\lambda v_{\text{mean}} C_{V,\text{m}}[\text{N}_2] \ [19\text{A}.13\text{b}] = \tfrac{1}{3}\left(\frac{1}{\sigma N_{\text{A}}[\text{N}_2]}\right)v_{\text{mean}} C_{V,\text{m}}[\text{N}_2] = \tfrac{1}{3}\left(\frac{C_{V,\text{m}}}{\sigma N_{\text{A}}}\right)v_{\text{mean}}$$

$$= \tfrac{1}{3}\left(\frac{C_{V,\text{m}}}{\sigma N_{\text{A}}}\right)\times\left(\frac{8RT}{\pi M}\right)^{1/2} \ [1\text{B}.8]$$

$$= \tfrac{1}{3}\left(\frac{20.8\ \text{J K}^{-1}\ \text{mol}^{-1}}{\left(0.43\times10^{-18}\ \text{m}^2\right)\times\left(6.022\times10^{23}\ \text{mol}^{-1}\right)}\right)\times\left(\frac{8\times\left(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}\right)\times\left(298\ \text{K}\right)}{\pi\times\left(28.02\times10^{-3}\ \text{kg mol}^{-1}\right)}\right)^{1/2}$$

$$= \boxed{1.3\times10^{-2}\ \text{J K}^{-1}\ \text{m}^{-1}\ \text{s}^{-1}}$$

Comment. This calculated value does not agree well with the value of κ listed in Table 19A.1.

Question. Can the differences between the calculated and experimental values of κ be accounted for by the difference in temperature ($298\,\text{K}$ here, $273\,\text{K}$ in Table 19A.1)? If not, what might be responsible for the difference?

19A.2(b) $D = \tfrac{1}{3}\lambda v_{\text{mean}}$ [19A.10]

$$= \tfrac{1}{3}\left(\frac{v_{\text{rel}}}{z}\right)v_{\text{mean}}\ [\text{1B.12}] = \tfrac{1}{3}\left(\frac{v_{\text{rel}}}{\sigma v_{\text{rel}}\,p/kT}\right)v_{\text{mean}}\ [\text{1B.11b}]$$

$$= \tfrac{1}{3}\left(\frac{kT}{\sigma p}\right)\times\left(\frac{8RT}{\pi M}\right)^{1/2}\ [\text{1B.8}]$$

$$= \tfrac{1}{3}\left(\frac{(1.381\times10^{-23}\ \text{J K}^{-1})\times(293.15\ \text{K})}{(0.43\times10^{-18}\ \text{m}^2)\times\text{Pa}}\right)\times\left(\frac{8\times(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(293.15\ \text{K})}{\pi\times(28.02\times10^{-3}\ \text{kg mol}^{-1})}\right)^{1/2}\times\frac{1}{p/\text{Pa}}$$

$$= (1.4\overline{8}\ \text{m}^2\ \text{s}^{-1})\times\frac{1}{p/\text{Pa}}$$

$$\frac{J_z}{N_{\text{A}}} = -\frac{D}{N_{\text{A}}}\frac{\text{d}\mathcal{N}}{\text{d}z}\ [\text{19A.3}] = -\frac{D}{N_{\text{A}}}\frac{\text{d}}{\text{d}z}\left(\frac{N_{\text{A}}p}{RT}\right)$$

$$= -\left(\frac{D}{RT}\right)\frac{\text{d}p}{\text{d}z}$$

$$= -\left(\frac{1}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(293.15\ \text{K})}\right)\times\left(\frac{1.4\overline{8}\ \text{m}^2\ \text{s}^{-1}}{p/\text{Pa}}\right)\times(1.20\times10^{5}\ \text{Pa m}^{-1})$$

$$= -\frac{72.\overline{9}\ \text{mol m}^{-2}\ \text{s}^{-1}}{p/\text{Pa}}$$

(i) $p = 100.0$ Pa, $\boxed{D = 1.5\ \text{m}^2\ \text{s}^{-1},\ J_z/N_{\text{A}} = -0.73\ \text{mol m}^{-2}\ \text{s}^{-1}}$

(ii) $p = 100$ kPa, $\boxed{D = 1.5\times10^{-5}\ \text{m}^2\ \text{s}^{-1},\ J_z/N_{\text{A}} = -7.3\times10^{-6}\ \text{mol m}^{-2}\ \text{s}^{-1}}$

(iii) $p = 20.0$ MPa, $\boxed{D = 1.5\times10^{-7}\ \text{m}^2\ \text{s}^{-1},\ J_z/N_{\text{A}} = -3.6\times10^{-6}\ \text{mol m}^{-2}\ \text{s}^{-1}}$

19A.3(b) For a perfect dihydrogen gas: $C_{V,\text{m}} = C_{p,\text{m}} - R = 28.824\ \text{J K}^{-1}\ \text{mol}^{-1} - R = 20.510\ \text{J K}^{-1}\ \text{mol}^{-1}$

and $\lambda = \dfrac{kT}{\sigma p}\ [\text{1B.13}] = \dfrac{RT}{\sigma N_{\text{A}}p} = \dfrac{1}{\sigma N_{\text{A}}[\text{H}_2]}$. Thus,

$$\kappa = \tfrac{1}{3}\lambda v_{\text{mean}}C_{V,\text{m}}[\text{H}_2]\ [\text{19A.13B}] = \tfrac{1}{3}\left(\frac{1}{\sigma N_{\text{A}}[\text{H}_2]}\right)v_{\text{mean}}C_{V,\text{m}}[\text{H}_2] = \tfrac{1}{3}\left(\frac{C_{V,\text{m}}}{\sigma N_{\text{A}}}\right)v_{\text{mean}}$$

$$= \tfrac{1}{3}\left(\frac{C_{V,\text{m}}}{\sigma N_{\text{A}}}\right)\times\left(\frac{8RT}{\pi M}\right)^{1/2}\ [\text{1B.8}]$$

$$= \tfrac{1}{3}\left(\frac{20.510\ \text{J K}^{-1}\ \text{mol}^{-1}}{(0.27\times10^{-18}\ \text{m}^2)\times(6.022\times10^{23}\ \text{mol}^{-1})}\right)\times\left(\frac{8\times(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(290\ \text{K})}{\pi\times(2.016\times10^{-3}\ \text{kg mol}^{-1})}\right)^{1/2}$$

$$= 7.3\overline{4}\times10^{-2}\ \text{J K}^{-1}\ \text{m}^{-1}\ \text{s}^{-1}$$

$$J_z = -\kappa\frac{\text{d}T}{\text{d}z}\ [\text{19A.4}]$$

$$= -(7.3\overline{4}\times10^{-2}\ \text{J K}^{-1}\ \text{m}^{-1}\ \text{s}^{-1})\times(8.5\ \text{K m}^{-1})$$

$$= \boxed{-0.62\ \text{J m}^{-2}\ \text{s}^{-1}}$$

19A.4(b) For a perfect dinitrogen gas: $C_{V,\text{m}} = C_{p,\text{m}} - R = 29.125\ \text{J K}^{-1}\ \text{mol}^{-1} - R = 20.811\ \text{J K}^{-1}\ \text{mol}^{-1}$

$$\kappa = \tfrac{1}{3}\lambda v_{\text{mean}}C_{V,\text{m}}[\text{N}_2]\ [\text{19A.13b}] = \tfrac{1}{3}\left(\frac{1}{\sigma N_{\text{A}}[\text{N}_2]}\right)v_{\text{mean}}C_{V,\text{m}}[\text{N}_2] = \tfrac{1}{3}\left(\frac{C_{V,\text{m}}}{\sigma N_{\text{A}}}\right)v_{\text{mean}}$$

$$= \tfrac{1}{3}\left(\frac{C_{V,\text{m}}}{\sigma N_{\text{A}}}\right)\times\left(\frac{8RT}{\pi M}\right)^{1/2}\ [\text{1B.8}]$$

Note: $\kappa_{298\text{ K}} \simeq \left(\dfrac{298\text{ K}}{273\text{ K}}\right)^{1/2} \kappa_{273\text{ K}} = \left(\dfrac{298\text{ K}}{273\text{ K}}\right)^{1/2} \times\left(24.0\times10^{-3}\text{ J K}^{-1}\text{ m}^{-1}\text{ s}^{-1}\right) = 25.1\times10^{-3}\text{ J K}^{-1}\text{ m}^{-1}\text{ s}^{-1}$

Solve for σ.

$$\sigma = \tfrac{1}{3}\left(\frac{C_{V,\text{m}}}{\kappa N_\text{A}}\right)\times\left(\frac{8RT}{\pi M}\right)^{1/2}$$

$$= \tfrac{1}{3}\left(\frac{20.811\text{ J K}^{-1}\text{ mol}^{-1}}{\left(25.1\times10^{-3}\text{ J K}^{-1}\text{ m}^{-1}\text{ s}^{-1}\right)\times\left(6.022\times10^{23}\text{ mol}^{-1}\right)}\right)\times\left(\frac{8\times\left(8.3145\text{ J K}^{-1}\text{ mol}^{-1}\right)\times\left(298\text{ K}\right)}{\pi\times\left(28.02\times10^{-3}\text{ kg mol}^{-1}\right)}\right)^{1/2}$$

$$= 2.18\times10^{-19}\text{ m}^2 = \boxed{0.218\text{ nm}^2}$$

The value reported in Table 1B.1 is 0.43 nm^2. Question: What approximations inherent in the equation used in the solution to this exercise are likely to cause a factor of 2 difference?

19A.5(b) The thermal energy flux (“heat” flux) is described by: $J_\text{z}(\text{energy}) = -\kappa\dfrac{\text{d}T}{\text{d}z}$ $[19\text{A}.4]$ 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

$$\frac{\text{d}E}{\text{d}t} = AJ_z\left(\text{energy}\right) = -\kappa A\frac{\text{d}T}{\text{d}z}$$

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,

$$\frac{\text{d}T}{\text{d}z} = \frac{\Delta T}{\Delta z} = \frac{\left\{(0)-(70)\right\}\text{ K}}{5.0\times10^{-2}\text{ m}} = -1.4\times10^3\text{ K m}^{-1}$$

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 19A.1: $\kappa \approx 0.0240\text{ J K}^{-1}\text{ m}^{-1}\text{ s}^{-1}$. Therefore, the rate of energy transfer, the rate of heat loss, toward the low temperature is

$$\frac{\text{d}E}{\text{d}t} \approx -\left(0.0240\text{ J K}^{-1}\text{ m}^{-1}\text{ s}^{-1}\right)\times\left(2.00\text{ m}^2\right)\times\left(-1.4\times10^3\text{ K m}^{-1}\right)$$

$$\approx 62\text{ J s}^{-1}\quad\text{or}\quad\boxed{62\text{ W}}$$

19A.6(b) $\eta = \dfrac{pMD}{RT}\ [19\text{A}.16\text{c}] = \left(\dfrac{pM}{RT}\right)\times\left(\dfrac{kT}{3\sigma p}\right)\times\left(\dfrac{8RT}{\pi M}\right)^{1/2}$

$$= \left(\frac{k}{3\sigma}\right)\times\left(\frac{8MT}{\pi R}\right)^{1/2}$$

Solve for σ.

$$\sigma = \left(\frac{k}{3\eta}\right)\times\left(\frac{8MT}{\pi R}\right)^{1/2}$$

$$= \tfrac{1}{3}\left(\frac{1.381\times10^{-23}\text{ J K}^{-1}}{166\times10^{-6}\times10^{-1}\text{ kg m}^{-1}\text{ s}^{-1}}\right)\times\left(\frac{8\times\left(28.02\times10^{-3}\text{ kg mol}^{-1}\right)\times\left(273\text{ K}\right)}{\pi\times\left(8.3145\text{ J K}^{-1}\text{ mol}^{-1}\right)}\right)^{1/2}$$

$$= 4.24\times10^{-19}\text{ m}^2 = \boxed{0.424\text{ nm}^2}$$

19A.7(b) $\eta = \dfrac{pMD}{RT}\ [19\text{A}.16\text{c}] = \left(\dfrac{pM}{RT}\right)\times\left(\dfrac{kT}{3\sigma p}\right)\times\left(\dfrac{8RT}{\pi M}\right)^{1/2}\ [19\text{A}.10] = \left(\dfrac{k}{3\sigma}\right)\times\left(\dfrac{8MT}{\pi R}\right)^{1/2}$

$$= \tfrac{1}{3}\left(\frac{1.381\times10^{-23}\text{ J K}^{-1}}{0.88\times10^{-18}\text{ m}^2}\right)\times\left(\frac{8\times\left(78.12\times10^{-3}\text{ kg mol}^{-1}\right)\times T}{\pi\times\left(8.3145\text{ J K}^{-1}\text{ mol}^{-1}\right)}\right)^{1/2}$$

$$= (8.09\times10^{-7}\text{ kg m}^{-1}\text{ s}^{-1})\times(T/\text{K})^{1/2} = (8.09\times10^{-6}\text{ P})\times(T/\text{K})^{1/2}$$

(i) At 273 K, $\boxed{\eta = 134\ \mu\text{P}}$

(ii) At 298 K, $\boxed{\eta = 140\ \mu\text{P}}$

(iii) At 1000 K, $\boxed{\eta = 256\ \mu\text{P}}$

19A.8(b) $A = (3.5\text{ cm}) \times (4.0\text{ cm}) = 1.4 \times 10^{-5}\text{ m}^2$

The collision frequency of the He gas molecules with surface area A equals $Z_\text{W}A$.

$$Z_\text{W}A = \frac{paN_\text{A}}{(2\pi MRT)^{1/2}}\ \text{[19A.17]}$$

$$= \frac{(111\text{ Pa}) \times (6.022 \times 10^{23}\text{ mol}^{-1}) \times (1.4 \times 10^{-5}\text{ m}^2)}{\left\{2\pi(4.00 \times 10^{-3}\text{ kg mol}^{-1}) \times (8.3145\text{ J K}^{-1}\text{ mol}^{-1}) \times (1500\text{ K})\right\}^{1/2}}$$

$$= 5.2\overline{9} \times 10^{19}\text{ s}^{-1}$$

The number of helium molecule collisions within A in time interval t equals $Z_\text{W}At$ if p does not change significantly during the period t.

$$Z_\text{W}At = (5.2\overline{9} \times 10^{19}\text{ s}^{-1}) \times (10\text{ s}) = \boxed{5.3 \times 10^{20}}$$

19A.9(b) The mass loss equals the effusion mass loss multiplied by the time period t:

m_loss = (rate of effusion) × t × m = (rate of effusion) × t × M / N_A.

$$m_\text{loss} = \left(\frac{pA_0N_\text{A}}{(2\pi MRT)^{1/2}}\right) \times \left(\frac{Mt}{N_\text{A}}\right)\ \text{[19A.17]}$$

$$= pA_0t \times \left(\frac{M}{2\pi RT}\right)^{1/2}$$

$$= (0.224\text{ Pa}) \times \left\{\pi(1.50 \times 10^{-3}\text{ m})^2\right\} \times (24 \times 3600\text{ s}) \times \left(\frac{0.300\text{ kg mol}^{-1}}{2\pi(8.3145\text{ J mol}^{-1}\text{ K}^{-1}) \times (450\text{ K})}\right)^{1/2}$$

$$= \boxed{0.489\text{ g}}$$

19A.10(b) The mass loss equals the effusion mass loss multiplied by the time period t:

m_loss = (rate of effusion) × t × m = (rate of effusion) × t × M / N_A.

$$m_\text{loss} = \left(\frac{pA_0N_\text{A}}{(2\pi MRT)^{1/2}}\right) \times \left(\frac{Mt}{N_\text{A}}\right)\ \text{[19A.17]} = pA_0t \times \left(\frac{M}{2\pi RT}\right)^{1/2}$$

Solving for p gives

$$p = \frac{m_\text{loss}}{A_0t}\left(\frac{2\pi RT}{M}\right)^{1/2}$$

$$= \frac{277 \times 10^{-6}\text{ kg}}{\left\{\pi(0.25 \times 10^{-3}\text{ m})^2\right\} \times (500\text{ s})}\left(\frac{2\pi(8.3145\text{ J mol}^{-1}\text{ K}^{-1}) \times (573\text{ K})}{0.200\text{ kg mol}^{-1}}\right)^{1/2}$$

$$= \boxed{1.09 \times 10^3\text{ Pa}}$$

19A.11(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, $N = pVN_\text{A}/RT$ where V and T are constants, reveals that the rate of effusion can be written as $(-N_\text{A}V/RT)\mathrm{d}p/\mathrm{d}t$. This formulation of the rate of effusion, along with eqn 19A.17, is used to find $p(t)$.

$$-\left(\frac{N_\text{A}V}{RT}\right)\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{pA_0N_\text{A}}{(2\pi MRT)^{1/2}}\ \text{[19A.17]}$$

$$\frac{\mathrm{d}p}{\mathrm{d}t} = -\frac{pA_0}{V}\left(\frac{RT}{2\pi M}\right)^{1/2}$$

$$\frac{\mathrm{d}p}{p}=-\frac{\mathrm{d}t}{\tau} \quad \text{where} \quad \tau=\frac{V}{A_0}\left(\frac{2\pi M}{RT}\right)^{1/2}$$

$$\int_{p_0}^{p}\frac{\mathrm{d}p}{p}=-\frac{1}{\tau}\int_0^t \mathrm{d}t \quad \text{where } p_0 \text{ is the initial pressure}$$

$$\ln\frac{p}{p_0}=-\frac{t}{\tau} \quad \text{or} \quad p(t)=p_0\mathrm{e}^{-t/\tau}$$

The nitrogen and unknown fluorocarbon data can be used to determine the relaxation time, τ, for each.

$$\tau_{\text{unk}}=\frac{t_{\text{unk}}}{\ln(p_0/p)_{\text{unk}}}=\frac{82.3\text{ s}}{\ln(65.1/42.1)}=189\text{ s}$$

$$\tau_{\mathrm{N}_2}=\frac{t_{\mathrm{N}_2}}{\ln(p_0/p)_{\mathrm{N}_2}}=\frac{18.5\text{ s}}{\ln(65.1/42.1)}=42.4\text{ s}$$

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,

$$\left(\frac{M_{\text{unk}}}{M_{\mathrm{N}_2}}\right)^{1/2}=\frac{\tau_{\text{unk}}}{\tau_{\mathrm{N}_2}}$$

$$M_{\text{unk}}=\left(\frac{\tau_{\text{unk}}}{\tau_{\mathrm{N}_2}}\right)^2 M_{\mathrm{N}_2}$$

$$=\left(\frac{189}{42.4}\right)^2\times(28.02\text{ g mol}^{-1})=\boxed{557\text{ g mol}^{-1}}$$

19A.12(b) In Exercise 19A.11(b) it is shown that

$$\ln\frac{p}{p_0}=-\frac{t}{\tau} \quad \text{or} \quad p(t)=p_0\mathrm{e}^{-t/\tau} \quad \text{where} \quad \tau=\frac{V}{A_0}\left(\frac{2\pi M}{RT}\right)^{1/2}$$

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 eqn.

$$t=\tau\ln(p_0/p)=(27\overline{6}\text{ days})\times\ln(122/105)=\boxed{41.\overline{4}\text{ days}}$$

Solutions to problems

19A.1 $\kappa=\tfrac{1}{3}\lambda v_{\text{mean}}C_{V,\text{m}}[\mathrm{N}_2]$ [19A.13b] $=\tfrac{1}{3}\left(\frac{1}{\sigma N_{\mathrm{A}}[\mathrm{N}_2]}\right)v_{\text{mean}}C_{V,\text{m}}[\mathrm{N}_2]=\tfrac{1}{3}\left(\frac{C_{V,\text{m}}}{\sigma N_{\mathrm{A}}}\right)v_{\text{mean}}$

$$=\tfrac{1}{3}\left(\frac{C_{V,\text{m}}}{\sigma N_{\mathrm{A}}}\right)\times\left(\frac{8RT}{\pi M}\right)^{1/2} \quad [1\mathrm{B}.8]$$

Thus, $$\frac{\kappa_{300\text{ K}}}{\kappa_{10\text{ K}}}=\frac{(C_{V,\text{m}}T^{1/2})_{300\text{ K}}}{(C_{V,\text{m}}T^{1/2})_{10\text{ K}}}$$

The molar heat capacities at the two temperatures are estimated with the equipartition theorem. At 300 K the dihydrogen molecule has are three translational degrees of freedom and two rotational degrees of freedom, which gives $C_{V,\text{m}}\approx(3+2)\tfrac{1}{2}R=\tfrac{5}{2}R$. At 10 K the rotational degrees of freedom are not significantly populated so there are three translational degrees of freedom alone, which gives $C_{V,\text{m}}\approx\tfrac{3}{2}R$.

$$\frac{\kappa_{300\text{ K}}}{\kappa_{10\text{ K}}}=\frac{\tfrac{5}{2}R(300\text{ K})^{1/2}}{\tfrac{3}{2}R(10\text{ K})^{1/2}}=\boxed{9.13}$$

19A.2 The number of molecules that escape in unit time is the number per unit time that would have collided with a wall section of area A equal to the area of the small hole. That is,

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -Z_{\mathrm{W}}A = \frac{-Ap}{(2\pi mkT)^{1/2}} \quad [19\mathrm{A}.6]$$

where p is the (constant) vapor pressure of the solid. The change in the number of molecules inside the cell in an interval Δt is therefore $\Delta N = -Z_{\mathrm{W}}A\Delta t$, and so the mass loss is

$$\Delta w = \Delta N m = -Ap\left(\frac{m}{2\pi kT}\right)^{1/2}\Delta t = -Ap\left(\frac{M}{2\pi RT}\right)^{1/2}\Delta t$$

Therefore, the vapor pressure of the substance in the cell is

$$p = \left(\frac{-\Delta w}{A\Delta t}\right)\times\left(\frac{2\pi RT}{M}\right)^{1/2}$$

For the vapor pressure of germanium

$$p = \left(\frac{43\times10^{-9}\ \mathrm{kg}}{\pi\times\left(0.50\times10^{-3}\ \mathrm{m}\right)^{2}\times\left(7200\ \mathrm{s}\right)}\right)\times\left(\frac{2\pi\times\left(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}\right)\times\left(1273\ \mathrm{K}\right)}{72.64\times10^{-3}\ \mathrm{kg\ mol^{-1}}}\right)^{1/2}$$

$$= 7.3\times10^{-3}\ \mathrm{Pa} = \boxed{7.3\ \mathrm{mPa}}$$

19A.3 An effusion oven has constant volume, fixed temperature, and effusion hole of area A. Gas escapes through the hole, which makes the effusion rate negative.

$$-\frac{\mathrm{d}N}{\mathrm{d}t} = Z_{\mathrm{W}}A = \frac{pAN_{\mathrm{A}}}{\left(2\pi MRT\right)^{1/2}} \quad [19\mathrm{A}.6]$$

For a perfect gas, $pV = nRT = NRT/N_{\mathrm{A}}$ and, therefore, $N = N_{\mathrm{A}}pV/RT$. Differentiation gives $\dfrac{\mathrm{d}N}{\mathrm{d}t} = \dfrac{N_{\mathrm{A}}V}{RT}\dfrac{\mathrm{d}p}{\mathrm{d}t}$.

Substitution yields:

$$\frac{N_{\mathrm{A}}V}{RT}\frac{\mathrm{d}p}{\mathrm{d}t} = -\frac{pAN_{\mathrm{A}}}{\left(2\pi MRT\right)^{1/2}}$$

$$\frac{\mathrm{d}p}{\mathrm{d}t} = -\left(\frac{RT}{2\pi M}\right)^{1/2}\frac{A}{V}p = -\frac{p}{\tau} \qquad \text{where the time constant is } \tau = \left(\frac{2\pi M}{RT}\right)^{1/2}\frac{V}{A}$$

$$\frac{\mathrm{d}p}{p} = -\frac{\mathrm{d}t}{\tau}$$

$$\int_{p_0}^{p}\frac{\mathrm{d}p}{p} = -\frac{1}{\tau}\int_0^t \mathrm{d}t$$

$$\ln\left(\frac{p}{p_0}\right) = -\frac{t}{\tau} \qquad \text{or} \qquad \boxed{p = p_0\mathrm{e}^{-t/\tau} \text{ where } \tau = \left(\frac{2\pi M}{RT}\right)^{1/2}\frac{V}{A}}$$

When $t = t_{1/2}$, $p = \tfrac{1}{2}p_0$. Substitution into the above equation gives

$$\ln\left(\frac{p_0}{2p_0}\right) = -\frac{t_{1/2}}{\tau} \qquad \text{or} \qquad \boxed{t_{1/2} = \tau\ln(2) = \left(\frac{2\pi M}{RT}\right)^{1/2}\frac{V}{A}\ln(2)}$$

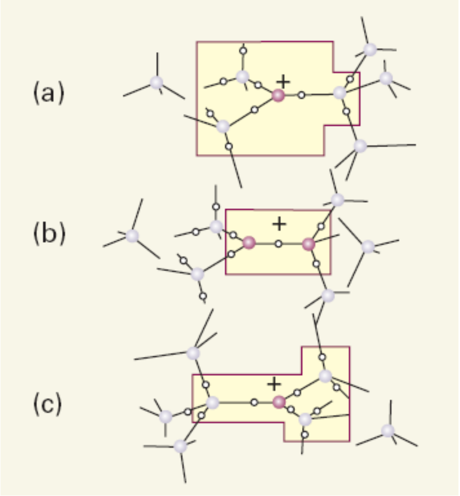
The final equation indicates that the half-life for effusive loss is independent of p_0. Furthermore, the half-life increases with both the V/A and $M^{1/2}$ factors. It decreases with the factor $T^{-1/2}$.

19B Motion in liquids

Answers to discussion questions

19B.2 According to the **Grotthuss mechanism**, there is an effective motion of a proton that involves the rearrangement of bonds in a group of water molecules. Attention now focuses on the $H_9O_4{}^+$ unit in which the nearly trigonal planar H_3O^+ ion is linked to three strongly solvating H_2O molecules. This cluster of atoms is itself hydrated, but the hydrogen bonds in the secondary sphere are weaker than in the primary sphere. It is envisaged that the rate-determining step is the cleavage of one of the weaker hydrogen bonds of this secondary sphere (Fig. 19B.1a). After this bond cleavage has taken place, and the released molecule has rotated through a few degrees (a process that takes about 1 ps), there is a rapid adjustment of bond lengths and angles in the remaining cluster, to form a $H_5O_2{}^+$ cation of structure $H_2O\cdots H^+\cdots OH_2$ (Fig. 19B.1b). Shortly after this reorganization has occurred, a new $H_9O_4{}^+$ cluster forms as other molecules rotate into a position where they can become members of a secondary hydration sphere, but now the positive charge is located one molecule to the right of its initial location (Fig. 19B.1c). According to this model, there is no coordinated motion of a proton along a chain of molecules, simply a very rapid hopping between neighbouring sites, with low activation energy. The model is consistent with the observation that the molar conductivity of protons increases as the pressure is raised, for increasing pressure ruptures the hydrogen bonds in water.

Figure 19B.1



Solutions to exercises

19B.1(b) We take the natural logarithm of eqn 19B.2 and solve for the activation energy, E_a.

$$\eta = \eta_0 e^{E_a/RT} \quad [19B.2]$$

$$\ln\eta = \ln\eta_0 + E_a/RT$$

$$\ln\eta_{T_1} - \ln\eta_{T_2} = \frac{E_a}{R}\times\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

Therefore,

$$E_a = \frac{R\ln\left(\eta_{T_1}/\eta_{T_2}\right)}{\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$$

$$= \frac{\left(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}\right)\times\ln\left(1.554/1.450\right)}{\left(\frac{1}{293\ \text{K}}-\frac{1}{313\ \text{K}}\right)} = \boxed{2.6\ \text{J mol}^{-1}}$$

19B.2(b) Molar ionic conductivity is related to mobility by

$$\lambda = zuF \quad [19\text{B}.13]$$

$$= 1\times\left(4.24\times10^{-8}\ \text{m}^2\ \text{s}^{-1}\ \text{V}^{-1}\right)\times\left(96485\ \text{C mol}^{-1}\right)$$

$$= \boxed{4.09\times10^{-3}\ \text{S m}^2\ \text{mol}^{-1}}$$

19B.3(b) $s = u\mathcal{E}$ [19B.11] and $\mathcal{E} = \dfrac{\Delta\phi}{l}$ [19B.7]

Therefore,

$$s = u\left(\frac{\Delta\phi}{l}\right)$$

$$= (4.01\times10^{-8}\ \text{m}^2\ \text{s}^{-1}\ \text{V}^{-1})\times\left(\frac{24.0\ \text{V}}{5.00\times10^{-3}\ \text{m}}\right)$$

$$= 1.92\times10^{-4}\ \text{m s}^{-1} \quad \text{or} \quad \boxed{192\ \mu\text{m s}^{-1}}$$

19B.4(b) The limiting molar conductivities of KF, KCH_3CO_2, and $Mg(CH_3CO_2)_2$ are 12.89 mS m^2 mol^{-1}, 11.44 mS m^2 mol^{-1} and 19B.78 mS m^2 mol^{-1}, respectively (all at 25 °C). What is the limiting molar conductivity of MgF_2 at this temperature?

The limiting molar conductivity of a dissolved salt is the sum of formula-weighted limiting molar conductivities of the formula ions, so

$$\Lambda_\text{m}^\text{o}\left(\text{MgF}_2\right) = \lambda\left(\text{Mg}^{2+}\right)+2\lambda\left(\text{F}^-\right) = \Lambda_\text{m}^\text{o}\left(\text{Mg}\left(\text{CH}_3\text{CO}\right)_2\right)+2\Lambda_\text{m}^\text{o}\left(\text{KF}\right)-2\Lambda_\text{m}^\text{o}\left(\text{K}\left(\text{CH}_3\text{CO}\right)_2\right)$$

$$= \left\{18.78+2\left(12.89\right)-2\left(11.44\right)\right\}\ \text{mS m}^2\ \text{mol}^{-1} = \boxed{21.68\ \text{mS m}^2\ \text{mol}^{-1}}$$

19B.5(b) $u = \dfrac{\lambda}{zF}$ [19B.13]; $z = 1$; $1\ \text{S} = 1\ \Omega^{-1} = 1\ \text{C V}^{-1}\ \text{s}^{-1}$

$$u(\text{F}^-) = \frac{5.54\ \text{mS m}^2\ \text{mol}^{-1}}{9.6485\times10^4\ \text{C mol}^{-1}} = 5.74\times10^{-5}\ \text{mS C}^{-1}\ \text{m}^2 = \boxed{5.74\times10^{-8}\ \text{m}^2\ \text{V}^{-1}\ \text{s}^{-1}}$$

$$u(\text{Cl}^-) = \frac{7.635\ \text{mS m}^2\ \text{mol}^{-1}}{9.6485\times10^4\ \text{C mol}^{-1}} = \boxed{7.913\times10^{-8}\ \text{m}^2\ \text{V}^{-1}\ \text{s}^{-1}}$$

$$u(\text{Br}^-) = \frac{7.81\ \text{mS m}^2\ \text{mol}^{-1}}{9.6485\times10^4\ \text{C mol}^{-1}} = \boxed{8.09\times10^{-8}\ \text{m}^2\ \text{V}^{-1}\ \text{s}^{-1}}$$

19B.6(b) $a = \dfrac{kT}{6\pi\eta D}$ [19B.19b]; $1\ \text{P} = 10^{-1}\ \text{kg m}^{-1}\ \text{s}^{-1}$

$$a = \frac{\left(1.381\times10^{-23}\ \text{J K}^{-1}\right)\times\left(298\ \text{K}\right)}{6\pi\times\left(1.00\times10^{-3}\ \text{kg m}^{-1}\ \text{s}^{-1}\right)\times\left(1.055\times10^{-9}\ \text{m}^2\ \text{s}^{-1}\right)} = 2.07\times10^{-10}\ \text{m} \quad \text{or} \quad \boxed{207\ \text{pm}}$$

19B.7(b) $D = \dfrac{uRT}{zF}$ [19B.16]; $z = 1$; $1\ \text{C V} = 1\ \text{J}$

$$D = \frac{\left(4.24\times10^{-8}\ \text{m}^2\ \text{V}^{-1}\ \text{s}^{-1}\right)\times\left(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}\right)\times\left(298\ \text{K}\right)}{1\times9.6485\times10^4\ \text{C mol}^{-1}} = \boxed{1.09\times10^{-9}\ \text{m}^2\ \text{s}^{-1}}$$

19B.4 $\eta \propto e^{E_a/RT}$ [19B.2]

$$\ln\eta = \text{constant} + E_a / RT,$$

Substitute the base 10 logarithm relationship ln(z) = log(z)×ln(10), thereby giving

$$\log\eta = \text{constant} + E_a / \ln(10)RT$$

The constant is evaluated with the viscosity at T_{20} = 293.15 K, thereby providing the relationship

$$\log(\eta/\eta_{20}) = \left(\frac{E_a}{\ln(10)R}\right)\times\left(\frac{1}{T}-\frac{1}{T_{20}}\right)$$

Inspection of the equation reveals that a plot of $\log(\eta/\eta_{20})$ against 1/T has a slope equal to E_a/ln(10)R. Thus, we prepare the requisite plot using the empirical relationship provided in the problem to compute $\log(\eta/\eta_{20})$ values in the range 20–100° C, and perform a linear regression fit of $\log(\eta/\eta_{20})$ against 1/T, shown in Fig. 19B.2. This yields the slope from which we calculate E_a with the expression E_a = slope×ln(10)R.

$$E_a = (774\ \text{K})\times\ln(10)\times(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) = \boxed{14.8\ \text{kJ mol}^{-1}}$$

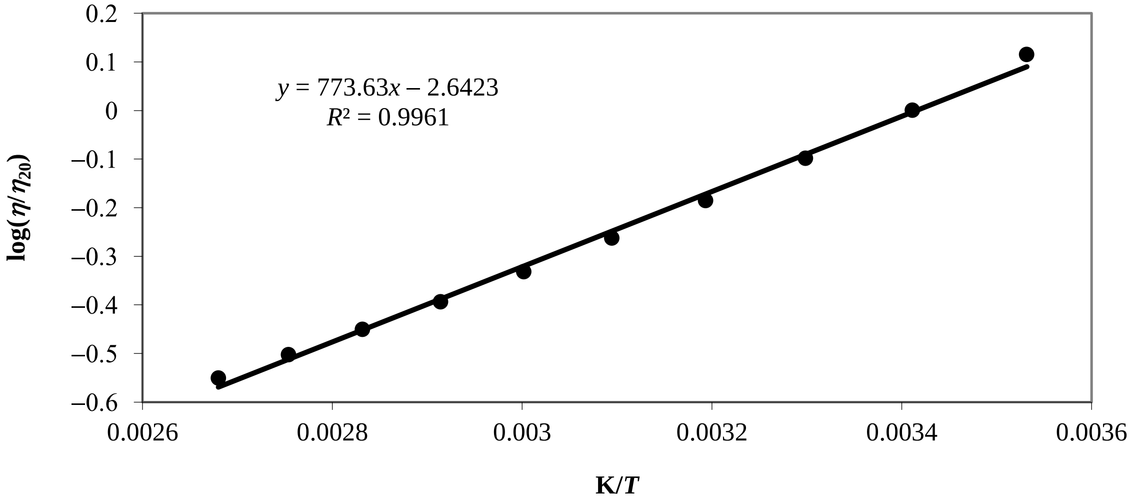


Figure 19B.2

19B.5 Conductivity is inversely proportional to resistance: $\kappa \propto \dfrac{1}{R}$ [19B.3]

Because both solutions are aqueous, their conductivities include a contribution of $76\ \text{mS m}^{-1}$ from the water. Therefore,

$$\frac{\kappa(\text{acid soln})}{\kappa(\text{KCl soln})} = \frac{\kappa(\text{acid})+\kappa(\text{water})}{\kappa(\text{KCl})+\kappa(\text{water})} = \frac{R(\text{KCl soln})}{R(\text{acid soln})} = \frac{33.21\ \Omega}{300.0\ \Omega}$$

Hence,

$$\kappa(\text{acid}) = \{\kappa(\text{KCl})+\kappa(\text{water})\}\times\left(\frac{33.21}{300.0}\right) - \kappa(\text{water})$$

$$= \left[\{1163.9+76\}\times\left(\frac{33.21}{300.0}\right)-76\right]\ \text{mS m}^{-1} = 61\ \text{mS m}^{-1}$$

$$\Lambda_m = \frac{\kappa}{c}\ [19B.4]$$

$$= \frac{61\ \text{mS m}^{-1}}{0.100\ \text{mol dm}^{-3}} = 61\times10^{1-3-3}\ \text{S m}^2\ \text{mol}^{-1} = 61\times10^{1-3-3+4}\ \text{S cm}^2\ \text{mol}$$

$$= \boxed{6.1\ \text{S cm}^2\ \text{mol}^{-1}}$$

19B.6 $s = u\mathcal{E}$ [19B.11] with $\mathcal{E} = \dfrac{\Delta\varphi}{l}$ [19B.7] $= \dfrac{100\ \text{V}}{5.00\ \text{cm}} = 20.0\ \text{V cm}^{-1}$

Table 19B.2 provides the ion mobilities, u.

$$s(\text{Li}^+) = (4.01\times10^{-4}\ \text{cm}^2\ \text{s}^{-1}\ \text{V}^{-1})\times(20.0\ \text{V cm}^{-1}) = \boxed{80.2\ \mu\text{m s}^{-1}}$$

$$s(\text{Na}^+) = (5.19\times10^{-4}\ \text{cm}^2\ \text{s}^{-1}\ \text{V}^{-1})\times(20.0\ \text{V cm}^{-1}) = \boxed{104\ \mu\text{m s}^{-1}}$$

$$s(\text{K}^+) = (7.62\times10^{-4}\ \text{cm}^2\ \text{s}^{-1}\ \text{V}^{-1})\times(20.0\ \text{V cm}^{-1}) = \boxed{152\ \mu\text{m s}^{-1}}$$

$$t(\text{Li}^+) = \frac{5.0\ \text{cm}}{80.2\ \mu\text{m s}^{-1}} = \boxed{623\ \text{s}}, \qquad t(\text{Na}^+) = \boxed{481\ \text{s}}, \qquad t(\text{K}^+) = \boxed{329\ \text{s}}$$

(a) For the distance moved during a half-cycle, write

$$d = \int_0^{1/2\nu} s\,\text{d}t = \int_0^{1/2\nu} u\mathcal{E}\,\text{d}t = u\mathcal{E}_0\int_0^{1/2\nu}\sin(2\pi\nu t)\,\text{d}t \quad [\mathcal{E} = \mathcal{E}_0\sin(2\pi\nu t)]$$

$$= \frac{u\mathcal{E}_0}{\pi\nu} = \frac{u\times(20.0\,\text{V cm}^{-1})}{\pi\times(2.0\times10^3\ \text{s}^{-1})}\ [\text{assume } \mathcal{E}_0 = 20\,\text{V}] = 3.18\times10^{-3}\ u\ \text{V s cm}^{-1}$$

That is, $d/\text{cm} = (3.18\times10^{-3})\times(u/\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1})$

$$d(\text{Li}^+) = (3.18\times10^{-3})\times(4.01\times10^{-4}\ \text{cm}) = \boxed{12.8\ \text{nm}}$$

$$d(\text{Na}^+) = \boxed{16.5\ \text{nm}}$$

$$d(\text{K}^+) = \boxed{24.2\ \text{nm}}$$

(b) These correspond to about $\boxed{43}$, $\boxed{55}$, and $\boxed{81}$ solvent molecule diameters, respectively.

19B.7 $D = \dfrac{uRT}{zF}$ [19B.16] and $a = \dfrac{ze}{6\pi\eta u}$ [19B.12]

$$D = \frac{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(298.15\ \text{K})\times u}{96485\ \text{C mol}^{-1}} = 2.569\times10^{-2}\ \text{V}\times u$$

So, $D/(\text{cm}^2\ \text{s}^{-1}) = (2.569\times10^{-2})\times u/(\text{cm}^2\ \text{s}^{-1}\ \text{V}^{-1})$

$$a = \frac{1.602\times10^{-19}\ \text{C}}{(6\pi)\times(0.891\times10^{-3}\ \text{kg m}^{-1}\ \text{s}^{-1})\times u}$$

$$= \frac{9.54\times10^{-18}\ \text{C kg}^{-1}\ \text{m s}}{u} = \quad (1\ \text{J} = 1\ \text{C V},\ 1\ \text{J} = 1\ \text{kg m}^2\ \text{s}^{-2})$$

$$a/\text{m} = \frac{9.54\times10^{-14}}{u/\text{cm}^2\ \text{s}^{-1}\ \text{V}^{-1}}$$

Therefore, $a/\text{pm} = \dfrac{9.54\times10^{-2}}{u/\text{cm}^2\ \text{s}^{-1}\ \text{V}^{-1}}$

We can now draw up the following table using data from Table 19B.2.

	Li^+	Na^+	K^+	Rb^+
$u/(10^{-4}\ \text{cm}^2\ \text{s}^{-1}\ \text{V}^{-1})$	4.01	5.19	7.62	7.92
$D/10^{-5}\ \text{cm}^2\ \text{s}^{-1}$	1.03	1.33	1.96	2.04
a/pm	238	184	125	120

The ionic radii themselves (i.e. their crystallographic radii) are

	Li^+	Na^+	K^+	Rb^+
r_+/pm	59	102	138	149

and it would seem that K^+ and Rb^+ have effective hydrodynamic radii that are smaller than their ionic radii. The effective hydrodynamic and ionic volumes of Li^+ and Na^+ are $\tfrac{4}{3}\pi a^3$ and $\tfrac{4}{3}\pi r_+^3$, respectively, and so the volumes occupied by hydrating water molecules are

(a) Li^+: $\Delta V = \tfrac{4}{3}\pi \times (238^3 - 59^3) \times 10^{-36}\ \text{m}^3 = 5.5\overline{6} \times 10^{-29}\ \text{m}^3$

(b) Na^+: $\Delta V = \tfrac{4}{3}\pi \times (184^3 - 102^3) \times 10^{-36}\ \text{m}^3 = 2.1\overline{6} \times 10^{-29}\ \text{m}^3$

The volume occupied by a single H_2O molecule is approximately $\tfrac{4}{3}\pi \times (150\,\text{pm})^3 = 1.4 \times 10^{-29}\ \text{m}^3$

Therefore, Li^+ has about $\boxed{\text{four}}$ firmly attached H_2O molecules whereas Na^+ has only $\boxed{\text{one to two}}$ (according to this analysis).

19B.8‡ $AB \rightleftharpoons A^+ + B^-$

$$K = K_\gamma K_c = K_\gamma \frac{(\alpha c)^2}{(1-\alpha)c} = K_\gamma \frac{\alpha^2 c}{1-\alpha} \quad \text{where } \alpha \text{ is the degree of ionization}$$

Thus, $\dfrac{K_\gamma c}{K} = \dfrac{1-\alpha}{\alpha^2}$

Now the molar conductivity is related to the degree of ionization by

$$\Lambda_\text{m} = (u_+ + u_-)F\alpha = \Lambda_{\text{m},\alpha=1}\alpha \quad \text{so that} \quad \alpha = \Lambda_\text{m} / \Lambda_{\text{m},\alpha=1}$$

Substitution into the equilibrium expression gives

$$K = K_\gamma c \left(\frac{\Lambda_\text{m}}{\Lambda_{\text{m},\alpha=1}}\right)^2 \left(\frac{1}{1-\dfrac{\Lambda_\text{m}}{\Lambda_{\text{m},\alpha=1}}}\right)$$

$$1 - \frac{\Lambda_\text{m}}{\Lambda_{\text{m},\alpha=1}} = \left(\frac{\Lambda_\text{m}}{\Lambda_{\text{m},\alpha=1}}\right)^2 \times \frac{K_\gamma c}{K} = \left(\frac{\Lambda_\text{m}}{\Lambda_{\text{m},\alpha=1}}\right)^2 \left(\frac{1-\alpha}{\alpha^2}\right)$$

and division by Λ_m gives the desired result.

$$\boxed{\frac{1}{\Lambda_\text{m}} = \frac{1}{\Lambda_{\text{m},\alpha=1}} + \frac{(1-\alpha)\Lambda_\text{m}}{\left(\alpha \Lambda_{\text{m},\alpha=1}\right)^2}}$$

We must also examine the meaning of $\Lambda_{\text{m},\alpha=1}$.

$$\Lambda_{\text{m},\alpha=1} = (u_+ + u_-)F = \frac{\kappa}{c_\text{ions}}\ [19\text{B}.4] = \frac{\kappa}{\alpha c} \quad \text{where } c_\text{ions} \text{ is the actual ion concentration}$$

Examination of the above relation tells us that $\Lambda_{\text{m},\alpha=1}$ is the molar conductivity of a solution for which ionization is complete but the preparation (analytical) concentration is αc. Consequently, by Kohlrausch's law (eqn 19B.5) we conclude that

$$\boxed{\Lambda_{\text{m},\alpha=1} = \Lambda_\text{m}^\text{o} - \mathcal{K}(\alpha c)^{1/2}}$$

19C Diffusion

Answers to discussion questions

19C.2 The **diffusion equation**, also called "Fick's second law of diffusion", relates the rate of change of concentration to the spatial variation of the concentration at that point:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}\ [19\text{C}.7]$$

Physically, the diffusion equation accounts for the observation that, when the curvature of the concentration gradient (i.e., $\dfrac{\partial}{\partial x}\left(\dfrac{\partial c}{\partial x}\right) = \dfrac{\partial}{\partial x}\nabla_x c$) is positive within a small, macroscopic volume, mass moves spontaneously into the volume so as to increase *c* at a rate governed by the diffusion coefficient. If the curvature is negative within a small, macroscopic volume, mass moves spontaneously out of the volume so as to decrease *c*. If the curvature is zero, there is a steady-state distribution such that *c* within the small volume does not change in time; the net inflow of mass is balanced by the net outflow.

Solutions to exercises

19C.1(b) Equation [19C.14], $\langle x^2 \rangle = 2Dt$, gives the mean square distance traveled in any one dimension in time *t*. We need the distance traveled 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.

$$r^2 = x^2 + y^2 + z^2 \text{ [Pythagorean theorem]},$$

$$\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle = 3\langle x^2 \rangle \text{ [independent motion]}$$

$$= 3 \times 2Dt \text{ [19C.14 for } \langle x^2 \rangle\text{]}$$

$$= 6Dt$$

Therefore, $t = \dfrac{\langle r^2 \rangle}{6D} = \dfrac{(0.010\text{ m})^2}{(6)\times(2.26\times10^{-9}\text{ m}^2\text{ s}^{-1})} = \boxed{7.4\times10^3\text{ s}}$

19C.2(b) The diffusion equation solution for these boundary conditions is provided in eqn 19C.11 with

$$n_0 = (10.0\text{ g})\times\left(\frac{1\text{ mol I}_2}{253.80\text{ g}}\right) = 3.94\times10^{-2}\text{ mol I}_2,$$

A = 10.0 cm^2, D = 4.05 × 10^{-9} m^2 s^{-1}, and x = 5 cm.

$$c(x,t) = \frac{n_0}{A(\pi Dt)^{1/2}}\mathrm{e}^{-x^2/4Dt} \text{ [19C.11]}$$

$$c(10\text{ cm},t) = \frac{3.94\times10^{-2}\text{ mol}}{\left(10.0\times10^{-4}\text{ m}^2\right)\times\left\{\pi\left(4.05\times10^{-9}\text{ m}^2\text{ s}^{-1}\right)\right\}^{1/2} t^{1/2}}\mathrm{e}^{-(0.050\text{ m})^2/4\times\left(4.05\times10^{-9}\text{ m}^2\text{ s}^{-1}\right)\times t}$$

$$= \left(3.49\times10^5\text{ mol m}^{-3}\right)\times(t/\text{s})^{-1/2}\,\mathrm{e}^{-\left(1.54\times10^5\right)/(t/\text{s})}$$

(i) t = 10 s:

$$c(5\text{ cm},10\text{ s}) = \left(3.49\times10^5\text{ mol m}^{-3}\right)\times(10)^{-1/2}\,\mathrm{e}^{-\left(1.54\times10^5\right)/(10)} = \boxed{0.00\text{ mol dm}^{-3}}$$

(ii) t = 24 × 3600 s = 8.64 × 10^4 s:

$$c\left(5\text{ cm},8.64\times10^4\text{ s}\right) = \left(3.49\times10^5\text{ mol m}^{-3}\right)\times\left(8.64\times10^4\right)^{-1/2}\mathrm{e}^{-\left(1.54\times10^5\right)/\left(8.64\times10^4\right)}$$

$$= 200.\text{ mol m}^{-3} = \boxed{0.0200\text{ mol dm}^{-3}}$$

19C.3(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 cm) = ½c_0.

$$A = \frac{c_0 - c(x)}{x^2} = \frac{c_0 - \tfrac{1}{2}c_0}{(8\text{ cm})^2} = \left(7.81\times10^{-3}\text{ cm}^{-2}\right)\times c_0 = \left(78.1\text{ m}^{-2}\right)\times c_0$$

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 19C.2b.

$$\mathcal{F}(x) = -\frac{RT}{c}\frac{\mathrm{d}c}{\mathrm{d}x} \text{ [19C.2b]} = -\frac{RT}{c}\frac{\mathrm{d}}{\mathrm{d}x}\left(c_0 - Ax^2\right) = \frac{2ARTx}{c}$$

$$= \frac{2\times\left(78.1\text{ m}^{-2}\right)\times\left(8.3145\text{ J K}^{-1}\text{ mol}^{-1}\right)\times(298\text{ K})\times x}{1-\left(7.81\times10^{-3}\text{ cm}^{-2}\right)\times x^2}$$

$$= \frac{\left(3.87\text{ kN mol}^{-1}\right)\times(x/\text{cm})}{1-\left(7.81\times10^{-3}\right)\times(x/\text{cm})^2}$$

$$\mathcal{F}(8\ \text{cm}) = \frac{(3.87\ \text{kN mol}^{-1})\times 8}{1-(7.81\times10^{-3})\times(8)^2} = \boxed{+61.9\ \text{kN mol}^{-1}}$$

$$\mathcal{F}(11\ \text{cm}) = \frac{(3.87\ \text{kN mol}^{-1})\times 11}{1-(7.81\times10^{-3})\times(11)^2} = \boxed{+774\ \text{kN mol}^{-1}}$$

The positive force indicates that the force points toward larger values of $|x|$ values.

19C.4(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 $c(10\ \text{cm}) = \tfrac{1}{2}c_0$.

$$A = \frac{\ln(c_0/c)}{x^2} = \frac{\ln 2}{(10\ \text{cm})^2} = (0.010\ \text{cm}^{-2})\times\ln 2 = (1.00\ \text{cm}^{-1}\ \text{m}^{-1})\times\ln 2$$

The thermodynamic force is determined with eqn 19C.2b.

$$\mathcal{F}(x) = -\frac{RT}{c}\frac{\mathrm{d}c}{\mathrm{d}x}\ [19\text{C}.2\text{b}] = -\frac{RT}{c}\frac{\mathrm{d}}{\mathrm{d}x}c_0\mathrm{e}^{-Ax^2} = 2ARTx$$

$$= 2\times(1.00\ \text{m}^{-1})\times\ln 2\times(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(291\ \text{K})\times(x/\text{cm})$$

$$= (3.35\ \text{kN mol}^{-1})\times(x/\text{cm})$$

$$\mathcal{F}(10\ \text{cm}) = (3.35\ \text{kN mol}^{-1})\times(10) = \boxed{33.5\ \text{kN mol}^{-1}}$$

19C.5(b) Equation [19C.14], $\langle x^2\rangle = 2Dt$, 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],

$$\langle r^2\rangle = \langle x^2\rangle + \langle y^2\rangle + \langle z^2\rangle = 3\langle x^2\rangle\ [\text{independent motion}]$$

$$= 3\times 2Dt\ [19\text{C}.14] = 6Dt\ .$$

Therefore, $t = \dfrac{\langle r^2\rangle}{6D} = \dfrac{(1.0\times10^{-2}\ \text{m})^2}{6\times(4.05\times10^{-9}\ \text{m}^2\ \text{s}^{-1})} = \boxed{4.1\times10^3\ \text{s}}$

19C.6(b) $a = \dfrac{kT}{6\pi\eta D}$ [19B.19b]; $1\ \text{P} = 10^{-1}\ \text{kg m}^{-1}\ \text{s}^{-1}$

$$a = \frac{(1.381\times10^{-23}\ \text{J K}^{-1})\times(298\ \text{K})}{6\pi\times(1.00\times10^{-3}\ \text{kg m}^{-1}\ \text{s}^{-1})\times(1.055\times10^{-9}\ \text{m}^2\ \text{s}^{-1})} = 2.07\times10^{-10}\ \text{m} = \boxed{207\ \text{pm}}$$

19C.7(b) The Einstein–Smoluchowski equation [19C.16] relates the diffusion constant to the jump distance λ and time τ required for a jump.

$$D = \frac{\lambda^2}{2\tau}\ [19\text{C}.16]\ \text{ so }\ \tau = \frac{\lambda^2}{2D}$$

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].

$$\lambda = 2a = 2\left(\frac{kT}{6\pi\eta D}\right)\ [19\text{B}.19\text{b}] = \frac{kT}{3\pi\eta D}$$

$$\tau = \frac{1}{2D}\times\left(\frac{kT}{3\pi\eta D}\right)^2\ [\eta_{\text{heptane}} = 0.386\times10^{-3}\ \text{kg m}^{-1}\ \text{s}^{-1}, \text{CRC } \textit{Handbook Chemistry and Physics}]$$

$$= \frac{1}{2\times(3.17\times10^{-9}\ \text{m}^2\ \text{s}^{-1})}\times\left\{\frac{(1.381\times10^{-23}\ \text{J K}^{-1})\times(298\ \text{K})}{3\pi\times(0.386\times10^{-3}\ \text{kg m}^{-1}\ \text{s}^{-1})\times(3.17\times10^{-9}\ \text{m}^2\ \text{s}^{-1})}\right\}^2$$

$$= 2.01\times10^{-11}\ \text{s} = \boxed{20.1\ \text{ps}}$$

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 19C.16 is $\tau = \lambda^2/6D$.
Question. Can you derive the equation? Use an analysis similar to that described in the solution to Exercise 19C.5(a and b).

19C.8(b) For three dimensional diffusion we use an equation analogous to eqn 19C.16 derived in Exercise 19C.5(a and b).

$$t = \frac{\langle r^2 \rangle}{6D}$$

(i) $\langle r^2 \rangle = (1.0\times10^{-3}\ \text{m})^2 = 1.0\times10^{-6}\ \text{m}^2$

For iodine in benzene [Data from Table 19B.3]: $t = \dfrac{1.0\times10^{-6}\ \text{m}^2}{6\times(2.13\times10^{-9}\ \text{m}^2\ \text{s}^{-1})} = \boxed{78\ \text{s}}$

For sucrose in water: $t = \dfrac{1.0\times10^{-6}\ \text{m}^2}{6\times(0.522\times10^{-9}\ \text{m}^2\ \text{s}^{-1})} = \boxed{31\bar{9}\ \text{s}}$

(ii) $\langle r^2 \rangle = (1.0\times10^{-2}\ \text{m})^2 = 1.0\times10^{-4}\ \text{m}^2$

For iodine in benzene [Data from Table 19B.3]: $t = \dfrac{1.0\times10^{-4}\ \text{m}^2}{6\times(2.13\times10^{-9}\ \text{m}^2\ \text{s}^{-1})} = 7.8\times10^{3}\ \text{s} = \boxed{2.2\ \text{h}}$

For sucrose in water: $t = \dfrac{1.0\times10^{-4}\ \text{m}^2}{6\times(0.522\times10^{-9}\ \text{m}^2\ \text{s}^{-1})} = 3.2\times10^{4}\ \text{s} = \boxed{8.9\ \text{h}}$

Solutions to problems

19C.9 $\mathcal{F} = -\dfrac{RT}{c}\times\dfrac{\mathrm{d}c}{\mathrm{d}x}$ [19C.2b] with the axis origin at the center of the tube

$RT = 2.48\times10^{3}\ \text{J mol}^{-1} = 2.48\times10^{3}\ \text{N m mol}^{-1}$

$c = c(x) = c_0 \mathrm{e}^{-ax^2}$ where $c_0 = 0.100\ \text{mol dm}^{-3}$ and $a = 0.10\ \text{cm}^{-2}$

$$\frac{\mathrm{d}c}{\mathrm{d}x} = -2axc_0\mathrm{e}^{-ax^2} = -2axc$$

Thus, the thermodynamic force per mole is given by the expression

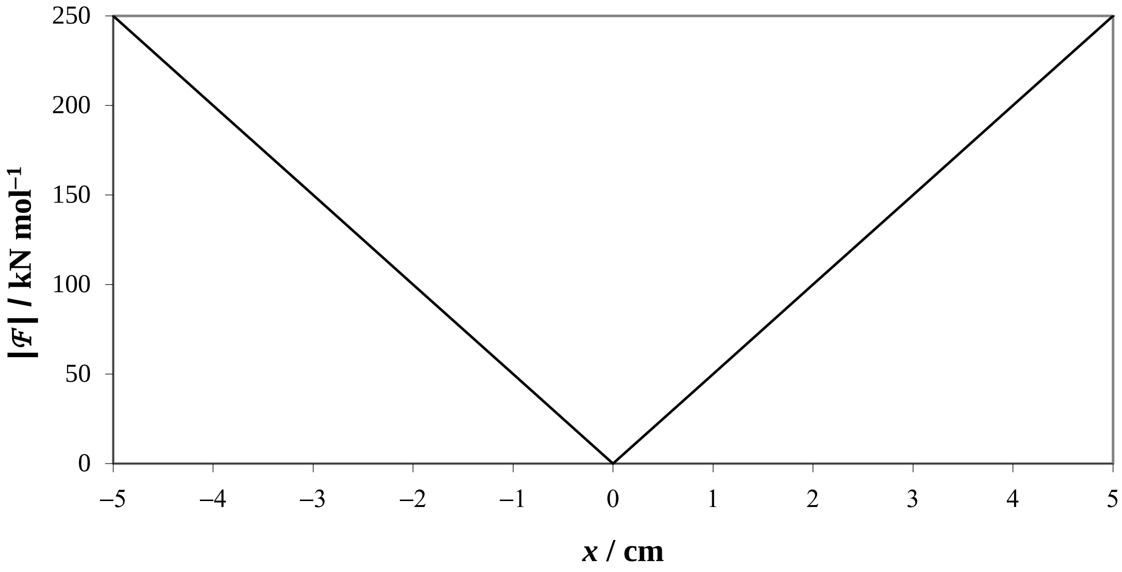
$$\mathcal{F} = 2aRTx = \boxed{(50.\ \text{kN cm}^{-1}\ \text{mol}^{-1})x}$$

while the force per molecule is given by

$$\mathcal{F} = 2aRTx/N_\text{A} = \boxed{(8.2\times10^{-23}\ \text{kN cm}^{-1}\ \text{molecule}^{-1})x}$$

A plot of the absolute force per mole against x is shown in Fig. 19C.1. It demonstrates that mass is pushed by the thermodynamic force toward the ends of the tube where the concentration is lowest; a negative force pushes toward the left (i.e., $x < 0$), positive force pushes toward the right (i.e., $x > 0$).

Figure 19C.1



19C.10 $c(r,t)=\dfrac{n_0}{8(\pi Dt)^{3/2}}\mathrm{e}^{-r^2/4Dt}$ [19C.12] where $n_0=(10.0\text{ g})\times(1\text{ mol}/342.3\text{ g})=0.0292\text{ mol}$

Using $D = 5.22\times10^{-6}\text{ cm}^2\text{ s}^{-1} = 5.22\times10^{-8}\text{ dm}^2\text{ s}^{-1}$ and $r = 10$ cm, the working equation becomes

$$c(10\text{ cm},t)=\frac{5.50\times10^{7}\text{ mol dm}^{-3}}{(t/\text{s})^{3/2}}\mathrm{e}^{-4.79\times10^6/(t/\text{s})}$$

(a) 1 hr = 3600 s

$$c(10\text{ cm},1\text{ hr})=\frac{5.50\times10^{7}\text{ mol dm}^{-3}}{(3600)^{3/2}}\mathrm{e}^{-4.79\times10^6/(3600)}=\boxed{0.00\text{ mol dm}^{-3}}$$

(b) 1 wk = 6.048×10^5 s

$$c(10\text{ cm},1\text{ wk})=\frac{5.50\times10^{7}\text{ mol dm}^{-3}}{(6.048\times10^5)^{3/2}}\mathrm{e}^{-4.79\times10^6/(6.048\times10^5)}=\boxed{4.25\times10^{-5}\text{ mol dm}^{-3}}$$

19C.11 The generalized diffusion equation is: $\dfrac{\partial c}{\partial t}=D\dfrac{\partial^2 c}{\partial x^2}-v\dfrac{\partial c}{\partial x}$ $[19\text{C}.10]$.

We confirm that $c(x,t)=\dfrac{a}{t^{1/2}}\mathrm{e}^{-b(x-x_0-vt)^2/t}$, where $a=\dfrac{c_0}{(4\pi D)^{1/2}}$ and $b=\dfrac{1}{4D}$, is a solution to the generalized diffusion equation by taking the partial derivative w/r/t time and both the first and second partials w/r/t position to find whether they are related by eqn 19C.10.

$$\frac{\partial c}{\partial t}=-\left(\frac{1}{2}\right)\times\left(\frac{a}{t^{3/2}}\right)\mathrm{e}^{-b(x-x_0-vt)^2/t}+\left(\frac{a}{t^{1/2}}\right)\times\left\{\frac{b(x-x_0-vt)}{t}\right\}\times\left\{2v+\frac{(x-x_0-vt)}{t}\right\}\mathrm{e}^{-b(x-x_0-vt)^2/t}$$

$$=-\frac{c}{2t}+\left\{\frac{b(x-x_0-vt)}{t}\right\}\times\left\{2v+\frac{(x-x_0-vt)}{t}\right\}\times c$$

$$\frac{\partial c}{\partial x}=\left(\frac{a}{t^{1/2}}\right)\times\left\{\frac{-2b(x-x_0-vt)}{t}\right\}\mathrm{e}^{-b(x-x_0-vt)^2/t}=\left\{\frac{-2b(x-x_0-vt)}{t}\right\}\times c$$

$$\frac{\partial^2 c}{\partial x^2}=\frac{\partial}{\partial x}\frac{\partial c}{\partial x}=\frac{\partial}{\partial x}\left[\left\{\frac{-2b\left(x-x_0-vt\right)}{t}\right\}\times c\right]$$

$$=\frac{-2b}{t}\times c+\left\{\frac{-2b\left(x-x_0-vt\right)}{t}\right\}\times\frac{\partial c}{\partial x}$$

$$=\frac{-2b}{t}\times c+\left\{\frac{-2b\left(x-x_0-vt\right)}{t}\right\}\times\left\{\frac{-2b\left(x-x_0-vt\right)}{t}\right\}\times c$$

$$=\frac{-2b}{t}\times c+\left\{\frac{2b\left(x-x_0-vt\right)}{t}\right\}^2\times c$$

Thus,

$$D\frac{\partial^2 c}{\partial x^2}-v\frac{\partial c}{\partial x}=D\left\{\frac{-2b}{t}\times c+\left\{\frac{2b\left(x-x_0-vt\right)}{t}\right\}^2\times c\right\}-v\left\{\frac{-2b\left(x-x_0-vt\right)}{t}\right\}\times c$$

$$=\frac{-1}{2t}\times c+b\left\{\frac{\left(x-x_0-vt\right)}{t}\right\}^2\times c+v\left\{\frac{2b\left(x-x_0-vt\right)}{t}\right\}\times c\quad\left[D=1/4b\right]$$

$$=\frac{-c}{2t}+\left\{\frac{b\left(x-x_0-vt\right)}{t}\right\}\times\left\{2v+\frac{\left(x-x_0-vt\right)}{t}\right\}\times c$$

$$=\frac{\partial c}{\partial t}\text{ as required.}$$

Initially the material is concentrated at $x=x_0$ because $c=0$ for $\left|x-x_0\right|>0$ when $t=0$ on account of the very strong exponential factor $\left(\mathrm{e}^{-b\left(x-x_0\right)^2/t}\to 0\text{ more strongly than }\frac{1}{t^{1/2}}\to\infty\right)$. The term $x_0 + v\,t$ in the concentration expression is the movement of the centroid due to fluid flow, x_{centroid}.

To prepare a very general set of concentration profiles at a series of times without specifying either x_0, v, or D, define z and C as follows.

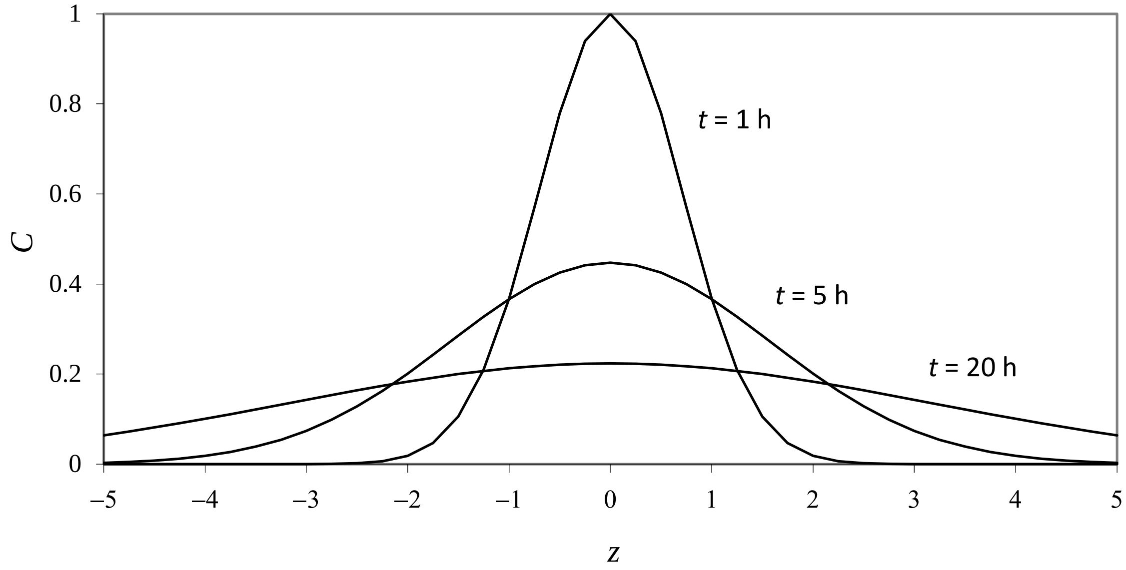
$$C\equiv\frac{c}{c_0/\left(4\pi D\ \mathrm{h}\right)^{1/2}}\ \text{ and }\ z\equiv\frac{x-x_{\text{centroid}}}{\left(4D\ \mathrm{h}\right)^{1/2}}$$

The hour (h) has been chosen for the unit because of the slow pace of diffusion activity. With these definitions the concentration expression becomes

$$C(z,t)=\frac{1}{\left(t/\mathrm{h}\right)^{1/2}}\mathrm{e}^{-z^2/\left(t/\mathrm{h}\right)}$$

Concentration profiles as C against t at various times (1, 5, and 20 h) are displayed in Fig. 19C.2.

Figure 19C.2



19C.12 $c(r,t)=\dfrac{n_0}{8(\pi Dt)^{3/2}}\mathrm{e}^{-r^2/4Dt}$ [19C.12] where $r^2=x^2+y^2+z^2$

$$\frac{\partial\ln c(r,t)}{\partial x}=\frac{1}{c(r,t)}\frac{\partial c(r,t)}{\partial x}=\frac{1}{c(r,t)}\frac{\partial c(r,t)}{\partial(r^2)}\frac{\partial(r^2)}{\partial x}$$

$$=\frac{1}{c(r,t)}\times\left\{\frac{-c(r,t)}{4Dt}\right\}\times(2x)=-\frac{x}{2Dt}$$

Likewise, $\dfrac{\partial\ln c(r,t)}{\partial y}=-\dfrac{y}{2Dt}$ and $\dfrac{\partial\ln c(r,t)}{\partial z}=-\dfrac{z}{2Dt}$

Thus,

$$\boldsymbol{\mathcal{F}}=-RT\nabla\ln c=\boxed{\frac{RT}{2Dt}\boldsymbol{r}\quad\text{where}\quad\boldsymbol{r}=x\boldsymbol{i}+y\boldsymbol{j}+z\boldsymbol{k}}$$

19C.13 Using the definitions $N=N_\mathrm{R}+N_\mathrm{L}$ and $n=N_\mathrm{R}-N_\mathrm{L}$, solve for N_R and N_L to find

$N_\mathrm{R}=½(N+n)$ and $N_\mathrm{L}=½(N-n)$

Following the discussion of Justification 19C.2, we then have

$$P(n\lambda)=\frac{\text{number of paths with }N_\mathrm{R}\text{ steps to the right}}{\text{total number of paths}}=\frac{N!}{(N_\mathrm{L})!N_\mathrm{R}!2^N}$$

$$=\frac{N!}{\{½(N+n)\}!\{½(N-n)\}!2^N}$$

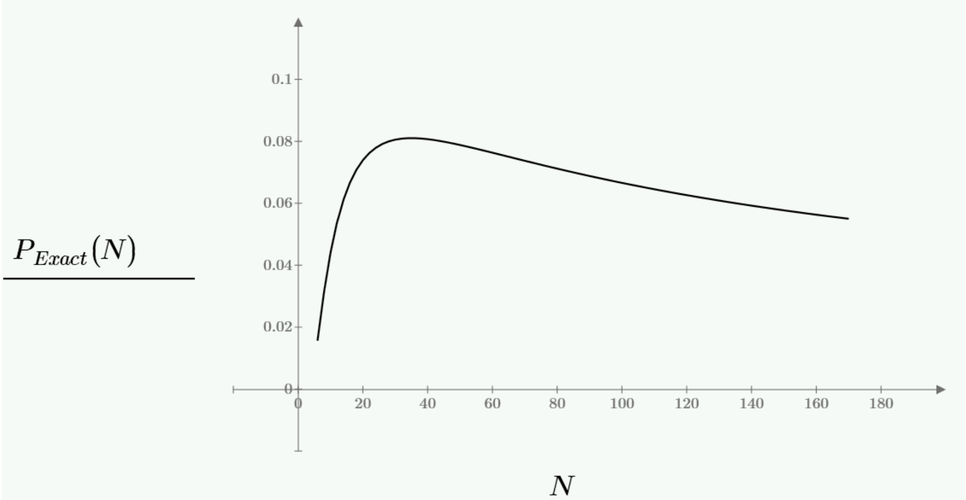
This is the "exact" random walk probability. After application of Stirling's approximation we have the "approximate" probability. P_Approx may be written in terms of the variables (x,t) or (n,N) because $x=n\lambda$ and $t=N\tau$.

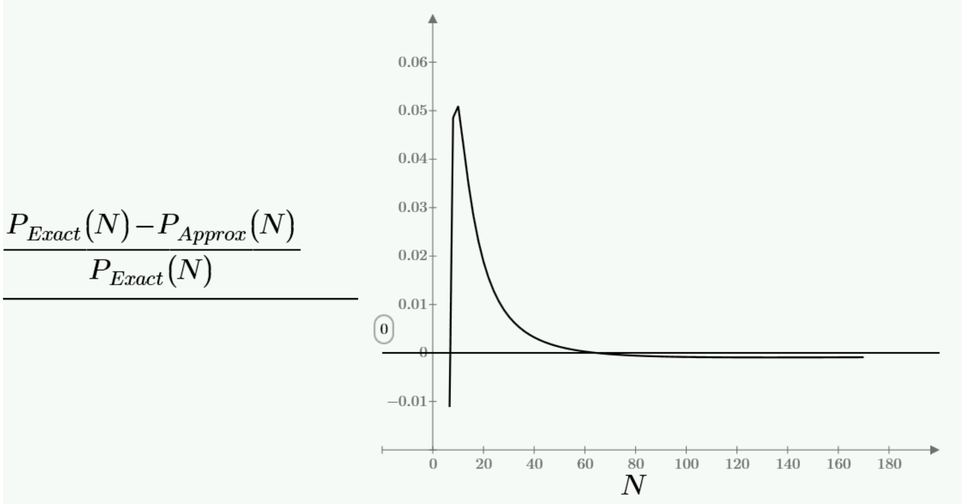
$$P_\text{Approx}=\left(\frac{2\tau}{\pi t}\right)^{1/2}\mathrm{e}^{-x^2\tau/2t\lambda^2}\ [\text{19C.15}]=\left(\frac{2}{\pi N}\right)^{1/2}\mathrm{e}^{-n^2/2N}$$

We calculate the probability P of being at $x=6\lambda$ for $N=6, 8,...180$ using Mathcad Prime 2 and we plot P_Exact against N. We include a plot of the fractional deviation of P_Approx against N from which we see that the deviation drops below 0.1% when $\boxed{N>60}$.

$$n := 6 \qquad P_{Exact}(N) := \frac{N!}{\left(\frac{1}{2}\cdot(N+n)\right)!\,\left(\frac{1}{2}\cdot(N-n)\right)!\,2^{N}} \qquad P_{Approx}(N) := \left(\frac{2}{\pi\cdot N}\right)^{\frac{1}{2}}\cdot e^{-\frac{n^2}{2\cdot N}}$$

$$N := 6, 8 \,..\, 180$$





19C.14 Eqn 19C.14, $\langle x^2 \rangle = 2Dt$, gives the mean square distance traveled in any one dimension in time t. We need the distance traveled 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.

$$r^2 = x^2 + y^2 + z^2 \text{ [Pythagorean theorem]}$$

$$\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle = 3\langle x^2 \rangle \text{ [independent motion]}$$

$$= 3\times 2Dt \text{ [81.14 for } \langle x^2 \rangle\text{]} = 6Dt$$

Therefore,

$$t = \frac{\langle r^2 \rangle}{6D} = \frac{(1.0\times10^{-6}\text{ m})^2}{6(1.0\times10^{-11}\text{ m}^2\text{ s}^{-1})} = \boxed{1.7\times10^{-2}\text{ s}}$$

Integrated activities

19B.2 The rate constant, k_r, for a transport process in which a molecule and its hydration sphere move a single step is governed by the activation energy for the step, E_a, where the general definition of activation energy is

$$E_a = RT^2\left(\frac{\mathrm{d}\ln k_r}{\mathrm{d}T}\right)$$

We expect that larger viscosities should retard the rate constant so let us assume that k_r is inversely proportional to the viscosity. Then,

$$\ln k_r = \text{constant} - \ln(\eta)$$

$$\frac{\mathrm{d}\ln k_r}{\mathrm{d}T} = -\frac{1}{\eta}\frac{\mathrm{d}\eta}{\mathrm{d}T}$$

$$E_a = -\frac{RT^2}{\eta}\frac{\mathrm{d}\eta}{\mathrm{d}T}$$

$$\frac{\mathrm{d}\eta}{\eta} = -\left(\frac{E_a}{R}\right)\frac{\mathrm{d}T}{T^2}$$

In the case for which E_a is independent of temperature, the above working equation can be integrated. We chose the lower integration limit to be the viscosity at a reference temperature T_{ref}, η_{ref}. The upper integration limit is the viscosity at temperature T, η.

$$\int_{\eta_{\text{ref}}}^{\eta}\frac{\mathrm{d}\eta}{\eta} = -\left(\frac{E_a}{R}\right)\int_{T_{\text{ref}}}^{T}\frac{\mathrm{d}T}{T^2}$$

$$\ln\left(\frac{\eta}{\eta_{\text{ref}}}\right) = \left(\frac{E_a}{R}\right)\times\left(\frac{1}{T}-\frac{1}{T_{\text{ref}}}\right) \quad \text{or} \quad \boxed{\eta = A\mathrm{e}^{E_a/RT} \text{ where } A = \eta_{\text{ref}}\,\mathrm{e}^{-E_a/RT_{\text{ref}}}}$$

Thus, we see that, when E_a is a constant, the pre-exponential factor A is a constant and $\eta \propto \mathrm{e}^{E_a/RT}$ [19B.2]. This demonstrates that the general definition $E_a = RT^2\left(\frac{\mathrm{d}\ln k_r}{\mathrm{d}T}\right)$ is compatible with eqn. [19B.2] when the activation energy is a constant.

We explore the possibility that the Problem 19B.2 empirical equation for the viscosity of water reflects an activation energy that has a dependence upon temperature by applying the above working equation prior to the constancy assumption. The reference temperature is 20° C and from the *CRC Handbook* (71st ed., 1990-1991) η_{20} = 1002 μPa s = 1.002 × 10^{-3} kg m^{-1} s^{-1} (the value is not actually necessary in the following calculations).

$$\eta(\theta) = \eta_{20}10^{\left\{a(20-\theta/{}^\circ\mathrm{C})-b(20-\theta/{}^\circ\mathrm{C})^2\right\}/(\theta/{}^\circ\mathrm{C}+c)} \quad \text{[Problem 19B.2] where } a = 1.3272,\ b = 0.001053,\ \text{and } c = 105$$

$$\eta(x) = \eta_{20}10^{f(x)} \text{ where } x = \theta/{}^\circ\ \mathrm{C} \text{ and } f(x) = \left\{a(20-x)-b(20-x)^2\right\}/(x+c)$$

$$\frac{\mathrm{d}\eta}{\mathrm{d}x} = \eta_{20}\frac{\mathrm{d}}{\mathrm{d}x}\left(10^{f(x)}\right) = \eta_{20}10^{f(x)}\times\ln(10)\times\frac{\mathrm{d}}{\mathrm{d}x}(f(x)) = \eta(x)\times\ln(10)\times\frac{\mathrm{d}}{\mathrm{d}x}(f(x))$$

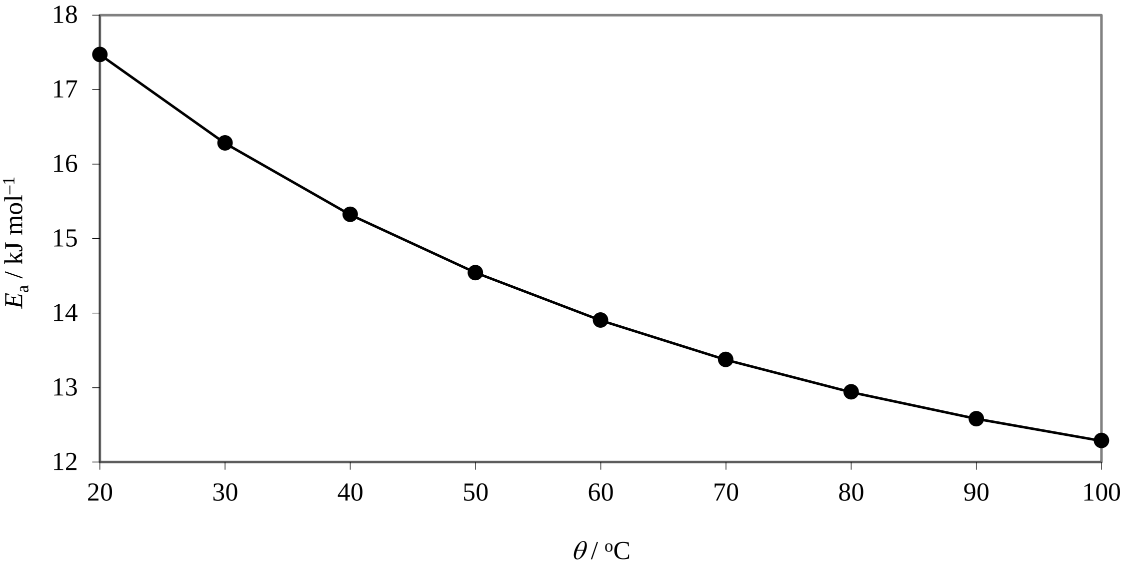
$$= \eta(x)\times\ln(10)\times\left\{\frac{-a+2b(20-x)}{x+c}-\frac{a(20-x)-b(20-x)^2}{(x+c)^2}\right\}$$

$$E_a = -\frac{RT^2}{\eta}\frac{\mathrm{d}\eta}{\mathrm{d}T} = -\frac{R\times(x+273.15)^2\ \mathrm{K}}{\eta(x)}\frac{\mathrm{d}\eta(x)}{\mathrm{d}(x)}$$

$$= -\left\{R\times(x+273.15)^2\ \mathrm{K}\right\}\times\ln(10)\times\left\{\frac{-a+2b(20-x)}{x+c}-\frac{a(20-x)-b(20-x)^2}{(x+c)^2}\right\}$$

This equation is used to make the plot of E_a against θ/°C (i.e., x) shown in Fig. 19.1. The activation energy drops from $\boxed{\text{17.5 kJ mol}^{-1}\text{ at 20° C to 12.3 kJ mol}^{-1}\text{ at 100° C}}$. This decrease may be caused by the density decrease that occurs across this temperature range because the increased average intermolecular distance may cause a decrease in the hydrogen bond strength between water molecules. There may also be a decrease in the hydration sphere of a molecule, thereby, making movement easier.

Figure I19.1



20 Chemical Kinetics

20A The rates of chemical reactions

Answers to discussion question

D20A.2 Reaction orders need not be integers, except for elementary reactions. Indeed, reaction orders can change during the course of the reaction. Consider the zero-order reaction mentioned in the text (Section 20A.2(c)), the decomposition of phosphine on hot tungsten. As long as enough phosphine is present, the rate of reaction is independent of that concentration; what limits the rate is the availability of catalytic sites on the tungsten. Clearly the integrated rate law for a zero-order reaction cannot be correct at long times, where it would predict negative concentrations. Before that unphysical situation would occur, the concentration of the reactant drops to such an extent that ***it*** limits the rate of reaction, and the reaction order changes from zero to a non-zero value. The text's treatment of the Lindemann–Hinshelwood mechanism (Section 20F.1) also illustrates how a reaction order can change from first- to second-order over the course of a reaction.

D20A.4 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

$$v = k_r'[A], \text{ where } k_r' = k_r[B]_0$$

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

$$\log v_0 = \log k_r + a \log [A]_0$$

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 lime 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 20B.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.

Solutions to exercises

E20A.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 $\alpha n_{\rm am}$, the amount of nitrogen consumed is $\alpha n_{\rm am}/2$, and the amount of hydrogen consumed is $3\alpha n_{\rm am}/2$. If we let $n_{\rm initial}$ be the total quantity of gas initially present (H_2 and N_2), then the total at any given time will be

$$n_{\rm total} = n_{\rm initial} - \alpha n_{\rm am}/2 - 3\alpha n_{\rm am}/2 + \alpha n_{\rm am} = n_{\rm initial} - \alpha n_{\rm am}$$

Thus, the total amount of gas changes from $n_{\rm initial}$ to $n_{\rm initial} - n_{\rm am}$ 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

$$\boxed{p_{\rm total} = p_{\rm initial} - \alpha p_{\rm am}}$$

E20A.2(b) $v = \dfrac{1}{\nu_{\rm J}}\dfrac{{\rm d}[{\rm J}]}{{\rm d}t}$ [20A.3b] so $\dfrac{{\rm d}[{\rm J}]}{{\rm d}t} = \nu_{\rm J} v$

Rate of consumption of A = v = $\boxed{2.7\ {\rm mol\ dm^{-3}\ s^{-1}}}$

Rate of consumption of B = $3v$ = $\boxed{8.1\ {\rm mol\ dm^{-3}\ s^{-1}}}$

Rate of formation of C = v = $\boxed{2.7\ {\rm mol\ dm^{-3}\ s^{-1}}}$

Rate of formation of D = $2v$ = $\boxed{5.4\ {\rm mol\ dm^{-3}\ s^{-1}}}$

E20A.3(b) $v = \dfrac{1}{\nu_{\rm J}}\dfrac{{\rm d}[{\rm J}]}{{\rm d}t}\ [20{\rm A.3b}] = \dfrac{1}{3}\dfrac{{\rm d}[{\rm B}]}{{\rm d}t} = \tfrac{1}{3}\times(2.7\,{\rm mol\ dm^{-3}\ s^{-1}}) = \boxed{0.9\,{\rm mol\,dm^{-3}\ s^{-1}}}$

Rate of formation of C = v = $\boxed{0.9\ {\rm mol\ dm^{-3}\ s^{-1}}}$

Rate of formation of D = $2v$ = $\boxed{1.8\ {\rm mol\ dm^{-3}\ s^{-1}}}$

Rate of consumption of A = v = $\boxed{0.9\ {\rm mol\ dm^{-3}\ s^{-1}}}$

Rate of consumption of B = $3v$ = $\boxed{2.7\ {\rm mol\ dm^{-3}\ s^{-1}}}$

E20A.4(b) The rate is expressed in mol dm^{-3} s^{-1}; therefore

mol dm^{-3} s^{-1} = $[k_{\rm r}]\times({\rm mol\ dm^{-3}})\times({\rm mol\ dm^{-3}})^2$

where $[k_{\rm r}]$ denotes units of $k_{\rm r}$, requires the units to be $\boxed{{\rm dm^6\ mol^{-2}\ s^{-1}}}$

(i) Rate of consumption of A = v = $\boxed{k_{\rm r}[{\rm A}][{\rm B}]^2}$

(ii) Rate of formation of C = v = $\boxed{k_{\rm r}[{\rm A}][{\rm B}]^2}$

E20A.5(b) Given $\dfrac{{\rm d}[{\rm C}]}{{\rm d}t} = k_{\rm r}[{\rm A}][{\rm B}][{\rm C}]^{-1}$

the rate of reaction is [20A.3b]

$$v = \frac{1}{\nu_{\rm J}}\frac{{\rm d}[{\rm J}]}{{\rm d}t} = \frac{{\rm d}[{\rm C}]}{{\rm d}t} = \boxed{k_{\rm r}[{\rm A}][{\rm B}][{\rm C}]^{-1}}$$

The units of $k_{\rm r}$, $[k_{\rm r}]$, must satisfy

mol dm^{-3} s^{-1} = $[k_{\rm r}]\times({\rm mol\ dm^{-3}})\times({\rm mol\ dm^{-3}})\times({\rm mol\ dm^{-3}})^{-1}$

Therefore, $[k_{\rm r}] = \boxed{{\rm s^{-1}}}$

E20A.6(b) **(i)** For a second-order reaction, denoting the units of $k_{\rm r}$ by $[k_{\rm r}]$

molecule m^{-3} s^{-1} = $[k_{\rm r}]\times({\rm molecule\ m^{-3}})^2$; therefore $[k_{\rm r}] = \boxed{{\rm m^3\ molecule^{-1}\ s^{-1}}}$ or $\boxed{{\rm m^3\ s^{-1}}}$

For a third-order reaction

molecule m^{-3} s^{-1} = $[k_{\rm r}]\times({\rm molecule\ m^{-3}})^3$; therefore $[k_{\rm r}] = \boxed{{\rm m^6\ molecule^{-2}\ s^{-1}}}$ or $\boxed{{\rm m^6\ s^{-1}}}$

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.

(ii) For a second-order reaction

Pa s^{-1} = $[k_{\rm r}]\times{\rm Pa}^2$; therefore $\boxed{[k_{\rm r}] = {\rm Pa^{-1}\ s^{-1}}}$

For a third-order reaction

Pa s^{-1} = $[k_r] \times \text{Pa}^3$; therefore $\boxed{[k_r] = \text{Pa}^{-2}\ \text{s}^{-1}}$

Solutions to problems

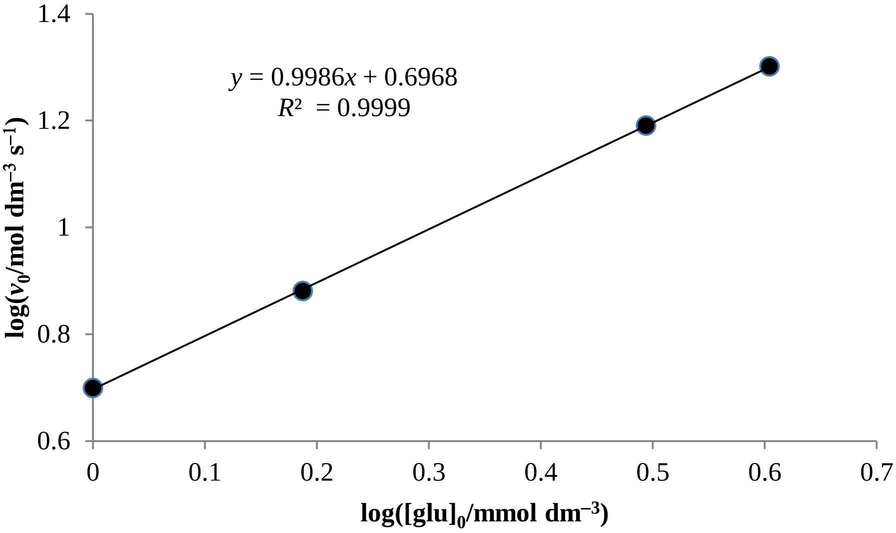
P20A.2 We suppose that the rate law for the reaction of isolated glucose (glu) with the enzyme hexokinase at 1.34 mmol dm^{-3} is $v = k_{r,eff}[\text{glu}]^a$. Evaluating this rate law at initial conditions and taking the logarithms gives

$$\log v_0 = \log k_{r,eff} + a \log[\text{glu}]_0$$

Thus, if the supposition is correct, a plot of $\log v_0$ against $\log[\text{glu}]_0$ with be linear with a slope equal to the reaction order a and an intercept equal to $\log k_{r,eff}$. We draw the following table with the requisite logarithm transformations, prepare the plot (see Figure 20A.1), and check whether the plot is linear.

$[\text{glu}]_0$ / mmol dm^{-3}	1.00	1.54	3.12	4.02
v_0 / mol dm^{-3} s^{-1}	5.0	7.6	15.5	20.0
log ($[\text{glu}]_0$/mmol dm^{-3})	0.00	0.188	0.494	0.604
log(v_0/mol dm^{-3} s^{-1})	0.699	0.881	1.19	1.30

Figure 20A.1



Inspection of the plot reveals that it is linear so we conclude that the supposed form of the rate law is valid and we perform the computation of the linear least squares regression fit of the data, which is shown in Figure 20A.1.

(a) The plot slope is extremely close to 1.00 so we conclude that the reaction order w/r/t glucose is $\boxed{1}$.

(b) The regression intercept tells us that $\log\left(k_{r,eff} / \text{mol dm}^{-3}\ \text{s}^{-1}\right)$ = 0.6968. Thus,

$k_{r,eff} = 10^{0.6968}$ mol dm^{-3} s^{-1} = $\boxed{5.0\ \text{mol dm}^{-3}\ \text{s}^{-1}}$.

E20A.4 **(a)** $\boxed{v = k_r\,[\text{ICl}]\,[\text{H}_2]}$

In order to deduce this rate law, compare experiments that have identical initial H_2 concentration then compare experiments that have identical initial ICl concentration. Experiments 1 and 2 have identical $[\text{H}_2]_0$ values but the 2nd has twice the $[\text{ICl}]_0$ value and an initial rate that is twice as large. The rate must be first-order in [ICl]. Similarly, Experiments 2 and 3 have identical $[\text{ICl}]_0$ values but the 3rd has thrice the $[H_2]_0$ value and an initial rate that is three times as large. Once again, the rate is proportional to the concentration so it must be first-order in $[H_2]$.

(b) $k_r = v / ([ICl]\,[H_2])$

$= 3.7\times10^{-7}\ \text{mol dm}^{-3}\ \text{s}^{-1} / (1.5\times10^{-3}\ \text{mol dm}^{-3})^2 = \boxed{0.16\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}$

(c) $v_0 = (0.16\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})\times(4.7\times10^{-3}\ \text{mol dm}^{-3})\times(2.7\times10^{-3}\ \text{mol dm}^{-3})$

$= \boxed{2.0\times10^{-6}\ \text{mol dm}^{-3}\ \text{s}^{-1}}$

20B Integrated rate laws

Answers to discussion questions

D20B.2 **(a)** $\dfrac{\mathrm{dA}}{\mathrm{d}t} = -k_r$, **(b)** $\dfrac{\mathrm{d[A]}}{\mathrm{d}t} = -k_r[\mathrm{A}]$, **(c)** $\dfrac{\mathrm{d[A]}}{\mathrm{d}t} = -k_r[\mathrm{A}]^2$

Solutions to exercises

E20B.1(b) Table 20B.3 gives a general expression for the half-life of a reaction of the type $\mathrm{A} \to \mathrm{P}$ 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:

$$\frac{t_{1/2}(p_{0,1})}{t_{1/2}(p_{0,2})} = \left(\frac{p_{0,1}}{p_{0,2}}\right)^{1-n} = \left(\frac{p_{0,2}}{p_{0,1}}\right)^{n-1}$$

Hence $\ln\left(\dfrac{t_{1/2}(p_{0,1})}{t_{1/2}(p_{0,2})}\right) = (n-1)\ln\left(\dfrac{p_{0,2}}{p_{0,1}}\right)$

or $\quad (n-1) = \dfrac{\ln\left(\dfrac{340\ \text{s}}{178\ \text{s}}\right)}{\ln\left(\dfrac{28.9\ \text{kPa}}{55.5\ \text{kPa}}\right)} = -0.992 \approx -1$

Therefore, $\boxed{n = 0}$

E20B.2(b) The rate law is

$$v = -\frac{1}{2}\frac{\mathrm{d[A]}}{\mathrm{d}t} = k_r[\mathrm{A}]$$

The half-life formula in eqn. 20B.2 is based on the assumption that

$$-\frac{\mathrm{d[A]}}{\mathrm{d}t} = k_r[\mathrm{A}]$$

That is, it would be accurate to take the half-life from the table and say

$$t_{1/2} = \frac{\ln 2}{k_r'}$$

where $k_r' = 2k_r$. Thus

$$t_{1/2} = \frac{\ln 2}{2(3.56\times10^{-7}\ \text{s}^{-1})} = \boxed{9.74\times10^5\ \text{s}}$$

Likewise, we modify the integrated rate law (eqn. 20B.1)), noting that pressure is proportional to concentration:

$$p = p_0 \mathrm{e}^{-2k_r t}$$

(i) Therefore, after 50 s, we have

$$p = (33.0\,\text{kPa})\,\mathrm{e}^{-2\times(3.56\times10^{-7}\ \text{s}^{-1})\times(50\,\text{s})} = \boxed{32.9\overline{99}\ \text{kPa}}$$

(ii) After 20 min,

$$p=(33.0\,\text{kPa})\,e^{-2\times(3.56\times10^{-7}\,\text{s}^{-1})\times(20\times60\,\text{s})}=\boxed{32.9\overline{7}\ \text{kPa}}$$

E20B.3(b) The integrated rate law is

$$k_\text{r}t=\frac{1}{[\text{B}]_0-2[\text{A}]_0}\ln\frac{[\text{A}]_0([\text{B}]_0-2[\text{C}])}{([\text{A}]_0-[\text{C}])[\text{B}]_0}\quad\text{[Table 20B.3]}$$

Solving for [C] yields, after some rearranging

$$[\text{C}]=\frac{[\text{A}]_0[\text{B}]_0\left(e^{k_\text{r}t([\text{B}]_0-2[\text{A}]_0)}-1\right)}{[\text{B}]_0e^{k_\text{r}t([\text{B}]_0-2[\text{A}]_0)}-2[\text{A}]_0}$$

so $$\frac{[\text{C}]}{\text{mol dm}^{-3}}=\frac{(0.027)\times(0.130)\times(e^{0.34\times(0.130-2\times0.027)\times t/\text{s}}-1)}{(0.130)\times e^{0.34\times(0.130-2\times0.027)\times t/\text{s}}-2\times(0.027)}=\frac{0.027\times(e^{0.026\times t/\text{s}}-1)}{e^{0.026\times t/\text{s}}-0.42}$$

(i) $$[\text{C}]=\frac{0.027\times(e^{0.026\times20}-1)}{e^{0.026\times20}-0.42}\ \text{mol dm}^{-3}=\boxed{0.014\ \text{mol dm}^{-3}}$$

(ii) $$[\text{C}]=\frac{0.027\times(e^{0.026\times15\times60}-1)}{e^{0.026\times15\times60}-0.42}\ \text{mol dm}^{-3}=\boxed{0.027\ \text{mol dm}^{-3}}$$

Comment. Note that part (ii) 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?

E20B.4(b) The rate law is

$$v=-\frac{1}{2}\frac{\text{d}[\text{A}]}{\text{d}t}=k_\text{r}[\text{A}]^3$$

which integrates to

$$2k_\text{r}t=\frac{1}{2}\left(\frac{1}{[\text{A}]^2}-\frac{1}{[\text{A}]_0^2}\right)\quad\text{so}\quad t=\frac{1}{4k_\text{r}}\left(\frac{1}{[\text{A}]^2}-\frac{1}{[\text{A}]_0^2}\right)$$

$$t=\left(\frac{1}{4(6.50\times10^{-4}\ \text{dm}^6\ \text{mol}^{-2}\ \text{s}^{-1})}\right)\times\left(\frac{1}{(0.015\,\text{mol dm}^{-3})^2}-\frac{1}{(0.067\,\text{mol dm}^{-3})^2}\right)$$

$$=\boxed{1.6\times10^6\ \text{s}}=\boxed{19\ \text{days}}.$$

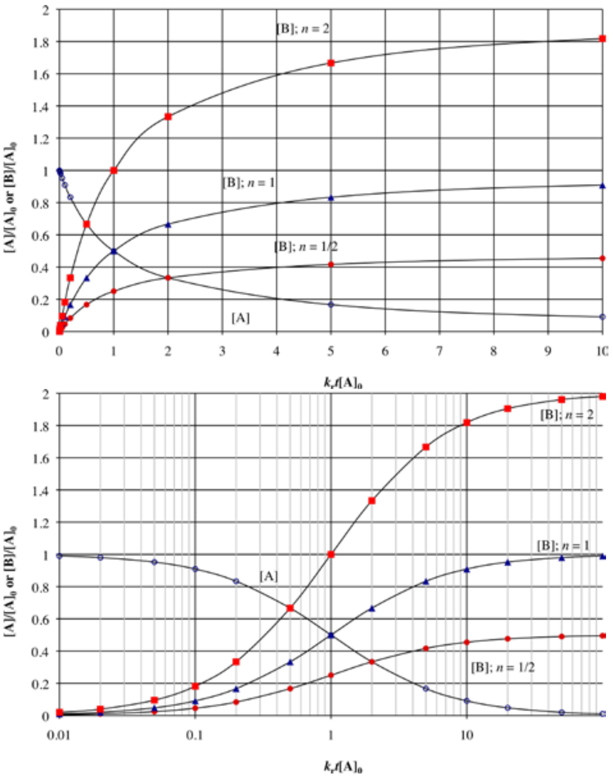
Solutions to problems

P20B.2 The concentration of A varies with time as

$$[\text{A}]=\frac{[\text{A}]_0}{1+k_\text{r}t[\text{A}]_0}\quad[20\text{B}.4]$$

Dimensionless concentrations $[\text{A}]/[\text{A}]_0$ and $[\text{B}]/[\text{A}]_0$ are plotted against the dimensionless time $k_\text{r}t[\text{A}]_0$ in Fig. 20B.1(a). The same variables are plotted against a logarithmic horizontal axis in Fig. 20B.1(b). The second-order plots have longer "tails" than the first-order plots of Problem 20B.1

Figures 20B.1(a) and (b)



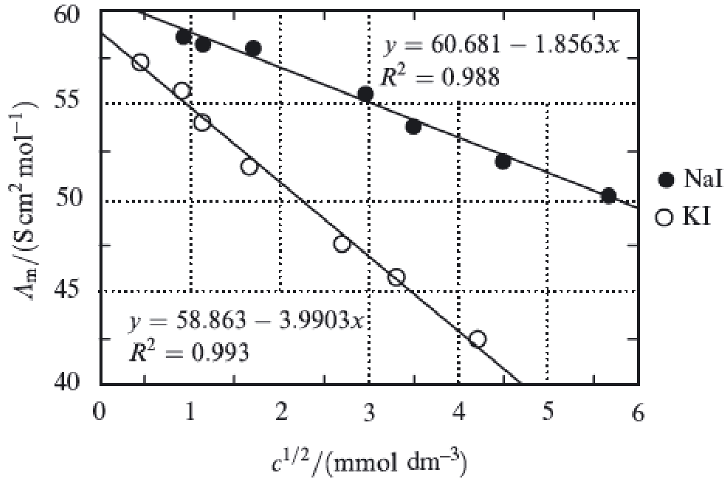
P20B.4 A simple but practical approach is to make an initial guess at the order by observing whether the half-life of the reaction appears to depend on concentration. If it does not, the reaction is first-order; otherwise refer to Table 20B.3. Visual inspection of the data seems to indicate that the half-life is roughly independent of the concentration. Therefore, we first try to fit the data to eqn. 20B.1:

$$\ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right) = -k_\mathrm{r}t$$

We plot $\ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right)$ against time to see if a straight line is obtained. We draw up the following table (A = $(CH_3)_3CBr$):

t / h	0	3.15	6.20	10.00	18.30	30.80
$[\mathrm{A}]/(10^{-2}\,\mathrm{mol\,dm^{-3}})$	10.39	8.96	7.76	6.39	3.53	2.07
$\frac{[\mathrm{A}]}{[\mathrm{A}]_0}$	1	0.862	0.747	0.615	0.340	0.199
$\ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right)$	0	–0.148	–0.292	–0.486	–1.080	–1.613
$\left(\frac{1}{[\mathrm{A}]}\right)/(\mathrm{dm^3\,mol^{-1}})$	9.62	11.16	12.89	15.65	28.3	48.3

Figure 20B.2



The data are plotted in Fig. 20B.2. 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:

$$k_r = 0.0542\,\mathrm{h^{-1}} = \boxed{1.51\times10^{-5}\ \mathrm{s^{-1}}}$$

At 43.8 h

$$\ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right) = -(0.0542\ \mathrm{h^{-1}})\times(43.8\ \mathrm{h}) = -2.374$$

$$[\mathrm{A}] = (10.39\times10^{-2}\ \mathrm{mol\ dm^{-3}})\times \mathrm{e}^{-2.359} = \boxed{9.67\times10^{-3}\ \mathrm{mol\ dm^{-3}}}$$

P20B.6 From Table 20B.3, we see that for A + 2B → P the integrated second-order rate law is

$$k_r t = \frac{1}{[\mathrm{B}]_0 - 2[\mathrm{A}]_0}\ln\left[\frac{[\mathrm{A}]_0([\mathrm{B}]_0 - 2[\mathrm{P}])}{([\mathrm{A}]_0 - [\mathrm{P}])[\mathrm{B}]_0}\right]$$

By the time [B] falls to 0.010 mol dm^{-3}, it has dropped by 0.020 mol dm^{-3}, so [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

$$k_r = \frac{1}{(3.6\times10^3\ \mathrm{s})\times(0.030-2\times0.050)\ \mathrm{mol\,dm^{-3}}}\times\ln\left[\frac{(0.050\times(0.030-2\times0.010)}{(0.050-0.010)\times0.030}\right]$$

$$= \boxed{3.5\times10^{-3}\mathrm{dm^3\ mol^{-1}\ s^{-1}}}$$

(b) The half-life in terms of A is the time when [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 [B] = $[\mathrm{B}]_0$/2 = 0.015 mol dm^{-3}

[A] = $[\mathrm{A}]_0$ – $[\mathrm{B}]_0$/4 = 0.0425 mol dm^{-3}, and [P] = $[\mathrm{B}]_0$/4 = 0.0075 mol dm^{-3}

$$t_{1/2}(\mathrm{B}) = \frac{1}{k_r([\mathrm{B}]_0 - 2[\mathrm{A}]_0)}\ln\left[\frac{[\mathrm{A}]_0([\mathrm{B}]_0 - 2[\mathrm{P}])}{([\mathrm{A}]_0 - [\mathrm{P}])[\mathrm{B}]_0}\right]$$

$$= \frac{1}{(3.5\times10^{-3}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}})\times(0.030-2\times0.050)\,\mathrm{mol\,dm^{-3}})}$$

$$\times\ln\left(\frac{0.050\times0.015}{0.0425\times0.030}\right)$$

$$= \boxed{2.2\times10^3\,\mathrm{s}} = \boxed{0.61\ \mathrm{h}}.$$

P20B.8 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; if it does, it may be second-order. Examination of the data shows that the half-life is roughly 90 minutes, but it is not exactly constant. (Compare the 60-150 minute data to the 150-240 minute data; in both intervals the concentration drops by roughly half. Then examine the 30-120 minute interval, where the concentration drops by less than half.) If the reaction is first-order, it will obey

$$\ln\left(\frac{c}{c_0}\right) = -k_r t \quad [20B.1]$$

If it is second-order, it will obey

$$\frac{1}{c} = k_r t + \frac{1}{c_0} \quad [20B.4]$$

See whether a first-order plot of ln c vs. time or a second-order plot of $1/c$ vs. time has a substantially better fit. We draw up the following table:

t / min	30	60	120	150	240	360	480
c / (ng cm^{-3})	699	622	413	292	152	60	24
(ng cm^{-3}) / c	0.00143	0.00161	0.00242	0.00342	0.00658	0.0167	0.0412
ln {c/(ng cm^{-3})}	6.550	6.433	6.023	5.677	5.024	4.094	3.178

Figure 20B.3(a)

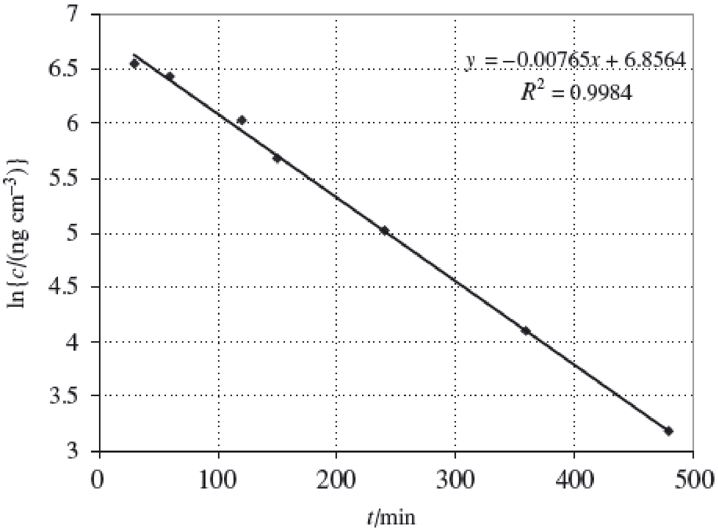
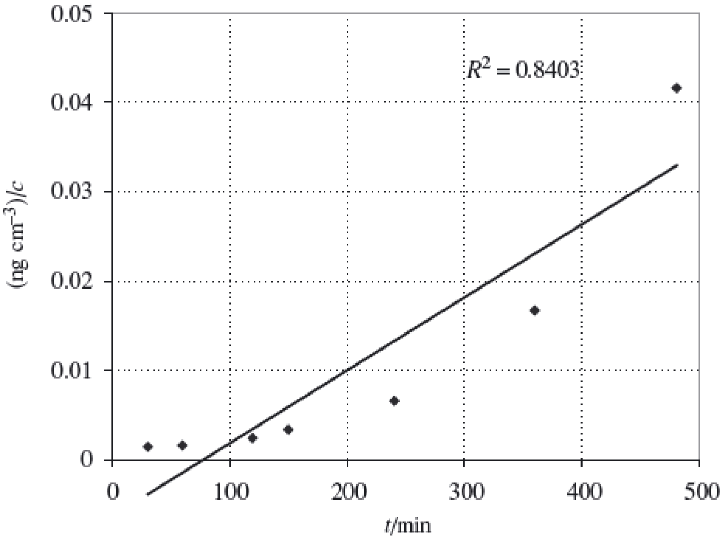


Figure 20B.3(b)



The data are plotted in Figs. 20B.3(a) and (b). The first-order plot fits closely to a straight line with just a hint of curvature near the outset. The second-order plot, conversely, is strongly curved throughout. Hence, the reaction is $\boxed{\text{first-order}}$. The rate constant is the negative of the slope of the first-order plot: $k_r = \boxed{0.00765\ \text{min}^{-1}} = \boxed{0.459\ \text{h}^{-1}}$. The half-life is (eqn. 20B.2)

$$t_{1/2} = \frac{\ln 2}{k_r} = \frac{\ln 2}{0.459\ \text{h}^{-1}} = \boxed{1.51\ \text{h}} = \boxed{91\ \text{min}}$$

Comment. As noted in the problem, the drug concentration is a result of absorption and elimination of the drug, two processes with distinct rates. Elimination is characteristically slower, so the later data points reflect elimination only, because absorption is effectively complete by then. The earlier data points, by contrast, reflect both absorption and elimination. It is, therefore, not surprising that the early points do not adhere so closely to the line so well defined by the later data.

P20B.10 Since both reactions are first-order,

$$-\frac{d[A]}{dt} = k_1[A] + k_2[A] = (k_1 + k_2)[A]$$

so $[A] = [A]_0 e^{-(k_1+k_2)t}$ [20B.1 with $k_r = k_1 + k_2$]

We are interested in the yield of ketene, CH_2CO; call it K:

$$\frac{d[K]}{dt} = k_2[A] = k_2[A]_0 e^{-(k_1+k_2)t}$$

Integrating yields

$$\int_0^{[K]} d[K] = k_2[A]_0 \int_0^t e^{-(k_1+k_2)t} dt$$

$$[K] = \frac{k_2[A]_0}{k_1 + k_2}(1 - e^{-(k_1+k_2)t}) = \frac{k_2}{k_1 + k_2}([A]_0 - [A])$$

The percent yield is the amount of K produced compared to complete conversion; since the stoichiometry of reaction (2) is one-to-one, we can write:

$$\%\ \text{yield} = \frac{[K]}{[A]_0} \times 100\% = \frac{k_2}{k_1 + k_2}(1 - e^{-(k_1+k_2)t}) \times 100\%$$

which has its maximum value when the reaction reaches completion

$$\text{max \% yield} = \frac{k_2}{k_1 + k_2} \times 100\% = \frac{4.65\ \text{s}^{-1}}{(3.74 + 4.65)\ \text{s}^{-1}} \times 100\% = \boxed{55.4\%}$$

Comment. If we are interested in yield of the desired product (ketene) compared to the products of side reactions (products of reaction 1), it makes sense to define the conversion ratio, the ratio of desired product formed to starting material *reacted*, namely

$$\frac{[K]}{[A]_0 - [A]}$$

which works out in this case to be independent of time

$$\frac{[\mathrm{K}]}{[\mathrm{A}]_0-[\mathrm{A}]}=\frac{k_2}{k_1+k_2}$$

If a substance reacts by parallel processes of the same order, then the ratio of the amounts of products will be constant and independent of the extent of the reaction, no matter what the order.

Question. Can you demonstrate the truth of the statement made in the above comment?

P20B.12 The stoichiometry of the reaction relates product and reaction concentrations as follows:

$$[\mathrm{A}]=[\mathrm{A}]_0-2[\mathrm{B}]$$

When the reaction goes to completion, $[\mathrm{B}] = [\mathrm{A}]_0/2$; hence $[\mathrm{A}]_0 = 0.624\ \mathrm{mol\ dm^{-3}}$. We can therefore tabulate [A], and examine its half-life. We see that the half-life of A from its initial concentration is approximately 20 min, and that its half-life from the concentration at 20 min is also 20 min. This indicates a first-order reaction. We confirm this conclusion by plotting the data accordingly (in Fig. 20B.4), using

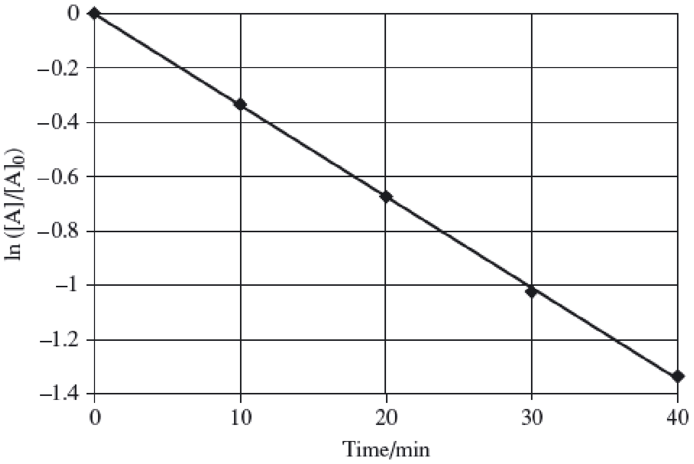
$$\ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]}=k_\mathrm{A}t\ \ [20\mathrm{B}.1]$$

which follows from

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}=-k_\mathrm{A}[\mathrm{A}]$$

t / min	0	10	20	30	40	∞
$[\mathrm{B}]/(\mathrm{mol\ dm^{-3}})$	0	0.089	0.153	0.200	0.230	0.312
$[\mathrm{A}]/(\mathrm{mol\ dm^{-3}})$	0.624	0.446	0.318	0.224	0.164	0
$\ln\frac{[\mathrm{A}]}{[\mathrm{A}]_0}$	0	–0.34	–0.67	–1.02	–1.34	

Figure 20B.4



The points lie on a straight line, which confirms $\boxed{\text{first-order}}$ kinetics. Since the slope of the line is $-3.4\times10^{-2}\ \mathrm{min^{-1}}$, we conclude that $k_\mathrm{A} = 3.4\times10^{-2}\ \mathrm{min^{-1}}$. To express the rate law in the form $v = k_\mathrm{r}[\mathrm{A}]$ we note that

$$v=-\frac{1}{2}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}=-\left(\tfrac{1}{2}\right)\times(-k_\mathrm{A}[\mathrm{A}])=\tfrac{1}{2}k_\mathrm{A}[\mathrm{A}]$$

and hence $k_\mathrm{r}=\tfrac{1}{2}k_\mathrm{A}=\boxed{1.7\times10^{-2}\ \mathrm{min^{-1}}}$

P20B.14 If the reaction is first-order the concentrations obey

$$\ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right) = -k_\mathrm{r}t \quad [20\mathrm{B}.1]$$

and, since pressures and concentrations of gases are proportional, the pressures should obey

$$\ln\frac{p_0}{p} = k_\mathrm{r}t$$

and $\frac{1}{t}\ln\frac{p_0}{p}$ should be a constant. We test this by drawing up the following table:

p_0 / Torr	200	200	400	400	600	600
t / s	100	200	100	200	100	200
p / Torr	186	173	373	347	559	520
$10^4\left(\frac{1}{t/\mathrm{s}}\right)\ln\frac{p_0}{p}$	7.3	7.3	7.0	7.1	7.1	7.2

The values in the last row of the table are virtually constant, and so (in the pressure range spanned by the data) the reaction has $\boxed{\text{first-order kinetics}}$ with $k_\mathrm{r} = \boxed{7.2\times10^{-4}\ \mathrm{s}^{-1}}$

P20B.16 The rate of change of [A] is

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_\mathrm{r}[\mathrm{A}]^n$$

Hence, $\displaystyle\int_{[\mathrm{A}]_0}^{[\mathrm{A}]}\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]^n} = -k_\mathrm{r}\int_0^t \mathrm{d}t = -k_\mathrm{r}t$

Therefore, $\displaystyle k_\mathrm{r}t = \left(\frac{1}{n-1}\right)\times\left(\frac{1}{[\mathrm{A}]^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right)$

At $t = t_{1/2}$, $[\mathrm{A}] = [\mathrm{A}]_0/2$

$$k_\mathrm{r}t_{1/2} = \left(\frac{1}{n-1}\right)\times\left(\frac{2^{n-1}}{[\mathrm{A}]_0^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right) = \left(\frac{2^{n-1}-1}{n-1}\right)\times\left(\frac{1}{[\mathrm{A}]_0^{n-1}}\right)$$

and $\displaystyle t_{1/2} = \boxed{\frac{2^{n-1}-1}{k_\mathrm{r}(n-1)[\mathrm{A}]_0^{n-1}}}$ [as in Table 20B.3]

Now let $t_{1/3}$ be the time at which $[\mathrm{A}] = [\mathrm{A}]_0/3$. Substitute these expressions into the integrated rate law:

$$k_\mathrm{r}t_{1/3} = \left(\frac{1}{n-1}\right)\times\left(\frac{3^{n-1}}{[\mathrm{A}]_0^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right) = \left(\frac{3^{n-1}-1}{n-1}\right)\times\left(\frac{1}{[\mathrm{A}]_0^{n-1}}\right)$$

and $\displaystyle t_{1/3} = \boxed{\frac{3^{n-1}-1}{k_\mathrm{r}(n-1)[\mathrm{A}]_0^{n-1}}}$

P20B.18 $\displaystyle\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -2k_\mathrm{r}[\mathrm{A}]^2[\mathrm{B}], \quad 2\mathrm{A}+\mathrm{B}\rightarrow\mathrm{P}$

(a) Let x represent [P] at time t, A_0 represent $[\mathrm{A}]_0$, and B_0 represent $[\mathrm{B}]_0$. Then

$$[\mathrm{A}] = A_0 - 2x \text{ and } [\mathrm{B}] = B_0 - x = \frac{A_0}{2} - x$$

Therefore, $\displaystyle\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -2\frac{\mathrm{d}x}{\mathrm{d}t} = -2k_\mathrm{r}(A_0-2x)^2\times(B_0-x)$

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_\mathrm{r}(A_0-2x)^2\times\left(\tfrac{1}{2}A_0 - x\right) = \tfrac{1}{2}k_\mathrm{r}(A_0-2x)^3$$

$$\frac{1}{2}k_\mathrm{r}t = \int_0^x \frac{dx}{(A_0-2x)^3} = \frac{1}{4}\times\left[\left(\frac{1}{A_0-2x}\right)^2 - \left(\frac{1}{A_0}\right)^2\right]$$

Therefore, $\boxed{k_\mathrm{r}t = \dfrac{2x(A_0-x)}{A_0^2(A_0-2x)^2}}$

(b) Now $B_0 = A_0$, so

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_\mathrm{r}(A_0-2x)^2\times(B_0-x) = k_\mathrm{r}(A_0-2x)^2\times(A_0-x)$$

$$k_\mathrm{r}t = \int_0^x \frac{dx}{(A_0-2x)^2\times(A_0-x)}$$

We proceed by the method of partial fractions (which is employed in the general case too), and look for the values of α, β, and γ such that

$$\frac{1}{(A_0-2x)^2\times(A_0-x)} = \frac{\alpha}{(A_0-2x)^2} + \frac{\beta}{A_0-2x} + \frac{\gamma}{A_0-x}$$

This requires that

$$\alpha(A_0-x) + \beta(A_0-2x)\times(A_0-x) + \gamma(A_0-2x)^2 = 1$$

Expand and gather terms by powers of x:

$$(A_0\alpha + A_0^2\beta + A_0^2\gamma) - (\alpha + 3\beta A_0 + 4\gamma A_0)x + (2\beta+4\gamma)x^2 = 1$$

This must be true for all x; therefore

$$A_0\alpha + A_0^2\beta + A_0^2\gamma = 1$$

$$\alpha + 3A_0\beta + 3A_0\gamma = 0$$

and $\quad 2\beta + 4\gamma = 0$

Solving this system yields $\alpha = \dfrac{2}{A_0}$, $\beta = \dfrac{-2}{A_0^2}$, and $\gamma = \dfrac{1}{A_0^2}$

Therefore,

$$k_\mathrm{r}t = \int_0^x \left(\frac{(2/A_0)}{(A_0-2x)^2} - \frac{(2/A_0^2)}{A_0-2x} + \frac{(1/A_0^2)}{A_0-x}\right)\mathrm{d}x$$

$$= \left(\frac{(1/A_0)}{A_0-2x} + \frac{1}{A_0^2}\ln(A_0-2x) - \frac{1}{A_0^2}\ln(A_0-x)\right)\Bigg|_0^x$$

$$= \boxed{\left(\frac{2x}{A_0^2(A_0-2x)}\right) + \left(\frac{1}{A_0^2}\right)\ln\left(\frac{A_0-2x}{A_0-x}\right)}$$

20C Reactions approaching equilibrium

Answers to discussion questions

D20C.2 If the equilibrium position shifts with pressure, pressure jumps, usually by ultrasonic methods, can be used to alter the rate of the reaction. $\Delta_\mathrm{r}V$ for the reaction must be non-zero.

Solutions to exercises

E20C.1(b) The equilibrium constant of the reaction is the ratio of rate constants of the forward and reverse reactions:

$$K = \frac{k_r}{k_r'} \text{ so } k_r = Kk_r'$$

The relaxation time for the temperature jump is (Example 20C.1):

$$\tau = \{k_r + k_r'([B]+[C])\}^{-1} \quad \text{so} \quad k_r = \tau^{-1} - k_r'([B]+[C])$$

Setting these two expressions for k_r equal yields

$$Kk_r' = \tau^{-1} - k_r'([B]+[C]) \quad \text{so} \quad k_r' = \frac{1}{\tau(K+[B]+[C])}$$

Hence $k_r' = \dfrac{1}{(3.0\times10^{-6}\,\text{s})\times(2.0\times10^{-16}+2.0\times10^{-4}+2.0\times10^{-4})\,\text{mol}\,\text{dm}^{-3}}$

$$= \boxed{8.3\times10^{8}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$$

and $\quad k_r = (2.0\times10^{-16}\,\text{mol}\,\text{dm}^{-3})\times(8.3\times10^{8}\,\text{dm}^3\,\text{mol}^{-1}\text{s}^{-1}) = \boxed{1.7\times10^{-7}\,\text{s}^{-1}}$

Solutions to problems

P20C.2 We proceed as in Section 20C.1. The individual reactions are (analogous to eqn. 84.1)

$\text{A} \rightarrow 2\,\text{B} \qquad v = k_r[\text{A}]$

and $\quad 2\,\text{B} \rightarrow \text{A} \qquad v = k_r'[\text{B}]^2$

The net rate of change of A is

$$\frac{d[A]}{dt} = -k_r[A] + k_r'[B]^2$$

If this reaction were run starting with no B and an initial concentration of A equal to $[\text{A}]_0$, then the reaction stoichiometry requires that

$[\text{B}] = 2([\text{A}]_0 - [\text{A}])$

Substituting this into the differential equation for [A] yields

$$\frac{d[A]}{dt} = -k_r[A] + 2k_r'\{[A]_0 - [A]\}^2 = \boxed{2k_r'[A]_0^2 - \{k_r + 4k_r'[A]_0\}[A] + 2k_r'[A]^2}$$

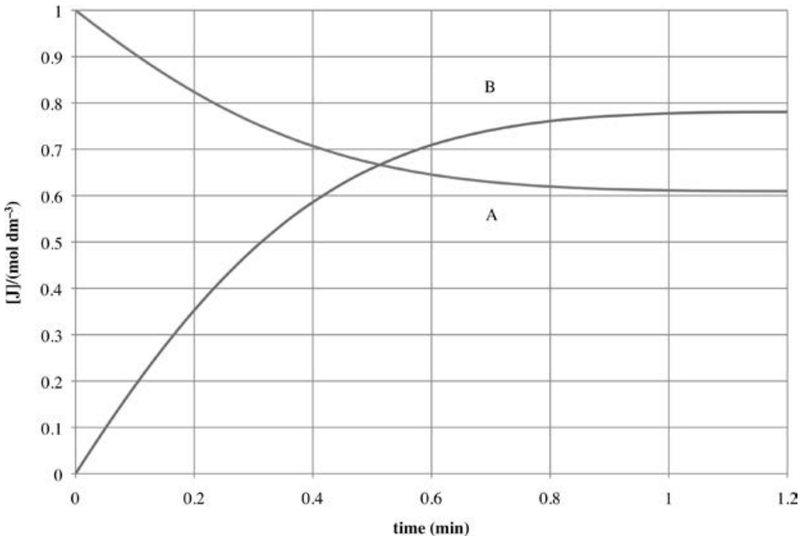
Note that the resulting equation is non-linear in [A]. Early on, the concentration of A would decay exponentially, but eventually the decay would slow as [A] approaches its equilibrium value. At equilibrium

$$\frac{d[A]}{dt} = 0 = -k_r[A] + k_r'[B]^2$$

so $\quad k_r[\text{A}]_{\text{eq}} = k_r'[\text{B}]_{\text{eq}}^2 \qquad$ and $\quad \dfrac{k_r}{k_r'} = \dfrac{[\text{B}]_{\text{eq}}^2}{[\text{A}]_{\text{eq}}} = K$

The approach of concentrations to their equilibrium values is plotted in Fig. 84.1 for initial concentration $[\text{A}]_0 = 1.0$ mol dm^{-3} (and no B initially) and rate constants $k_r = 1.0$ min^{-1} and $k_r' = 1.0$ dm^3 mol min^{-1}.

Figure 20C.1



P20C.4 Consider a two-step equilibrium involving an intermediate I:

$\mathrm{A} \rightleftharpoons \mathrm{I}$ with rate constants k_1 and k_1'

$\mathrm{I} \rightleftharpoons \mathrm{B}$ with rate constants k_2 and k_2'

The rate of change of [A] is

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_1[\mathrm{A}] + k_1'[\mathrm{I}]$$

and at equilibrium

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = 0 = -k_1[\mathrm{A}]_{\mathrm{eq}} + k_1'[\mathrm{I}]_{\mathrm{eq}} \qquad \text{so} \qquad \frac{[\mathrm{I}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{k_1}{k_1'}$$

But we wish to express our equilibrium constant in terms of reactant and product concentrations, eliminating intermediates. So consider the rate of change of [B]:

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_2[\mathrm{I}] - k_2'[\mathrm{B}]$$

and at equilibrium

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = 0 = k_2[\mathrm{I}]_{\mathrm{eq}} - k_2'[\mathrm{B}]_{\mathrm{eq}} \qquad \text{so} \qquad \frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{I}]_{\mathrm{eq}}} = \frac{k_2}{k_2'}$$

Multiplying these two expressions together yields the desired expression:

$$\frac{[\mathrm{I}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}}\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{I}]_{\mathrm{eq}}} = \frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{k_2}{k_2'}\frac{k_1}{k_1'}$$

Now suppose B is also an intermediate and there is another step to arrive at a final product C:

$\mathrm{B} \rightleftharpoons \mathrm{C}$ with rate constants k_3 and k_3'

Now consider the rate of change of [C]:

$$\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = k_3[\mathrm{B}] - k_3'[\mathrm{C}]$$

and at equilibrium

$$\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = 0 = k_3[\mathrm{B}]_{\mathrm{eq}} - k_3'[\mathrm{C}]_{\mathrm{eq}} \qquad \text{so} \qquad \frac{[\mathrm{C}]_{\mathrm{eq}}}{[\mathrm{B}]_{\mathrm{eq}}} = \frac{k_3}{k_3'}$$

Multiplying this expressions with the previous one yields:

$$\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}}\frac{[\mathrm{C}]_{\mathrm{eq}}}{[\mathrm{B}]_{\mathrm{eq}}} = \frac{[\mathrm{C}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{k_3}{k_3'}\frac{k_2}{k_2'}\frac{k_1}{k_1'}$$

It should be clear that this process can be carried on for any number of steps, if the procedure to this point is correct. One possible objection is worth addressing here, and that is that once B becomes an intermediate rather than a final product, the expression for its rate of change becomes more complicated, namely

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t}=k_2[\mathrm{I}]-k_2'[\mathrm{B}]-k_3[\mathrm{B}]+k_3'[\mathrm{C}]$$

This is true in general. However, at equilibrium, forward and reverse rates of reaction are equal ***for each step***. Therefore it is still true that each of the following is true separately

$$0=k_2[\mathrm{I}]_{\mathrm{eq}}-k_2'[\mathrm{B}]_{\mathrm{eq}} \qquad \text{and} \qquad 0=k_3[\mathrm{B}]_{\mathrm{eq}}-k_3'[\mathrm{C}]_{\mathrm{eq}}$$

and the same would be true for any additional steps.

P20C.6 $2\,\mathrm{A} \underset{k_\mathrm{r}'}{\overset{k_\mathrm{r}}{\rightleftharpoons}} \mathrm{A}_2$ $\qquad \frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}=-2k_\mathrm{r}[\mathrm{A}]^2+2k_\mathrm{r}'[\mathrm{A}_2]$

Define the deviation from equilibrium, x, by the following equations, which satisfy the law of mass conservation.

$$[\mathrm{A}]=[\mathrm{A}]_{\mathrm{eq}}+2x \qquad \text{and} \qquad [\mathrm{A}_2]=[\mathrm{A}_2]_{\mathrm{eq}}-x$$

Then,

$$\frac{\mathrm{d}([\mathrm{A}]_{\mathrm{eq}}+2x)}{\mathrm{d}t}=-2k_\mathrm{r}([\mathrm{A}]_{\mathrm{eq}}+2x)^2+2k_\mathrm{r}'([\mathrm{A}_2]_{\mathrm{eq}}-x)$$

$$\frac{\mathrm{d}x}{\mathrm{d}t}=-k_\mathrm{r}([\mathrm{A}]_{\mathrm{eq}}+2x)^2+k_\mathrm{r}'([\mathrm{A}_2]_{\mathrm{eq}}-x)=-k_\mathrm{r}\left([\mathrm{A}]_{\mathrm{eq}}^2+4[\mathrm{A}]_{\mathrm{eq}}x+4x^2\right)+k_\mathrm{r}'\left([\mathrm{A}_2]_{\mathrm{eq}}-x\right)$$

$$=-\left\{4k_\mathrm{r}x^2+\left(k_\mathrm{r}'+4k_\mathrm{r}[\mathrm{A}]_{\mathrm{eq}}\right)x+k_\mathrm{r}[\mathrm{A}]_{\mathrm{eq}}^2-k_\mathrm{r}'[\mathrm{A}_2]_{\mathrm{eq}}\right\}$$

$$\approx-\left\{\left(k_\mathrm{r}'+4k_\mathrm{r}[\mathrm{A}]_{\mathrm{eq}}\right)x+k_\mathrm{r}[\mathrm{A}]_{\mathrm{eq}}^2-k_\mathrm{r}'[\mathrm{A}_2]_{\mathrm{eq}}\right\}$$

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.

$$\int\frac{\mathrm{d}w}{aw+b}=\frac{1}{a}\ln\left(aw+b\right)$$

$$\int\frac{\mathrm{d}x}{\left(k_\mathrm{r}'+4k_\mathrm{r}[\mathrm{A}]_{\mathrm{eq}}\right)x+k_\mathrm{r}[\mathrm{A}]_{\mathrm{eq}}^2-k_\mathrm{r}'[\mathrm{A}_2]_{\mathrm{eq}}}=-\int\mathrm{d}t$$

$$\frac{1}{\left(k_\mathrm{r}'+4k_\mathrm{r}[\mathrm{A}]_{\mathrm{eq}}\right)}\ln\left\{\left(k_\mathrm{r}'+4k_\mathrm{r}[\mathrm{A}]_{\mathrm{eq}}\right)x+k_\mathrm{r}[\mathrm{A}]_{\mathrm{eq}}^2-k_\mathrm{r}'[\mathrm{A}_2]_{\mathrm{eq}}\right\}=-t+\text{constant.}$$

Let $\ln\left(\frac{y}{y_0}\right)=-\left(k_\mathrm{r}'+4k_\mathrm{r}[\mathrm{A}]_{\mathrm{eq}}\right)t$ where $y=\left(k_\mathrm{r}'+4k_\mathrm{r}[\mathrm{A}]_{\mathrm{eq}}\right)x+k_\mathrm{r}[\mathrm{A}]_{\mathrm{eq}}^2-k_\mathrm{r}'[\mathrm{A}_2]_{\mathrm{eq}}$

Then $y=y_0\mathrm{e}^{-\left(k_\mathrm{r}'+4k_\mathrm{r}[\mathrm{A}]_{\mathrm{eq}}\right)t}$

Comparison of the above exponential to the decay equation $y=y_0\mathrm{e}^{-t/\tau}$ reveals that

$$\tau=\boxed{\frac{1}{k_\mathrm{r}'+4k_\mathrm{r}[\mathrm{A}]_{\mathrm{eq}}}}$$

Comment. Note that this equation can be used as the basis of an alternate derivation of the equation discussed in Problem 20C.5. The manipulations use the facts that $K=[\mathrm{A}_2]_{\mathrm{eq}}/[\mathrm{A}]_{\mathrm{eq}}^2=k_\mathrm{r}/k_\mathrm{r}'$ 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

$$[\mathrm{A}]_{\mathrm{tot}}=[\mathrm{A}]_{\mathrm{eq}}+\frac{2k_\mathrm{r}}{k_\mathrm{r}'}[\mathrm{A}]_{\mathrm{eq}}^2 \qquad \text{or} \qquad \frac{2k_\mathrm{r}}{k_\mathrm{r}'}[\mathrm{A}]_{\mathrm{eq}}^2+[\mathrm{A}]_{\mathrm{eq}}-[\mathrm{A}]_{\mathrm{tot}}=0$$

This quadratic equation can be solved for $[\mathrm{A}]_{\mathrm{eq}}$.

$$[\mathrm{A}]_{\mathrm{eq}}=\frac{k_\mathrm{r}'}{4k_\mathrm{r}}\left(\sqrt{1+\frac{8k_\mathrm{r}[\mathrm{A}]_{\mathrm{tot}}}{k_\mathrm{r}'}}-1\right)$$

Substitution of this equation into $\frac{1}{\tau^2}=\left(k_\mathrm{r}'+4k_\mathrm{r}[\mathrm{A}]_{\mathrm{eq}}\right)^2$ and some algebraic manipulation yields the result of Problem 20C.5: $\frac{1}{\tau^2}=k_\mathrm{r}'^2+8k_\mathrm{r}k_\mathrm{r}'[\mathrm{A}]_{\mathrm{tot}}$

20D The Arrhenius equation

Answers to discussion question

D20D.2 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

$$E_\mathrm{a} = RT^2\left(\frac{\mathrm{d}\ln k}{\mathrm{d}T}\right) \text{ [20D.3]}$$

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 (Section 8A) is playing a significant role in the reaction. In biological reactions it might signal that an enzyme has undergone a structural change and has become less efficient. A reaction with a very small or zero activation energy, so that $k_\mathrm{r} = A$, such as for some radical recombination reactions in the gas phase, has a rate that is largely temperature independent.

Solutions to exercises

E20D.1(b) The Arrhenius equation for two different temperatures can be rearranged to yield the activation energy:

$$E_\mathrm{a} = \frac{R\ln\dfrac{k_{\mathrm{r},2}}{k_{\mathrm{r},1}}}{\left(\dfrac{1}{T_1}-\dfrac{1}{T_2}\right)} = \frac{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\ln\dfrac{4.01\times10^{-2}}{2.25\times10^{-3}}}{\left(\dfrac{1}{(273+29)\ \mathrm{K}}-\dfrac{1}{(273+37)\ \mathrm{K}}\right)}$$

$$= \boxed{5.62\times10^4\ \mathrm{J\ mol^{-1}}} = \boxed{56.2\ \mathrm{kJ\ mol^{-1}}}$$

With the activation energy in hand, the pre-exponential factor can be found from either rate constant by rearranging eqn. 20D.4.

$$A = k_\mathrm{r}\mathrm{e}^{E_\mathrm{a}/RT} = (2.25\times10^{-2}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}})\mathrm{e}^{5.62\times10^4\ \mathrm{J\ mol^{-1}}/(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(273+29)\ \mathrm{K}}$$

$$A = \boxed{1.19\times10^8\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}}$$

Computing *A* from both provides a useful check on the calculation.

$$A = k_\mathrm{r}\mathrm{e}^{E_\mathrm{a}/RT} = (4.01\times10^{-2}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}})\mathrm{e}^{5.62\times10^4\ \mathrm{J\ mol^{-1}}/(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(273+37)\ \mathrm{K}}$$

$$A = \boxed{1.19\times10^8\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}}$$

E20D.2(b) Proceed as in Exercise 20D.1(b):

$$E_\mathrm{a} = \frac{R\ \ln\left(\dfrac{k_\mathrm{r}(T_2)}{k_\mathrm{r}(T_1)}\right)}{\left(\dfrac{1}{T_1}-\dfrac{1}{T_2}\right)} = \frac{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times\ln 2}{\dfrac{1}{298\,\mathrm{K}}-\dfrac{1}{308\,\mathrm{K}}} = \boxed{53\,\mathrm{kJ\,mol^{-1}}}$$

Solutions to problems

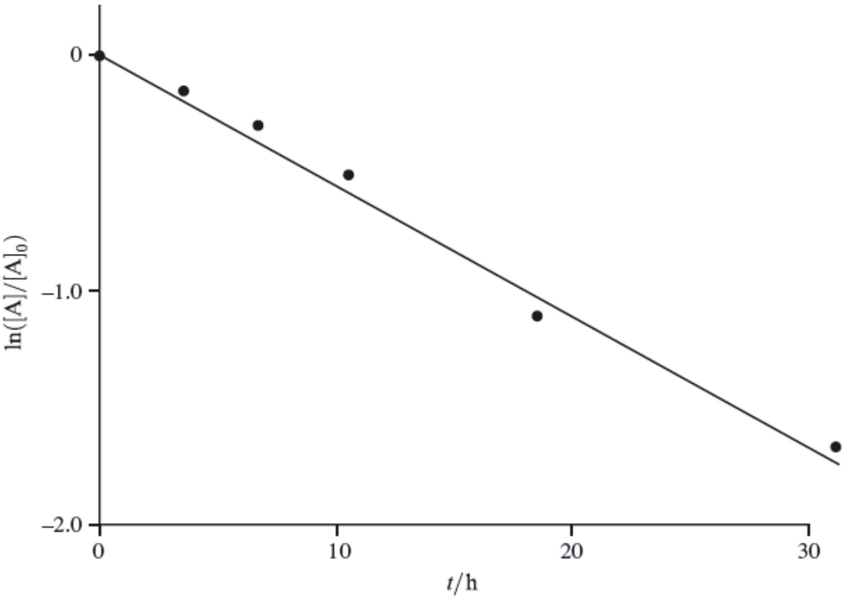
P20D.2 A simple but practical approach is to make an initial guess at the order by observing whether the half-life of the reaction appears to depend on concentration. If it does not, the reaction is first-order; otherwise refer to Table 20B.3. Visual inspection of the data seems to indicate that the half-life is roughly independent of the concentration. Therefore, we first try to fit the data to eqn. 20B.1:

$$\ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right) = -k_\mathrm{r}t$$

As in Example 20B.1 we plot $\ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right)$ against time to see if a straight line is obtained. We draw up the following table (A = $(\mathrm{CH_3})_3\mathrm{CBr}$):

t / h	0	3.15	6.20	10.00	18.30	30.80
$[\mathrm{A}]/(10^{-2}\,\mathrm{mol\,dm^{-3}})$	10.39	8.96	7.76	6.39	3.53	2.07
$\frac{[\mathrm{A}]}{[\mathrm{A}]_0}$	1	0.862	0.747	0.615	0.340	0.199
$\ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right)$	0	–0.148	–0.292	–0.486	–1.080	–1.613
$\left(\frac{1}{[\mathrm{A}]}\right)/(\mathrm{dm^3\,mol^{-1}})$	9.62	11.16	12.89	15.65	28.3	48.3

Figure 20D.1



The data are plotted in Fig. 20D.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:

$$k_\mathrm{r} = 0.0542\,\mathrm{h^{-1}} = \boxed{1.51\times10^{-5}\ \mathrm{s^{-1}}}$$

At 43.8 h

$$\ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right) = -(0.0542\ \mathrm{h^{-1}})\times(43.8\ \mathrm{h}) = -2.374$$

$$[\mathrm{A}] = (10.39\times10^{-2}\ \mathrm{mol\,dm^{-3}})\times \mathrm{e}^{-2.359} = \boxed{9.67\times10^{-3}\,\mathrm{mol\,dm^{-3}}}$$

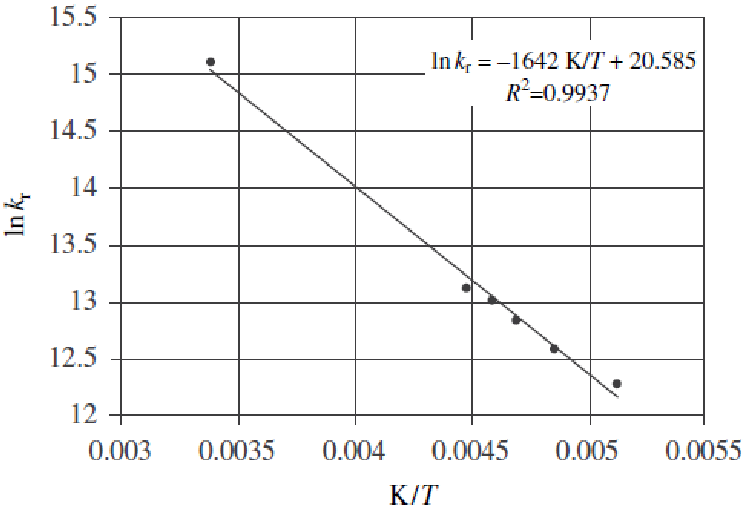
P20D.4 The Arrhenius expression for the rate constant is (eqn. 20D.1)

$$\ln k_r = \ln A - E_a/RT$$

A plot of ln k_r versus $1/T$ will have slope $-E_a/R$ and y-intercept ln A. The transformed data and plot (Fig. 85.2) follow:

T / K	295	223	218	213	206	200	195
$10^{-6}k_r/(\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$	3.55	0.494	0.452	0.379	0.295	0.241	0.217
$\ln k_r/(\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$	15.08	13.11	13.02	12.85	12.59	12.39	12.29
10^{-3} K / T	3.39	4.48	4.59	4.69	4.85	5.00	5.13

Figure 20D.2



So $E_a = -(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (-1642\ \text{K}) = 1.37\times10^4\ \text{J mol}^{-1} = \boxed{13.7\ \text{kJ mol}^{-1}}$

and $A = \text{e}^{20.585}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} = \boxed{8.7\times10^8\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}$

20E Reaction mechanisms

Answers to discussion questions

D20E.2 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

D20E.4 Refer to Table 20B.3. We will consider only reactions whose rates depend on the concentration of a single reactant.

In a first-order reaction, the rate of reaction is directly proportional to the concentration of the reactant:

$v = k_r[A]$ and $\ln [A] = \ln [A]_0 - k_r t$ [20B.1]

A plot of the logarithm of reactant concentration against time is a straight line.

In a zero-order reaction, the rate of reaction is constant, independent of the reactant concentration:

$v = k_r$ and $[A] = [A]_0 - k_r t$ [based on Table 20D.3]

A plot of the reactant concentration itself against time is a straight line.

In a second-order reaction, the rate of reaction is proportional to the square of the reactant concentration:

$v = k_r[A]^2$ and $\dfrac{1}{[A]} = \dfrac{1}{[A]_0} + k_r t$

A plot of the reciprocal of reactant concentration against time is a straight line.

Reaction orders need not be integers, except for elementary reactions. Indeed, reaction orders can change during the course of the reaction. Consider the zero-order reaction mentioned in the text (Section 20A.2(c)), the decomposition of phosphine on hot tungsten. As long as enough phosphine is present, the rate of reaction is independent of that concentration; what limits the rate is the availability of catalytic sites on the tungsten. Clearly the integrated rate law for a zero-order reaction cannot be correct at long times, where it would predict negative concentrations. Before that unphysical situation would occur, the concentration of the reactant drops to such an extent that ***it*** limits the rate of reaction, and the reaction order changes from zero to a non-zero value. The text's treatment of the Lindemann–Hinshelwood mechanism (Section 20F.1) also illustrates how a reaction order can change from first- to second-order over the course of a reaction.

D20E.6 Yes, a negative activation energy is quite possible for composite reactions. The rate constant of a composite reaction can be a product or ratio of rate constants and equilibrium constants of elementary reactions that contribute to the composite reaction, as illustrated in Section 20E.5. In general, elementary reactions that have a positive activation energy whose rate constants appear in the denominator of a composite rate constant tend to reduce the activation energy of the overall reaction, as illustrated in eqn 20E.13. There is no reason why that reduction cannot be to a negative value.

The most common molecular interpretation of the activation energy is as the "height" of an energy barrier that must be overcome by reactants in order to form products, as discussed in connection with collision theory in Section 21A. Among the limitations of collision theory is that it is only applicable to elementary reactions, those which can possibly occur in one collision or reactive molecular encounter. Thus, it is no surprise that this interpretation fails to apply to composite reactions. The more general interpretation of the activation energy, as a measure of the temperature-dependence of the reaction rate (eqn. 20D.3), does apply.

Question. Show that the following mechanism leads to an overall negative activation energy for the rate of formation of P if $E_a(2) > E_a(3)$.

$A \rightarrow I$ k_1 (slow)

$I \rightarrow B$ k_2

$I \rightarrow P$ k_3

Solutions to exercises

E20E.1(b) Call the stable double helix S and the unstable one U. The rate of the overall reaction is

$$v = \frac{d[S]}{dt} = k_2[U]$$

however, we cannot have the concentration of an intermediate in the overall rate law.

(i) Assume a pre-equilibrium with

$K = \dfrac{[U]}{[A][B]}$, which implies $[U] = K[A][B]$

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:

$$\frac{\mathrm{d}[\mathrm{U}]}{\mathrm{d}t} \approx 0 = k_1[\mathrm{A}][\mathrm{B}] - k_1'[\mathrm{U}] - k_2[\mathrm{U}]$$

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 $k_1' >> k_2$, 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 $k_1' << k_2$, in which case $k_{\mathrm{eff}} \approx k_1$, implying that the first step is rate limiting.

E20E.2(b) Let the steps be

$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{I}$ (fast: k_{a}, k_{a}')

and $\mathrm{I} \rightarrow \mathrm{P}$ (k_{b})

Then the rate of reaction is

$$v = \frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = k_{\mathrm{b}}[\mathrm{I}]$$

Applying the pre-equilibrium approximation yields

$$\frac{[\mathrm{I}]}{[\mathrm{A}][\mathrm{B}]} = K = \frac{k_{\mathrm{a}}}{k_{\mathrm{a}}'} \quad \text{so} \quad [\mathrm{I}] = \frac{k_{\mathrm{a}}[\mathrm{A}][\mathrm{B}]}{k_{\mathrm{a}}'}$$

and $v = \dfrac{k_{\mathrm{a}}k_{\mathrm{b}}[\mathrm{A}][\mathrm{B}]}{k_{\mathrm{a}}'} = k_{\mathrm{r}}[\mathrm{A}][\mathrm{B}]$ with $k_{\mathrm{r}} = \dfrac{k_{\mathrm{a}}k_{\mathrm{b}}}{k_{\mathrm{a}}'}$

Thus $E_{\mathrm{a}} = E_{\mathrm{a,a}} + E_{\mathrm{a,b}} - E_{\mathrm{a,a}}'$ [20E.13] = $(27 + 15 - 35)\ \mathrm{kJ\ mol^{-1}} = \boxed{7\ \mathrm{kJ\ mol^{-1}}}$

Solutions to problems

P20E.2 Using spreadsheet software to evaluate eqns. 20E.4a, 20E.4b, and 20E.4c, one can draw up a plot [A], [I], and [P] against time. Figs. 20E.1(a), 20E.1(b), and 20E.1(c) show plots of these concentrations (scaled by $[\mathrm{A}]_0$) vs. the dimensionless time $k_{\mathrm{b}}t$. What differs in the three plots is the ratio of rate constants $k_{\mathrm{a}}/k_{\mathrm{b}}$; it drops from 0.99 in the first plot (to avoid indeterminate forms in eqns. 20E.4b and 20E.4c when $k_{\mathrm{a}}/k_{\mathrm{b}} = 1$) to 0.10 in the second and 0.01 in the third. The curves for A and P are remarkably similar in all three plots, although the time scale becomes successively longer. (After all, [A] decays with rate constant k_{a}, which becomes successively smaller compared to k_{b}.) The dramatic difference is in the curve for I, whose concentration becomes successively more suppressed. In each successive plot, I is consumed more and more quickly compared to the rate at which it is formed. The steady-state approximation, illustrated in Fig. 20E.2 of the main text, becomes successively a better approximation.

Figure 20E.1(a)

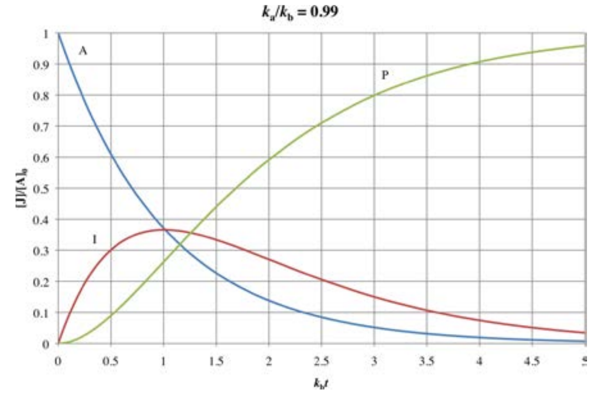


Figure 20E.1(b)

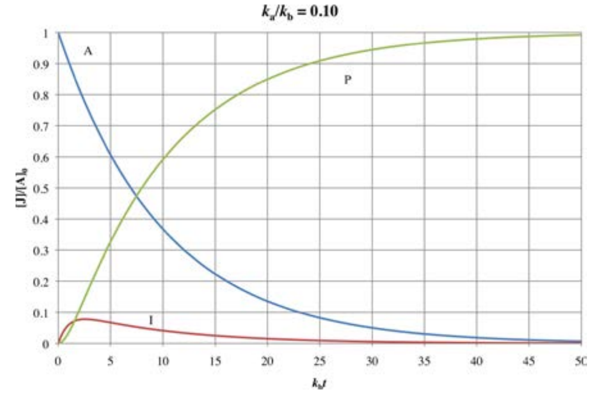
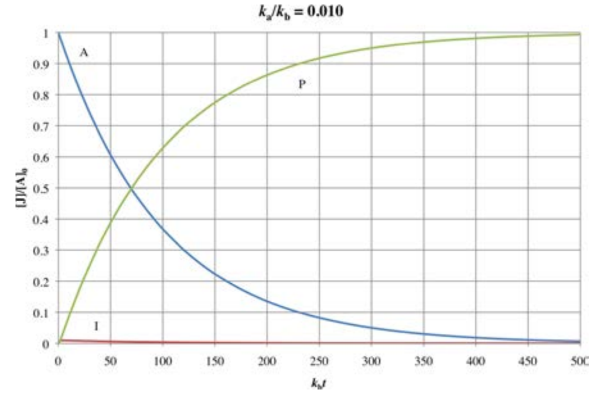


Figure 20E.1(c)



P20E.4 Let the forward rates be written as

$$r_1 = k_1[\mathrm{A}], \qquad r_2 = k_2[\mathrm{B}], \qquad r_3 = k_3[\mathrm{C}]$$

and the reverse rates as

$$r_1' = k_1'[\mathrm{B}], \qquad r_2' = k_2'[\mathrm{C}], \qquad r_3' = k_3'[\mathrm{D}]$$

The net rates are then

$$R_1 = k_1[\mathrm{A}] - k_1'[\mathrm{B}], \qquad R_2 = k_2[\mathrm{B}] - k_2'[\mathrm{C}], \qquad R_3 = k_3[\mathrm{C}] - k_3'[\mathrm{D}]$$

But $[\mathrm{A}] = [\mathrm{A}]_0$ and $[\mathrm{D}] = 0$, so that the steady-state equations for the net rates of the individual steps are

$$k_1[\mathrm{A}]_0 - k_1'[\mathrm{B}] = k_2[\mathrm{B}] - k_2'[\mathrm{C}] = k_3[\mathrm{C}]$$

From the second of these equations we find

$$[\mathrm{C}] = \frac{k_2[\mathrm{B}]}{k_2' + k_3}$$

After inserting this expression for $[\mathrm{C}]$ into the first of the steady-state equations we obtain

$$[\mathrm{B}]=\frac{k_1[\mathrm{A}]_0+k_2'[\mathrm{C}]}{k_1'+k_2}=\frac{k_1[\mathrm{A}]_0+k_2'\left(\dfrac{k_2[\mathrm{B}]}{k_2'+k_3}\right)}{k_1'+k_2}$$

which yields, upon isolating [B],

$$[\mathrm{B}]=[\mathrm{A}]_0\times\frac{k_1}{k_1'+k_2-\left(\frac{k_2k_2'}{k_2'+k_3}\right)}$$

Thus, at the steady-state

$$R_1=R_2=R_3=[\mathrm{A}]_0k_1\times\left(1-\frac{k_1}{k_1'+k_2-\left(\frac{k_2k_2'}{k_2'+k_3}\right)}\right)=\boxed{\frac{k_1k_2k_3[\mathrm{A}]_0}{k_1'k_2'+k_1'k_3+k_2k_3}}$$

Comment. At steady-state, not only are the net rates of reactions 1, 2, and 3 steady but so are the concentrations [B] and [C]. That is,

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t}=k_1[\mathrm{A}]_0-(k_1'+k_2)[\mathrm{B}]+k_2'[\mathrm{C}]\approx 0$$

and $$\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t}=k_2[\mathrm{B}]-(k_2'+k_3)[\mathrm{C}]\approx 0$$

In fact, another approach to solving the problem is to solve *these* equations for [B] and [C].

P20E.6 **(a)** For the mechanism

$$hhhh...\underset{k_{\mathrm{a}}'}{\overset{k_{\mathrm{a}}}{\rightleftarrows}}hchh...$$

$$hchh...\underset{k_{\mathrm{b}}'}{\overset{k_{\mathrm{b}}}{\rightleftarrows}}cccc...$$

the rate equations are

$$\frac{\mathrm{d}[hhhh...]}{\mathrm{d}t}=-k_{\mathrm{a}}[hhhh...]+k_{\mathrm{a}}'[hchh...]$$

$$\frac{\mathrm{d}[hchh...]}{\mathrm{d}t}=k_{\mathrm{a}}[hhhh...]-k_{\mathrm{a}}'[hchh...]-k_{\mathrm{b}}[hchh...]+k_{\mathrm{b}}'[cccc...]$$

$$\frac{\mathrm{d}[cccc...]}{\mathrm{d}t}=k_{\mathrm{b}}[hchh...]-k_{\mathrm{b}}'[cccc...]$$

(b) Apply the steady-state approximation to the intermediate:

$$\frac{\mathrm{d}[hchh...]}{\mathrm{d}t}=k_{\mathrm{a}}[hhhh...]-k_{\mathrm{a}}'[hchh...]-k_{\mathrm{b}}[hchh...]+k_{\mathrm{b}}'[cccc...]=0$$

so $$[hchh...]=\frac{k_{\mathrm{a}}[hhhh...]+k_{\mathrm{b}}'[cccc...]}{k_{\mathrm{a}}'+k_{\mathrm{b}}}$$

Therefore, $$\frac{\mathrm{d}[hhhh...]}{\mathrm{d}t}=-k_{\mathrm{a}}[hhhh...]+k_{\mathrm{a}}'\left(\frac{k_{\mathrm{a}}[hhhh...]+k_{\mathrm{b}}'[cccc...]}{k_{\mathrm{a}}'+k_{\mathrm{b}}}\right)$$

$$=[hhhh...]\left(\frac{k_{\mathrm{a}}k_{\mathrm{a}}'-k_{\mathrm{a}}(k_{\mathrm{a}}'+k_{\mathrm{b}})}{k_{\mathrm{a}}'+k_{\mathrm{b}}}\right)+k_{\mathrm{a}}'\left(\frac{k_{\mathrm{b}}'[cccc...]}{k_{\mathrm{a}}'+k_{\mathrm{b}}}\right)$$

$$=-\frac{k_{\mathrm{a}}k_{\mathrm{b}}}{k_{\mathrm{a}}'+k_{\mathrm{b}}}[hhhh...]+\frac{k_{\mathrm{a}}'k_{\mathrm{b}}'}{k_{\mathrm{a}}'+k_{\mathrm{b}}}[cccc...]$$

This rate expression may be compared to that given in the text [Section 21.4] for the mechanism $\mathrm{A}\underset{k_{\mathrm{r}}'}{\overset{k_{\mathrm{r}}}{\rightleftarrows}}\mathrm{B}$

Here $hhhh...\underset{k_{\mathrm{eff}}'}{\overset{k_{\mathrm{eff}}}{\rightleftarrows}}cccc...$ with $$k_{\mathrm{eff}}=\frac{k_{\mathrm{a}}k_{\mathrm{b}}}{k_{\mathrm{a}}'+k_{\mathrm{b}}}\quad k_{\mathrm{eff}}'=\frac{k_{\mathrm{a}}'k_{\mathrm{b}}'}{k_{\mathrm{a}}'+k_{\mathrm{b}}}$$

20F Examples of reaction mechanisms

Answers to discussion questions

D20F.2 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

$$\langle N\rangle = 1 + k_r t[\mathrm{A}]_0 \quad [20\mathrm{F}.12]$$

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:

$$\langle N\rangle = 2k_r[\mathrm{M}][\mathrm{In}]^{-1/2} \quad [20\mathrm{F}.16]$$

where $k_r = (1/2)k_p(fk_ik_t)^{-1/2}$, 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.

Solutions to exercises

E20F.1(b) $\dfrac{1}{k_r} = \dfrac{k_a'}{k_a k_b} + \dfrac{1}{k_a p_A}$ [analogous to 20F.8]

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 $$k_a = \left(\frac{1}{p_1} - \frac{1}{p_2}\right)\left(\frac{1}{k_r(p_1)} - \frac{1}{k_r(p_2)}\right)^{-1}$$

$$= \left(\frac{1}{1.09\times10^3\ \mathrm{Pa}} - \frac{1}{25\,\mathrm{Pa}}\right)\times\left(\frac{1}{1.7\times10^{-3}\ \mathrm{s}^{-1}} - \frac{1}{2.2\times10^{-4}\ \mathrm{s}^{-1}}\right)^{-1}$$

$$= \boxed{9.9\times10^{-6}\mathrm{s}^{-1}\ \mathrm{Pa}^{-1}} = \boxed{9.9\ \mathrm{s}^{-1}\ \mathrm{MPa}^{-1}}.$$

E20F.2(b) The degree of polymerization is [20F.12]

$$\langle N\rangle = 1 + k_r t[\mathrm{A}]_0$$

$$= 1 + (2.80\times10^{-2}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}})\times 10.00\ \mathrm{h}\times 3600\ \mathrm{s\ h^{-1}}\times 5.00\times10^{-2}\ \mathrm{mol\ dm^{-3}}$$

$$= \boxed{51.4}.$$

The fraction condensed is related to the degree of polymerization by

$$\langle N\rangle = \frac{1}{1-p} \qquad \text{so} \qquad p = \frac{\langle N\rangle - 1}{\langle N\rangle} = \frac{51.4-1}{51.4} = \boxed{0.981}$$

E20F.3(b) The kinetic chain length varies with concentration as

$\nu = k_r[\mathrm{M}][\mathrm{In}]^{-1/2}$ [20F.13]

so the ratio of kinetic chain lengths under different concentrations is

$$\frac{\nu_2}{\nu_1} = \frac{[\mathrm{M}]_2}{[\mathrm{M}]_1} \times \left(\frac{[\mathrm{In}]_1}{[\mathrm{In}]_2}\right)^{1/2} = 5.0 \times (10.0)^{1/2} = \boxed{15.8}$$

Solutions to problems

P20F.2 In termination by disproportionation, the chain carriers do not combine. The average number of monomers in a polymer molecule equals the average number in a chain carrier when it terminates, namely, the kinetic chain length, ν.

$$\langle N \rangle = \nu = \boxed{k_r[\cdot\mathrm{M}][\mathrm{In}]^{-1/2}}$$

Comment. Contrast this result to the reasoning before eqn. 20F.16 in the text, in which the average number is the **sum** of the average numbers of a pair of combining radicals.

20G Photochemistry

Answers to discussion questions

D20G.2 The shortening of the lifetime of an excited state is called quenching. Quenching effects may be studied by monitoring the emission from the excited state that is involved in the photochemical process. The addition of a quencher opens up an additional channel for the deactivation of the excited singlet state.

Three common mechanisms for bimolecular quenching of an excited singlet (or triplet) state are:

Collisional deactivation: $\mathrm{S}^* + \mathrm{Q} \rightarrow \mathrm{S} + \mathrm{Q}$

Energy transfer: $\mathrm{S}^* + \mathrm{Q} \rightarrow \mathrm{S} + \mathrm{Q}^*$

Electron transfer: $\mathrm{S}^* + \mathrm{Q} \rightarrow \mathrm{S}^+ + \mathrm{Q}^-$ or $\mathrm{S}^- + \mathrm{Q}^+$

Collisional quenching is particularly efficient when Q is a heavy species, such as an iodide ion, which receives energy from S^* and then decays primarily by internal conversion to the ground state. Pure collisional quenching can be detected by the appearance of vibrational and rotational excitation in the spectrum of the acceptor.

In many cases, it is possible to prove that energy transfer is the predominant mechanism of quenching if the excited state of the acceptor fluoresces or phosphoresces at a characteristic wavelength. In a pulsed laser experiment, the rise in fluorescence intensity from Q^* with a characteristic time which is the same as that for the decay of the fluorescence of S^* is often taken as an indication of energy transfer from S to Q.

Electron transfer can be studied by time-resolved spectroscopy. The oxidized and reduced products often have electronic absorption spectra distinct from those of their neutral parent compounds. Therefore, the rapid appearance of such known features in the absorption spectrum after excitation by a laser pulse may be taken as an indication of quenching by electron transfer.

Solutions to exercises

E20G.1(b) The quantum yield tells us that each mole of photons absorbed causes 1.2×10^2 moles of A to react [20G.1a]; the stoichiometry tells us that 1 mole of B is formed for every mole of A which reacts. From the yield of 1.77 mmol B, we infer that 1.77 mmol A reacted, caused by the absorption of

$$\frac{(1.77\times10^{-3}\ \mathrm{mol})\times(6.022\times10^{23}\ \mathrm{einstein}^{-1})}{1.2\times10^{2}\ \mathrm{mol\,einstein}^{-1}} = \boxed{4.4\times10^{18}}\ \text{photons}$$

E20G.2(b) The Stern-Volmer equation [20G.8] relates the ratio of fluorescence quantum yields in the absence and presence of quenching

$$\frac{\phi_{F,0}}{\phi_F}=1+\tau_0 k_Q[Q]=\frac{I_{F,0}}{I_F}$$

The last equality reflects the fact that fluorescence intensities are proportional to quantum yields. Solve this equation for [Q]:

$$[Q]=\frac{(I_{F,0}/I_F)-1}{\tau_0 k_Q}=\frac{(100/75)-1}{(3.5\times10^{-9}\ \mathrm{s})\times(2.5\times10^{9}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}})}=\boxed{0.038\ \mathrm{mol\ dm^{-3}}}$$

Solutions to problems

P20G.2 The rate of reaction is the rate at which ozone absorbs photons times the quantum yield. The rate at which ozone absorbs photons is the rate at which photons impinge on the ozone times the fraction of photons absorbed. That fraction is 1 – *T*, where *T* is the transmittance. *T* is related to the absorbance *A* by

$$A=-\log T=\varepsilon cL \qquad \text{so} \qquad 1-T=1-10^{-\varepsilon cL}$$

and $$1-T=1-10^{-\{(260\,\mathrm{dm^3\ mol^{-1}\ cm^{-1}})\times(8\times10^{-9}\ \mathrm{mol\,dm^{-3}})\times(10^5\ \mathrm{cm})\}}=0.38$$

If we let *F* stand for the flux of photons (the rate at which photons impinge on our sample of ozone), then the rate of reaction is

$$v=\phi(1-T)F=(0.94)\times(0.38)\times\frac{(1\times10^{14}\ \mathrm{cm^{-2}\ s^{-1}})\times(1000\,\mathrm{cm^3\ dm^{-3}})}{(6.022\times10^{23}\ \mathrm{mol^{-1}})\times(10^5\ \mathrm{cm})}$$

$$=\boxed{5.9\times10^{-13}\ \mathrm{mol\,dm^{-3}\,s^{-1}}}$$

P20G.4

$$\mathrm{M}+h\nu_i\to\mathrm{M}^*, \qquad I_{abs}\ [\mathrm{M}=\text{benzophenone}]$$

$$\mathrm{M}^*+\mathrm{Q}\to\mathrm{M}+\mathrm{Q}, \qquad k_Q$$

$$\mathrm{M}^*\to\mathrm{M}+h\nu_f, \qquad k_F$$

$$\frac{d[\mathrm{M}^*]}{dt}=I_{abs}-k_F[\mathrm{M}^*]-k_Q[\mathrm{Q}][\mathrm{M}^*]\approx0\ \ \text{[steady state]}$$

and hence $$[\mathrm{M}^*]=\frac{I_{abs}}{k_F+k_Q[\mathrm{Q}]}$$

Then $$I_F=[\mathrm{M}^*]=\frac{k_F I_{abs}}{k_F+k_Q[\mathrm{Q}]}$$

and so $$\boxed{\frac{1}{I_F}=\frac{1}{I_{abs}}+\frac{k_Q[\mathrm{Q}]}{I_F I_{abs}}}$$

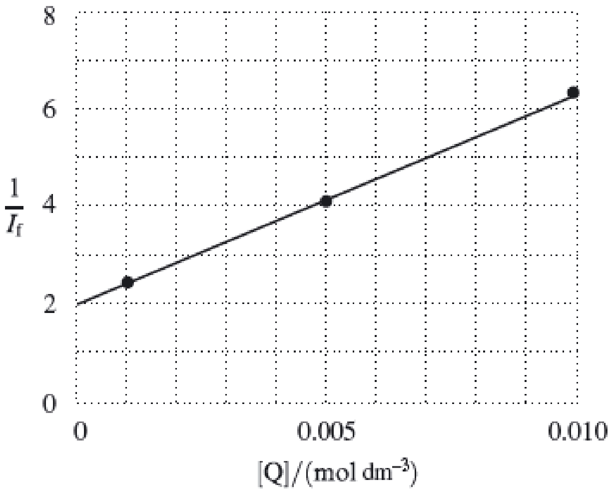
If the exciting light is extinguished, [M*], and hence I_F, decays as $e^{-k_F t}$ in the absence of a quencher. Therefore we can measure $k_Q/k_F I_{abs}$ from the slope of $1/I_F$ plotted against [Q], and then use k_F to determine k_Q.

We draw up the following table:

10^3[Q] / M	1	5	10
1 / I_F	2.4	4.0	6.3

The points are plotted in Fig. 20G.1.

Figure 20G.1



The intercept lies at 2.0, and so $I_{\text{abs}} = \frac{1}{2.0} = 0.50$. The slope is 430, and so

$$\frac{k_Q}{k_F I_{\text{abs}}} = 430\,\text{dm}^3\ \text{mol}^{-1}$$

Then, since $I_{\text{abs}} = 0.50$ and $k_F = \frac{\ln 2}{t_{1/2}}$

$$k_Q = (0.50)\times\left(430\,\text{dm}^3\ \text{mol}^{-1}\right)\times\left(\frac{\ln 2}{29\times10^{-6}\ \text{s}}\right) = \boxed{5.1\times10^6\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}$$

P20G.6 The efficiency of resonance energy transfer is given by [20G.9]

$$\eta_T = 1-\frac{\phi_F}{\phi_{F,0}} = 0.15$$

Förster theory relates this quantity to the distance R between donor-acceptor pairs by

$$\eta_T = \frac{R_0{}^6}{R_0{}^6+R^6}\quad [20\text{G}.10]$$

where R_0 is an empirical parameter listed in Table 20G.3. Solving for the distance yields

$$R = R_0\left(\frac{1}{\eta_T}-1\right)^{1/6} = (2.2\ \text{nm})\times\left(\frac{1}{0.15}-1\right)^{1/6} = \boxed{2.9\ \text{nm}}$$

P20G.8 We approach the lifetime via the efficiency of resonant energy transfer:

$$\eta_T = 1-\frac{\phi_F}{\phi_{F,0}}[20\text{G}.9] = 1-\frac{\tau}{\tau_0}$$

and $$\eta_T = \frac{R_0^6}{R_0^6+R^6}\quad [20\text{G}.10]$$

Equating these two expressions for η_T and solving for R gives:

$$\frac{R_0^6}{R_0^6+R^6} = 1-\frac{\tau}{\tau_0} = \frac{\tau_0-\tau}{\tau_0}\qquad \text{so}\qquad \frac{R_0^6+R^6}{R_0^6} = \frac{\tau_0}{\tau_0-\tau}$$

$$\left(\frac{R}{R_0}\right)^6 = \frac{\tau_0}{\tau_0-\tau}-1 = \frac{\tau_0-\tau_0+\tau}{\tau_0-\tau} = \frac{\tau}{\tau_0-\tau}\qquad \text{or}\qquad R = R_0\left(\frac{\tau}{\tau_0-\tau}\right)^{1/6}$$

$\tau/\tau_0 = 10\ \text{ps} / 10^3\ \text{ps} = 0.010$ and $R = 5.6\ \text{nm}\left(\frac{0.010}{1-0.010}\right)^{1/6} = \boxed{2.6\ \text{nm}}$

20H Enzymes

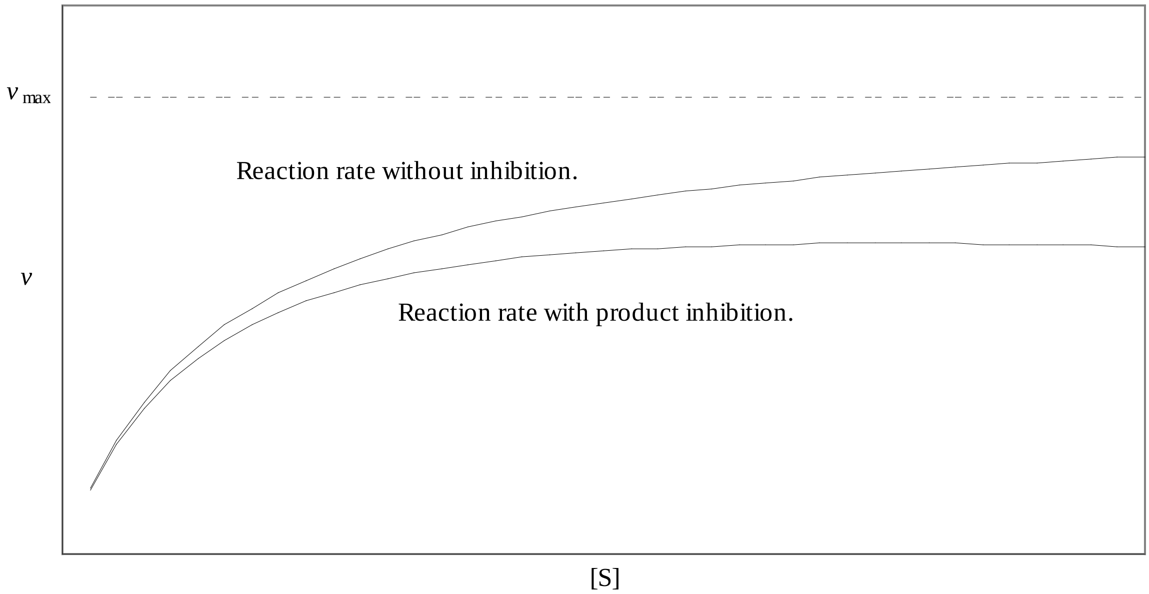
Answers to discussion questions

D20H.2 As temperature increases we expect the rate of an enzyme-catalyzed reaction to increase. However, at a sufficiently high temperature the enzyme **denatures** and a decrease in the reaction rate is observed. Temperature related denaturation is caused by the action of vigorous vibrational motion, which destroys secondary and tertiary protein structure. Electrostatic, internal hydrogen bonding, and van der Waals interactions that hold the protein in its active, folded shape are broken with the protein unfolding into a **random coil**. The active site and enzymatic activity is lost.

The rate of a particular enzyme-catalyzed reaction may also appear to decrease at high temperature in the special case in which an alternative substrate reaction, which has a relatively slow rate at low temperature, has the faster rate increase with increasing temperature. A temperature may be reached at which the alternative reaction predominates.

D20H.4 Figure 20H.1 is a sketch of the enzyme-catalyzed reaction rate against substrate concentration both with and without product inhibition. Inhibition reduces the reaction rate and lowers the maximum achievable reaction rate.

Figure 20H.1



Solutions to exercises

E20H.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

$$\frac{\mathrm{d[P]}}{\mathrm{d}t} = k_\mathrm{b}[\mathrm{HAH^+}][\mathrm{B}] = \boxed{k_\mathrm{b}K[\mathrm{HA}][\mathrm{H^+}][\mathrm{B}]}\,.$$

E20H.2(b) Since $\nu = \dfrac{\nu_{\max}}{1+K_{\mathrm{M}}/[\mathrm{S}]_0}$ [20H.3a],

$$\begin{aligned}\nu_{\max} &= \left(1+K_{\mathrm{M}}/[\mathrm{S}]_0\right)\nu \\ &= \left(1+0.032/0.875\right)\times\left(0.205\ \mathrm{mmol\ dm^{-3}\ s^{-1}}\right) \\ &= \boxed{0.212\ \mathrm{mmol\ dm^{-3}\ s^{-1}}}\end{aligned}$$

E20H.3(b) Eqn 20H.7 describes competitive inhibition as the case for which $\alpha = 1+[\mathrm{I}]/K_{\mathrm{I}}$ and $\alpha' = 1$. Thus,

$$\nu = \frac{\nu_{\max}}{1+\alpha K_{\mathrm{M}}/[\mathrm{S}]_0}.$$

By setting the ratio ν([I]=0)/ν([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%.

$$\frac{\nu\left([\mathrm{I}]=0\right)}{\nu\left([\mathrm{I}]\right)} = \frac{1+\alpha K_{\mathrm{M}}/[\mathrm{S}]_0}{1+K_{\mathrm{M}}/[\mathrm{S}]_0} = 4.00$$

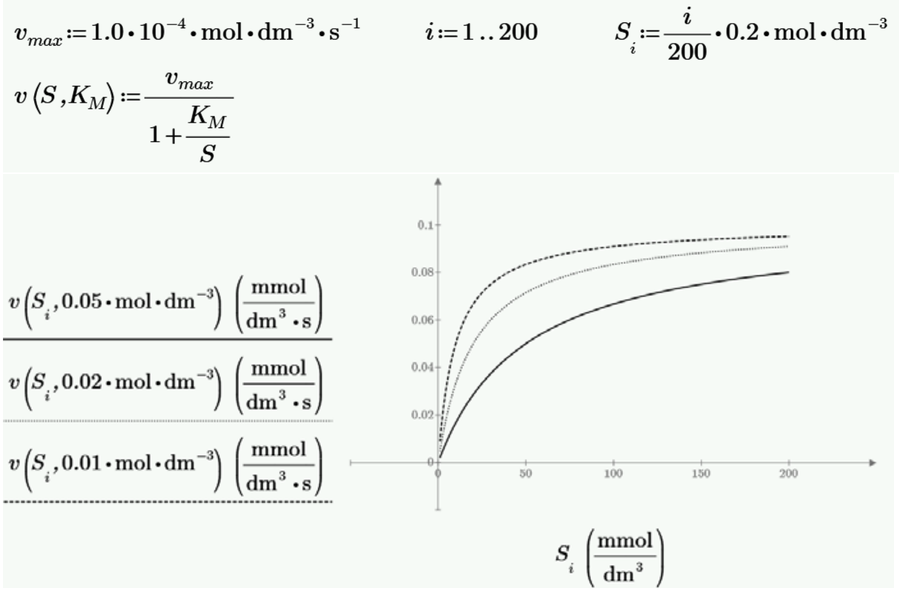
$$\begin{aligned}\alpha &= \frac{1.333\left(1+K_{\mathrm{M}}/[\mathrm{S}]_0\right)-1}{K_{\mathrm{M}}/[\mathrm{S}]_0} \\ &= \frac{4.00\left(1+7.5/1.0\right)-1}{7.5/1.0} = 4.40\end{aligned}$$

$$\begin{aligned}[\mathrm{I}] &= \left(\alpha-1\right)K_{\mathrm{I}} \\ &= 3.40\times\left(0.56\ \mathrm{mmol\ dm^{-3}}\right) = \boxed{1.90\ \mathrm{mmol\ dm^{-3}}}\end{aligned}$$

Solutions to problems

P20H.2 Mathcad Prime 2 worksheets are present with easily changed parameters for studying the effect of property variations.

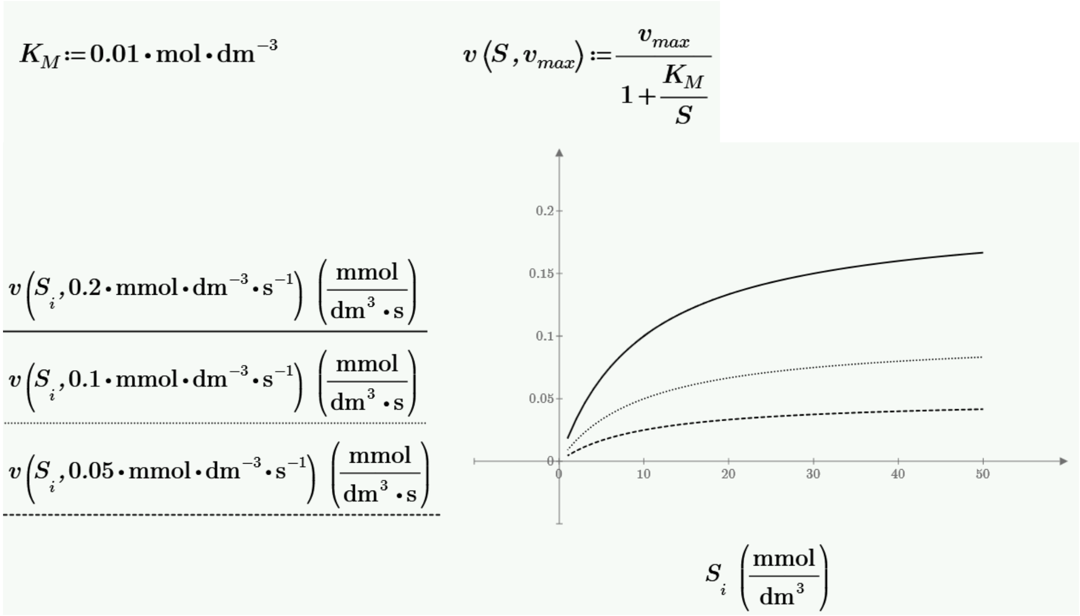
(a) $v_{\max}$ is constant:



$v_{max} := 1.0 \cdot 10^{-4} \cdot \mathrm{mol} \cdot \mathrm{dm}^{-3} \cdot \mathrm{s}^{-1}$ $i := 1\,..\,200$ $S_i := \dfrac{i}{200} \cdot 0.2 \cdot \mathrm{mol} \cdot \mathrm{dm}^{-3}$

$$v\left(S, K_M\right) := \frac{v_{max}}{1+\dfrac{K_M}{S}}$$

K_{M} is constant:

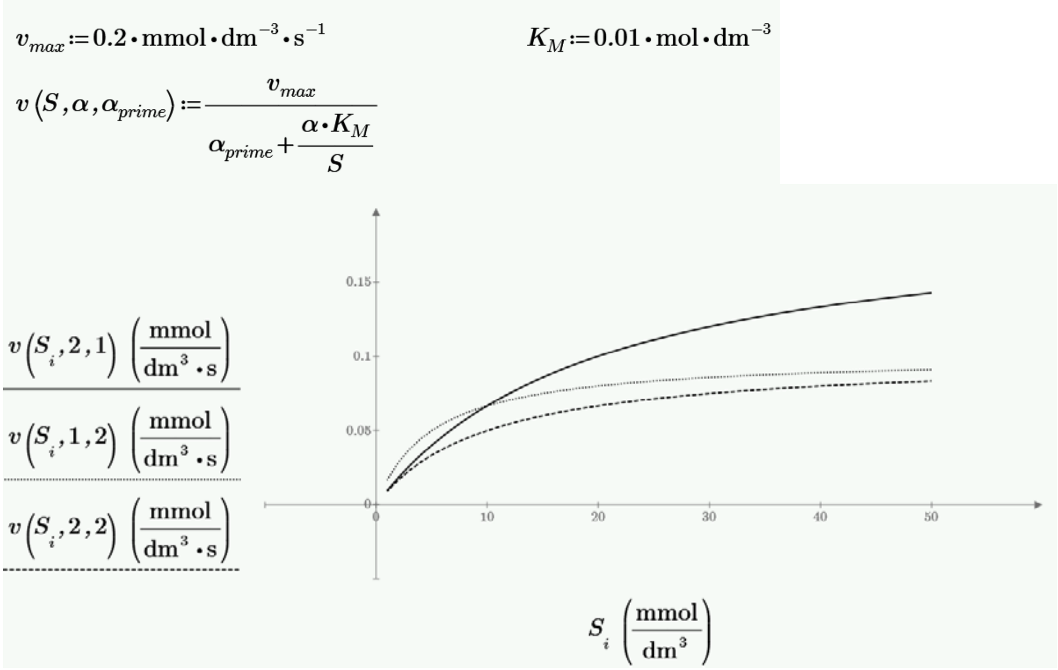


$$K_M := 0.01 \cdot \mathrm{mol} \cdot \mathrm{dm}^{-3} \qquad v(S, v_{max}) := \frac{v_{max}}{1 + \frac{K_M}{S}}$$

(b) Competitive inhibition: $\alpha > 1$ and $\alpha' = 1$

Uncompetitive inhibition: $\alpha = 1$ and $\alpha' > 1$

Non-competitive inhibition: $\alpha > 1$ and $\alpha' > 1$



$$v_{max} := 0.2 \cdot \mathrm{mmol} \cdot \mathrm{dm}^{-3} \cdot \mathrm{s}^{-1} \qquad K_M := 0.01 \cdot \mathrm{mol} \cdot \mathrm{dm}^{-3}$$

$$v(S, \alpha, \alpha_{prime}) := \frac{v_{max}}{\alpha_{prime} + \frac{\alpha \cdot K_M}{S}}$$

P20H.4 (a) $k_{\mathrm{cat}} = v_{\mathrm{max}} / [\mathrm{E}]_0$ [20H.4]

$$= \left(0.0224 \text{ mmol dm}^{-3} \text{ s}^{-1}\right) / \left(1.60 \times 10^{-6} \text{ mmol dm}^{-3}\right) = \boxed{1.40 \times 10^{4} \text{ s}^{-1}}$$

(b)

$\eta = k_{\mathrm{cat}} / K_{\mathrm{M}}$ [20H.5]

$$= \left(1.40 \times 10^{4} \text{ s}^{-1}\right) / \left(9.0 \times 10^{5} \text{ mol dm}^{-3}\right) = \boxed{0.015 \text{ dm}^{3} \text{ mol}^{-1} \text{ s}^{-1}}$$

Diffusion limits the **catalytic efficiency**, η, to a maximum of about 10^8–10^9 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'.

P20H.6 **(a)** We add to the Michaelis−Menten mechanism the inhibition by the substrate

$$\mathrm{SES} \rightleftharpoons \mathrm{ES} + \mathrm{S} \qquad K_\mathrm{I} = [\mathrm{ES}][\mathrm{S}]/[\mathrm{SES}]$$

where the inhibited enzyme, SES, forms when S binds to ES and, thereby, prevents the formation of product. This inhibition might possibly occur when S is at a very high concentration. Enzyme mass balance is written in terms of [ES], K_I, K_M (= [E][S]/[ES]), and [S]. (For practical purposes the free substrate concentration is replaced by $[\mathrm{S}]_0$ because the substrate is typically in large excess relative to the enzyme.)

$$\begin{aligned}[\mathrm{E}]_0 &= [\mathrm{E}] + [\mathrm{ES}] + [\mathrm{SES}] \\ &= \frac{K_\mathrm{M}[\mathrm{ES}]}{[\mathrm{S}]} + [\mathrm{ES}] + \frac{[\mathrm{ES}][\mathrm{S}]}{K_\mathrm{I}} \\ &= \left(1 + \frac{K_\mathrm{M}}{[\mathrm{S}]} + \frac{[\mathrm{S}]}{K_\mathrm{I}}\right)[\mathrm{ES}]\end{aligned}$$

Thus,

$$[\mathrm{ES}] = \frac{[\mathrm{E}]_0}{\left(1 + \frac{K_\mathrm{M}}{[\mathrm{S}]} + \frac{[\mathrm{S}]}{K_\mathrm{I}}\right)}$$

and the expression for the rate of product formation becomes

$$v = k_\mathrm{b}[\mathrm{ES}] = \frac{v_\mathrm{max}}{1 + \frac{K_\mathrm{M}}{[\mathrm{S}]_0} + \frac{[\mathrm{S}]_0}{K_\mathrm{I}}} \qquad \text{where} \qquad v_\mathrm{max} = k_\mathrm{b}[\mathrm{E}]_0 \,.$$

The denominator term $[\mathrm{S}]_0/K_\mathrm{I}$ reflects a reduced reaction rate caused by inhibition as the concentration of S becomes very large.

(b) To examine the effect that substrate inhibition has on the double reciprocal, **Lineweaver-Burk plot** of $1/v$ against $1/[\mathrm{S}]_0$ take the inverse of the above rate expression and compare it to the uninhibited expression [20H.3b]:

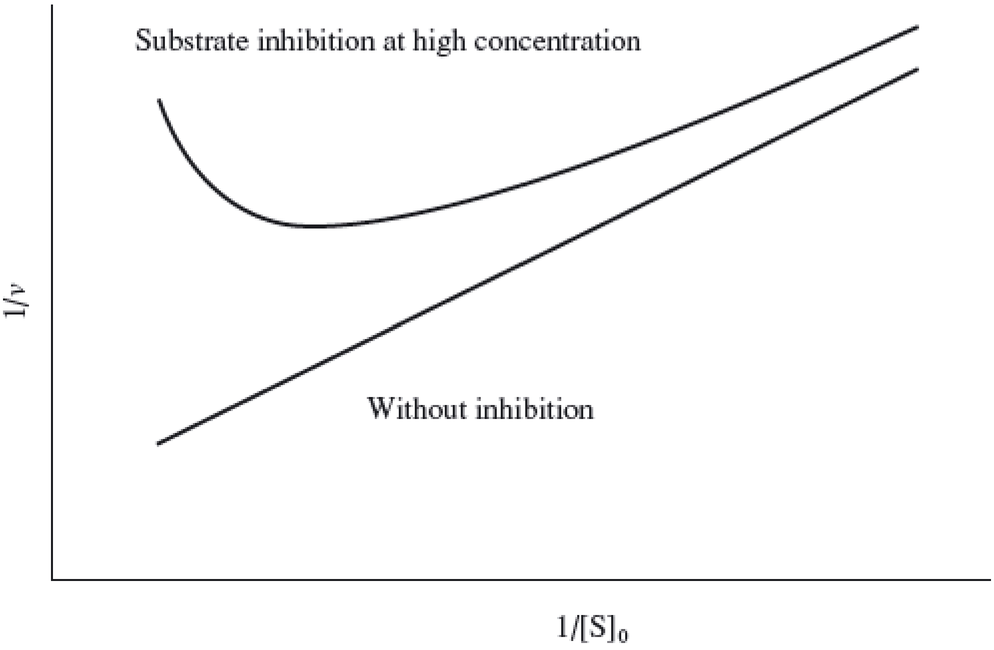
$$\frac{1}{v} = \frac{1}{v_\mathrm{max}} + \left(\frac{K_\mathrm{M}}{v_\mathrm{max}}\right)\frac{1}{[\mathrm{S}]_0} \quad .$$

The inverse of the inhibited rate law is

$$\begin{aligned}\frac{1}{v} &= \frac{1}{v_\mathrm{max}} + \left(\frac{K_\mathrm{M}}{v_\mathrm{max}}\right)\frac{1}{[\mathrm{S}]_0} + \left(\frac{[\mathrm{S}]_0^{\,2}}{v_\mathrm{max}K_\mathrm{I}}\right)\frac{1}{[\mathrm{S}]_0} \\ &= \frac{1}{v_\mathrm{max}} + \left(\frac{K_\mathrm{M}}{v_\mathrm{max}} + \frac{[\mathrm{S}]_0^{\,2}}{v_\mathrm{max}K_\mathrm{I}}\right)\frac{1}{[\mathrm{S}]_0}.\end{aligned}$$

The uninhibited and inhibited line shapes are sketched in Figure 20H.1.

Figure 20H.1



Comparing the two expressions, we see that the two curves match at high values of $1/[S]_0$. However, as the concentration of $[S]_0$ increases ($1/[S]_0$ decreases) the $1/\nu$ curve with inhibition curves upward because the reaction rate is decreasing.

Integrated activities

20.2 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 auto catalytic, $I(0)\neq 0$.

$$\left(\frac{dI}{dt}\right)_{t\,=\,0}=\left(rS_0-a\right)I_0$$

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,

$\boxed{\frac{a}{r}<S_0}$ [infection spreads] and $\boxed{\frac{a}{r}>S_0}$ [infection dies out].

20.4 The number-average molar mass of the polymer is the average chain length times the molar mass of the monomer

$$\langle M\rangle = \langle N\rangle M_1 = \frac{M_1}{1-p} \quad [20F.12(a)]$$

The probability P_N that a polymer consists of N monomers is equal to the probability that it has $N-1$ reacted end groups and one unreacted end group. The former probability is p^{N-1}; the latter $1-p$. Therefore, the total probability of finding an N-mer is

$$P_N = p^{N-1}(1-p)$$

We need this probability to get at $\langle M^2\rangle$, again using number averaging:

$$\langle M^2\rangle = M_1^2\langle N^2\rangle = M_1^2\sum_N N^2 P_N = M_1^2(1-p)\sum_N N^2 p^{N-1}$$

$$= M_1^2(1-p)\frac{\mathrm{d}}{\mathrm{d}p}p\frac{\mathrm{d}}{\mathrm{d}p}\sum_N p^N = M_1^2(1-p)\frac{\mathrm{d}}{\mathrm{d}p}p\frac{\mathrm{d}}{\mathrm{d}p}(1-p)^{-1} = \frac{M_1^2(1+p)}{(1-p)^2}$$

Thus $$\langle M^2\rangle_N - \langle M\rangle_N^2 = M_1^2\left(\frac{1+p}{(1-p)^2} - \frac{1}{(1-p)^2}\right) = \frac{pM_1^2}{(1-p)^2}$$

and $$\boxed{\left(\langle M^2\rangle_N - \langle M\rangle_N^2\right)^{1/2} = \frac{p^{1/2}M_1}{1-p}}$$

The time dependence is obtained from

$$p = \frac{k_\mathrm{r}t[\mathrm{A}]_0}{1+k_\mathrm{r}t[\mathrm{A}]_0} \quad [20F.11]$$

and $$\langle N\rangle = \frac{1}{1-p} = 1 + k_\mathrm{r}t[\mathrm{A}]_0 \quad [20F.12]$$

Hence $$\frac{p^{1/2}}{1-p} = p^{1/2}(1+k_\mathrm{r}t[\mathrm{A}]_0) = \left\{k_\mathrm{r}t[\mathrm{A}]_0(1+k_\mathrm{r}t[\mathrm{A}]_0)\right\}^{1/2}$$

and $$\left(\langle M^2\rangle_N - \langle M\rangle_N^2\right)^{1/2} = \boxed{M_1\left\{kt[\mathrm{A}]_0(1+kt[\mathrm{A}]_0)\right\}^{1/2}}$$

20.6 The rates of the individual steps are

$$\mathrm{A} \rightarrow \mathrm{B} \quad \frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = I_\mathrm{a}$$

$$\mathrm{B} \rightarrow \mathrm{A} \quad \frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = -k_\mathrm{r}[\mathrm{B}]^2$$

In the photostationary state, $I_\mathrm{a} - k_\mathrm{r}[\mathrm{B}]^2 = 0$. Hence,

$$[\mathrm{B}] = \boxed{\left(\frac{I_\mathrm{a}}{k_\mathrm{r}}\right)^{1/2}}$$

This concentration can differ significantly from an equilibrium distribution because changing the illumination may change the rate of the forward reaction without affecting the reverse reaction. Contrast this situation to the corresponding equilibrium expression, in which $[\mathrm{B}]_\mathrm{eq}$ depends on a ratio of rate constants for the forward and reverse reactions. In the equilibrium case, the rates of forward and reverse reactions cannot be changed **independently**.

21 Reaction dynamics

21A Collision theory

Answers to discussion questions

21A.2 To the extent that real gases deviate from perfect gas behavior, they do so because of intermolecular interactions. Interactions tend to be more important at high pressures, when the size of the molecules themselves is not negligible compared to the average intermolecular distance (mean free path). Attractive interactions, might enhance a reaction rate compared to the predictions of collision theory, particularly if the parts of the molecules that are attracted to each other are the reactive sites. (In that case, the both the collision frequency and the steric factor might be enhanced.) Similarly, repulsive interactions might reduce the frequency of collisions compared to what would be predicted for perfect gases. In supercritical fluids, densities can be comparable to those of liquids, so the considerations explored in the next topic (Diffusion-controlled reactions, Topic 21B) for reactions in solution might be more relevant than those of a perfect gas.

21A.4 The RRK theory proposes a *P*-factor that is more related to statistical energetic considerations than to geometric ("steric") ones. The *P*-factor in RRK theory is [21A.10a]:

$$P=\left(1-\frac{E^*}{E}\right)^{s-1}$$

where *E** is the energy required to break a bond (leading to reaction), *E* the energy of the collision, and *s* the number of modes over which the energy can be dissipated. Like more geometric interpretations of the *P*-factor, the RRK theory assigns smaller *P* factors to complex molecules than to simple ones, but for different reasons. A more geometric theory would say that an active site is only a small fraction of the "surface area" of a complex molecule, whereas RRK theory says that complex molecules are much more effective than simple ones at dispersing energy away from the reactive site.

Solutions to exercises

21A.1(b) The collision frequency is [1B.11a]

$$z=\sigma v_{\text{rel}}\mathcal{N}$$

where $v_{\text{rel}}=\left(\frac{16kT}{\pi m}\right)^{1/2}$ [1B.10a & 1B.9], $\sigma=\pi d^2=4\pi R^2$, and $\mathcal{N}=\frac{p}{kT}$

$$\text{Therefore, } z=\sigma\mathcal{N}\left(\frac{16kT}{\pi m}\right)^{1/2}=16pR^2\left(\frac{\pi}{mkT}\right)^{1/2}$$

$$=16\times(120\times10^3\ \text{Pa})\times(180\times10^{-12}\ \text{m})^2$$

$$\times\left(\frac{\pi}{28.01\,m_{\text{u}}\times1.661\times10^{-27}\ \text{kg}\,m_{\text{u}}^{-1}\times1.381\times10^{-23}\ \text{J K}^{-1}\times303\ \text{K}}\right)^{1/2}$$

$$=\boxed{7.90\times10^9\ \text{s}^{-1}}$$

The collision density is [*Justification* 21A.1]

$$Z=\frac{z\mathcal{N}_{\text{A}}}{2}=\frac{z}{2}\left(\frac{p}{kT}\right)=\frac{7.90\times10^9\ \text{s}^{-1}}{2}\left(\frac{120\times10^3\ \text{Pa}}{1.381\times10^{-23}\ \text{J K}^{-1}\times303\ \text{K}}\right)$$

$$=\boxed{1.13\times10^{35}\ \text{s}^{-1}\ \text{m}^{-3}}$$

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 $$\frac{\delta z}{z}=\frac{\delta Z}{Z}\approx\frac{\delta T}{2T}=\frac{1}{2}\left(\frac{10\text{ K}}{303\text{ K}}\right)=0.017$$

so both z and Z increase by about $\boxed{1.7\%}$.

21A.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. 21A.9) those factors that can be identified as belonging to the steric factor or collision rate: $f=\mathrm{e}^{-E_\mathrm{a}/RT}$

(i) (1) $$f=\exp\left(\frac{-15\times10^3\text{ J mol}^{-1}}{(8.3145\text{ J K}^{-1}\text{ mol}^{-1})\times(300\text{ K})}\right)=\boxed{2.4\times10^{-3}}$$

(2) $$f=\exp\left(\frac{-15\times10^3\text{ J mol}^{-1}}{(8.3145\text{ J K}^{-1}\text{ mol}^{-1})\times(800\text{ K})}\right)=\boxed{0.10\overline{5}}$$

(ii) (1) $$f=\exp\left(\frac{-150\times10^3\text{ J mol}^{-1}}{(8.3145\text{ J K}^{-1}\text{ mol}^{-1})\times(300\text{ K})}\right)=\boxed{7.7\times10^{-27}}$$

(2) $$f=\exp\left(\frac{-150\times10^3\text{ J mol}^{-1}}{(8.3145\text{ J K}^{-1}\text{ mol}^{-1})\times(800\text{ K})}\right)=\boxed{1.6\times10^{-10}}$$

21A.3(b) A straightforward approach would be to compute $f=\mathrm{e}^{-E_\mathrm{a}/RT}$ at the new temperature and compare it to that at the old temperature. An approximate approach would be to note that f changes from $f_0=\mathrm{e}^{-E_\mathrm{a}/RT}$ to $\exp\left(\frac{-E_\mathrm{a}}{RT(1+x)}\right)$, where x is the fractional increase in the temperature. If x is small, the exponent changes from $-E_\mathrm{a}/RT$ to approximately $-E_\mathrm{a}(1-x)/RT$ and f changes from f_0 to

$$f\approx\mathrm{e}^{-E_\mathrm{a}(1-x)/RT}=\mathrm{e}^{-E_\mathrm{a}/RT}\left(\mathrm{e}^{-E_\mathrm{a}/RT}\right)^{-x}=f_0f_0^{-x}$$

Thus the new fraction is the old one times a factor of f_0^{-x} . The increase in f expressed as a percentage is

$$\frac{f-f_0}{f_0}\times100\%=\frac{f_0f_0^{-x}-f_0}{f_0}\times100\%=(f_0^{-x}-1)\times100\%$$

(1) (1) $f_0^{-x}=(2.4\times10^{-3})^{-10/300}=1.2$ and the percentage change is $\boxed{20\%}$.

(2) $f_0^{-x}=(0.10\overline{5})^{-10/800}=1.03$ and the percentage change is $\boxed{3\%}$.

(ii) (1) $f_0^{-x}=(7.7\times10^{-27})^{-10/300}=7.4$ and the percentage change is $\boxed{640\%}$.

(2) $f_0^{-x}=(1.6\overline{1}\times10^{-10})^{-10/800}=1.3\overline{3}$ and the percentage change is $\boxed{33\%}$.

21A.4(b) $$k_\mathrm{r}=P\sigma\left(\frac{8kT}{\pi\mu}\right)^{1/2}N_\mathrm{A}\mathrm{e}^{-E_\mathrm{a}/RT}\quad[21\text{A}.9]$$

We take P = 1, so

$$k_\mathrm{r}=[0.30\times(10^{-9}\text{ m})^2]\times\left(\frac{8(1.381\times10^{-23}\text{ J K}^{-1})\times(450\text{ K})}{\pi(3.930\,m_\mathrm{u})\times(1.661\times10^{-27}\text{ kg }m_\mathrm{u}^{-1})}\right)^{1/2}$$

$$\times(6.022\times10^{23}\text{ mol}^{-1})\times\exp\left(\frac{-200\times10^3\text{ J mol}^{-1}}{(8.3145\text{ J K}^{-1}\text{ mol}^{-1})\times(450\text{ K})}\right)$$

$$=\boxed{1.7\times10^{-15}\text{ m}^3\text{ mol}^{-1}\text{ s}^{-1}}=\boxed{1.7\times10^{-12}\text{ dm}^3\text{ mol}^{-1}\text{s}^{-1}}.$$

21A.5(b) The steric factor, P, is

$$P=\frac{\sigma^*}{\sigma}\ [\text{Topic 21A.1(c)}]$$

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:

$$d_A = (\sigma_A/\pi)^{1/2} \quad \text{and} \quad d_B = (\sigma_B/\pi)^{1/2},$$

so $$\sigma = \frac{\pi}{4}\left\{\left(\frac{\sigma_A}{\pi}\right)^{1/2} + \left(\frac{\sigma_B}{\pi}\right)^{1/2}\right\}^2 = \frac{\left(\sigma_A^{1/2}+\sigma_B^{1/2}\right)^2}{4} = \frac{\left\{(0.88\ \text{nm}^2)^{1/2}+(0.40\ \text{nm}^2)^{1/2}\right\}^2}{4}$$

$$= \boxed{0.62\ \text{nm}^2}.$$

Therefore, $P = \dfrac{8.7\times10^{-22}\ \text{m}^2}{0.62\times(10^{-9}\ \text{m})^2} = \boxed{1.41\times10^{-3}}$

21A.6(b) According to RRK theory, the steric *P*-factor is given by eqn. 21A.10a

$$P = \left(1-\frac{E^*}{E}\right)^{s-1}$$

where *s* is the number of vibrational modes in the reacting molecule. For a non-linear molecule composed of *N* atoms, the number of modes is [Topic 12E.1]

$$s = 3N - 6 = 3\times4 - 6 = 6.$$

Rearranging eqn. 21A.10a yields

$$\frac{E^*}{E} = 1 - P^{\frac{1}{s-1}} = 1-(0.025)^{\frac{1}{5}} = \boxed{0.52}$$

21A.7(b) According to RRK theory, the steric *P*-factor is given by eqn. 21A.10a

$$P = \left(1-\frac{E^*}{E}\right)^{s-1} = \left(1-\frac{300\ \text{kJ mol}^{-1}}{500\ \text{kJ mol}^{-1}}\right)^{12-1} = \boxed{4.2\times10^{-5}}$$

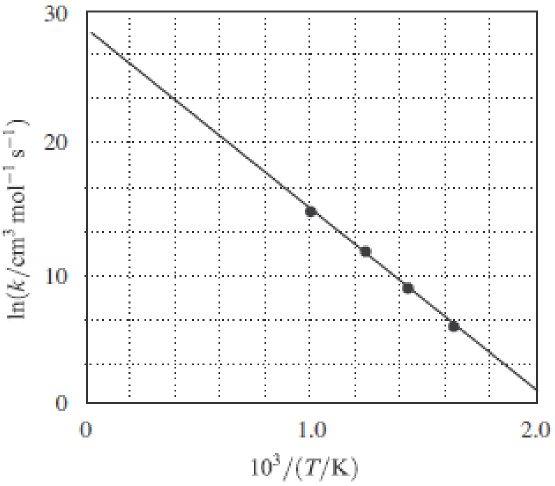
Solutions to problems

21A.2 Draw up the following table as the basis of an Arrhenius plot:

T / K	600	700	800	1000
10^3 K / T	1.67	1.43	1.25	1.00
k_r / (cm^3 mol^{-1} s^{-1})	4.6×10^2	9.7×10^3	1.3×10^5	3.1×10^6
ln (k_r / cm^3 mol^{-1} s^{-1})	6.13	9.18	11.8	14.9

The points are plotted in Figure 21A.1.

Figure 21A.1



The least-squares intercept is at 28.3, which implies that

$$A / (\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = e^{28.3} = 2.0\times10^{12}$$

But comparison of eqn. 21A.9 to the Arrhenius equation tells us that $A = N_A P\sigma\left(\frac{8kT}{\pi\mu}\right)^{1/2}$

so $$P = \frac{A}{N_A\sigma}\left(\frac{\pi\mu}{8kT}\right)^{1/2}$$

The reduced mass is

$$\mu = m(\mathrm{NO_2})/2 = 46\, m_u \times (1.661\times10^{-27}\ \mathrm{kg}\ m_u^{-1}) / 2 = 3.8\times10^{-26}\ \mathrm{kg}$$

so, evaluating P in the center of the range of temperatures spanned by the data,

$$P = \frac{2.0\times10^{12}\times(10^{-2}\ \mathrm{m})^3\ \mathrm{mol^{-1}\ s^{-1}}}{(6.022\times10^{23}\ \mathrm{mol^{-1}})\times0.60\times(10^{-9}\ \mathrm{m})^2}\times\left(\frac{\pi\times3.8\times10^{-26}\ \mathrm{kg}}{8\times1.381\times10^{-23}\ \mathrm{J\ K^{-1}}\times800\ \mathrm{K}}\right)^{1/2}$$

$$= \boxed{6.5\times10^{-3}}.$$

$$\sigma^* = P\sigma = (6.5\times10^{-3})\times(0.60\ \mathrm{nm^2}) = \boxed{3.9\times10^{-3}\ \mathrm{nm^2}} = \boxed{3.9\times10^{-21}\ \mathrm{m^2}}$$

21A.4 Example 21A.1 estimates a steric factor within the harpoon mechanism:

$$\frac{\sigma^*}{\sigma}\approx\left(\frac{e^2}{4\pi\varepsilon_0 d(I-E_{ea})}\right)^2$$

Taking $\sigma = \pi d^2$ gives

$$\sigma^*\approx\pi\left(\frac{e^2}{4\pi\varepsilon_0[I(\mathrm{M})-E_{ea}(\mathrm{X_2})]}\right)^2 = \frac{6.5\ \mathrm{nm^2}}{\{(I-E_{ea})/\mathrm{eV}\}^2}$$

Thus, σ^* is predicted to increase as $I - E_{ea}$ decreases. We construct the following table from the data:

σ^* /nm^2	Cl_2	Br_2	I_2
Na	0.45	0.42	0.56
K	0.72	0.68	0.97
Rb	0.77	0.72	1.05
Cs	0.97	0.90	1.34

All values of σ^* in the table are smaller than the experimental ones, but they do show the correct trends down the columns. The variation with E_{ea} across the table is not so good.

21A.6 Collision theory gives for a rate constant with no energy barrier

$$k_r = P\sigma\left(\frac{8kT}{\pi\mu}\right)^{1/2}N_A\ [21A.9]\quad\text{so}\quad P=\frac{k_r}{\sigma N_A}\left(\frac{\pi\mu}{8kT}\right)^{1/2}$$

$$P = \frac{k_r/(\mathrm{dm^3\ mol^{-1}\,s^{-1}})\times(10^{-3}\ \mathrm{m^3\,dm^{-3}})}{(\sigma/\mathrm{nm^2})\times(10^{-9}\ \mathrm{m})^2\times(6.022\times10^{23}\ \mathrm{mol^{-1}})}$$
$$\times\left(\frac{\pi\times(\mu/\mathrm{u})\times(1.66\times10^{-27}\ \mathrm{kg})}{8\times(1.381\times10^{-23}\ \mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}\right)^{1/2}$$
$$=\frac{(6.61\times10^{-13})k_r/(\mathrm{dm^3\ mol^{-1}\,s^{-1}})}{(\sigma/\mathrm{nm^2})\times(\mu/m_u)^{1/2}}$$

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 *Data Section*. 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

$$\sigma=\frac{(0.40^{1/2}+0.64^{1/2})^2}{4}\mathrm{nm^2}=0.51\,\mathrm{nm^2}$$

$$\mu = \frac{m_O m_{et}}{m_O + m_{et}} = \frac{(32.0\,m_u)\times(29.1\,m_u)}{(32.0+29.1)\,m_u} = 15.2\,m_u$$

so $$P = \frac{(6.61\times10^{-13})\times(4.7\times10^{9})}{(0.51)\times(15.2)^{1/2}} = \boxed{1.6\times10^{-3}}$$

For O_2 with cyclohexyl

$$\sigma = \frac{(0.40^{1/2}+0.88^{1/2})^2}{4}\,\text{nm}^2 = 0.62\,\text{nm}^2$$

$$\mu = \frac{m_O m_C}{m_O + m_C} = \frac{(32.0\,m_u)\times(77.1\,m_u)}{(32.0+77.1)\,m_u} = 22.6\,m_u$$

so $$P = \frac{(6.61\times10^{-13})\times(8.4\times10^{9})}{(0.62)\times(22.6)^{1/2}} = \boxed{1.8\times10^{-3}}$$

21B Diffusion-controlled reactions

Answer to discussion question

D21B.2 In the cage effect, a pair of molecules may be held in close proximity for an extended period of time (extended on the microscopic scale, mind you) by the presence of other neighboring molecules, typically solvent molecules. Such a pair is called an encounter pair, and their time near each other an “encounter” as opposed to a simple collision. An encounter may include a series of collisions. Furthermore, an encounter pair may pick up enough energy to react from collisions with neighboring molecules, even though the pair may not have had enough energy at the time of its initial collision.

Solutions to exercises

21B.1(b) The rate constant for a diffusion-controlled bimolecular reaction is

$k_d = 4\pi R^* D N_A$ [21B.3]

where $D = D_A + D_B = 2\times(5.2\times10^{-9}\ \text{m}^2\ \text{s}^{-1}) = 1.04\times10^{-8}\ \text{m}^2\ \text{s}^{-1}$

$k_d = 4\pi\times(0.4\times10^{-9}\ \text{m})\times(1.04\times10^{-8}\ \text{m}^2\ \text{s}^{-1})\times(6.022\times10^{23}\ \text{mol}^{-1})$

$$k_d = \boxed{3.\bar{1}\times10^{7}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}} = \boxed{3.\bar{1}\times10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}$$

21B.2(b) The rate constant for a diffusion-controlled bimolecular reaction is

$$k_d = \frac{8RT}{3\eta}\ [21A.4] = \frac{8\times(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(298\ \text{K})}{3\eta} = \frac{6.61\times10^{3}\ \text{J mol}^{-1}}{\eta}$$

(i) For decylbenzene, $\eta = 3.36\ \text{cP} = 3.36\times10^{-3}\ \text{kg m}^{-1}\ \text{s}^{-1}$

$$k_d = \frac{6.61\times10^{3}\ \text{J mol}^{-1}}{3.36\times10^{-3}\ \text{kg m}^{-1}\ \text{s}^{-1}} = \boxed{1.97\times10^{6}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}} = \boxed{1.97\times10^{9}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}$$

(ii) In concentrated sulfuric acid, $\eta = 27\ \text{cP} = 27\times10^{-3}\ \text{kg m}^{-1}\ \text{s}^{-1}$

$$k_d = \frac{6.61\times10^{3}\ \text{J mol}^{-1}}{27\times10^{-3}\ \text{kg m}^{-1}\ \text{s}^{-1}} = \boxed{2.4\times10^{5}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}} = \boxed{2.4\times10^{8}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}$$

21B.3(b) The rate constant for a diffusion-controlled bimolecular reaction is [21B.4]

$$k_d = \frac{8RT}{3\eta} = \frac{8\times(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(320\,\text{K})}{3\times(0.601\times10^{-3}\,\text{kg}\,\text{m}^{-1}\text{s}^{-1})}$$

$$= \boxed{1.18\times10^{7}\ \text{m}^3\ \text{mol}^{-1}\text{s}^{-1}} = \boxed{1.18\times10^{10}\ \text{dm}^3\ \text{mol}^{-1}\text{s}^{-1}}$$

Since this reaction is elementary bimolecular it is second-order; hence

$$t_{1/2} = \frac{1}{2k_{\mathrm{d}}[\mathrm{A}]_0} \quad \text{[Table 20B.3, with } k_{\mathrm{r}} = 2k_{\mathrm{d}} \text{ because 2 atoms are consumed]}$$

so $$t_{1/2} = \frac{1}{2\times(1.18\times10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}})\times(2.0\times10^{-3}\ \mathrm{mol\ dm^{-3}})} = \boxed{2.1\times10^{-8}\ \mathrm{s}}$$

21B.4(b) Since the reaction is diffusion-controlled, the rate-limiting step is bimolecular and therefore second-order; hence

$$\frac{\mathrm{d[P]}}{\mathrm{d}t} = k_{\mathrm{d}}[\mathrm{A}][\mathrm{B}]$$

where $k_{\mathrm{d}} = 4\pi R^{*}DN_{\mathrm{A}}[88.3] = 4\pi N_{\mathrm{A}}R^{*}(D_{\mathrm{A}} + D_{\mathrm{B}})$

$$= 4\pi N_{\mathrm{A}} \times (R_{\mathrm{A}} + R_{\mathrm{B}}) \times \frac{kT}{6\pi\eta}\left(\frac{1}{R_{\mathrm{A}}} + \frac{1}{R_{\mathrm{B}}}\right)[19\mathrm{B}.19\mathrm{b}] = \frac{2RT}{3\eta}(R_{\mathrm{A}} + R_{\mathrm{B}}) \times \left(\frac{1}{R_{\mathrm{A}}} + \frac{1}{R_{\mathrm{B}}}\right)$$

$$k_{\mathrm{d}} = \frac{2\times(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(293\,\mathrm{K})}{3\times(1.35\times10^{-3}\ \mathrm{kg\ m^{-1}\ s^{-1}})} \times (421+945) \times \left(\frac{1}{421} + \frac{1}{945}\right)$$

$$= 5.64\times10^{6}\ \mathrm{m^3\ mol^{-1}\ s^{-1}} = 5.64\times10^{9}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}.$$

Therefore, the initial rate is

$$\frac{\mathrm{d[P]}}{\mathrm{d}t} = (5.64\times10^{9}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}})\times(0.155\,\mathrm{mol\ dm^{-3}})\times(0.195\,\mathrm{mol\ dm^{-3}})$$

$$= \boxed{1.71\times10^{8}\ \mathrm{mol\ dm^{-3}\ s^{-1}}}$$

Comment. If the approximation of eqn. 21B.4 is used, $k_{\mathrm{d}} = 4.81\times10^{9}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$. In this case the approximation results in a difference of about 15% compared to the expression used above.

Solutions to problems

21B.2 See *Brief illustration* 21B.3 for a sample scenario. In the graphs shown here, the same parameters are used, except for the value of the rate constant. That is, n_0 = 3.9 mmol of I_2, A = 5.0 cm^2, and $D = 4.1\times10^{-9}\ \mathrm{m^2\ s^{-1}}$. Using these parameters, we will plot the spatial variation in concentration at 10^2 s, 10^3 s, and 10^4 s. In Figure 21B.1(a), the concentration is plotted against position in the absence of reaction. That is, $k_{\mathrm{r}} = 0$. The concentration profile spreads with time. That is, the maximum concentration (which stays at the origin throughout) decreases, but the distance over which there is appreciable concentration increases. Introducing a first-order reaction with a rate constant $k_{\mathrm{r}} = 4.0\times10^{-5}\ \mathrm{s^{-1}}$, as in the *Brief illustration*, has a barely noticeable effect on the concentration profiles (plotted in Figure 21B.1(b)); the longer-time profiles are very slightly depressed. Making the rate constant a factor of 10 greater suppresses the 10^4-s profile: by that time the material has practically all reacted away (Figure 21B.1(c)). Speeding up the reaction by a further factor of 10 (Figure 21B.1(d)) suppresses the 10^3-s profile practically completely as well, and even the 10^2-s is visibly lower.

Figure 21B.1(a)

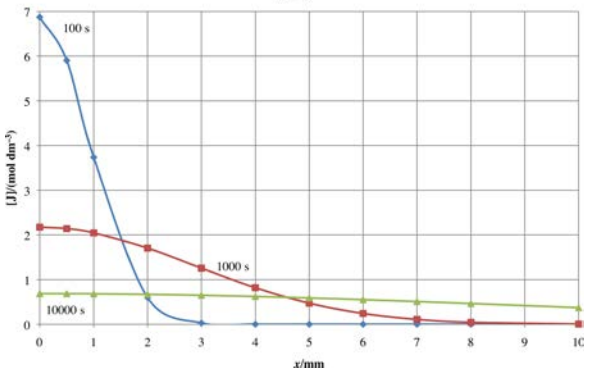


Figure 21B.1(b)

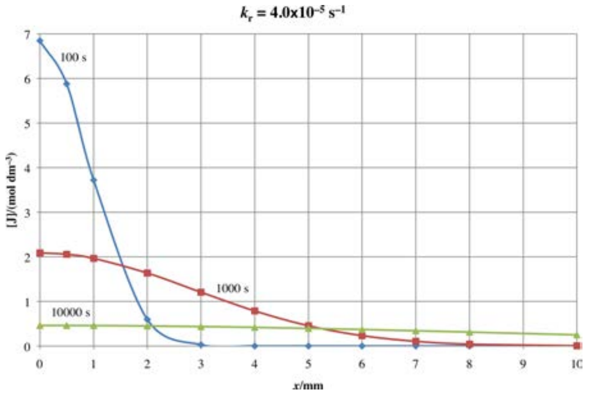


Figure 21B.1(c)

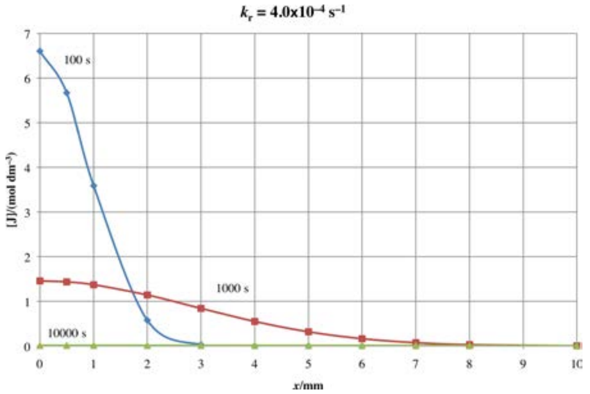
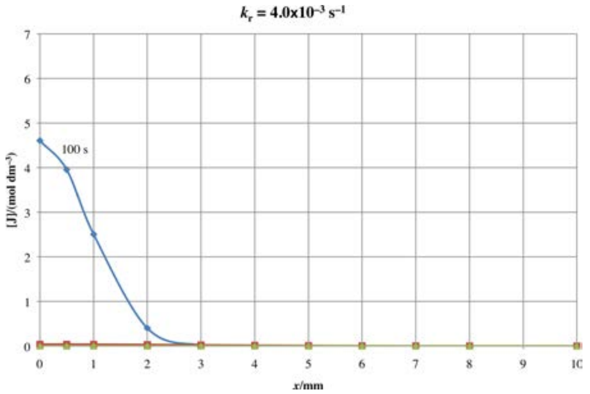


Figure 21B.1(d)



Examination of eqn. 21B.9 suggests that the spatial variation is **not** significantly changed by reaction; it is merely scaled equally at all positions by the factor $e^{-k_r t}$.

21B.4 **(a)** The rate constant of a diffusion-limited reaction is

$$k_\mathrm{d}=\frac{8RT}{3\eta}[21\mathrm{B}.4]=\frac{8\times(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(298\ \mathrm{K})}{3\times(1.06\times10^{-3}\ \mathrm{kg\ m^{-1}\ s^{-1}})}$$

$$=\boxed{6.23\times10^{6}\ \mathrm{m^{3}\ mol^{-1}\ s^{-1}}}=\boxed{6.23\times10^{9}\ \mathrm{dm^{3}\ mol^{-1}s^{-1}}}$$

(b) The rate constant is related to the diffusion constants and reaction distance by

$k_\mathrm{d} = 4\pi R^*DN_\mathrm{A}$ [21B.3]

so $$R^*=\frac{k_\mathrm{d}}{4\pi DN_\mathrm{A}}=\frac{(2.77\times10^{9}\ \mathrm{dm^{3}\ mol^{-1}\ s^{-1}})\times(10^{-3}\ \mathrm{m^{3}\ dm^{-3}})}{4\pi\times(1\times10^{-9}\ \mathrm{m^{2}\ s^{-1}})\times(6.022\times10^{23}\ \mathrm{mol^{-1}})}$$

$$=\boxed{4\times10^{-10}\ \mathrm{m}}=\boxed{0.4\ \mathrm{nm}}$$

21C Transition-state theory

Answers to discussion questions

21C.2 See Topic 21C.1(e) for detailed examples of how femtosecond spectroscopy has been used to detect activated complexes and transition states of reactions. Because the activated complexes are not even local minima on potential energy surfaces, they are extremely transitory, and laser pulses of duration less than 1 ps are needed in order to detect them. Typically one very short pulse will initiate the reaction under investigation, thereby creating a dissociative activated complex, and a second pulse will detect a reaction product. Not only must the pulses themselves be very short, but the delay between the creation of the complex and the detection of its effects must also be short. By such techniques, investigators have been able to determine just how stretched the bond in ICN must get before it breaks (yielding free CN). Also, decay of the ion pair $\mathrm{Na^+I^-}$ has been studies in detail, revealing the existence of two potential energy surfaces, one largely ionic and one corresponding to a covalent NaI.

21C.4 The primary isotope effect is the change in rate constant of a reaction in which the breaking of a bond involving the isotope occurs. The reaction coordinate in a C–H bond-breaking process corresponds to the stretching of that bond. The vibrational energy of the stretching depends upon the effective mass of the C and H atoms (μ_CH). Upon deuteration, the zero point energy of the bond is lowered due to the greater mass of the deuterium atom. However, the height of the energy barrier is not much changed because the relevant vibration in the activated complex has a very low force constant (bonding in the complex is very weak), so there is little zero point energy associated with the complex and little change in its zero point energy upon deuteration. The net effect is an increase in the activation energy of the reaction. We then expect that the rate constant for the reaction will be lowered in the deuterated molecule and that is what is observed. See the derivation leading to eqns 21C.19 and 21C.20 for a quantitative description of the effect.

Sometimes the rate of reaction is lowered upon deuteration to an extent even greater than can be accounted for by these equations. In such cases, quantum-mechanical tunneling (Topic 8A) may be part of the reaction mechanism. The probability of tunneling is highly sensitive to mass, so it is much less likely (and therefore much slower) for deuterium than for ^{1}H.

If the rate of a reaction is altered by isotopic substitution it implies that the substituted site plays an important role in the mechanism of the reaction. For example, an observed effect on the rate can identify bond breaking events in the rate determining step of the mechanism. On the other hand, if no isotope effect is observed, the site of the isotopic substitution may play no critical role in the mechanism of the reaction.

Solutions to exercises

21C.1(b) The enthalpy of activation for a bimolecular solution reaction is [Topic 21C.2(a) footnote]

$$\Delta^{\ddagger}H = E_\mathrm{a} - RT = 8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}\times(5925\ \mathrm{K} - 298\ \mathrm{K}) = \boxed{46.9\ \mathrm{kJ\ mol^{-1}}}$$

$$k_r = B\mathrm{e}^{\Delta^{\ddagger}S/R}\mathrm{e}^{-\Delta^{\ddagger}H/RT}, \quad B = \left(\frac{kT}{h}\right)\times\left(\frac{RT}{p^{\ominus}}\right) = \frac{kRT^2}{hp^{\ominus}}$$

$$= B\mathrm{e}^{\Delta^{\ddagger}S/R}\mathrm{e}^{-E_a/RT}\mathrm{e} = A\mathrm{e}^{-E_a/RT}$$

Therefore, $A = \mathrm{e}\,B\mathrm{e}^{\Delta^{\ddagger}S/R}$, implying that $\Delta^{\ddagger}S = R\left(\ln\frac{A}{B} - 1\right)$

$$B = \frac{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})^2}{6.626\times10^{-34}\,\mathrm{J\,s}\times10^{5}\,\mathrm{Pa}}$$

$$= 1.54\times10^{11}\,\mathrm{m^3\,mol^{-1}\,s^{-1}} = 1.54\times10^{14}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$$

and hence $\Delta^{\ddagger}S = R\left[\ln\left(\frac{6.92\times10^{12}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}}{1.54\times10^{14}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}}\right) - 1\right]$

$$= 8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}\times(-4.10) = \boxed{-34.1\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

21C.2(b) The enthalpy of activation for a bimolecular solution reaction is [Topic 21C.2(a) footnote]

$$\Delta^{\ddagger}H = E_a - RT = 8.3145\,\mathrm{J\,mol^{-1}\,K^{-1}}\times(4972\,\mathrm{K} - 298\,\mathrm{K}) = \boxed{38.9\,\mathrm{kJ\,mol^{-1}}}$$

The entropy of activation is [Exercise 21C.1(b)]

$$\Delta^{\ddagger}S = R\left(\ln\frac{A}{B} - 1\right)$$

with $B = \frac{kRT^2}{hp^{\ominus}} = 1.59\times10^{14}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$

Therefore, $\Delta^{\ddagger}S = 8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}\times\left[\ln\left(\frac{4.98\times10^{13}}{1.54\times10^{14}}\right) - 1\right] = -17.7\,\mathrm{J\,K^{-1}\,mol^{-1}}$

Hence, $\Delta^{\ddagger}G = \Delta^{\ddagger}H - T\Delta^{\ddagger}S = \{38.9 - (298)\times(-17.7\times10^{-3})\}\,\mathrm{kJ\,mol^{-1}} = \boxed{+44.1\,\mathrm{kJ\,mol^{-1}}}$

21C.3(b) Use eqn. 21C.15(a) to relate a bimolecular gas-phase rate constant to activation energy and entropy:

$$k_r = \mathrm{e}^2 B\mathrm{e}^{\Delta^{\ddagger}S/R}\mathrm{e}^{-E_a/RT}$$

where $B = \left(\frac{kT}{h}\right)\times\left(\frac{RT}{p^{\ominus}}\right)$ [21C.14]

$$= \frac{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(338\,\mathrm{K})^2\times(8.3145\,\mathrm{J\,mol^{-1}\,K^{-1}})}{(6.626\times10^{-34}\,\mathrm{J\,s})\times(10^5\,\mathrm{Pa})}$$

$$= 1.98\times10^{11}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$$

Solve for the entropy of activation:

$$\Delta^{\ddagger}S = R\left(\ln\frac{k_r}{B} - 2\right) + \frac{E_a}{T}$$

Hence $\Delta^{\ddagger}S = 8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}\times\left(\ln\frac{0.35\,\mathrm{m^3\,mol^{-1}\,s^{-1}}}{1.98\times10^{11}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}} - 2\right) + \frac{39.7\times10^3\,\mathrm{J\,mol^{-1}}}{338\,\mathrm{K}}$

$$= \boxed{-124\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

21C.4(b) For a bimolecular gas-phase reaction [Exercise 21C.3(b)],

$$\Delta^{\ddagger}S = R\left(\ln\frac{k_r}{B} - 2\right) + \frac{E_a}{T} = R\left(\ln\frac{A}{B} - \frac{E_a}{RT} - 2\right) + \frac{E_a}{T} = R\left(\ln\frac{A}{B} - 2\right)$$

where $B = \frac{kRT^2}{hp^{\ominus}}$

For two structureless particles, the rate constant is the same as that of collision theory

$$k_r = N_A\sigma^*\left(\frac{8kT}{\pi\mu}\right)^{1/2}\mathrm{e}^{-\Delta E_0/RT} \quad \text{[Example 21C.1]}$$

The activation energy is [20D.3]

$$E_a = RT^2 \frac{\mathrm{d}\ln k_r}{\mathrm{d}T} = RT^2 \frac{\mathrm{d}}{\mathrm{d}T}\left(\ln N_A \sigma^* + \frac{1}{2}\ln\frac{8k}{\pi\mu} + \frac{1}{2}\ln T - \frac{\Delta E_0}{RT} \right)$$

$$= RT^2\left(\frac{1}{2T} + \frac{\Delta E_0}{RT^2} \right) = \Delta E_0 + \frac{RT}{2},$$

so the prefactor is

$$A = k_r e^{E_a/RT} = N_A \sigma^* \left(\frac{8kT}{\pi\mu}\right)^{1/2} e^{-\Delta E_0/RT}\left(e^{\Delta E_0/RT}e^{1/2}\right) = N_A\sigma^*\left(\frac{8kT}{\pi\mu}\right)^{1/2} e^{1/2}$$

Hence $\Delta^{\ddagger}S = R\left\{ \ln N_A\sigma^*\left(\frac{8kT}{\pi\mu}\right)^{1/2} + \frac{1}{2} - \ln\frac{kRT^2}{p^{\ominus}h} - 2 \right\} = R\left\{ \ln\frac{\sigma^* p^{\ominus} h}{(kT)^{3/2}}\left(\frac{8}{\pi\mu}\right)^{1/2} - \frac{3}{2} \right\}.$

For identical particles,

$$\mu = m/2 = (92\ \mathrm{u})(1.661\times10^{-27}\ \mathrm{kg\ u^{-1}})/2 = 7.6\times10^{-26}\ \mathrm{kg}\ ,$$

and hence

$$\Delta^{\ddagger}S = 8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

$$\times\left\{ \ln\frac{0.45\times(10^{-9}\ \mathrm{m})^2\times10^5\ \mathrm{Pa}\times6.626\times10^{-34}\ \mathrm{J\ s}}{(1.381\times10^{-23}\ \mathrm{J\ K^{-1}}\times450\ \mathrm{K})^{3/2}}\left(\frac{8}{\pi\times7.6\times10^{-26}\ \mathrm{kg}}\right)^{1/2} - \frac{3}{2} \right\}$$

$$= \boxed{-79\ \mathrm{J\ K^{-1}\ mol^{-1}}}.$$

21C.5(b) At low pressure, the reaction can be assumed to be bimolecular. (The rate constant is certainly second-order.)

(a) $\Delta^{\ddagger}S = R\left(\ln\frac{A}{B} - 2\right)$ [Exercise 21C.4(b)]

where $B = \frac{kRT^2}{hp^{\ominus}}$ [Exercise 21C.4(b)] $= \frac{1.381\times10^{-23}\ \mathrm{J\ K^{-1}}\times8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}\times(298\ \mathrm{K})^2}{6.626\times10^{-34}\ \mathrm{J\ s}\times10^5\ \mathrm{Pa}}$

$$= 1.54\times10^{11}\ \mathrm{m^3\ mol^{-1}\ s^{-1}} = 1.54\times10^{14}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}.$$

Hence $\Delta^{\ddagger}S = 8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}\times\left(\ln\frac{2.3\times10^{13}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}}{1.54\times10^{14}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}} - 2\right)$

$$= \boxed{-32\ \mathrm{J\ K^{-1}\ mol^{-1}}}$$

(b) The enthalpy of activation for a bimolecular gas-phase reaction is [Topic 21C.2(a) footnote]

$\Delta^{\ddagger}H = E_a - 2RT = 30.0\ \mathrm{kJ\ mol^{-1}} - 2\times8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}}\times298\ \mathrm{K} = \boxed{25.0\ \mathrm{kJ\ mol^{-1}}}$

(c) The Gibbs energy of activation at 298 K is

$\Delta^{\ddagger}G = \Delta^{\ddagger}H - T\Delta^{\ddagger}S = 25.0\ \mathrm{kJ\ mol^{-1}} - (298\ \mathrm{K})\times(-32\times10^{-3}\ \mathrm{kJ\ K^{-1}\ mol^{-1}})$

$\Delta^{\ddagger}G = \boxed{+34.7\ \mathrm{kJ\ mol^{-1}}}$

21C.6(b) Use eqn. 21C.18 to examine the effect of ionic strength on a rate constant:

$\log k_r = \log k_r^\circ + 2A|z_Az_B|I^{1/2}$

Hence $\log k_r^\circ = \log k_r - 2A|z_Az_B|I^{1/2} = \log 1.55 - 2\times0.509\times|1\times1|\times(0.0241)^{1/2} = 0.032$,

and $k_r^\circ = \boxed{1.08\ \mathrm{dm^6\ mol^{-2}\ min^{-1}}}$.

Solutions to problems

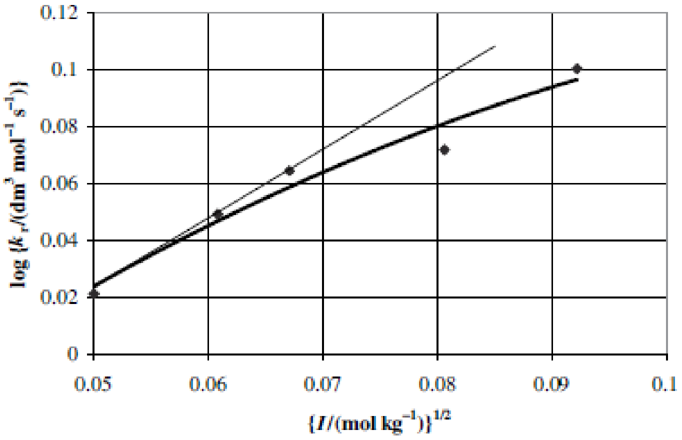
21C.2 $\log k_r = \log k_r^\circ + 2Az_Az_BI^{1/2}$ [21C.18]

This expression suggests that we should plot $\log k_r$ against $I^{1/2}$ and determine z_B from the slope, since we know that $|z_A| = 1$. We draw up the following table:

I / (mol kg^{-1})	0.0025	0.0037	0.0045	0.0065	0.0085
$\{I$ / (mol kg^{-1})$\}^{1/2}$	0.050	0.061	0.067	0.081	0.092
$\log\{k_r$ / (dm^3 mol^{-1} s^{-1})$\}$	0.021	0.049	0.064	0.072	0.100

These points are plotted in Figure 21C.1.

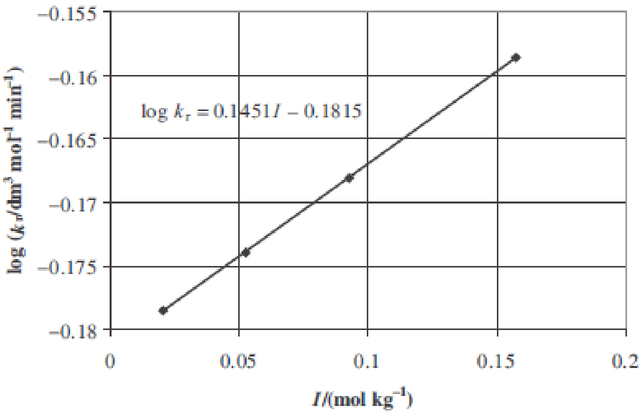
Figure 21C.1



The slope of the limiting line in Figure 21C.1 is approximately 2.5. Since this slope is equal to $2Az_Az_B \times (\text{mol dm}^{-3})^{1/2} = 1.018 z_Az_B$, we have $z_Az_B \approx 2.5$. But $|z_A| = 1$, and so $|z_B| = 2$. Furthermore, z_A and z_B have the same sign because $z_Az_B > 0$. (In fact, the data refer to I^- and $S_2O_8^{2-}$.)

21C.4 Figure 21C.2 shows that log k_r is proportional to the ionic strength even when one of the reactants is a neutral molecule.

Figure 21C.2



From the graph, the intercept at $I = 0$ is –0.182, so the limiting value of k_r is

$$k_r° = 10^{-0.182} = \boxed{0.658\ \text{dm}^3\ \text{mol}^{-1}\ \text{min}^{-1}}$$

Compare the equation of the best-fit line to eqn 21C.16b:

$$\log k_r = \log k_r° - \log K_\gamma = \log k_r° - \log \frac{\gamma_{C^\ddagger}}{\gamma_{I^-}\gamma_{H_2O_2}} = \log k_r° + \log \frac{\gamma_{I^-}\gamma_{H_2O_2}}{\gamma_{C^\ddagger}}$$

which implies that $\log \dfrac{\gamma_{I^-}\gamma_{H_2O_2}}{\gamma_{C^\ddagger}} = 0.145I$

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 $\log \gamma_{H_2O_2} = 0.145I$, that is, that the activity coefficient of a neutral molecule depends on ionic strength.

21C.6 $$K_{\mathrm{a}}=\frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]\gamma_{\mathrm{HA}}}\gamma_{\pm}^2\approx\frac{[\mathrm{H}^+][\mathrm{A}^-]\gamma_{\pm}^2}{[\mathrm{HA}]}$$

Therefore, $[\mathrm{H}^+]=\dfrac{[\mathrm{HA}]K_{\mathrm{a}}}{[\mathrm{A}^-]\gamma_{\pm}^2}$

and $$\log[\mathrm{H}^+]=\log K_{\mathrm{a}}+\log\frac{[\mathrm{HA}]}{[\mathrm{A}^-]}-2\log\gamma_{\pm}=\boxed{\log K_{\mathrm{a}}+\log\frac{[\mathrm{HA}]}{[\mathrm{A}^-]}+2AI^{1/2}}$$

Write $v=k_{\mathrm{r}}[\mathrm{H}^+][\mathrm{B}]$.

Then $$\begin{aligned}\log v&=\log(k_{\mathrm{r}}[\mathrm{B}])+\log[\mathrm{H}^+]\\&=\log(k_r[\mathrm{B}])+\log\frac{[\mathrm{HA}]}{[\mathrm{A}^-]}+2AI^{1/2}+\log K_{\mathrm{a}}\\&=\log v^{\circ}+2AI^{1/2},\quad v^{\circ}=k_{\mathrm{r}}\frac{[\mathrm{B}][\mathrm{HA}]K_{\mathrm{a}}}{[\mathrm{A}^-]}.\end{aligned}$$

That is, the logarithm of the rate should depend linearly on the square root of the ionic strength.

$$\log\frac{v}{v^{\circ}}=2AI^{1/2}\quad\text{so}\quad v=\boxed{v^{\circ}\times10^{2AI^{1/2}}}$$

That is, the rate depends exponentially on the square root of the ionic strength.

21C.8 We use the Eyring equation (combining eqns. 21C.9 and 21C.10) to compute the bimolecular rate constant

$$k_{\mathrm{r}}=\kappa\frac{kT}{h}\left(\frac{RT}{p^{\ominus}}\right)\frac{N_{\mathrm{A}}\bar{q}_{\mathrm{C}^{\ddagger}}^{\ominus}}{q_{\mathrm{H}}^{\ominus}q_{\mathrm{D}_2}^{\ominus}}\exp\left(\frac{-\Delta E_0}{RT}\right)\approx\frac{(RT)^2\bar{q}_{\mathrm{C}^{\ddagger}}^{\ominus}}{hp^{\ominus}q_{\mathrm{H}}^{\ominus}q_{\mathrm{D}_2}^{\ominus}}\exp\left(\frac{-\Delta E_0}{RT}\right)$$

We are to consider a variety of activated complexes, but the reactants, (H and D_2) and their partition functions do not change. Consider them first. The partition function of H is solely translational:

$$q_{\mathrm{H}}^{\ominus}=\frac{RT}{p^{\ominus}\Lambda_{\mathrm{H}}^3}\text{ and }\Lambda_H=\left(\frac{h^2}{2\pi kTm_{\mathrm{H}}}\right)^{1/2}\text{ so }q_{\mathrm{H}}^{\ominus}=\frac{RT(2\pi kTm_{\mathrm{H}})^{3/2}}{p^{\ominus}h^3}$$

We have neglected the spin degeneracy of H, which will cancel the spin degeneracy of the activated complex. The partition function of D_2 has a rotational term as well.

$$q_{\mathrm{D}_2}^{\ominus}=\frac{RT}{p^{\ominus}\Lambda_{\mathrm{D}_2}^3}\times\frac{kT}{\sigma hcB_{\mathrm{D}_2}}=\frac{RkT^2(2\pi kTm_{\mathrm{D}_2})^{3/2}}{2p^{\ominus}h^4cB_{\mathrm{D}_2}}$$

We have neglected the vibrational partition function of D_2, which is very close to unity at the temperature in question. The symmetry number σ is 2 for a homonuclear diatomic, and the rotational constant is 30.44 cm^{-1}. Now, the partition function of the activated complex will have a translational piece that is the same regardless of the model:

$$\bar{q}_{\mathrm{C}^{\ddagger}}^{\ominus}=q_{\mathrm{C}^{\ddagger}}^{\mathrm{T}\ominus}\times q_{\mathrm{C}^{\ddagger}}^{\mathrm{R}}\times\bar{q}_{\mathrm{C}^{\ddagger}}^{\mathrm{V}}$$

where $$q_{\mathrm{C}^{\ddagger}}^{\mathrm{T}\ominus}=\frac{RT(2\pi kTm_{\mathrm{HD}_2})^{3/2}}{p^{\ominus}h^3}$$

Let us aggregate the model-independent factors into a single term, F where

$$\begin{aligned}F&=\frac{(RT)^2\bar{q}_{\mathrm{C}^{\ddagger}}^{\mathrm{T}\ominus}}{hp^{\ominus}q_{\mathrm{H}}^{\ominus}q_{\mathrm{D}_2}^{\ominus}}\exp\left(\frac{-\Delta E_0}{RT}\right)=\frac{2h^3cB_{\mathrm{D}_2}m_{\mathrm{HD}_2}{}^{3/2}}{kT(2\pi m_{\mathrm{H}}m_{\mathrm{D}_2}kT)^{3/2}}\exp\left(\frac{-\Delta E_0}{RT}\right)\\&=h^3cB_{\mathrm{D}_2}\left(\frac{5^3}{2m_{\mathrm{H}}{}^3(4)^3p^3T^3k^5}\right)^{1/2}\exp\left(\frac{-\Delta E_0}{RT}\right)=2.71\times10^4\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}\end{aligned}$$

where we have taken $m_{\mathrm{HD}_2}=5m_{\mathrm{H}}$ and $m_{\mathrm{D}_2}=4m_{\mathrm{H}}$.

Now $$k_{\mathrm{r}}=F\times q_{\mathrm{C}^{\ddagger}}^{\mathrm{R}}\times\bar{q}_{\mathrm{C}^{\ddagger}}^{\mathrm{V}}$$

The number of vibrational modes in the activated complex is 3×3–6=3 for a non-linear complex, one more for a linear complex; however, in either case, one mode is the reaction coordinate, and is removed from the partition function. Therefore, assuming all real vibrations to have the same wavenumber $\tilde{\nu}$

$$\bar{q}^{\mathrm{V}}_{\mathrm{C}^{\ddagger}} = q^{2}_{\mathrm{mode}}\text{(non-linear) or } q^{3}_{\mathrm{mode}}\text{(linear)}$$

where $$q_{\mathrm{mode}} = \left[1-\exp\left(\frac{-hc\tilde{\nu}}{kT}\right)\right]^{-1} = 1.028$$

if the vibrational wavenumbers are 1000 cm^{-1} . The rotational partition function is

$$q^{\mathrm{R}}_{\mathrm{C}^{\ddagger}} = \frac{kT}{\sigma hc\tilde{B}}\text{(linear) or } \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2} \text{ (non-linear)}$$

where the rotational constants are related to moments of inertia by

$$\tilde{B} = \frac{\hbar}{4\pi cI} \text{ where } I = \sum mr^{2}$$

and r is the distance from an atom to a rotational axis.

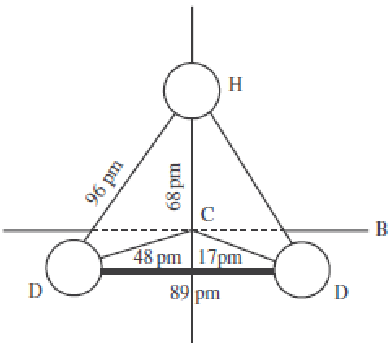
(a) The first model for the activated complex is triangular, with two equal sides of

$$s = 1.30 \times 74 \text{ pm} = 96 \text{ pm}$$

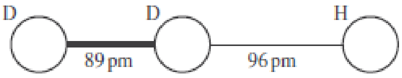
and a base of

$$b = 1.20 \times 74 \text{ pm} = 89 \text{ pm}$$

Complex (a)



Complex (b)



The moment of inertia about the axis of the altitude of the triangle (z axis) is

$$I_{1} = 2m_{\mathrm{D}}(b/2)^{2} = m_{\mathrm{H}}b^{2} \text{ so } \tilde{A} = \frac{\hbar}{4\pi cm_{\mathrm{H}}b^{2}} = 21.2 \text{ cm}^{-1}$$

To find the other moments of inertia, we need to find the center of mass. Clearly it is in the plane of the molecule and on the z axis; the center of mass is the position z at which

$$\sum_{i} m_{i}(z_{i}-z) = 0 = 2(2m_{\mathrm{H}})(0-z) + m_{\mathrm{H}}(H-z)$$

where H is the height of the triangle,

$$H = [s^{2}-(b/2)^{2}]^{1/2} = 85 \text{ pm}$$

so the center of mass is $z = H/5$.

The moment of inertia about the axis in the plane of the triangle perpendicular to the altitude is

$$I_{2} = 2(2m_{\mathrm{H}})(H/5)^{2} + m_{\mathrm{H}}(4H/5)^{2} = (4m_{\mathrm{H}}/5)H^{2}$$

so $$\tilde{B} = \frac{\hbar}{4\pi c(4m_{\mathrm{H}}/5)H^{2}} = 28.3 \text{ cm}^{-1}$$

The distance from the center of mass to the D atoms is

$$r_{\mathrm{D}} = [(H/5)^{2} + (b/2)^{2}]^{1/2} = 48 \text{ pm}$$

and the moment of inertia about the axis perpendicular to the plane of the triangle is

$$I_{3} = 2(2m_{\mathrm{H}})r_{\mathrm{D}}^{2} + m_{\mathrm{H}}(4H/5)^{2} = 2(2m_{\mathrm{H}})[(H/5)^{2} + (b/2)^{2}] + m_{\mathrm{H}}(4H/5)^{2}$$
$$= (4m_{\mathrm{H}}/5)(s^{2}+b^{2}).$$

so

$$\tilde{C} = \frac{\hbar}{4\pi c(4m_{\mathrm{H}}/5)(s^2+b^2)} = 12.2\ \mathrm{cm}^{-1}$$

The rotational partition function is

$$q_{\mathrm{C}^\ddagger}^{\mathrm{R}} = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2} = 47.7$$

(The symmetry number σ is 2 for this model.) The vibrational partition function is

$$\bar{q}_{\mathrm{C}^\ddagger}^{\mathrm{V}} = q_{\mathrm{mode}}^2 = 1.057$$

So the rate constant is:

$$k_{\mathrm{r}} = F \times q_{\mathrm{C}^\ddagger}^{\mathrm{R}} \times \bar{q}_{\mathrm{C}^\ddagger}^{\mathrm{V}} = \boxed{1.37\times10^6\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}}$$

(b) To compute the moment of inertia, we need the center of mass. Let the terminal D atom be at $x = 0$, the central D atom at $x = b$, and the H atom at $x = b + s$. The center of mass is the position X at which

$$\sum_i m_i(x_i - X) = 0 = 2m_{\mathrm{H}}(0-X) + 2m_{\mathrm{H}}(b-X) + m_{\mathrm{H}}(s+b-X)$$

$$5X = 3b + s \ so\ x = (3b+s)/5$$

The moment of inertia is

$$I = \sum_i m_i(x_i - X)^2 = 2m_{\mathrm{H}}X^2 + 2m_{\mathrm{H}}(b-X)^2 + m_{\mathrm{H}}(s+b-X)^2$$

$$= 3.97\times10^{-47}\,\mathrm{m\ kg^2}$$

and $$\tilde{B} = \frac{\hbar}{4\pi cI} = 7.06\ \mathrm{cm}^{-1}$$

The rotational partition function is

$$q_{\mathrm{C}^\ddagger}^{\mathrm{R}} = \frac{kT}{\sigma hc\tilde{B}} = 39.4$$

(The symmetry number σ is 1 for this model.) The vibrational partition function is

$$\bar{q}_{\mathrm{C}^\ddagger}^{\mathrm{V}} = q_{\mathrm{mode}}^3 = 1.09$$

So the rate constant is

$$k_{\mathrm{r}} = F \times q_{\mathrm{C}^\ddagger}^{\mathrm{R}} \times \bar{q}_{\mathrm{C}^\ddagger}^{\mathrm{V}} = \boxed{1.16\times10^6\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}}$$

(c) Both models are already pretty good, coming within a factor of 3 to 4 of the experimental result, and neither model has much room for improvement. Consider how to try to change either model to reduce the rate constant toward the experimental value. The factor F is model-independent. The factor $\bar{q}_{\mathrm{C}^\ddagger}^{\mathrm{V}}$ is nearly at its minimum possible value, 1, so stiffening the vibrational modes will have almost no effect. Only the factor $q_{\mathrm{C}^\ddagger}^{\mathrm{R}}$ is amenable to lowering, and even that not by much. It would be decreased if the rotational constants were increased, which means decreasing the moments of inertia and the bond lengths. Reducing the lengths s and b in the models to the equilibrium bond length of H_2 would only drop k_{r} to 6.5×10^5 (model a) or 6.9×10^5 (model b) $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$, even with a stiffening of vibrations. Reducing the HD distance in model (a) to 80% of the H_2 bond length does produce a rate constant of $4.2\times10^5\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ (assuming stiff vibrations of 2000 $\mathrm{cm^{-1}}$); such a model is not intermediate in structure between reactants and products, though. It appears that the rate constant is rather insensitive to the geometry of the complex.

21C.10 Eqn. 21C.18 may be written in the form:

$$z_{\mathrm{A}}^2 = \frac{1}{2A}\frac{\log\left(k_{\mathrm{r}}/k_{\mathrm{r}}^{\circ}\right)}{I^{1/2}}$$

where we have used $z_{\mathrm{A}} = z_{\mathrm{B}}$ for the cationic protein. This equation suggests that z_{A} can be determined through analysis that uses the mean value of $\frac{\log\left(k_{\mathrm{r}}/k_{\mathrm{r}}^{\circ}\right)}{I^{1/2}}$ from several experiments over a range of various ionic strengths.

$$z_A = \sqrt{\frac{1}{2A}\left\langle\frac{\log\left(k_r / k_r^o\right)}{I^{1/2}}\right\rangle}$$

We draw up a table that contains data rows needed for the computation:

I	0.0100	0.0150	0.0200	0.0250	0.0300	0.0350
k_r/k_r^o	8.10	13.30	20.50	27.80	38.10	52.00
$\log(k_r/k_r^o) / I^{1/2}$	9.08	9.18	9.28	9.13	9.13	9.17

$$\left\langle\frac{\log\left(k_r / k_r^o\right)}{I^{1/2}}\right\rangle = 9.17$$

$$z_A = \sqrt{\frac{1}{2A}\left\langle\frac{\log\left(k_r / k_r^o\right)}{I^{1/2}}\right\rangle} = \sqrt{\frac{9.16}{2(0.509)}} = \boxed{+3.0}$$

We used the positive root because the protein is cationic.

21D The dynamics of molecular collisions

Answers to discussion questions

21D.2 The saddle point on the potential energy surface corresponds to the transition state of a reaction. The saddle-point energy is the minimum energy required for reaction; it is the minimum energy for a path on the potential energy surface that leads from reactants to products. Because many paths on the surface between reactants and products do not pass through the saddle point, they necessarily pass through points of greater energy, so the activation energy can be greater than the saddle-point energy. Thus, the saddle-point energy is a lower limit to the activation energy.

21D.4 Attractive and repulsive potential-energy surfaces are discussed in Section 21D.4(b). An attractive surface is one whose saddle point is closer to reactants than to products, so that the transition state occurs early in the reaction. On such a surface, trajectories in which excess energy is translational tend to end in products whereas trajectories in which the reactant is vibrationally excited tend not to cross the saddle point and end in products. Conversely, on a repulsive surface, the oscillatory motion of a trajectory that has excess vibrational energy in the reactant enhances the likelihood that the trajectory will end in products rather than simply reflect back to reactants.

Solutions to exercises

21D.1(b) Refer to Figure 21D.20 of the main text, which shows a repulsive potential energy surface as well as trajectories of both a successful reaction and an unsuccessful one. The trajectories begin in the lower right, representing reactants. The successful trajectory passes through the transition state (marked by a circle with the symbol ‡ near it). The unsuccessful trajectory is fairly straight from the lower right through the transition state, indicating little or no vibrational excitation in the reactant. Therefore most of its energy is in translation. That trajectory runs up a steep portion of the surface and rolls back down the valley representing the reactant. Without vibrational energy, it cannot go around the corner to the transition state. The successful trajectory, conversely, is able to turn that corner only because it has a substantial amount of energy in vibration (which is represented by side to side motion in the valley representing reactants). That is, the $\boxed{\text{reactant is relatively high in vibrational energy}}$. Once that successful trajectory passes through the transition state, it rolls pretty much straight into the valley representing products, so the $\boxed{\text{product is high in translational energy and low in vibrational energy}}$.

21D.2(b) The numerator of eqn. 21D.6 is

$$\int_0^{\infty} \bar{P}(E)\mathrm{e}^{-E/RT}\mathrm{d}E = \int_0^{V} \mathrm{e}^{-E/RT}\mathrm{d}E = -\frac{1}{RT}\left(\mathrm{e}^{-E/RT}\right)\Big|_{E=0}^{E=-V} = \frac{1}{RT}\left(1-\mathrm{e}^{-V/RT}\right)$$

Thus, if the cumulative reaction probability were a step function that vanishes at high temperature, then the numerator would decrease with increasing temperature. (The exponential term increases with increasing temperature, but it diminishes the expression because of the negative sign in front of it. The $1/T$ factor also decreases with increasing temperature.) The rate constant, then, would also decrease with increasing temperature. (In fact, the rate constant would decrease with increasing temperature even faster, because the denominator of eqn. 21D.6 would increase with increasing temperature.)

Comment: The cumulative reaction probability is more likely to be a step function in the opposite sense, one that vanishes for energies **below** a threshold.

Comment: The solution to Exercise 21D.2(a) can be obtained from this solution by taking the limit $V \to \infty$.

Solutions to problems

21D.2 The number density of scatterers ($\mathcal{N}_s$) and the path length L are the same in the two experiments. Because

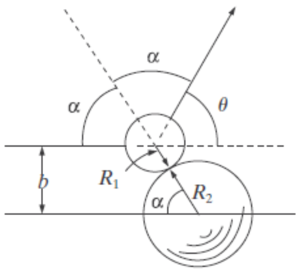
$$I = I_0\mathrm{e}^{-\sigma\mathcal{N}L} \text{ [Problem 21D.1]} \qquad \text{so} \qquad \ln\frac{I}{I_0} = -\sigma\mathcal{N}L\,,$$

we have $\dfrac{\sigma(\mathrm{CH_2F_2})}{\sigma(\mathrm{Ar})} = \dfrac{\ln 0.6}{\ln 0.9} = \boxed{5}$

CH_2F_2 is a polar molecule; Ar is not. CsCl is a polar ion pair and is scattered more strongly by the polar CH_2F_2.

21D.4 Refer to Figure 21D.1.

Figure 21D.1



The scattering angle is $\theta = \pi - 2\alpha$ if specular reflection occurs in the collision (angle of impact equal to angle of departure from the surface). For $b \le R_1 + R_2$, $\sin\alpha = \dfrac{b}{R_1 + R_2(v)}$

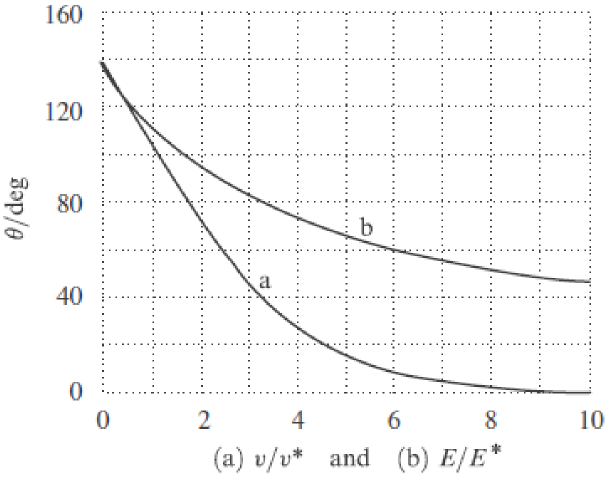
$$\theta(v) = \begin{cases} \pi - 2\arcsin\left(\dfrac{b}{R_1 + R_2(v)}\right) & b \le R_1 + R_2(v) \\ 0 & b > R_1 + R_2(v) \end{cases}$$

where $R_2(v) = R_2\mathrm{e}^{-v/v^*}$, $R_1 = R_2/2 = b$.

(a) $\theta(v) = \pi - 2\arcsin\left(\dfrac{1}{1+2\mathrm{e}^{-v/v^*}}\right)$

(Note: The restriction $b \le R_1 + R_2(v)$ transforms into $R_2/2 \le R_2/2 + R_2\mathrm{e}^{-v/v^*}$, which is valid for all v.) This function is plotted as curve (a) in Figure 21D.2.

Figure 21D.2



(b) The kinetic energy of approach is $E = mv^2/2$, so

$$\theta(E) = \pi - 2\arcsin\left(\frac{1}{1+2\mathrm{e}^{-(E/E^*)^{1/2}}}\right) \qquad \text{where} \quad E^* = m(v^*)^2/2 \ .$$

This function is plotted as curve (b) in Figure 21.6.

21E Electron transfer in homogeneous systems

Answer to discussion question

21E.2 Electron tunneling plays an important role in electron transfer. From considerations in Topic 8A, we would expect that tunneling would be more important for electrons than any other particles that participate in chemical reactions because they are so much lighter than even the lightest atoms or ions. Tunneling is responsible for the exponential distance dependence of the factor $H_{\mathrm{et}}(d)^2$ (eqn. 21E.4), which is directly proportional to the electron-transfer rate constant (eqn. 21E.5). A more thorough discussion can be found in Topic 21E.2(a).

Solutions to exercises

21E.1(b) For a donor–acceptor pair separated by a constant distance, assuming that the reorganization energy is constant, eqn. 21E.9 holds:

$$\ln k_{\mathrm{et}} = -\frac{(\Delta_{\mathrm{r}}G^{\ominus})^2}{4RT\Delta E_{\mathrm{R}}} - \frac{\Delta_{\mathrm{r}}G^{\ominus}}{2RT} + \text{constant}$$

or, using molecular units rather than molar units,

$$\ln k_{\mathrm{et}} = -\frac{(\Delta_{\mathrm{r}}G^{\ominus})^2}{4kT\Delta E_{\mathrm{R}}} - \frac{\Delta_{\mathrm{r}}G^{\ominus}}{2kT} + \text{constant}$$

Two sets of rate constants and reaction Gibbs energies can be used to generate two equations (eqn. 21E.9 applied to the two sets) in two unknowns, ΔG_{r} and the constant.

$$\ln k_{\mathrm{et},1} + \frac{(\Delta_{\mathrm{r}}G_1^{\ominus})^2}{4kT\Delta E_{\mathrm{R}}} + \frac{\Delta_{\mathrm{r}}G_1^{\ominus}}{2kT} = \text{constant} = \ln k_{\mathrm{et},2} + \frac{(\Delta_{\mathrm{r}}G_2^{\ominus})^2}{4kT\Delta E_{\mathrm{R}}} + \frac{\Delta_{\mathrm{r}}G_2^{\ominus}}{2kT}$$

so $$\frac{(\Delta_{\mathrm{r}}G_1^{\ominus})^2 - (\Delta_{\mathrm{r}}G_2^{\ominus})^2}{4kT\Delta E_{\mathrm{R}}} = \ln\frac{k_{\mathrm{et},2}}{k_{\mathrm{et},1}} + \frac{\Delta_{\mathrm{r}}G_2^{\ominus} - \Delta_{\mathrm{r}}G_1^{\ominus}}{2kT}$$

and $$\Delta E_{\mathrm{R}} = \frac{(\Delta_{\mathrm{r}}G_1^{\ominus})^2 - (\Delta_{\mathrm{r}}G_2^{\ominus})^2}{4kT\ln\dfrac{k_{\mathrm{et},2}}{\mathrm{k}_{\mathrm{et},1}} + 2\left(\Delta_{\mathrm{r}}G_2^{\ominus} - \Delta_{\mathrm{r}}G_1^{\ominus}\right)}$$

$$\Delta E_{\mathrm{R}} = \frac{(-0.665\ \mathrm{eV})^2 - (-0.975\ \mathrm{eV})^2}{\dfrac{4(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})(298\ \mathrm{K})}{1.602\times10^{-19}\ \mathrm{J\ eV^{-1}}}\ln\dfrac{3.33\times10^{6}}{2.02\times10^{5}} - 2(0.975-0.665)\ \mathrm{eV}} = \boxed{1.53\ \mathrm{eV}}$$

If we knew the activation Gibbs energy, we could use eqn. 21E.5 to compute $H_{\mathrm{et}}(d)$ from either rate constant, and we *can* compute the activation Gibbs energy from eqn. 21E.6:

$$\Delta^{\ddagger}G = \frac{(\Delta_{\mathrm{r}}G^{\ominus} + \Delta E_{\mathrm{r}})^2}{4\Delta E_{\mathrm{r}}} = \frac{\{(-0.665+1.53)\ \mathrm{eV}\}^2}{4(1.53\ \mathrm{eV})} = 0.123\ \mathrm{eV}$$

Now $$k_{\mathrm{et}} = \frac{2\{H_{\mathrm{et}}(d)\}^2}{h}\left(\frac{\pi^3}{4kT\Delta E_{\mathrm{R}}}\right)^{1/2}\exp\left(\frac{-\Delta^{\ddagger}G}{kT}\right)$$

$$H_{\mathrm{et}}(d) = \left(\frac{hk_{\mathrm{et}}}{2}\right)^{1/2}\left(\frac{4kT\Delta E_{\mathrm{R}}}{\pi^3}\right)^{1/4}\exp\left(\frac{\Delta^{\ddagger}G}{2kT}\right)$$

$$= \left(\frac{(6.626\times10^{-34}\ \mathrm{J\ s})(2.02\times10^{5}\ \mathrm{s^{-1}})}{2}\right)^{1/2}$$

$$\times\left(\frac{4(1.53\ \mathrm{eV})(1.602\times10^{-19}\ \mathrm{J\ eV^{-1}})(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})(298\ \mathrm{K})}{\pi^3}\right)^{1/4}$$

$$\times\exp\left(\frac{(0.123\ \mathrm{eV})(1.602\times10^{-19}\ \mathrm{J\ eV^{-1}})}{2(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})(298\ \mathrm{K})}\right)$$

so $$= \boxed{9.6\times10^{-24}\ \mathrm{J}}$$

21E.2(b) Equation 21E.8 applies:

$$\ln k_{\mathrm{et}} = -\beta d + \text{constant}$$

The slope of a plot of k_{et} versus d is $-\beta$. The slope of a line defined by two points is:

$$\text{slope} = \frac{\Delta y}{\Delta x} = \frac{\ln k_{\mathrm{et,2}} - \ln k_{\mathrm{et,1}}}{d_2 - d_1} = -\beta = \frac{\ln\ 4.51\times10^{4} - \ln\ 2.02\times10^{5}}{(1.23-1.11)\ \mathrm{nm}}$$

so $$\beta = 12.\bar{5}\ \mathrm{nm^{-1}}$$

Inserting data from either rate constant allows calculation of the constant:

$$\text{constant} = \ln 2.02\times10^{5} + (12.\bar{5}\ \mathrm{nm^{-1}})(1.11\ \mathrm{nm}) = 26.1$$

Taking the exponential of eqn. 21E.8 yields:

$$k_{\mathrm{et}} = \mathrm{e}^{-\beta d\ +\ \text{constant}}\ \mathrm{s^{-1}} = \mathrm{e}^{-(12.\bar{5}/\mathrm{nm})(1.59\,\mathrm{nm})+26.1}\,\mathrm{s^{-1}} = \boxed{5.0\times10^{2}\ \mathrm{s^{-1}}}$$

Solutions to problems

21E.2 Estimate the bimolecular rate constant k_{r} for the reaction

$$\mathrm{Ru(bpy)_3}^{3+} + \mathrm{Fe(H_2O)_6}^{2+} \rightarrow \mathrm{Ru(bpy)_3}^{2+} + \mathrm{Fe(H_2O)_6}^{3+}$$

by using the approximate Marcus cross-relation:

$$k_{\mathrm{r}} \approx (k_{\mathrm{DD}}k_{\mathrm{AA}}K)^{1/2}$$

The standard cell potential for the reaction is

$$E^{\ominus} = E^{\ominus}_{\mathrm{red}}(\mathrm{Ru(bpy)_3}^{3+}) - E^{\ominus}_{\mathrm{red}}(\mathrm{Fe(H_2O)_6}^{3+}) = (1.26-0.77)\mathrm{V} = 0.49\ \mathrm{V}$$

so the equilibrium constant is

$$K = \exp\left(\frac{\nu F E^{\ominus}}{RT}\right) = \exp\left(\frac{(1)(96485\ \mathrm{C\ mol^{-1}\ s^{-1}})(0.49\,\mathrm{V})}{(8.3145\,\mathrm{J\ K^{-1}\ mol^{-1}})(298\,\mathrm{K})}\right) = 1.9\times10^{8}$$

The rate constant is approximately

$$k_{\mathrm{r}} \approx \{(4.0\times10^{8}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}})(4.2\ \mathrm{dm^3\ mol^{-1}\ s^{-1}})(1.9\times10^{8})\}^{1/2}$$

$$k_{\mathrm{r}} \approx \boxed{5.7\times10^{8}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}}$$

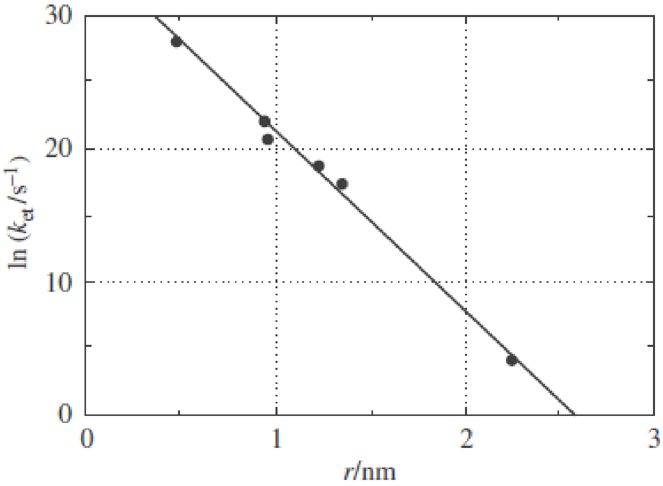
21E.4 Does eqn. 21E.8

$$\ln k_{\mathrm{et}} = -\beta d + \text{constant}$$

apply to these data? Draw the following table and plot $\ln k_{\mathrm{et}}$ vs. d (Figure 21E.1):

d / nm	k_{et} / s^{-1}	ln k_{et} / s^{-1}
0.48	1.58×10^{12}	28.1
0.95	3.98×10^{9}	22.1
0.96	1.00×10^{9}	20.7
1.23	1.58×10^{8}	18.9
1.35	3.98×10^{7}	17.5
2.24	6.31×10^{1}	4.14

Figure 21E.1



The data fall on a good straight line, so the equation $\boxed{\text{appears to apply}}$. The least-squares linear fit equation is:

$$\ln k_{\mathrm{et}} / \mathrm{s} = 34.7 - 13.4d / \mathrm{nm} \quad R^2 (\text{correlation coefficient}) = 0.991$$

so we identify $\beta = \boxed{13.4\ \mathrm{nm}^{-1}}$

21F Processes at electrodes

Answer to discussion question

21F.2 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 electode-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 treated in Topic 21F.2(a).

Solutions to exercises

21F.1(b) The conditions are in the limit of large, positive overpotentials, so eqn 21F.5b applies:

$$\ln j = \ln j_0 + (1-\alpha)f\eta$$

where $f = \dfrac{F}{RT} = \dfrac{96845\ \mathrm{C\ mol^{-1}}}{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (298\ \mathrm{K})} = 38.9\ \mathrm{V^{-1}}$

Subracting 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

$$\eta'=\eta+\frac{\ln(j'/j)}{(1-\alpha)f}=(105\times10^{-3}\ \mathrm{V})+\frac{\ln(72/17.0)}{(1-0.42)\times(38.9\ \mathrm{V})^{-1}}=\boxed{0.169\ \mathrm{V}}$$

21F.2(b) Use eqn 21F.5a; then

$$j_0=j\,\mathrm{e}^{-(1-\alpha)\eta f}=(17.0\ \mathrm{mA\ cm^{-2}})\times\mathrm{e}^{-(1\text{-}0.42)\times0.105\ \mathrm{V}\times38.9/\mathrm{V}}=\boxed{1.59\ \mathrm{mA\ cm^{-2}}}\,.$$

21F.3(b) In the high overpotential limit [21F.5a]

$$j=j_0\mathrm{e}^{(1-\alpha)f\eta}\quad\text{so}\quad\frac{j_1}{j_2}=\mathrm{e}^{(1-\alpha)f(\eta_1-\eta_2)}\quad\text{and}\quad j_2=j_1\mathrm{e}^{(1-\alpha)f(\eta_2-\eta_1)}\,.$$

So the current density at 0.60 V

$$j_2=(1.22\,\mathrm{mA\,cm^{-2}})\times\mathrm{e}^{(1-0.50)\times(0.60\,\mathrm{V}-0.50\,\mathrm{V})\times(38.9/\mathrm{V})}=\boxed{8.5\,\mathrm{mA\,cm^{-2}}}$$

about a 7-fold increase compared to the current at 0.50 V.

21F.4(b) **(i)** The Butler–Volmer equation is [21F.1]

$$j=j_0(\mathrm{e}^{(1-\alpha)f\eta}-\mathrm{e}^{-\alpha f\eta})$$

$$=(2.5\times10^{-3}\ \mathrm{A\,cm^{-2}})\times(\mathrm{e}^{(1-0.58)\times(0.30\,\mathrm{V})\times(38.9/\mathrm{V})}-\mathrm{e}^{-0.58\times(0.30\,\mathrm{V})\times(38.9/\mathrm{V})})=\boxed{0.34\ \mathrm{A\ cm^{-2}}}$$

(ii) Eqn 21F.5a (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 $\eta\to0$.
The validity of the Tafel equation improves as the overpotential increases.

21F.5(b) The Butler–Volmer equation (21F.1]), with transfer coefficients from Table 21F.1, 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 (6C.4):

$$E=E^{\ominus}-\frac{RT}{vF}\ln Q=E^{\ominus}-\frac{1}{f}\ln\frac{a(\mathrm{Fe^{2+}})}{a(\mathrm{Fe^{3+}})}=0.77\ \mathrm{V}-\frac{1}{f}\ln\frac{a(\mathrm{Fe^{2+}})}{a(\mathrm{Fe^{3+}})}$$

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 $j=(2.5\,\mathrm{mA\,cm^{-2}})\times(\mathrm{e}^{0.42\,fE'-0.42\,f\times0.77\ \mathrm{V}}-\mathrm{e}^{-0.58\,fE'+0.58\,f\times0.77\ \mathrm{V}})$.

Evaluating the constant parts of the exponentials (with $f=38.9\ \mathrm{V^{-1}}$). and incorporating them as numerical factors yields

$$j=\boxed{(8.6\times10^{-6}\ \mathrm{mA\,cm^{-2}})\times\mathrm{e}^{0.42\,fE'}-(8.8\times10^{-7}\ \mathrm{mA\,cm^{-2}})\mathrm{e}^{-0.58\,fE'}}$$

21F.6(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 21F.1, and recall that $1\ \mathrm{A}=1\ \mathrm{C\ s^{-1}}$.

For Cu | H_2 | H^+ $j_0=1.0\times10^{-6}\ \mathrm{A\ cm^{-2}}$

$$\frac{j_0}{e}=\frac{1.0\times10^{-6}\ \mathrm{A\ cm^{-2}}}{1.602\times10^{-19}\ \mathrm{C}}=\boxed{6.2\times10^{12}\ \mathrm{cm^{-2}\ s^{-1}}}$$

For Pt | Ce^{4+}, Ce^{3+} $j_0=4.0\times10^{-5}\ \mathrm{mA\ cm^{-2}}$

$$\frac{j_0}{e}=\frac{4.0\times10^{-5}\ \mathrm{A\ cm^{-2}}}{1.602\times10^{-19}\ \mathrm{C}}=\boxed{2.5\times10^{14}\ \mathrm{cm^{-2}\ s^{-1}}}$$

There are approximately $\frac{(1.0\times10^{-2}\text{ m})^2}{(260\times10^{-12}\text{ m})^2}=1.5\times10^{15}$ atoms in each square centimeter of surface. The numbers of electrons per atom are therefore $\boxed{4.2\times10^{-3}\ \text{s}^{-1}}$ and $\boxed{0.17\ \text{s}^{-1}}$, respectively.

21F.7(b) When the overpotential is small, its relation to the current density is [21F.4]

$$\eta=\frac{RTj}{Fj_0}=\frac{j}{fj_0}$$

which implies that the current through surface area S is

$$I=Sj=Sj_0f\eta\,.$$

An ohmic resistance r obeys $\eta=Ir$, and so we can identify the resistance as

$$r=\frac{\eta}{I}=\frac{1}{Sj_0f}=\frac{1}{1.0\text{ cm}^2\times38.9\text{ V}^{-1}\times j_0}=\frac{2.57\times10^{-2}\,\Omega}{(j_0/\text{A cm}^{-2})}\quad[1\text{V}=1\text{A}\,\Omega]$$

(a) Pb | H_2 | H^+ $\quad j_0=5.0\times10^{-12}$ A cm^{-2}

$$r=\frac{2.57\times10^{-2}\,\Omega}{5.0\times10^{-12}}=\boxed{5.1\times10^{9}\ \Omega}=5.1\text{ G}\Omega$$

(b) Pt | Fe^{3+}, Fe^{2+} $\quad j_0=2.5\times10^{-3}$ mA cm^{-2}

$$r=\frac{2.57\times10^{-2}\,\Omega}{2.5\times10^{-3}}=\boxed{10.\ \Omega}$$

21F.8(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

$$j=j_0e^{-\alpha f\eta}\ [21F.6a]=(0.79\text{ mA cm}^{-2})\times e^{-0.5\times(38.9/\text{V})\times(-0.76\text{ V})}=2.1\times10^{6}\text{ mA cm}^{-2}$$

This current density is much too large to allow deposition of zinc; that is, H_2 would begin being evolved, and fast, long before zinc began to deposit.

Solutions to problems

21F.2 Deposition may occur when the potential falls to below E. (Recall that $\eta<0$ for cathodic processes.) E is given by the Nernst equation (6C.4):

$$E=E^{\ominus}+\frac{RT}{zF}\ln a(\text{M}^+)$$

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

$$\ln\frac{a(\text{Sn}^{2+})}{a(\text{Pb}^{2+})}=\left(\frac{2F}{RT}\right)\{E^{\ominus}(\text{Pb},\text{Pb}^{2+})-E^{\ominus}(\text{Sn},\text{Sn}^{2+})\}$$

$$=2\times(38.9\text{ V}^{-1})\times(-0.126+0.136)\text{ V}=0.78$$

That is, we require $a(\text{Sn}^{2+})=e^{0.78}a(\text{Pb}^{2+})=2.2a(\text{Pb}^{2+})$.

21F.4 This problem differs somewhat from the simpler one-electron transfers considered in the text. In place of Ox + e^- → Red we have here

$$\text{In}^{3+}+3\,e^-\rightarrow\text{In}$$

namely, a three-electron transfer. Therefore equations that contain the Faraday constant F (or f, which is proportional to F) need to be modified by including the factor z (in this case 3). In place of eqns 21F.5b and 21F.6b, we have

$\ln j=\ln j_0+z(1-\alpha)f\eta$ anode

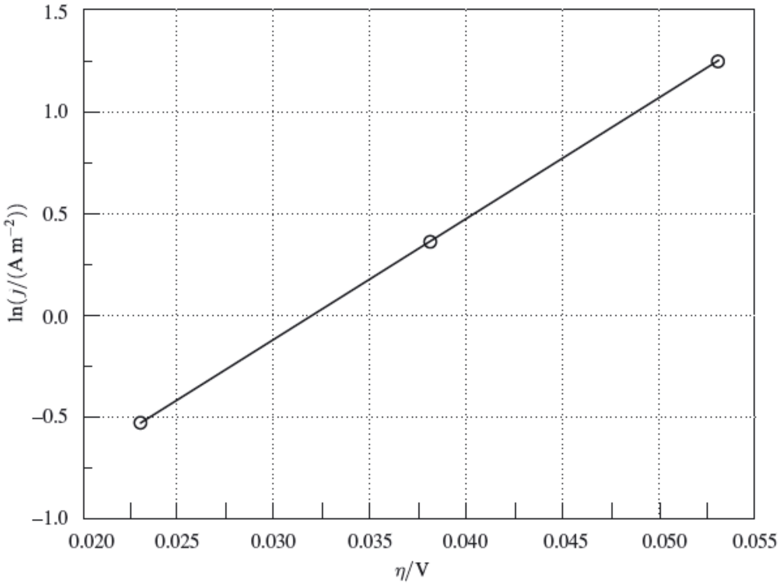
$\ln(-j)=\ln j_0-z\alpha f\eta$ cathode

We draw up the following table

j/(A m^{-2})	$-E$/V	η/V	ln (j/A m^{-2})
0	0.388	0	
0.590	0.365	0.023	–0.5276
1.438	0.350	0.038	0.3633
3.507	0.335	0.053	1.255

We carry out a linear regression of ln j against η with the following results (see Figure 20F.1).

Figure 20F.1



slope = $z(1-\alpha)f$ = 59.42 V^{-1}, standard deviation = 0.0154
y-intercept = ln j_0 = –1.894, standard deviation = 0.0006
R = 1 almost exactly

The fit of the three data points to the Tafel equation is almost exact. Solving for α from the slope, we obtain

$$\alpha = 1-\frac{59.42\ \mathrm{V^{-1}}}{3f} = 1-\left(\frac{59.42\ \mathrm{V^{-1}}}{3\times(38.9\ \mathrm{V^{-1}})}\right) = \boxed{0.50}$$

which matches the usual value of α exactly.

$j_0 = \mathrm{e}^{-1.894}$ A m^{-2} = $\boxed{0.150\ \mathrm{A\ m^{-2}}}$.

The cathodic current density at E = –0.365 V is obtained from

$$\ln(-j_c) = \ln j_0 - z\alpha f\eta$$
$$= -1.894-(3\times 0.50\times 0.023\ \mathrm{V})\times(38.9\ \mathrm{V^{-1}}) = -3.2\overline{6}$$

so $j_c = \mathrm{e}^{-3.2\overline{6}} = \boxed{0.038\,\mathrm{A\,m^{-2}}}$

21F.6 Start from the Butler-Volmer equation (21F.1), and expand it in powers of η:

$$j = j_0(e^{(1-\alpha)f\eta}-e^{-\alpha f\eta})$$
$$= j_0\{1+(1-\alpha)\eta f+\tfrac{1}{2}(1-\alpha)^2\eta^2 f^2+\cdots-1+\alpha f\eta-\frac{1}{2}\alpha^2\eta^2 f^2+\cdots\}$$
$$= j_0\{\eta f+\tfrac{1}{2}(\eta f)^2(1-2\alpha)+\cdots\}$$

Average over one cycle (of period $2\pi/\omega$):

$$\langle j\rangle = j_0\left\{\langle\eta\rangle f+\tfrac{1}{2}(1-2\alpha)f^2\langle\eta^2\rangle+\cdots\right\}$$

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,

$$\begin{aligned}\langle I\rangle &= \tfrac{1}{4}(1-2\alpha)f^2 S j_0 \eta_0^2\\ &= \frac{1-0.76}{4}\times(1.0\ \mathrm{cm}^2)\times(7.90\times10^{-4}\ \mathrm{A\ cm}^{-2})\times(0.0389\ \mathrm{mV}^{-1})\times(10\,\mathrm{mV})^2\\ &= \boxed{7.2\ \mu A}\end{aligned}$$

21F.8 **(a)** The roughly symmetrically distributed positive maximum and negative minimum suggest a reversible one-electron transfer. Compare to Figures 21F.12 and 21F.13(b) of the main part of the chapter as discussed in Topic 21F.3 and Example 21F.2.

(b) There are two roughly symmetrically distributed positive maxima and negative minima, suggesting a reversible two-electron transfer brought about by sequential reversible one-electron transfers.

(c) The shape is typical of an irreversible reduction: the positive maximum has no corresponding negative minimum. Compare to Figure 21F.13(a) of the main part of the chapter as discussed in Example 21F.2.

(d) Two reductions are apparent in this voltammogram, the second of which is reversible and the first not. (The first positive maximum has no corresponding minimum; the second does.) Compare to Figure 21F.14 of the main part of the text.

Integrated activity

21.2 Both the Marcus theory of photo-induced electron transfer (Topic 21E) and the Förster theory of resonance energy transfer (Topic 20G) 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).

22 Processes on surfaces

22A An introduction to solid surfaces

Answers to discussion questions

22A.2 AFM, atomic force microscopy, drags a sharp stylus attached to a cantilever across a surface and monitors the deflection of a laser beam from the back of the cantilever. Tiny changes in deflection indicate attraction to or repulsion from atoms on a sample surface. Since no current is involved, both conductive and nonconductive surfaces may be viewed. Surface damage is avoided by using a cantilever that has a very small spring constant. The method does not require a vacuum, and it has been applied in a liquid environment. Biological polymers may be viewed and nanometre resolutions have been achieved. However, an incorrect probe choice may cause image artifacts and distortions. Thermal drift of adsorbates may result in image distortions during relatively slow surface scans.

FIM, field-ionization microscopy, points a tip, with a point radius of about 50 nm, toward a fluorescent screen in a chamber containing about 1 mTorr to 1 nTorr of either hydrogen or helium. A positive 2-20 kV potential applied to the tip causes the hydrogen or helium gas adsorbate molecules to ionize and accelerate to the fluorescent screen. The image portrays the electrical characteristics of the tip surface and surface diffusion characteristics of the adsorbate are deduced. See the very interesting historical review of the technique in the issue of *C&EN* 83, no. 48 (November 28, 2005): 13-16.

LEED, low-energy electron diffraction, uses electrons with energies in the range 10-200 eV, which ensures diffraction from atoms only on or near the sample surface. Diffraction intensities depend on the vertical location of the atoms. The diffraction pattern is sharp if the surface is well-ordered for long distances compared with the wavelength of the incident electrons. Diffuse patterns indicate a poorly ordered surface or the presence of impurities. If the LEED pattern does not correspond to the pattern expected by extrapolation of the bulk to the surface, then either a reconstruction of the surface has occurred or there is order in the arrangement of an adsorbed layer. The interpretation of LEED data can be very complicated.

SAM, scanning Auger electron microscopy, uses a focused 1-5 keV electron beam to probe and map surface composition to a resolution of about 50 nm. The high energy impact causes the ejection of an electron from a low-lying orbital, and an upper electron falls into it. The energy this releases may result either in the generation of **X-ray fluorescence** or in the ejection of a second electron, the **Auger effect**. The emissions are used to identify chemical constituents at interfaces and surfaces of conducting and semiconducting materials to a depth of 1-5 nm.

SEM, scanning electron microscopy, uses magnetic fields to focus and scan a beam of electrons across a sample surface. Scattered electrons from a small irradiated area are detected and the electrical signal is sent to a video screen. Resolution is typically between 1.5 and 3.0 nm. Nonconductive materials require a thin conductive coating to prevent electrical charging of the sample.

STM, scanning tunnelling microscopy, reveals atomic details of surface and adsorbate structure. Surface chemical reactions can be viewed as they happen. The tip of the STM, which may end in a single atom, can also be used to manipulate adsorbed atoms on a surface, making possible the fabrication of complex and yet very tiny structures, such as nanometre-sized electronic devices. The method is based upon the quantum mechanical tunneling effect in the presence of a bias voltage between the STM tip and sample surface. A piezoelectric scanner is used to position and move the tip in very close proximity to the surface, and the electrical current of tunneling generates an image of the surface topography with a resolution in the nanometre range. Images of surface electronic states may be generated. A host of very interesting STM images can be viewed at http://www.almaden.ibm.com/vis/stm/gallery.html.

TEM, transmission electron microscopy, passes an electron beam through the sample and collects the image on a screen. Electron wavelengths can be as short as 10 pm and typical resolutions are about 2 nm so the method cannot resolve individual atoms. Samples must be very thin cross-sections of a dry (therefore, nonliving) sample. Electron microscopy is very useful in the study of internal structures of cells.

Solutions to exercises

22A.1(b) The collision frequency, Z_W, of gas molecules with an ideally smooth surface area is given by eqn 22A.1.

$$
\begin{aligned}
Z_W &= \frac{p}{(2\pi MkT/N_A)^{1/2}} \quad [\text{22A.1; } m = M/N_A] \\
&= \frac{p\times\left\{\left(\mathrm{kg\ m^{-1}\ s^{-2}}\right)/\mathrm{Pa}\right\}\times\left(10^{-4}\ \mathrm{m^2/cm^2}\right)}{\left\{2\pi\times\left(1.381\times10^{-23}\ \mathrm{J\ K^{-1}}\right)\times(298.15\ \mathrm{K})\times\left(\mathrm{kg\ mol^{-1}}\right)/\left(6.022\times10^{23}\ \mathrm{mol^{-1}}\right)\right\}^{1/2}\left\{M/\left(\mathrm{kg\ mol^{-1}}\right)\right\}^{1/2}} \\
&= 4.825\times10^{17}\left(\frac{p/\mathrm{Pa}}{\left\{M/\left(\mathrm{kg\ mol^{-1}}\right)\right\}^{1/2}}\right)\mathrm{cm^{-2}\ s^{-1}} \quad \text{at } 25°\ \mathrm{C}
\end{aligned}
$$

(i) Nitrogen ($M = 0.02802\ \mathrm{kg\ mol^{-1}}$)

$p = 10.0$ Pa, $Z_W = \boxed{3.88\times10^{19}\ \mathrm{cm^{-2}\ s^{-1}}}$

$p = 0.150\ \mu$Torr $= 2.00\times10^{-5}$ Pa, $Z_W = \boxed{5.76\times10^{13}\ \mathrm{cm^{-2}\ s^{-1}}}$

(ii) Methane ($M = 0.01604\ \mathrm{kg\ mol^{-1}}$)

$p = 10.0$ Pa, $Z_W = \boxed{3.81\times10^{19}\ \mathrm{cm^{-2}\ s^{-1}}}$

$p = 0.150\ \mu$Torr $= 2.00\times10^{-5}$ Pa, $Z_W = \boxed{7.62\times10^{13}\ \mathrm{cm^{-2}\ s^{-1}}}$

22A.2(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 is $Z_WA = 5.00\times10^{19}\ \mathrm{s^{-1}}$.

$$
\begin{aligned}
Z_WA &= \frac{p}{(2\pi MkT/N_A)^{1/2}}A \ [\text{95.1; } m = M/N_A] \\
p &= (Z_WA)\times(2\pi MkT/N_A)^{1/2}/A \\
&= \left(5.0\times10^{19}\ \mathrm{s^{-1}}\right) \\
&\quad\times\left\{2\pi\left(28.02\times10^{-3}\ \mathrm{kg\ mol^{-1}}\right)\times\left(1.381\times10^{-23}\ \mathrm{J\ K^{-1}}\right)\times(525\ \mathrm{K})/\left(6.022\times10^{23}\ \mathrm{mol^{-1}}\right)\right\}^{1/2}/\left(3.14\times10^{-6}\ \mathrm{m^2}\right) \\
&= \boxed{733\ \mathrm{Pa}}
\end{aligned}
$$

Solutions to problems

22A.2 $Z_W = \dfrac{p}{(2\pi MkT/N_A)^{1/2}}$ [22A.1; $m = M/N_A$]

$$
\begin{aligned}
&= \frac{p\times\left\{\left(\mathrm{kg\ m^{-1}\ s^{-2}}\right)/\mathrm{Pa}\right\}\times\left(10^{-4}\ \mathrm{m^2/cm^2}\right)}{\left\{2\pi\times\left(1.381\times10^{-23}\ \mathrm{J\ K^{-1}}\right)\times(300\ \mathrm{K})\times\left(0.03200\ \mathrm{kg\ mol^{-1}}\right)/\left(6.022\times10^{23}\ \mathrm{mol^{-1}}\right)\right\}^{1/2}} \\
&= 2.69\times10^{18}\times(p/\mathrm{Pa})\ \mathrm{cm^{-2}\ s^{-1}} \qquad \text{for } O_2 \text{ at } 300\ \mathrm{K}
\end{aligned}
$$

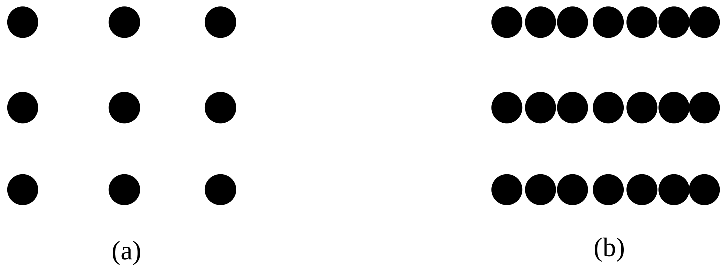
(a) At 100 kPa, $\boxed{Z_W = 2.69\times10^{23}\ \mathrm{cm^{-2}\ s^{-1}}}$ **(b)** at 1.000 Pa, $\boxed{Z_W = 2.69\times10^{18}\ \mathrm{cm^{-2}\ s^{-1}}}$

The nearest neighbor in titanium is 291 pm, so the number of atoms per 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 $Z_W/\left(1.4\times10^{15}\ \mathrm{cm^{-2}}\right)$.

(a) When $p = 100\,\mathrm{kPa}$, $Z_{\mathrm{atom}} = \boxed{2.0\times10^{8}\ \mathrm{s^{-1}}}$ **(b)** When $p = 1.000\,\mathrm{Pa}$, $Z_{\mathrm{atom}} = \boxed{2.0\times10^{3}\ \mathrm{s^{-1}}}$

22A.4 The farther apart the atoms responsible for the pattern, the closer the spots appear in the pattern (see

Example 22A.1). Tripling the horizontal separation between atoms of the unreconstructed face, which has LEED pattern (a), yields a reconstructed surface that gives LEED pattern (b).



22B Adsorption and desorption

Answers to discussion questions

22B.2 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 neighboring sites.

For the **BET isotherm** condition number 1 above is removed and the isotherm applies to multi-layer coverage.

In Example 22B.1 it is shown that a gas exhibits the characteristics of a Langmuir adsorption isotherm when

$$\frac{p}{V}=\frac{p}{V_\infty}+\frac{1}{\alpha V_\infty}$$

where V is the volume of the adsorbate and V_∞ completes the monolayer coverage. Hence, a plot of p/V against p should give a straight line of slope $1/V_\infty$ and intercept $1/\alpha V_\infty$.

In contrast the BET adsorption isotherm is followed when, as shown in Example 22B.3,

$$\frac{z}{(1-z)V}=\frac{1}{cV_{\text{mon}}}+\frac{(c-1)z}{cV_{\text{mon}}}$$

where $z = p/p^*$ and p^* is the vapour pressure above a layer of adsorbate that is more than one molecule thick and which resembles a pure bulk liquid, V_{mon} is the volume corresponding to monolayer coverage, and c is a constant. Thus, the BET adsorption mechanism is indicated when a plot of $z/\{(1-z)V\}$ against z is linear.

Solutions to exercises

22B.1(b) $\theta=\frac{V}{V_\infty}=\frac{V}{V_{\text{mon}}}=\frac{\alpha p}{1+\alpha p}$ [22B.2]

This rearranges to [Example 22B.1]

$$\frac{p}{V}=\frac{p}{V_{\text{mon}}}+\frac{1}{\alpha V_{\text{mon}}}$$

Hence, $\frac{p_2}{V_2}-\frac{p_1}{V_1}=\frac{p_2}{V_{\text{mon}}}-\frac{p_1}{V_{\text{mon}}}$

Solving for V_{mon}:

$$V_{\text{mon}}=\frac{p_2-p_1}{(p_2/V_2-p_1/V_1)}=\frac{(108\text{–}56.4)\text{ kPa}}{(108/2.77-56.4/1.52)\text{ kPa cm}^{-3}}=\boxed{27\,\text{cm}^3}$$

22B.2(b) The enthalpy of adsorption is typical of $\boxed{\text{chemisorption}}$ (Table 22A.2) for which $\tau_0 \approx 10^{-14}$ s because the adsorbate-substrate bond is stiff (see Brief illustration 22B.2). The half-life for remaining on the surface is

$$t_{1/2} = \tau_0 \mathrm{e}^{E_{\mathrm{a,des}}/RT} \ [22\mathrm{B}.13] \approx (10^{-14}\ \mathrm{s}) \times (\mathrm{e}^{155\times 10^3/(8.3145\times 500)}) \ [E_{\mathrm{d}} \approx -\Delta_{\mathrm{ad}}H] \approx \boxed{200\ \mathrm{s}}$$

22B.3(b) $\dfrac{m_1}{m_2} = \dfrac{\theta_1}{\theta_2} = \dfrac{p_1}{p_2} \times \dfrac{1+\alpha p_2}{1+\alpha p_1}$ [22B.2 and $V \propto m/p$]

which solves to

$$\alpha = \frac{(m_1 p_2 / m_2 p_1) - 1}{p_2 - (m_1 p_2 / m_2)} = \frac{(m_1/m_2)\times(p_2/p_1) - 1}{1-(m_1/m_2)} \times \frac{1}{p_2}$$

$$= \frac{(0.63/0.21)\times(4/36.0) - 1}{1-(0.63/0.21)} \times \frac{1}{4.0\ \mathrm{kPa}} = 0.083\ \mathrm{kPa}^{-1}$$

Therefore,

$$\theta_1 = \frac{(0.083\ \mathrm{kPa}^{-1})\times(36.0\ \mathrm{kPa})}{(1)+(0.083\ \mathrm{kPa}^{-1})\times(36.0\ \mathrm{kPa})} = \boxed{0.75} \quad [22\mathrm{b}.2] \quad \text{and} \quad \theta_2 = \frac{(0.083)\times(4.0)}{(1)+(0.083)\times(4.0)} = \boxed{0.25}$$

22B.4(b) $\theta = \dfrac{Kp}{1+Kp}$ [22B.1, $\alpha = K = k_{\mathrm{a}}/k_{\mathrm{d}}$], which implies that $p = \left(\dfrac{\theta}{1-\theta}\right)\dfrac{1}{K}$.

(a) $p = (0.20/0.80)/0.548\ \mathrm{kPa}^{-1} = \boxed{0.46\ \mathrm{kPa}}$

(b) $p = (0.75/0.25)/0.548\ \mathrm{kPa}^{-1} = \boxed{5.5\ \mathrm{kPa}}$

22B.5(b)

$$\left(\frac{\partial \ln(p/p^{\ominus})}{\partial(1/T)}\right)_{\theta} = \frac{\Delta_{\mathrm{ad}}H^{\ominus}}{R} = -\frac{\Delta_{\mathrm{des}}H^{\ominus}}{R} \quad [\text{Example 22B.2, } \Delta_{\mathrm{ad}}H = -\Delta_{\mathrm{des}}H = -12.2\ \mathrm{J}/1.00\ \mathrm{mmol}]$$

Assuming that $\Delta_{\mathrm{des}}H$ is independent of temperature, integration and evaluation gives

$$\ln\frac{p_2}{p_1} = -\frac{\Delta_{\mathrm{des}}H}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) = -\left(\frac{12.2\ \mathrm{kJ\ mol^{-1}}}{8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}}\right)\times\left(\frac{1}{318\ \mathrm{K}}-\frac{1}{298\ \mathrm{K}}\right) = 0.310$$

which implies that $p_2 = (8.86\ \mathrm{kPa})\times(\mathrm{e}^{0.310}) = \boxed{12.1\ \mathrm{kPa}}$.

22B.6(b) $\left(\dfrac{\partial \ln(p/p^{\ominus})}{\partial(1/T)}\right)_{\theta} = \dfrac{\Delta_{\mathrm{ad}}H^{\ominus}}{R}$ [Example 22B.2]

Assuming that $\Delta_{\mathrm{ad}}H$ is independent of temperature, integration and evaluation gives

$$\ln\frac{p_2}{p_1} = \frac{\Delta_{\mathrm{ad}}H}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$\Delta_{\mathrm{ad}}H = R\left(\frac{1}{T_2}-\frac{1}{T_1}\right)^{-1}\ln\frac{p_2}{p_1}$$

$$= (8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times\ln\left(\frac{1.02\times 10^3\ \mathrm{kPa}}{350\ \mathrm{kPa}}\right)\times\left(\frac{1}{240\ \mathrm{K}}-\frac{1}{180\ \mathrm{K}}\right)^{-1}$$

$$= \boxed{-6.4\bar{0}\ \mathrm{kJ\ mol^{-1}}}$$

22B.7(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:

$$t(2)/t(1) = t_{1/2}(2)/t_{1/2}(1) = \mathrm{e}^{E_{\mathrm{a,des}}/RT_2} / \mathrm{e}^{E_{\mathrm{a,des}}/RT_1} \ [22\mathrm{B}.13] = \mathrm{e}^{E_{\mathrm{a,des}}(1/T_2-1/T_1)/R}$$

Solving for the activation energy for desorption, $E_{\mathrm{a,des}}$, gives:

$$\begin{aligned} E_{\text{a,des}} &= R\ln\{t(2)/t(1)\}(1/T_2 - 1/T_1)^{-1} \\ &= (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times\ln\left(\frac{8.44\ \text{s}}{1856\ \text{s}}\right)\times\left(\frac{1}{1012\ \text{K}}-\frac{1}{873\ \text{K}}\right)^{-1} \\ &= \boxed{285\ \text{kJ mol}^{-1}} \end{aligned}$$

The desorption time, *t*, for the same volume at temperature *T* is given by:

$$\begin{aligned} t = t(1)\mathrm{e}^{E_{\text{a,des}}(1/T-1/T_1)/R} &= (1856\ \text{s})\exp\left\{(285\times10^3\ \text{J mol}^{-1})\times\left(\frac{1}{T}-\frac{1}{873\ \text{K}}\right)/(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\right\} \\ &= (1856\ \text{s})\exp\left\{(34.3)\times\left(\frac{1}{T/1000\ \text{K}}-\frac{1}{0.873}\right)\right\} \end{aligned}$$

(i) At 298 K, $t = \boxed{1.56\times10^{36}\ \text{s}}$

(ii) At 1500 K, $t = \boxed{1.37\times10^{-4}\ \text{min}}$

22B.8(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:

$$t(2)/t(1) = t_{1/2}(2)/t_{1/2}(1) = \mathrm{e}^{E_{\text{a,des}}/RT_2}\ /\ \mathrm{e}^{E_{\text{a,des}}/RT_1}\ \ [22\text{B}.13] = \mathrm{e}^{E_{\text{a,des}}(1/T_2-1/T_1)/R}$$

Solving for the activation energy for desorption, $E_{\text{a,des}}$, gives:

$$\begin{aligned} E_{\text{a,des}} &= R\ln\{t(2)/t(1)\}(1/T_2-1/T_1)^{-1} = R\ln\{0.65\times t(1)/t(1)\}(1/T_2-1/T_1)^{-1} = R\ln\{0.65\}(1/T_2-1/T_1)^{-1} \\ &= (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times\ln(0.65)\times\left(\frac{1}{1000\ \text{K}}-\frac{1}{600\ \text{K}}\right)^{-1} \\ &= \boxed{5.34\ \text{kJ mol}^{-1}} \end{aligned}$$

22B.9(b) At 298 K: $t_{1/2} = \tau_0\mathrm{e}^{E_{\text{a,des}}/RT}\ [22\text{B}.13] = (0.12\ \text{ps})\times\mathrm{e}^{0.404E_{\text{a,des}}/\text{kJ mol}^{-1}}$

At 800 K: $t_{1/2} = \tau_0\mathrm{e}^{E_{\text{a,des}}/RT}\ [22\text{B}.13] = (0.12\ \text{ps})\times\mathrm{e}^{0.150E_{\text{a,des}}/\text{kJ mol}^{-1}}$

(i) $E_{\text{a,des}} = 20\ \text{kJ mol}^{-1}$

$t_{1/2}(298\ \text{K}) = (0.12\ \text{ps})\times\mathrm{e}^{0.404\times20} = \boxed{38\bar{8}\ \text{ps}}$, $t_{1/2}(800\ \text{K}) = (0.12\ \text{ps})\times\mathrm{e}^{0.150\times20} = \boxed{2.4\ \text{ps}}$.

(ii) $E_{\text{a,des}} = 200\ \text{kJ mol}^{-1}$

$t_{1/2}(298\ \text{K}) = (0.12\ \text{ps})\times\mathrm{e}^{0.404\times200} = \boxed{1.5\times10^{22}\ \text{s}}$, $t_{1/2}(800\ \text{K}) = (0.12\ \text{ps})\times\mathrm{e}^{0.150\times200} = \boxed{1.3\ \text{s}}$

22B.10(b) The Langmuir isotherm would be

(i) $\theta = \dfrac{\alpha p}{1+\alpha p}$

(ii) $\theta = \dfrac{(\alpha p)^{1/2}}{1+(\alpha p)^{1/2}}$

(iii) $\theta = \dfrac{(\alpha p)^{1/3}}{1+(\alpha p)^{1/3}}$

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

Solutions to Problems

22B.2 We follow Example 22B.1 of the text, where it is shown that for a Langmuir isotherm:

$$\frac{p}{V} = \frac{p}{V_\infty}+\frac{1}{KV_\infty}\quad[\alpha = K]$$

Since this expression predicts that a plot of *p*/*V* against *p* is linear with intercept $1/KV_\infty$ and slope equal to $1/V_\infty$, we draw up the following table.

p / Pa	25	129	253	540	1000	1593
p/V / Pa cm^{-3}	595	791	1145	1682	2433	3382

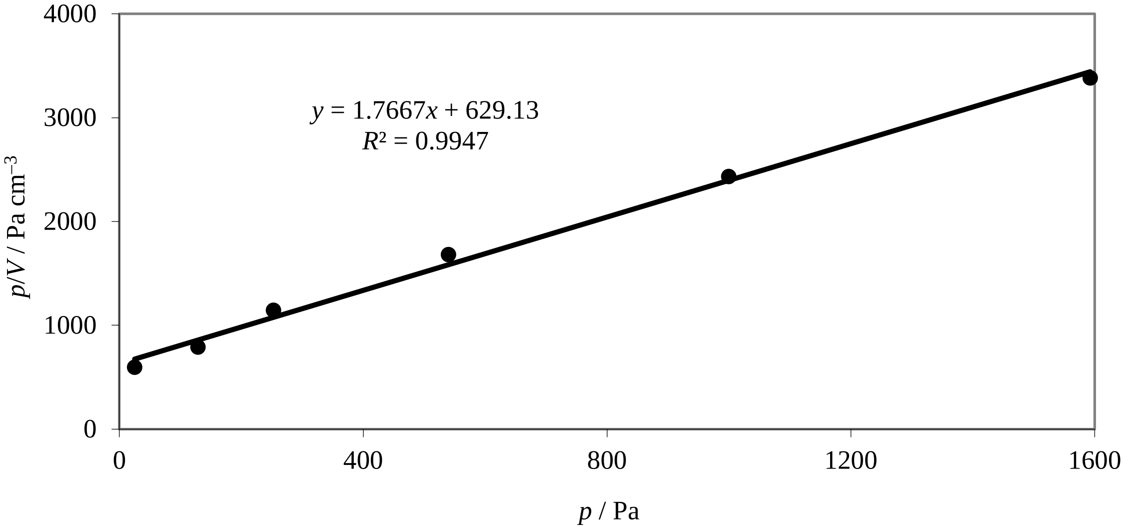
p/V is plotted against p in Fig. 22B.1. The plot is observed to be linear so we conclude that the data fits the Langmuir isotherm for these low pressures and, therefore, low coverage. The regression slope equals $1/V_\infty$; the regression intercept equals $1/KV_\infty$. Thus,

$$V_\infty = 1/\text{slope} = 1/(1.77\ \text{cm}^{-3}) = \boxed{0.565\ \text{cm}^3}$$

and $$K = 1/(V_\infty \times \text{intercept}) = 1/(0.565\ \text{cm}^3 \times 629\ \text{Pa cm}^{-3}) = \boxed{2.81 \times 10^{-3}\ \text{Pa}^{-1}}$$

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 22B.4 for adsorption data at higher pressures

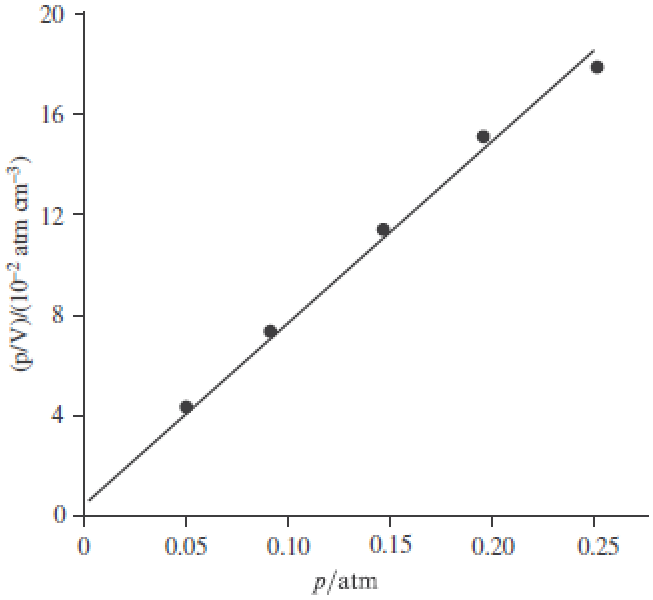
Figure 22B.1



22B.4 We assume that the data fit the Langmuir isotherm; to confirm this we plot p/V against p and expect a straight line [Example 22B.1]. We draw up the following table and a data plot is shown in Fig. 22B.2:

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	1.47	17.9

Figure 22B.2



The plot fits closely to a straight line with slope 0.720 dm^{-3}. Hence,

$$V_\infty = 1/\text{slope} = \boxed{1.3\overline{9}\ \text{cm}^{-3}} = 1.3\overline{9}\times 10^{-3}\ \text{dm}^{-3} \approx V_\text{mon}$$

The number of H_2 molecules corresponding to this volume is

$$N_{H_2} = \frac{pVN_A}{RT} = \frac{(1.00\,\text{atm})\times(1.3\overline{9}\times10^{-3}\text{dm}^3)\times(6.02\times10^{23}\ \text{mol}^{-1})}{(0.0821\text{dm}^3\ \text{atm}\,\text{K}^{-1}\ \text{mol}^{-1})\times(273\,\text{K})} = 3.73\times10^{19}$$

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.

$$A = \pi\left(\frac{3V}{4\pi}\right)^{2/3} = \pi\left(\frac{3M}{4\pi\rho N_A}\right)^{2/3} \quad \left[V = \text{volume of molecule} = \frac{M}{\rho N_A}\right]$$

$$= \pi\left(\frac{3\times(2.02\ \text{g mol}^{-1})}{4\pi\times(0.708\ \text{g cm}^{-3})\times(6.022\times10^{23}\ \text{mol}^{-1}}\right)^{2/3}$$

$$= 3.41\times10^{-16}\ \text{cm}^2$$

Area occupied = $(3.73\times10^{19})\times(3.41\times10^{-16}\ \text{cm}^2) = (1.3\times10^4\ \text{cm}^2) = \boxed{1.3\ \text{m}^2}$

Comment. The value for V_∞ calculated here may be compared to the value obtained in Problem 22B.2. The agreement is not good and illustrates the point that these kinds of calculations provide only rough value surface areas.

22B.6 For the Langmuir and BET isotherm (using p^* = 200 kPa) tests we draw up the following table using eqns 22B.2 and 22B.6 with the methods of Examples 22B.1 and 22B.3.

p/kPa	13.3	26.7	40.0	53.3	66.7	80.0
$p/V\ /\ (\text{kPa cm}^{-3})$	0.743	0.809	0.851	0.877	0.886	0.876
$10^3 z$	67	134	200	267	334	400

$\dfrac{10^3 z}{(1-z)(V/\text{cm}^3)}$	3.98	4.67	5.32	5.98	6.65	7.30

p/V is plotted against p is in Fig. 22B.3. $z/(1-z)V$ is plotted against z in Fig. 22B.4.

Figure 22B.3

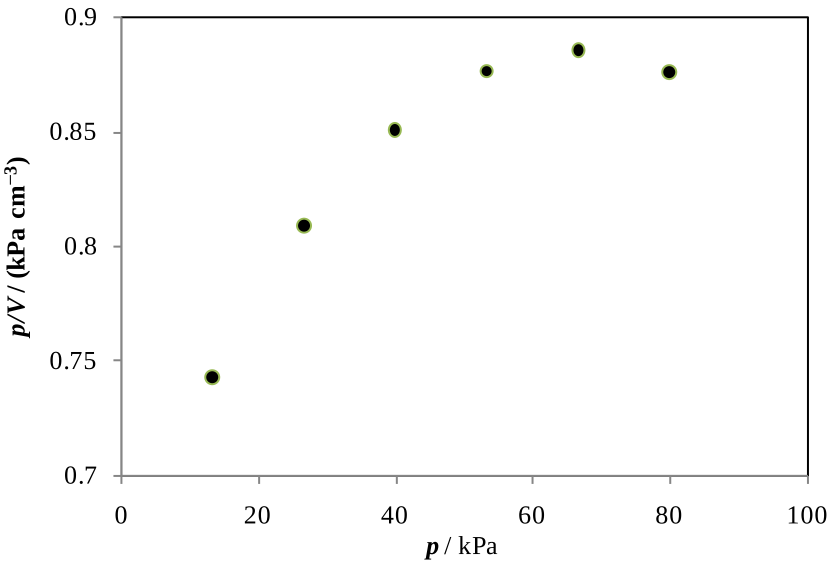
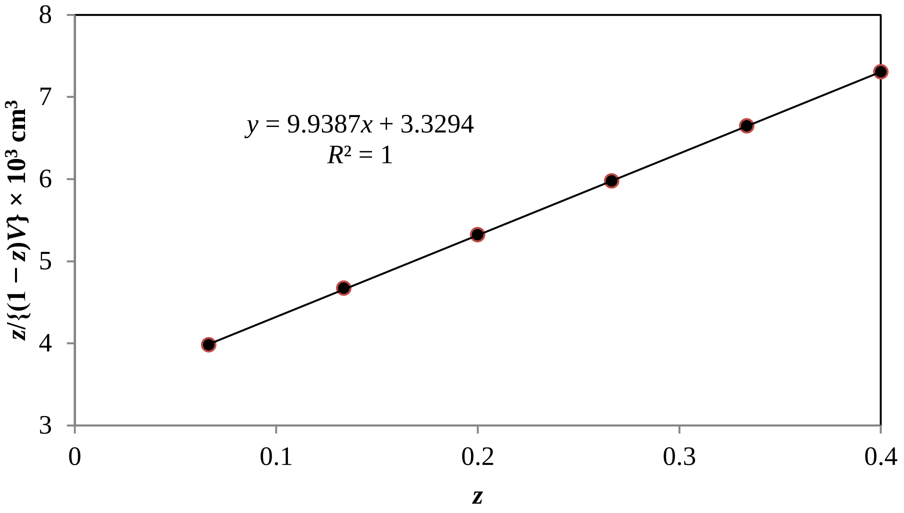


Figure 22B.4



We see that the plot of p/V against p is non-linear so we reject the proposition that it is described by a Langmuir isotherm. The plot of $z/(1-z)V$ against z appears to be linear so we accept the proposition that it is described by the BET isotherm and the linear regression fit is summarized in Fig. 22B.4.

The BET isotherm has an intercept of 3.33×10^{-3} cm^{-3} and a slope of 9.94×10^{-3} cm^{-3}. Since $1/cV_{\text{mon}}$ equals the intercept of a BET isotherm and $(c-1)/cV_{\text{mon}}$ equals the slope, we find that

$$c = 1 + \text{slope/intercept} = 1 + 9.94/3.33 = \boxed{3.96}$$

and

$$V_{\text{mon}} = 1/(c \times \text{intercept}) = 1/(3.96 \times 3.33 \times 10^{-3}\ \text{cm}^{-3}) = \boxed{75.8\ \text{cm}^3}$$

22B.8‡ Equilibrium constants vary with temperature according to the van’t Hoff equation [22B.5, $K = \alpha p$] which can be written in the form

$$\frac{K_2}{K_1} = \mathrm{e}^{-\left[\Delta_{\mathrm{ad}}H^{\ominus}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)/R\right]} \quad \text{[Integration of eqn 22B.5 at constant } \Delta_{\mathrm{ad}}H^{\ominus} \text{ and } \theta.\text{]}$$

or

$$\frac{K_2}{K_1} = \exp\left[\frac{160\times10^3\,\mathrm{J\,mol^{-1}}}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\left(\frac{1}{773\,\mathrm{K}}-\frac{1}{673\,\mathrm{K}}\right)\right] = \boxed{0.0247}$$

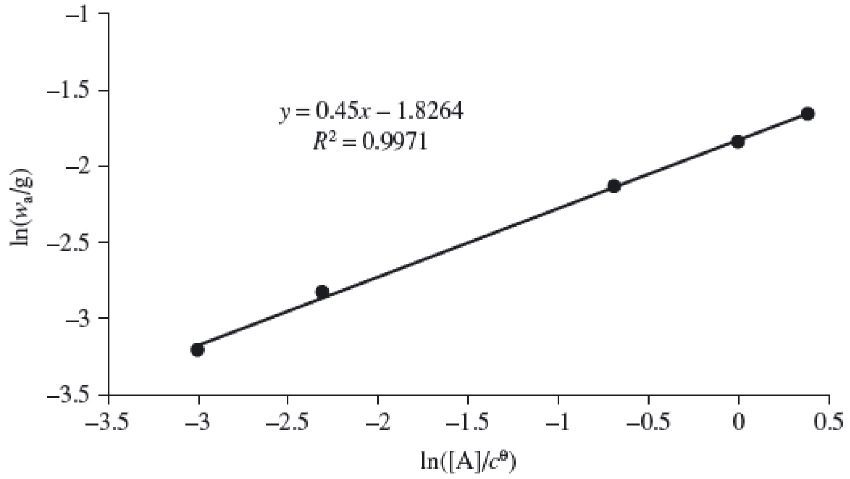
As measured by the equilibrium constant of absorption, NO is less strongly absorbed by a factor of 0.0247 at 500°C than at 400°C.

22B.10 $\theta = c_1 p^{1/c_2}$ [Freundlich isotherm, 22B.10]

We adapt the Freundlich gas isotherm to a liquid by noting that $w_{\mathrm{a}} \propto \theta$ and replacing p by $[\mathrm{A}]/c^{\ominus}$, the concentration of the acid divided by the standard concentration $c^{\ominus} = 1\ \mathrm{mol\ dm^3}$. Then $w_{\mathrm{a}} = c_1\left([\mathrm{A}]/c^{\ominus}\right)^{1/c_2}$ (with c_1, c_2 modified constants), and hence $\ln(w_{\mathrm{a}}/\mathrm{g}) = \ln(c_1/\mathrm{g}) + \frac{1}{c_2}\times\ln\left([\mathrm{A}]/c^{\ominus}\right)$. A plot of $\ln(w_{\mathrm{a}}/\mathrm{g})$ against $\ln\left([\mathrm{A}]/c^{\ominus}\right)$ is predicted to be linear in a Freundlich isotherm with intercept $\ln(c_1/\mathrm{g})$ and slope $1/c_2$. We draw up the following table and prepared the desired plot, shown in Figure 22B.5.

$[\mathrm{A}]/(\mathrm{mol\ dm^{-3}})$	0.05	0.10	0.50	1.0	1.5
$w_{\mathrm{a}}/\mathrm{g}$	0.04	0.06	0.12	0.16	0.19
$\ln([\mathrm{A}]/\mathrm{mol\ dm^{-3}})$	–3.00	–2.30	–0.693	–0.00	0.405
$\ln(w_{\mathrm{a}}/\mathrm{g})$	–3.22	–2.81	–2.12	–1.83	–1.66

Figure 22B.5



Since the plot is linear, the linear regression fit shown in Figure 22B.5 is appropriate and the Freundlich coefficients are

$$c_1 = \mathrm{e}^{intercept}\ \mathrm{g} = \mathrm{e}^{-1.83} = \boxed{0.16\ \mathrm{g}}$$

$$c_2 = 1/slope = 1/0.45 = \boxed{2.2}$$

22B.12‡ We must adapt the Langmuir gas adsorption isotherm, $\frac{p}{V} = \frac{p}{V_\infty} + \frac{1}{KV_\infty}$ [Example 22B.1, $K = \alpha$], so that it describes adsorption from solution. This can be done with the transforms: p → concentration, c and V → amount adsorbed per gram adsorbent, s. This gives

Langmuir isotherm and regression analysis:

$$\frac{c}{s}=\frac{c}{s_\infty}+\frac{1}{Ks_\infty}\quad \text{[Langmuir solution isotherm]}$$

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

$$slope=\frac{1}{s_\infty}=0.163\ \text{g mmol}^{-1}\text{, standard deviation = 0.017 g mmol}^{-1}$$

$$intercept=\frac{1}{Ks_\infty}=35.6\ (\text{mmol dm}^{-3})\times(\text{g mmol}^{-1})\text{, std. dev.}=5.9\ (\text{mmol dm}^{-3})\times(\text{g mmol}^{-1})$$

$$\boxed{R(\text{Langmuir}) = 0.973}$$

$$K=\frac{slope}{intercept}=\frac{0.163\ \text{g mmol}^{-1}}{35.6\ (\text{mmol dm}^{-3})\times(\text{g mmol}^{-1})}=0.0046\ \text{dm}^3\ \text{mmol}^{-1}$$

Similarly, the Freundlich solution isotherm [22B.10] and regression analysis of the data is:

$$s=c_1\left(c/\text{mmol dm}^{-3}\right)^{1/c_2}\qquad\text{or}\qquad \ln\left(s/\text{mmol g}^{-1}\right)=\ln\left(c_1/\text{mmol g}^{-1}\right)+\tfrac{1}{c_2}\ln\left(c/\text{mmol dm}^{-3}\right)$$

This says that a plot of $\ln\left(s/\text{mmol g}^{-1}\right)$ against $\ln\left(c/\text{mmol dm}^{-3}\right)$ should be linear and we find that the linear regression fit of the data gives

$$c_1=\mathrm{e}^{intercept}\ \text{mmol dm}^{-3}=0.139\ \text{mmol dm}^{-3}\text{, standard deviation = 0.012 mmol dm}^{-3}$$

$$slope=\frac{1}{c_2}=0.539,\qquad \text{standard deviation = 0.003}$$

$$\boxed{R(\text{Freundlich}) = 0.999\ 94}$$

The Temkin solution isotherm [22B.9] and regression analysis gives:

$$s=c_1\ln(c_2c/\text{mmol dm}^{-3})$$

$$c_1=1.08\ \text{mmol dm}^{-3},\quad \text{standard deviation = 0.14 mmol dm}^{-3}$$

$$c_2=0.074,\quad \text{standard deviation = 0.023}$$

$$\boxed{R(\text{Temkin}) = 0.9590}$$

The correlation coefficients and standard deviations indicate that the $\boxed{\text{Freundlich isotherm}}$ provides the best fit of the data.

22B.14‡ We write the isotherms in the following forms where q is milligrams of solvent sorbed per gram of ground rubber (g_R) and K, K_F, K_L, and M are empirical constants.

Linear isotherm: $q=K\times\left(c_{\text{eq}}/\text{mg dm}^{-3}\right)$

Freundlich isotherm: $q=K_F\times\left(c_{\text{eq}}/\text{mg dm}^{-3}\right)^{1/n}$ or $\ln\left(q/\text{mg g}_R^{-1}\right)=\ln\left(K_F/\text{mg g}_R^{-1}\right)+\tfrac{1}{n}\ln\left(c_{\text{eq}}/\text{mg dm}^{-3}\right)$

Langmuir isotherm: $q=K_LMc_{\text{eq}}/\left(1+Mc_{\text{eq}}\right)$ or $\dfrac{1}{q}=\dfrac{1}{K_L}+\left(\dfrac{1}{K_LM}\right)\times\dfrac{1}{c_{\text{eq}}}$

(a) K unit: $\text{mg g}_R{}^{-1}$ [g_R = mass (grams) of rubber]

K_F unit: $\text{mg g}_R{}^{-1}$

K_L unit: $\text{mg g}_R{}^{-1}$

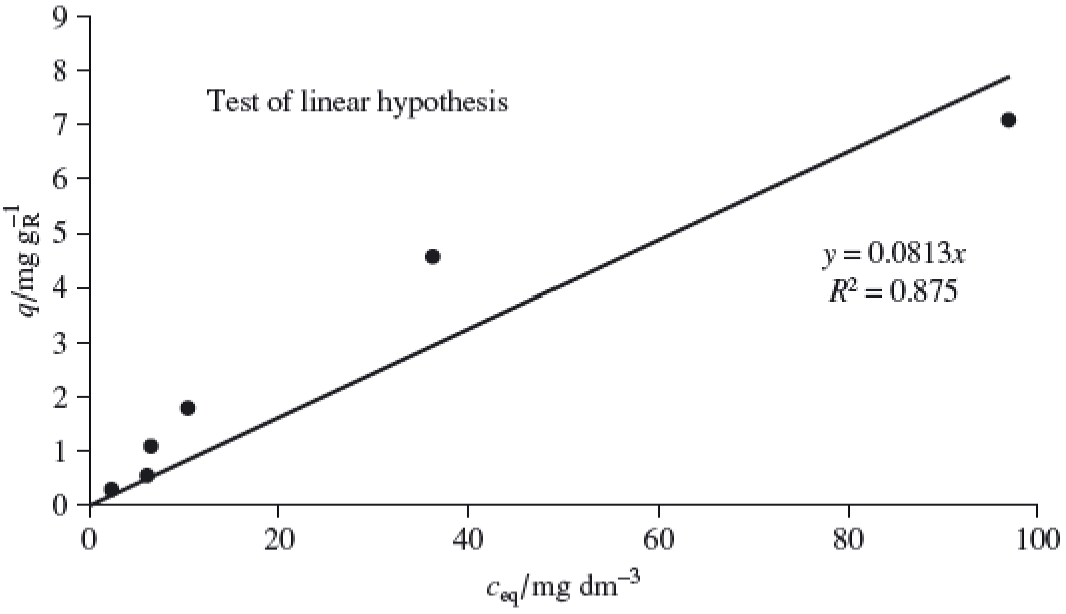
M unit: $\text{mg}^{-1}\ \text{dm}^3$

(b) Determination of best description of data. Data analysis with the linear sorption isotherm. Since $K = q/c_{\text{eq}}$, we calculate q/c_{eq} and calculate the average and standard deviation.

$$K=0.126\ \text{mg g}_R{}^{-1}\quad[\text{standard deviation} = 0.041\ \text{mg g}_R{}^{-1}]$$

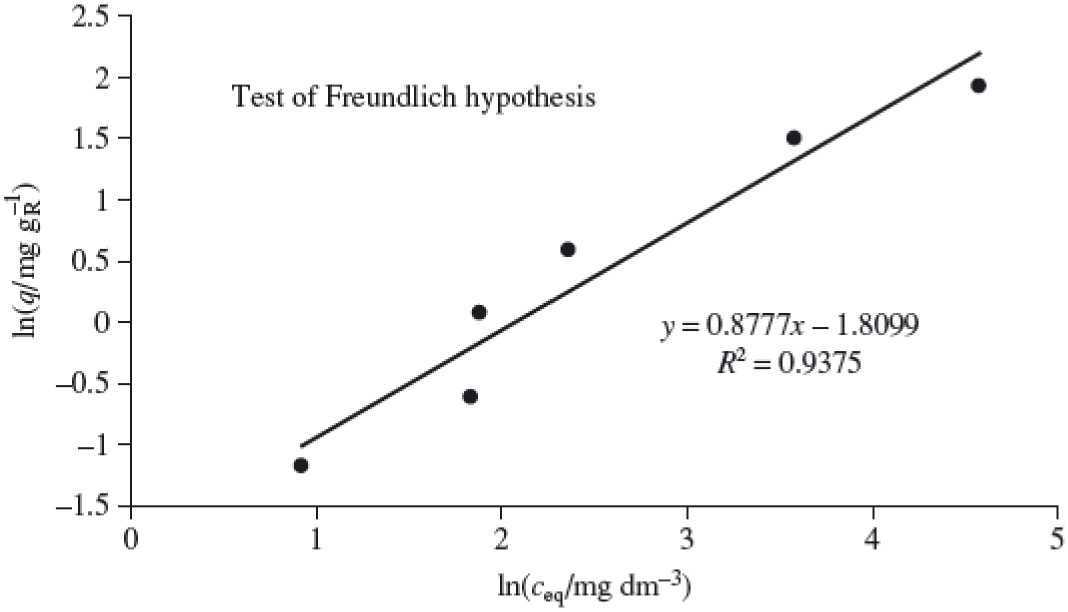
The standard deviation is a large percentage of K, which may indicate some combination of random and/or systematic variation. A test of a relationship is often facilitated by checking the appearance of a plot. To further test the linear hypothesis between q and c, we prepare the plot, shown in Figure 22B.6, with the constraint that the intercept equal zero. The plot appears to have a systematic non-linear component and only 88% of the variation is explained by the linear regression. However, with the small number of data points random error could give this appearance so we tentatively reject the linear hypothesis.

Figure 22B.6



Data analysis with the Freundlich isotherm. To test the Freundlich hypothesis between q and c, we prepare the plot of ln$q$ against lnc_{eq}, shown in Figure 22B.7. The appearance of the plot appears to be linear with considerable random scatter but there is no definitive visual indicator of systematic non-linearity. 94% of the variation is explained by the linear regression fit.

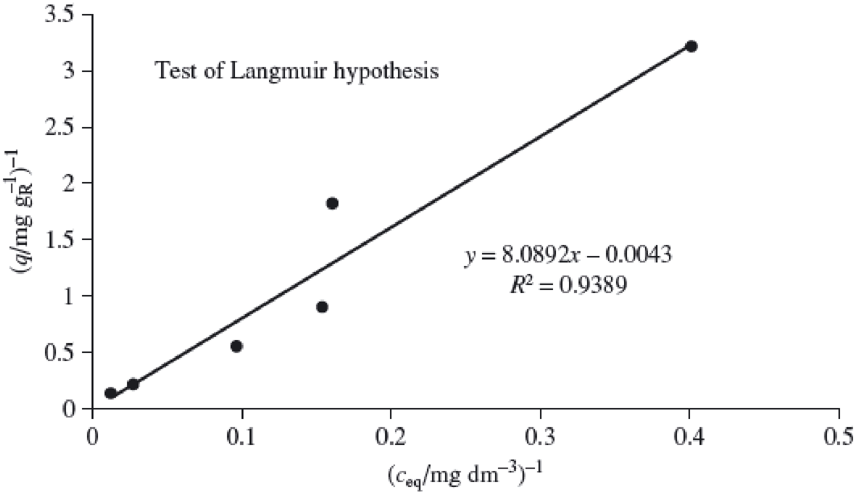
Figure 22B.7



Data analysis with the Langmuir isotherm. To test the Langmuir hypothesis between q and c, we prepare the plot of 1/q against 1/c_{eq}, shown in Figure 22B.8. The appearance of the plot appears to be linear with considerable random scatter but there is no definitive visual indicator of systematic non-linearity. 94% of the variation is explained by the linear regression fit. However, the negative, but very small, intercept of the regression fit implies either that $K_L < 0$ or that K_L is so small that it has been swamped by the random scatter.

We further recognize that a Langmuir isotherm must have a positive K_L because it is an equilibrium constant. The data, such as it is, does not firmly support the Langmuir isotherm hypothesis.

Figure 22B.8



Summary: Only the Freundlich isotherm gives an adequate description of the data. The empirical constants for this isotherm are calculated with the linear regression fit shown as an insert in the Freundlich plot.
Freundlich constants:

$$K_F = e^{intercept}\ \mathrm{mg\ g_R}^{-1} = e^{-1.81}\ \mathrm{mg\ g_R}^{-1} = \boxed{0.164\ \mathrm{mg\ g_R}^{-1}}$$

$$n = 1/slope = 1/0.878 = \boxed{1.14}$$

(c) The ratio of rubber-to-charcoal Freundlich sorption isotherms is $\dfrac{q_{\text{rubber}}}{q_{\text{charcoal}}} = \dfrac{0.164c_{\text{eq}}^{0.878}}{c_{\text{eq}}^{1.6}} = \boxed{0.164\ c_{\text{eq}}^{-0.72}}$

The sorption efficiency of ground rubber is much less than that of activated charcoal and drops significantly with increasing concentration. The only advantage of the ground rubber is it’s exceedingly low cost relative to activated charcoal, which might convert to a lower cost per gram of contaminant adsorbed.

22C Heterogeneous catalysis

Answers to discussion questions

22C.2 Heterogeneous catalysis on a solid surface requires the reacting molecules or fragments to encounter each other by adsorption on the surface. Therefore, the rate of the catalyzed reaction is determined by the sticking probabilities of the species on the surface as described by Fig. 22C.2 of the text.

Solutions to exercises

22C.1(b) Let us assume that the carbon monoxide molecules are close-packed, as shown in Fig. 22C.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 1B.1 ($\sigma \sim \sigma_{\text{dinitrogen}} = 0.43\ \mathrm{nm^2} = 4\pi r^2$) gives a reasonable estimate of r: $r = (\sigma/4\pi)^{1/2}$. With these assumptions the surface area occupied by one molecule is:

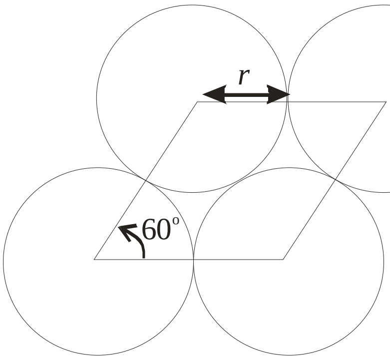
$$A_{\text{molecule}} = 2\sqrt{3}\,(\sigma/4\pi) = \sqrt{3}\,\sigma/2\pi$$
$$= \sqrt{3}\left(0.43\ \text{nm}^2\right)/2\pi = 0.12\ \text{nm}^2$$

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.

$$N = \frac{pV}{kT} = \frac{\left(1.00\times10^5\ \text{Pa}\right)\times\left(3.75\times10^{-6}\ \text{m}^3\right)}{\left(1.381\times10^{-23}\ \text{J K}^{-1}\right)\times\left(273.15\ \text{K}\right)} = 9.94\times10^{19}$$

$$A_{\text{molecule}}N = \left(0.12\times10^{-18}\ \text{m}^2\right)\times\left(9.94\times10^{19}\right) = \boxed{12\ \text{m}^2}$$

Figure 22C.1



Integrated activities

22.2 Electron microscopes can obtain images with much higher resolution than optical microscopes because of the short wavelength obtainable from a beam of electrons. For electrons moving at speeds close to c, the speed of light, the expression for the de Broglie wavelength (eqn 7A.14, $\lambda = h/p$) needs to be corrected for relativistic effects:

$$\lambda = \frac{h}{\left\{2m_{\text{e}}e\Delta\phi\left(1+\frac{e\Delta\phi}{2m_{\text{e}}c^2}\right)\right\}^{1/2}}$$

where c is the speed of light in vacuum and $\Delta\phi$ is the potential difference through which the electrons are accelerated. (a) Use the expression above to calculate the de Broglie wavelength of electrons accelerated through 50 kV. (b) Is the relativistic correction important?

(a) The shortest de Broglie wavelength as estimated without relativistic correction is calculated as follows:

$$\lambda_{\text{non-relativistic}} = \frac{h}{p} = \frac{h}{\left(2m_{\text{e}}E_{\text{k}}\right)^{1/2}} = \frac{h}{\left(2m_{\text{e}}eV\right)^{1/2}}$$
$$= \frac{6.626\times10^{-34}\ \text{J s}}{\left\{2\left(9.109\times10^{-31}\ \text{kg}\right)\times\left(1.602\times10^{-19}\ \text{C}\right)\times\left(50.0\times10^{3}\ \text{V}\right)\right\}^{1/2}}$$
$$= 5.48\ \text{pm}$$

The relativistic de Broglie wavelength is

$$\lambda_{\text{relativistic}} = \frac{h}{\left\{2m_eeV\left(1+\dfrac{eV}{2m_ec^2}\right)\right\}^{1/2}}$$

$$= \frac{\lambda_{\text{non-relativistic}}}{\left(1+\dfrac{eV}{2m_ec^2}\right)^{1/2}} = \frac{5.48\ \text{pm}}{\left\{1+\dfrac{(1.602\times10^{-19}\ \text{C})(50.0\times10^3\ \text{V})}{2(9.109\times10^{-31}\ \text{kg})(3.00\times10^8\ \text{m s}^{-1})^2}\right\}^{1/2}}$$

$$= \boxed{5.35\ \text{pm}}$$

(b) For an electron accelerated through 50 kV the non-relativistic de Broglie wavelength is calculated to be high by 2.4%. This error may be insignificant for many applications. However, should an accuracy of 1% or better be required, use the relativistic equation at accelerations through a potential above 20.4 kV as demonstrated in the following calculation:

$$\frac{\lambda_{\text{non-relativistic}}-\lambda_{\text{relativistic}}}{\lambda_{\text{relativistic}}} = \frac{\lambda_{\text{non-relativistic}}}{\lambda_{\text{relativistic}}}-1 = \left(1\ +\ \frac{eV}{2m_ec^2}\right)^{1/2}-1$$

$$= \cancel{1}\ +\ \frac{1}{2}\left(\frac{eV}{2m_ec^2}\right)\ -\ \frac{1}{2\cdot4}\left(\frac{eV}{2m_ec^2}\right)^2\ +\ \frac{1\cdot3}{2\cdot4\cdot6}\left(\frac{eV}{2m_ec^2}\right)^3 - \cdots\cdots \cancel{-1}$$

$$\simeq \frac{1}{2}\left(\frac{eV}{2m_ec^2}\right) \qquad \text{because 2}^{\text{nd}}\text{ and 3}^{\text{rd}}\text{ order terms are very small.}$$

The largest value of V for which the non-relativistic equation yields a value that has less than 1% error:

$$V \simeq 2\left(\frac{2m_ec^2}{e}\right)\times\left(\frac{\lambda_{\text{non-relativistic}}-\lambda_{\text{relativistic}}}{\lambda_{\text{relativistic}}}\right) = 2\left(\frac{2m_ec^2}{e}\right)(0.01) = 20.4\ \text{kV}$$

22.4 $V - E = 2.00\ \text{eV} = 3.20\times10^{-19}\ \text{J}$

$$\kappa = \{2m_e(V-E)\}^{1/2}/\hbar\ \ [8\text{A}.20]$$

$$= \{2\times(9.109\times10^{-31}\ \text{kg})\times(3.20\times10^{-19}\ \text{J})\}^{1/2}/(1.055\times10^{-34}\ \text{J s})$$

$$= 7.24\times10^9\ \text{m}^{-1}$$

Since $\kappa L \gg 1$ for the distances of this problem, we use eqn 8A.23B for the transmission probability T.

$$T \approx\ 16\varepsilon(1\ -\varepsilon)\text{e}^{-2\kappa L}\ \text{ where } \varepsilon = E/V$$

We regard the tunnelling current to be proportional to the transmission probability, so the ratio of the currents at different distances is equal to the ratio of transmission probabilities.

$$\frac{\text{current at } L_2}{\text{current at } L_1} = \frac{T(L_2)}{T(L_1)} = \frac{\text{e}^{-2\kappa L_2}}{\text{e}^{-2\kappa L_1}} = \text{e}^{-2\kappa(L_2-L_1)}$$

$$= \text{e}^{-2\times(7.24\times10^9\ \text{m}^{-1})\times(1.00\times10^{-10}\ \text{m})}$$

$$= \boxed{0.235}$$

We conclude that, at the distance of 0.60 nm between the surface and the needle, the current is about 24% of the value measured when the distance is 0.50 nm.

Solutions to a) exercises

Foundations

Topic A

EA.1(a)

	Example	Element	Ground-state Electronic Configuration
(i)	Group 2	Ca, calcium	[Ar]$4s^2$
(ii)	Group 7	Mn, manganese	[Ar]$3d^5 4s^2$
(iii)	Group 15	As, arsenic	[Ar]$3d^{10} 4s^2 4p^3$

EA.2(a) (i) Chemical formula and name: $MgCl_2$, magnesium chloride
ions: Mg^{2+} and Cl^-
oxidation numbers of the elements: magnesium, +2; chlorine, –1

(ii) Chemical formula and name: FeO, iron(II) oxide
ions: Fe^{2+} and O^{2-}
oxidation numbers of the elements: iron, +2; oxygen, –2

(iii) Chemical formula and name: Hg_2Cl_2, mercury(I) chloride
ions: Cl^- and $Hg_2{}^{2+}$ (a polyatomic ion)
oxidation numbers of the elements: mercury, +1; chlorine, –1

EA.8(a) (i) CO_2 is a linear, nonpolar molecule. (ii) SO_2 is a bent, polar molecule. (iii) N_2O is linear, polar molecule. (iv) SF_4 has a seesaw molecule and it is a polar molecule.

EA.9(a) In the order of increasing dipole moment: CO_2, N_2O, SF_4, SO_2

EA.10(a) (i) Mass is an extensive property. (ii) Mass density is an intensive property. (iii) Temperature is an intensive property. (iv) Number density is an intensive property.

EA.11(a) (i) 0.543 mol (ii) 3.27×10^{23} molecules

EA.12(a) (i) 180. g (ii) 1.77 N

EA.13(a) 0.43 bar

EA.14(a) 0.42 atm

EA.15(a) 1.47×10^{5} Pa

EA.16(a) $T = 310.2$ K

EA.17(a) $\theta / ^\circ\mathrm{C} = {}^{5}\!/_{9} \times (\theta_\mathrm{F} / ^\circ\mathrm{F} - 32)$ or $\theta_\mathrm{F} / ^\circ\mathrm{F} = {}^{9}\!/_{5} \times \theta / ^\circ\mathrm{C} + 32$, $\theta_\mathrm{F} = 173\ ^\circ\mathrm{F}$

EA.18(a) 105 kPa

EA.19(a) S_8

EA.20(a) 1.8 MPa

EA.21(a) 4.6×10^{5} Pa , 6.9×10^{5} Pa

Topic B

EB.1(a) (i) $9.81\ \mathrm{m\ s^{-1}}$, 48 mJ (ii) $29.4\ \mathrm{m\ s^{-1}}$, 0.43 J

EB.2(a) $s_\text{terminal} = \dfrac{ze\mathcal{E}}{6\pi\eta R}$

EB.4(a) (i) 2.25×10^{-20} J (ii) 9.00×10^{-20} J

EB.5(a) (i) $1.88\times10^{8}\ \mathrm{m\ s^{-1}}$, 100 keV

EB.6(a) 1.15×10^{-18} J , 1.48×10^{-20} J

EB.7(a) -2.40 V

EB.8(a) 24.1 kJ , 28.8 °C

EB.9(a) 27.2 K or 27.2 °C

EB.10(a) 128 J

EB.11(a) $2.4194\ \mathrm{J\ K^{-1}\ g^{-1}}$

EB.12(a) $75.3\ \mathrm{J\ K^{-1}\ mol^{-1}}$

EB.13(a) $8.3145\ \mathrm{kJ\ mol^{-1}}$

EB.14(a) $S_{\mathrm{H_2O(g)}} > S_{\mathrm{H_2O(l)}}$

EB.15(a) $S_{\mathrm{Fe(3000\ K)}} > S_{\mathrm{Fe(300\ K)}}$

EB.17(a) (i) 1.6×10^{-17} (ii) 0.021

EB.19(a) 4.631×10^{-6}

EB.21(a) 1.07

EB.22(a) 1.25

EB.23(a)	0.47 kJ
EB.24(a)	(i) 1.38 kJ (ii) 4.56 kJ
EB.25(a)	12.47 J mol^{-1} K^{-1}
EB.26(a)	(i) 20.79 J mol^{-1} K^{-1} (ii) 24.94 J mol^{-1} K^{-1}

Topic C

EC.1(a)	2.26×10^{8} m s^{-1}
EC.2(a)	4.00 μm, 7.50×10^{13} Hz

Chapter 1

Topic 1A

E1A.1(a)	24 atm, no
E1A.2(a)	(i) 3.42 bar (ii) 3.38 atm
E1A.3(a)	30 lb in^{-2}
E1A.4(a)	4.20×10^{-2}
E1A.5(a)	0.50 m^{3}
E1A.6(a)	102 kPa
E1A.7(a)	8.3147 J K^{-1} mol^{-1}
E1A.8(a)	S_8
E1A.9(a)	6.2 kg
E1A.10(a)	(i) 0.762, 0.238, 0.752 bar, 0.235 bar (ii) 0.782, 0.208, 0.0099 bar, 0.772 bar, 0.205 bar
E1A.11(a)	169 g mol^{-1}
E1A.12(a)	273°C
E1A.13(a)	(i) 0.67, 0.33 (ii) 2.0 atm, 1.0 atm (iii) 3.0 atm

Topic 1B

E1B.1(a)	(i) 9.975

E1B.2(a)	1.90×10^{3} m s^{-1} = 1.90 km s^{-1}, 458 m s^{-1}
E1B.3(a)	0.00687
E1B.4(a)	333 m s^{-1}, 375 m s^{-1}, 596 m s^{-1}
E1B.5(a)	(i) 475 m s^{-1} (ii) 8.3×10^{-8} m (iii) 8.1×10^{-9} s^{-1}
E1B.6(a)	$0.19\overline{5}$ Pa
E1B.7(a)	1.4×10^{-6} m

Topic 1C

E1C.1(a)	(i) 1.0 atm (ii) 1.8×10^{3} atm
E1C.2(a)	$7.61\times10^{-2}\ \text{kg m}^{5}\ \text{s}^{-2}\ \text{mol}^{-2}$, $2.26\times10^{-5}\ \text{m}^{3}\ \text{mol}^{-1}$
E1C.3(a)	(i) 0.88 (ii) 1.2 dm^{3} mol^{-1}, attractive
E1C.4(a)	140 atm
E1C.5(a)	(i) 50.7 atm (ii) 35.1 atm, 0.692
E1C.6(a)	1.78 dm^{6} atm mol^{-2}, 0.0362 dm^{3} mol^{-1}, 0.122nm
E1C.7(a)	(i) 1.41×10^{3} K (ii) 0.139nm
E1C.8(a)	(i) 3.64×10^{3} K, 8.7 atm (ii) 2.62×10^{3} K, 4.5 atm (iii) 47K, 0.18 atm
E1C.9(a)	$0.46\times10^{-4}\ \text{m}^{3}\ \text{mol}^{-1}$, 0.66

Chapter 2

Topic 2A

E2A.1(a)	(i) $\frac{7}{2}R$, $8.671\ \text{kJ mol}^{-1}$ (ii) $3R$, $7.436\ \text{kJ mol}^{-1}$ (iii) $7R$, $17.35\ \text{kJ mol}^{-1}$
E2A.2(a)	(i) Pressure, (ii) temperature, and (iv) enthalpy are state functions.
E2A.3(a)	$-75\,\text{J}$
E2A.4(a)	(i) $\Delta U = \Delta H = 0$, $-2.68\,\text{kJ}$, $+2.68\,\text{kJ}$ (ii) $\Delta U = \Delta H = 0$, $-1.62\,\text{kJ}$, $+1.62\,\text{kJ}$ (iii) $\Delta U = \Delta H = 0$ $w = 0$, 0
E2A.5(a)	$1.33\,\text{atm}$, $+1.25\,\text{kJ}$, $w = 0$, $+1.25\,\text{kJ}$
E2A.6(a)	(i) $-88\,\text{J}$ (ii) $-167\,\text{J}$

Topic 2B

E2B.1(a)	$30\ \mathrm{J\,K^{-1}\,mol^{-1}}$, $22\,\mathrm{J\,K^{-1}\,mol^{-1}}$
E2B.2(a)	(i) $1.07\times10^{4}\,\mathrm{J} = +10.7\ \mathrm{kJ}$, $-0.624\times10^{3}\,\mathrm{J} = -0.624\ \mathrm{kJ}$, $+10.1\,\mathrm{kJ}$ (ii) $+10.7\ \mathrm{kJ}$, $+10.1\,\mathrm{kJ}$, $w = 0$, $+10.1\,\mathrm{kJ}$
E2B.3(a)	$+2.2\ \mathrm{kJ}$, $+2.2\ \mathrm{kJ}$, $+1.6\,\mathrm{kJ}$

Topic 2C

E2C.1(a)	$22.5\ \mathrm{kJ}$, $-1.6\ \mathrm{kJ}$, $20.9\ \mathrm{kJ}$
E2C.2(a)	$-4564.7\,\mathrm{kJ\ mol^{-1}}$
E2C.3(a)	$+53\,\mathrm{kJ\,mol^{-1}}$, $-33\,\mathrm{kJ\,mol^{-1}}$
E2C.4(a)	$-167\ \mathrm{kJ/mol^{-1}}$
E2C.5(a)	$-5152\,\mathrm{kJ\,mol^{-1}}$, $1.58\,\mathrm{kJ\,K^{-1}}$, $+3.08\,\mathrm{K}$
E2C.6(a)	(i) $-114.40\,\mathrm{kJ\,mol^{-1}}$, $-111.92\,\mathrm{kJ\,mol^{-1}}$ (ii) $-92.31\,\mathrm{kJ\,mol^{-1}}$, $-241.82\,\mathrm{kJ\,mol^{-1}}$
E2C.7(a)	$-1368\,\mathrm{kJ\,mol^{-1}}$
E2C.8(a)	(i) $+131.29\,\mathrm{kJ\,mol^{-1}}$, $+128.81\,\mathrm{kJ\,mol^{-1}}$ (ii) $+134.14\,\mathrm{kJ\,mol^{-1}}$, $+130.17\,\mathrm{kJ\,mol^{-1}}$
E2C.9(a)	$-803.07\ \mathrm{kJ\ mol^{-1}}$
E2C.10(a)	$-1892\,\mathrm{kJ\,mol^{-1}}$

Topic 2D

E2D.1(a)	5.03 mbar
E2D.2(a)	$+130.\bar{1}\ \mathrm{J\ mol^{-1}}$, $+7.52\times10^{3}\,\mathrm{J\,mol^{-1}}$, $-7.39\times10^{3}\,\mathrm{J\,mol^{-1}}$
E2D.3(a)	$1.31\times10^{-3}\,\mathrm{K^{-1}}$
E2D.4(a)	2.0×10^{3} atm
E2D.5(a)	$-7.2\,\mathrm{J\,atm^{-1}\,mol^{-1}}$, $+6.1\,\mathrm{kJ}$

Topic 2E

E2E.1(a) Closer , closer

E2E.2(a) $13\bar{1}$ K

E2E.3(a) $0.0084\bar{6}\ \mathrm{m^3}$, $25\bar{7}$ K , -0.89×10^3 J

E2E.4(a) $-194\,\mathrm{J}$

E2E.5(a) $9.7\,\mathrm{kPa}$

Chapter 3

Topic 3A

E3A.1(a) Not spontaneous.

E3A.2(a) $T_c = 191.2$ K

E3A.3(a) (i) $366\ \mathrm{J\,K^{-1}}$ (ii) $309\,\mathrm{J\,K^{-1}}$

E3A.4(a) I_2(g)

E3A.5(a) $3.1\ \mathrm{J\,K^{-1}}$

E3A.6(a) 30.0 kJ/mol^{-1}

E3A.7(a) $152.67\,\mathrm{J\,K^{-1}\,mol^{-1}}$

E3A.9(a) $\Delta H = 0$, $+2.7\ \mathrm{J\,K^{-1}}$, $\Delta H_{\mathrm{tot}} = 0$

E3A.10(a) (i) $+2.9\,\mathrm{J\,K^{-1}}$, $-2.9\,\mathrm{J\,K^{-1}}$, 0 (ii) $+2.9\ \mathrm{J\,K^{-1}}$, 0, $+2.9\,\mathrm{J\,K^{-1}}$ (iii) 0, 0, 0

E3A.11(a) (i) $+87.8\,\mathrm{J\,K^{-1}\,mol^{-1}}$ (ii) $-87.8\,\mathrm{J\,K^{-1}\,mol^{-1}}$

E3A.12(a) $\Delta S = 92.2\ \mathrm{J\,K^{-1}}$

Topic 3B

E3B.1(a) (i) 9.13 J K^{-1} mol^{-1} (ii) 13.4 J K^{-1} mol^{-1} (iii) 14.9 J K^{-1} mol^{-1}

E3B.2(a) (i) $-386.1\,\mathrm{J\,K^{-1}\,mol^{-1}}$ (ii) $+92.6\,\mathrm{J\,K^{-1}\,mol^{-1}}$ (iii) $-153.1\,\mathrm{J\,K^{-1}\,mol^{-1}}$

Topic 3C

E3C.1(a)	(i) $-521.5\,\mathrm{kJ\,mol^{-1}}$	(ii) $+25.8\,\mathrm{kJ\,mol^{-1}}$	(iii) $-178.7\,\mathrm{kJ\,mol^{-1}}$
E3C.2(a)	$-480.98\,\mathrm{kJ\,mol^{-1}}$		
E3C.3(a)	$817.90\,\mathrm{kJ\,mol^{-1}}$		
E3C.4(a)	(i) $-522.1\,\mathrm{kJ\,mol^{-1}}$	(ii) $+25.78\,\mathrm{kJ\,mol^{-1}}$	(iii) $-178.6\,\mathrm{kJ\,mol^{-1}}$
E3C.5(a)	$-340\ \mathrm{kJ\ mol^{-1}}$		

Topic 3D

E3D.1(a)	$-17\,\mathrm{J}$
E3D.2(a)	$-36.5\,\mathrm{J\,K^{-1}}$
E3D.3(a)	$+10\,\mathrm{kJ}$, $1.6\ \mathrm{kJ\ mol^{-1}}$
E3D.4(a)	$+11\ \mathrm{kJ\,mol^{-1}}$

Chapter 4

Topic 4A

E4A.1(a)	(a) Single phase	(b) two phases	(c) three phases	(d) two phases
E4A.2(a)	0.71 J			
E4A.3(a)	4			

Topic 4B

E4B.1(a)	$-1.0\times10^{-4}\ \mathrm{K}$
E4B.2(a)	$5.2\times10^{3}\ \mathrm{J\ mol^{-1}}\ =\ 5.2\ \mathrm{kJ\ mol^{-1}}$
E4B.3(a)	$70\ \mathrm{J\ mol^{-1}}$
E4B.4(a)	$2.71\,\mathrm{kPa}$
E4B.5(a)	$+45.2\bar{3}\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $+16\,\mathrm{kJ\,mol^{-1}}$
E4B.6(a)	304 K, 31°C

E4B.7(a)	$+20.80\,\text{kJ mol}^{-1}$
E4B.8(a)	(i) $+34.08\,\text{kJ mol}^{-1}$ (ii) 350.5 K
E4B.9(a)	281.8 K or 8.7°C
E4B.10(a)	$25\ \text{g s}^{-1}$
E4B.11(a)	(i) 1.7×10^3 g (ii) 31×10^3 g (iii) 1.4 g
E4B.12(a)	(i) $+4.9\times10^4\ \text{J mol}^{-1} = +49\ \text{kJ mol}^{-1}$ (ii) $21\bar{5}\,°\text{C}$, $+101\ \text{J K}^{-1}\ \text{mol}^{-1}$
E4B.13(a)	272.80 K
E4B.14(a)	0.0763

Chapter 5

Topic 5A

E5A.1(a)	0, $(35.6774 - 0.91846x + 0.051975x^2)\ \text{cm}^3\ \text{mol}^{-1}$
E5A.2(a)	$17.5\ \text{cm}^3\ \text{mol}^{-1}$, $18.\overline{07}\ \text{cm}^3\ \text{mol}^{-1}$
E5A.3(a)	$-1.2\ \text{J mol}^{-1}$
E5A.4(a)	-0.35 kJ, $+1.2\ \text{J K}^{-1}$
E5A.5(a)	$+4.70\ \text{J K}^{-1}\ \text{mol}^{-1}$
E5A.6(a)	6.7 kPa
E5A.7(a)	$886.8\ \text{cm}^3$
E5A.8(a)	$56\ \text{cm}^3\ \text{mol}^{-1}$
E5A.9(a)	6.4×10^3 kPa
E5A.10(a)	$3.67\times10^{-3}\ \text{mol dm}^{-3}$
E5A.11(a)	(i) $3.4\times10^{-3}\ \text{mol kg}^{-1}$ (ii) $3.37\times10^{-2}\ \text{mol kg}^{-1}$
E5A.12(a)	$0.17\ \text{mol dm}^{-3}$

Topic 5B

E5B.1(a)	1.3×10^2 kPa

E5B.2(a)	$85\ \text{g mol}^{-1}$
E5B.3(a)	$3.8\times10^{2}\ \text{g mol}^{-1}$
E5B.4(a)	–0.09°C
E5B.5(a)	$-3.10\ \text{kJ}$, $+10.4\ \text{J K}^{-1}$, 0
E5B.6(a)	(i) $\frac{1}{2}$ (ii) 0.8600
E5B.7(a)	$0.135\ \text{mol kg}^{-1}$, 24.0 g anthracene
E5B.8(a)	$87\ \text{kg mol}^{-1}$
E5B.9(a)	32.2 Torr, 6.1 Torr, 38.3 Torr, 0.840, 0.160
E5B.10(a)	0.92, 0.08, 0.97, 0.03
E5B.11(a)	0.267, 0.733, 58.6 kPa
E5B.12(a)	(i) solution is ideal (ii) 0.830, 0.1703
E5B.13(a)	(i) 20.6 kPa (ii) 0.668, 0.332

Topic 5C

E5C.1(a)	(i) $y_M = 0.36$ (ii) $y_M = 0.80$ (*i.e.*, $y_O = 0.20$)
E5C.4(a)	0.25, 193°C
E5C.6(a)	(i) 76% (ii) 52% (iii) 1.11, 1.46
E5C.7(a)	(ii) 620 Torr (iii) 490 Torr (iv) 0.50, 0.72 (v) 0.50, 0.30

Chapter 6

Topic 6A

E6A.1(a)	0.9 mol, 1.2 mol
E6A.2(a)	$-0.64\ \text{kJ}$
E6A.3(a)	5.80×10^{5}
E6A.4(a)	2.85×10^{-6}
E6A.5(a)	(i) 0.141 (ii) 13.5
E6A.6(a)	(i) $-68.26\ \text{kJ mol}^{-1}$, 9.13×10^{11} (ii) 1.32×10^{9}, $-69.8\ \text{kJ mol}^{-1}$

E6A.7(a) $K = K_c \times \left(c^{\ominus} RT / p^{\ominus}\right)$

E6A.8(a) (i)

	A	B	C	D	Total
Initial amounts / mol	1.00	2.00	0	1.00	4.00
Stated change / mol			+0.90		
Implied change / mol	–0.60	–0.30	+0.90	+0.60	
Equilibrium amounts / mol	0.40	1.70	0.90	1.60	4.60
Mole fractions	0.087	0.370	0.196	0.348	1.001

(ii) 0.33 (iii) 0.33 (iv) $+2.8\ \text{kJ mol}^{-1}$

E6A.9(a) $+12.3\ \text{kJ mol}^{-1}$

E6A.10(a) $-14.4\ \text{kJ mol}^{-1}$, toward the ammonia product

E6A.11(a) $-1108\ \text{kJ mol}^{-1}$

Topic 6B

E6B.1(a) 0.045, $15\overline{00}$ K

E6B.2(a) $+2.77\ \text{kJ mol}^{-1}$, $-16.5\ \text{J K}^{-1}\ \text{mol}^{-1}$

E6B.3(a) 50%

E6B.4(a) 0.9039, 0.0961

E6B.5(a) (i) $52.89\ \text{kJ mol}^{-1}$ (ii) $-52.89\ \text{kJ mol}^{-1}$

E6B.6(a) 1110 K

E6B.7(a) $70.2\ \text{kJ mol}^{-1}$, $110\ \text{kJ mol}^{-1}\ \text{K}^{-1}$, $-6.3\ \text{kJ mol}^{-1}$, 3.0

Topic 6C

E6C.2(a) (i) +1.10 V (ii) +0.22 V (iii) +1.23 V

E6C.3(a) (i) $\text{Cd}^{2+}(\text{aq}) + 2\text{Br}^{-}(\text{aq}) + 2\ \text{Ag(s)} \rightarrow \text{Cd(s)} + 2\ \text{AgBr(s)}$ (iii) –0.62 V

Topic 6D

E6D.1(a) (i) 6.5×10^{9} (ii) 1.4×10^{12}

E6D.2(a) (i) 8.47×10^{-17} (ii) $9.20\times10^{-9}\ \text{mol dm}^{-3}$ or $2.16\ \mu\text{g dm}^{-3}$

Chapter 7

Topic 7A

E7A.1(a) (i) 6.6×10^{-19} J, 4.0×10^{2} kJ mol^{-1} (ii) 6.6×10^{-20} J, 40 kJ mol^{-1} (iii) 6.6×10^{-34} J, 4.0×10^{-13} kJ mol^{-1}

E7A.2(a)

λ / nm	E / aJ	E_m / (kJ mol^{-1})
(i) 600	331	199
(ii) 550	361	218
(iii) 400	497	299

E7A.3(a)

λ / nm	E_{photon} / aJ	v / (km s^{-1})
(i) 600	331	19.9
(ii) 550	361	20.8
(iii) 400	497	24.4

E7A.4(a) 21 m s^{-1}

E7A.5(a) (i) 2.77×10^{18} (ii) 2.77×10^{20}

E7A.6(a) (i) no electron ejection (ii) 3.19×10^{-19} J, 837 km s^{-1}

E7A.7(a) 6.96 keV, 6.96 keV

E7A.8(a) 7.27×10^{6} m s^{-1}, 150 V

E7A.9(a) 0.024 m s^{-1}

E7A.10(a) 332 pm

E7A.11(a) (i) 6.6×10^{-29} m (ii) 6.6×10^{-36} m (iii) 99.7 pm

Topic 7B

E7B.3(a)	$N = \left(\dfrac{1}{2\pi}\right)^{1/2}$
E7B.4(a)	$(1/2\pi)\,\mathrm{d}\phi$
E7B.5(a)	$\dfrac{1}{2}$

Topic 7C

E7C.1(a)	$\hat{V} = \tfrac{1}{2}k_\mathrm{f}x^2$
E7C.5(a)	$\dfrac{L}{2}$
E7C.7(a)	$1.1\times10^{-28}\ \mathrm{m\,s^{-1}}$, $1.1\times10^{-27}\ \mathrm{m}$
E7C.8(a)	700 pm
E7C.9(a)	(i) $-\dfrac{1}{x^2}$ (ii) $2x$

Chapter 8

Topic 8A

E8A.1(a)	$5\times10^{-20}\ \mathrm{J}$
E8A.2(a)	$A\mathrm{e}^{\mathrm{i}kx}$
E8A.3(a)	(i) $1.81\times10^{-19}\ \mathrm{J}$, $1.13\ \mathrm{eV}$, $9100\ \mathrm{cm^{-1}}$, $109\ \mathrm{kJ\,mol^{-1}}$ (ii) $6.6\times10^{-19}\ \mathrm{J}$, $4.1\ \mathrm{eV}$, $33\,000\ \mathrm{cm^{-1}}$, $400\ \mathrm{kJ\,mol^{-1}}$
E8A.4(a)	(i) 0.04 (ii) 0
E8A.5(a)	$\dfrac{h^2}{4L^2}$
E8A.6(a)	$L^2\left(\dfrac{1}{3}-\dfrac{1}{2\pi^2}\right)$
E8A.7(a)	$\dfrac{h}{8^{1/2}m_\mathrm{e}c} = \dfrac{\lambda_\mathrm{C}}{8^{1/2}}$
E8A.8(a)	$\dfrac{L}{6}, \dfrac{L}{2}$ and $\dfrac{5L}{6}$

E8A.9(a)	–17.4%
E8A.10(a)	$\dfrac{2kTmL^2}{h^2}-\dfrac{1}{2}$
E8A.11(a)	$n_1=1$, $n_2=4$
E8A.12(a)	3
E8A.13(a)	0.8

Topic 8B

E8B.1(a)	4.30×10^{-21} J
E8B.2(a)	278 N m^{-1}
E8B.3(a)	2.64 μm
E8B.4(a)	8.3673×10^{-28} kg , 1.6722×10^{-27} kg , 93.3 THz
E8B.5(a)	(i) 3.3×10^{-34} J (ii) 3.3×10^{-33} J
E8B.6(a)	5.61×10^{-21} J
E8B.7(a)	$\pm0.525\alpha$ or $\pm1.65\alpha$
E8B.8(a)	$\pm\alpha$
E8B.9(a)	0.056, 0.112

Topic 8C

E8C.1(a)	0, $\pm\hbar$
E8C.2(a)	$\left(\dfrac{1}{2\pi}\right)^{1/2}$
E8C.3(a)	3.32×10^{-22} J
E8C.4(a)	2.11×10^{-22} J
E8C.5(a)	4.22×10^{-22} J
E8C.6(a)	$2^{1/2}\hbar$, 1.49×10^{-34} J s
E8C.8(a)	7

Chapter 9

Topic 9A

E9A.1(a) (i) $g = 1$ (ii) $g = 9$ (iii) $g = 25$

E9A.2(a) $N = \dfrac{2}{a_0^{3/2}}$

E9A.3(a) $4a_0$, $r = 0.$

E9A.4(a) $r = 0.35a_0$

E9A.5(a) 101 pm and 376 pm

E9A.6(a) $2E_{1s}$, $-E_{1s}$

E9A.7(a) $5.24\dfrac{a_0}{\mathrm{Z}}$

E9A.8(a) $r = 2a_0 / Z$

E9A.10(a) $6a_0 / Z$, *xy* plane, $\theta = \pi/2$, *yz*, $\theta = 0$, xz, $\theta = 0$

Topic 9B

E9B.2(a) (i) $[\mathrm{Ar}]3\mathrm{d}^8$ (ii) $S = 1, 0$, $M_S = -1, 0, +1$, $M_S = 0$

Topic 9C

E9C.1(a) 9.118×10^{-6} cm, 1.216×10^{-5} cm

E9C.2(a) 3.292×10^{5} cm^{-1}, 3.038×10^{-6} cm, 9.869×10^{15} s^{-1}

E9C.3(a) 14.0 eV

E9C.4(a) (i) Forbidden (ii) allowed (iii) allowed

E9C.5(a) (i) $\tfrac{5}{2}, \tfrac{3}{2}$ (ii) $\tfrac{7}{2}, \tfrac{5}{2}$

E9C.6(a) $l = 1$

E9C.7(a) $L = 2,\ S = 0,\ J = 2$

E9C.8(a) (i) $1, 0$, $3, 1$ (ii) $\tfrac{3}{2}, \tfrac{1}{2}$, and $\tfrac{1}{2}$, $4, 2, 2$

E9C.9(a) $^3D_3$, $^3D_2$, $^3D_1$, $^1D_2$, ^3D set of terms are the lower in energy

E9C.10(a) (i) $J = 0$, 1state (ii) $J = \frac{3}{2}, \frac{1}{2}$, 4, 2 states respectively (iii) $J = 2, 1, 0$, 5, 3, 1 states respectively

E9C.11(a) (i) $^2S_{1/2}$ (ii) $^2P_{3/2}$ and $^2P_{1/2}$

E9C.12(a) (i) Allowed (ii) forbidden (iii) allowed

Chapter 10

Topic 10A

E10A.1(a) $\{s(1)p_z(2)+s(2)p_z(1)\} \times \{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}$

E10A.2(a) $\psi = a\psi_{\mathrm{VB}} + b\psi_{\mathrm{H^-F^+}} + c\psi_{\mathrm{H^+F^-}}$

E10A.6(a) $N = 3^{-1/2}$, $\psi = 3^{-1/2}(\mathrm{s} + 2^{1/2}\mathrm{p})$

Topic 10B

E10B.1(a) $N = \left(\dfrac{1}{1+2\lambda S+\lambda^2}\right)^{1/2}$

E10B.2(a) $N = 1.12$, $\psi_1 = 0.163A + 0.947B$, $b = 0.412$, $a = -1.02$, $\psi_2 = -1.02A + 0.412B$

E10B.3(a) 1.9 eV, 130 pm

E10B.4(a) u, g

Topic 10C

E10C.1(a) (i) $1\sigma_g^2$, b=1 (ii) $1\sigma_g^2 1\sigma_u^2$, b=0 (iii) $1\sigma_g^2 1\sigma_u^2 1\pi_u^4$, b=2

E10C.2(a) C_2

E10C.3(a) F_2^+

E10C.4(a) b=1, b=0, b=1, b=2, b=3, b=2, b=1

E10C.5(a) $1\sigma_g$, $1\sigma_u$, $1\pi_u$, $1\pi u$, $2\sigma_g$, $1\pi_g$, $1\pi_g$, $1\sigma_u$, $1\pi_u$, $1\pi_u$, $2\sigma_g$, $1\pi_g$, $1\pi_g$, $2\sigma_u$

E10C.6(a) $4\times10^5\ \mathrm{m\ s^{-1}}$

E10C.7(a) (i) 2.1×10^{-10} m = 0.21 nm (ii) 1.0×10^{-10} m = 0.10 nm

Topic 10D

E10D.1(a) (i) $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2$ (ii) $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 2\pi^1$ (iii) $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2$

E10D.3(a) NO^+

E10D.5(a) 7.2, 8.3

E10D.6(a) -6.6 or -8.9

E10D.7(a) –5.0 or –10.7 eV

Topic 10E

E10E.2(a) (i) $a_{2u}{}^2 e_{1g}{}^4 e_{2u}{}^1$, $7\alpha + 7\beta$ (ii) $a_{2u}{}^2 e_{1g}{}^3$, $5\alpha + 7\beta$

E10E.3(a) (i) 7β, 0 (ii) 7β, 2β

E10E.5(a) (i) $14\alpha + 19.314\beta$ (ii) $14\alpha + 19.448\beta$

Chapter 11

Topic 11A

E11A.1(a) Identity E, C_3 axis, three vertical mirror planes σ_v

E11A.2(a) D_{2h}, $3C_2$ axes, a centre of inversion, $3\sigma_h$ mirror planes

E11A.3(a) (i) R_3 (ii) C_{2v} (iii) D_{3h} (iv) $D_{\infty h}$

E11A.4(a) (i) C_{2v} (ii) $C_{\infty v}$ (iii) C_{3v} (iv) D_{2h}

E11A.5(a) (i) C_{2v} (ii) C_{2h}

E11A.6(a) (i) pyridine (ii) nitroethane

E11A.7(a)

Isomers and Point Groups of *m*,*n*-Dichloronaphthalene

m,*n*	1,2	1,3	1,4	1,5	1,6	1,7	1,8	2,3	2,6	2,7
Point Group	C_s	C_s	C_{2v}	C_{2h}	C_s	C_s	C_{2v}	C_{2v}	C_{2h}	C_{2v}

E11A.8(a) $i,\ \sigma_{\mathrm{h}}$

Topic 11B

E11B.1(a) $$\boldsymbol{D}(\sigma_{\mathrm{h}})=\begin{pmatrix}-1 & 0 & 0 & 0\\ 0 & -1 & 0 & 0\\ 0 & 0 & -1 & 0\\ 0 & 0 & 0 & -1\end{pmatrix}$$

E11B.2(a) $$\begin{pmatrix}-1 & 0 & 0 & 0\\ 0 & 0 & -1 & 0\\ 0 & 0 & 0 & -1\\ 0 & -1 & 0 & 0\end{pmatrix}=\boldsymbol{D}(S_3)$$

Topic 11C

E11C.4(a) no N orbitals, d_{xy}

E11C.6(a) $2A_1 + B_1 + E$

E11C.7(a) (i) Either E_{1u} or A_{2u} (ii) B_{3u} (x-polarized), B_{2u} (y-polarized), B_{1u} (z – polarized)

E11C.8(a) zero

Chapter 12

Topic 12A

E12A.1(a) (i) $0.0469\,\mathrm{J\,m^{-3}\,s}$ (ii) $1.33\times10^{-13}\,\mathrm{J\,m^{-3}s}$ (iii) $4.50\times10^{-28}\,\mathrm{J\,m^{-3}\,s}$

E12A.2(a) 82.9 %

E12A.3(a) $5.34\times10^{3}\ \mathrm{dm^{3}\ mol^{-1}\ cm^{-1}}$

E12A.4(a) $1.09\ \mathrm{mmol\ dm^{-3}}$

E12A.5(a)	$450\ \mathrm{dm^3\ mol^{-1}\ cm^{-2}}$
E12A.6(a)	$15\overline{9}\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$, 23 per cent
E12A.7(a)	(i) $0.87\ \mathrm{m}$ (ii) $2.9\ \mathrm{m}$
E12A.8(a)	$1.3\times10^{8}\ \mathrm{dm^3\ mol^{-1}\ cm^{-2}}$
E12A.9(a)	(i) $5\times10^{7}\ \mathrm{dm^3\ mol^{-1}\ cm^{-2}}$ (ii) $2.5\times10^{6}\ \mathrm{dm^3\ mol^{-1}\ cm^{-2}}$
E12A.10(a)	$0.9999\times\lambda$
E12A.11(a)	(i) $27\ \mathrm{ps}$ (ii) $2.7\ \mathrm{ps}$
E12A.12(a)	(i) $\delta\tilde{\nu} = 53\ \mathrm{cm^{-1}}$ (ii) $\delta\tilde{\nu} = 0.53\ \mathrm{cm^{-1}}$

Topic 12B

E12B.1(a)	$6.33\times10^{-46}\ \mathrm{kg\ m^2}$, $0.4421\ \mathrm{cm^{-1}}$
E12B.3(a)	(i) Asymmetric (ii) oblate symmetric (iii) spherical (iv) prolate symmetric
E12B.4(a)	$106.5\ \mathrm{pm}$, $115.6\ \mathrm{pm}$
E12B.5(a)	$2.073\times10^{-4}\ \mathrm{cm^{-1}}$, 0.1253

Topic 12C

E12C.2(a)	$3.07\times10^{11}\ \mathrm{Hz}$
E12C.3(a)	$127.4\ \mathrm{pm}$
E12C.4(a)	$4.442\times10^{-47}\ \mathrm{kg\ m^2}$, $165.9\ \mathrm{pm}$
E12C.5(a)	(i) 20 (ii) 23
E12C.6(a)	(iii) CH_4 is inactive, (i), (ii), and (iv) are active.
E12C.7(a)	$20\ 475\ \mathrm{cm^{-1}}$
E12C.8(a)	$198.9\ \mathrm{pm}$
E12C.9(a)	$\frac{5}{3}$

Topic 12D

E12D.1(a)	$1.6\times10^{2}\ \mathrm{N\,m^{-1}}$
E12D.2(a)	1.077 %
E12D.3(a)	$328.7\ \mathrm{N\ m^{-1}}$
E12D.4(a)	967.0, 515.6, 411.8, 314.2
E12D.5(a)	(i) 0.067 (ii) 0.20
E12D.6(a)	$1580.38\ \mathrm{cm^{-1}}$, 7.644×10^{-3}
E12D.7(a)	5.13 eV

Topic 12E

E12E.3(a)	127
E12E.4(a)	$\tfrac{1}{2}\left(\tilde{\nu}_1+\tilde{\nu}_2+\tilde{\nu}_3\right)$
E12E.6(a)	Raman active
E12E.7(a)	$4\mathrm{A}_1+\mathrm{A}_2+2\mathrm{B}_1+2\mathrm{B}_2$
E12E.8(a)	$\mathrm{A}_1,\mathrm{B}_1$ and B_2 are infrared active, all modes are Raman active

Chapter 13

Topic 13A

E13A.1(a)	3, u
E13A.2(a)	(i) Allowed (ii) allowed (iii) forbidden (iv) forbidden (v) allowed
E13A.3(a)	$\dfrac{2\sqrt{2}}{3}\mathrm{e}^{-2ax_0^2/3}$
E13A.4(a)	$\dfrac{1}{32}\left(3+\dfrac{4}{\pi}\right)^2$
E13A.5(a)	$\tfrac{1}{2}\left(\tilde{B}'+\tilde{B}\right)/\left(\tilde{B}'-\tilde{B}\right)$
E13A.6(a)	$\tfrac{1}{2}\left(\tilde{B}'+\tilde{B}\right)/\left\lvert\left(\tilde{B}'-\tilde{B}\right)\right\rvert-1$, 7
E13A.7(a)	$30.4\ \mathrm{cm^{-1}}<\tilde{B}'<40.5\ \mathrm{cm^{-1}}$, greater
E13A.8(a)	$\Delta_{\mathrm{O}}=P-\tilde{\nu}$, $14\times10^{3}\ \mathrm{cm^{-1}}$

E13A.9(a)	$\frac{3}{8}\left(\frac{a^3}{b-\frac{1}{2}a}\right)^{1/2}$
E13A.10(a)	$\frac{1}{4}\mathrm{e}^{-1/16}a$

Topic 13B

13B.1(a)	(i) Lower, $\tilde{\nu} \approx 1800\,\mathrm{cm}^{-1}$ (ii) no information

Topic 13C

E13C.1(a)	λ = 2.0 cm (ν = 15.0 GHz)
E13C.2(a)	20 ps, 70 MHz

Chapter 14

Topic 14A

E14A.1(a)	$\mathrm{s}^{-1}\ \mathrm{T}^{-1}$		
E14A.2(a)	9.133×10^{-35} J s, $\pm5.273\times10^{-35}$ J s, $\pm0.9553\ \mathrm{rad} = \pm54.74^\circ$		
E14A.3(a)	574 MHz		
E14A.4(a)	$-1.473\times10^{-26}\ \mathrm{J}\times m_I$		
E14A.5(a)	165 MHz		
E14A.6(a)	(i) 3.98×10^{-25} J	(ii) 6.11×10^{-26} J, (a).	
E14A.7(a)	(i) 1×10^{-6}	(ii) 5.1×10^{-6}	(iii) 3.4×10^{-5}
E14A.8(a)	13		
E14A.9(a)	2×10^{2} T,	10 mT	

Topic 14B

E14B.1(a)	(i) Independent	(ii) 13

E14B.2(a)	(i) $11\,\mu\text{T}$	(ii) $110\,\mu\text{T}$	
E14B.5(a)	753 MHz		
E14B.9(a)	0.39 ms, $2.6\times10^{3}\,\text{s}^{-1}$		

Topic 14C

E14C.1(a)	9.40×10^{-4} T , 6.25 μs
E14C.2(a)	0.21 s
E14C.3(a)	1.234

Topic 14D

E14D.1(a)	2.0022	
E14D.2(a)	2.3 mT , $2.002\overline{5}$	
E14D.3(a)	Equal intensity , 330.2 mT, 332.2 mT, 332.8 mT, 334.8 mT	
E14D.5(a)	(i) 332.3 mT	(ii) 1.206 T
E14D.6(a)	$I=\frac{3}{2}$	

Chapter 15

Topic 15A

E15A.1(a)	21621600		
E15A.2(a)	(i) 40320	(ii) 5.63×10^{3}	(iii) 3.99×10^{4}
E15A.3(a)	1		
E15A.4(a)	524 K		
E15A.5(a)	7.43		
E15A.6(a)	$35\overline{4}$ K		

Topic 15B

E15B.1(a)	(i) 8.23×10^{-12} m, 8.23 pm, 2.60×10^{-12} m, 2.60 pm (ii) 1.79×10^{27}, 5.67×10^{28}
E15B.2(a)	0.3574
E15B.3(a)	72.2
E15B.4(a)	(i) 7.97×10^{3} (ii) 1.12×10^{4}
E15B.5(a)	18 K
E15B.6(a)	37 K
E15B.7(a)	4.5 K
E15B.8(a)	(i) 1 (ii) 2 (iii) 2 (iv) 12 (v) 3
E15B.9(a)	660.6
E15B.10(a)	4500 K
E15B.11(a)	2.571
E15B.12(a)	42.3
E15B.13(a)	4.292, 0.0353 to 0.0377 to 1

Topic 15C

E15C.1(a)	8.16×10^{-22} J
E15C.2(a)	18.5 K
E15C.3(a)	25 K
E15C.4(a)	4.5 K
E15C.5(a)	4600 K
E15C.6(a)	10500 K
E15C.7(a)	6500 K
E15C.8(a)	4.033×10^{-21} J

Topic 15D

E15D.1(a)	He gas, CO gas, H_2O vapour

Topic 15E

E15E.1(a)	(i) $\frac{7}{2}R$ (ii) $3R$ (iii) $7R$
E15E.2(a)	Closer, closer
E15E.3(a)	(i) 4.158 (ii) 4.489
E15E.4(a)	(i) 14.93 J K^{-1} mol^{-1} (ii) 25.65 J K^{-1} mol^{-1}
E15E.5(a)	(i) 126 J K^{-1} mol^{-1} (ii) 169 J K^{-1} mol^{-1}
E15E.6(a)	2.35×10^{3} K
E15E.7(a)	43.1, 22.36 K, 43.76 J K^{-1} mol^{-1}
E15E.8(a)	11.5 J K^{-1} mol^{-1}
E15E.9(a)	(i) 34.72 J K^{-1} mol^{-1} (ii) 119.06 J K^{-1} mol^{-1}

Topic 15F

E15F.1(a)	-13.8 kJ mol^{-1}, -0.20 kJ mol^{-1}
E15F.2(a)	(i) -6.42 kJ mol^{-1} (ii) -14.0 kJ mol^{-1}
E15F.3(a)	3.70×10^{-3}

Chapter16

Topic 16A

E16A.1(a)	CIF_3, O_3, H_2O_2
E16A.2(a)	1.4 D
E16A.3(a)	37 D, $11.\overline{7}°$
E16A.4(a)	1.66 D, 1.01×10^{-39} J^{-1} C^2 m^2, 9.06×10^{-30} m^3
E16A.5(a)	4.75
E16A.6(a)	1.42×10^{-39} J^{-1} C^2 m^2
E16A.7(a)	1.34
E16A.8(a)	17.7

Topic 16B

E16B.1(a)	$1.07\times10^{3}\ \text{kJ mol}^{-1}$
E16B.2(a)	$\dfrac{6l^{4}Q_{1}^{2}}{\pi\varepsilon_{0}r^{5}}$
E16B.3(a)	$0.071\ \text{J mol}^{-1}$
E16B.4(a)	$28\overline{9}\ \text{kJ mol}^{-1}$

Topic 16C

E16C.1(a)	2.6 kPa
E16C.2(a)	$72.8\ \text{mN m}^{-1}$
E16C.3(a)	728 kPa

Chapter 17

Topic 17A

E17A.1(a)	27 nm
E17A.2(a)	3.08 μm , 30.8 nm
E17A.3(a)	2.4×10^{3}
E17A.4(a)	0.017
E17A.5(a)	6.4×10^{-3}
E17A.6(a)	+41.42% , +182.8%
E17A.7(a)	+895 % when $N = 1000$, $+9.84\times10^{4}$ % when $N = 1000$
E17A.8(a)	1.6×10^{2} pm

Topic 17B

E17B.1(a)	$-19\ \text{mJ mol}^{-1}\ \text{K}^{-1}$
E17B.2(a)	3.7×10^{-14} N

Topic 17C

E17C.1(a)	3.43

Topic 17D

E17D.1(a)	$70\ \mathrm{kg\ mol^{-1}}$, $71\ \mathrm{kg\ mol^{-1}}$
E17D.2(a)	(i) $18\ \mathrm{kg\ mol^{-1}}$ (ii) $20\ \mathrm{kg\ mol^{-1}}$
E17D.3(a)	100
E17D.4(a)	$64\ \mathrm{kg\ mol^{-1}}$
E17D.5(a)	$0.73\ \mathrm{mm\ s^{-1}}$
E17D.6(a)	$31\ \mathrm{kg\ mol^{-1}}$
E17D.7(a)	$3.4\times10^{3}\ \mathrm{kg\ mol^{-1}}$

Chapter 18

Topic 18A

E18A.1(a)	$N=4$, $4.01\ \mathrm{g\ cm^{-3}}$
E18A.2(a)	(323) and (110)
E18A.3(a)	229 pm , 397 pm , 115 pm
E18A.4(a)	220 pm
E18A.5(a)	70.7 pm
E18A.6(a)	10.1° , 14.4° , 17.7°
E18A.7(a)	8.16° , 4.82° , $11.7\bar{5}^\circ$
E18A.8(a)	$f_{\mathrm{Br^-}}=36$
E18A.9(a)	$f_{\mathrm{Br^-}}=36$
E18A.10(a)	f
E18A.11(a)	$3f$ for $h+k$ even and $-f$ for $h+k$ odd
E18A.15(a)	$6.1\ \mathrm{km\ s^{-1}}$

E18A.16(a) 233 pm

Topic 18B

E18B.1(a) 0.9069

E18B.2(a) (i) 0.5236 (ii) 0.6802 (iii) 0.7405

E18B.3(a) (i) 74.9 pm (ii) 132 pm

E18B.4(a) Expansion

E18B.5(a) 3500. kJ mol^{-1}

Topic 18C

E18C.1(a) $9.3\times10^{-4}\ \text{cm}^3$

E18C.2(a) n-type; the dopant, arsenic, belongs to Group 15 whereas germanium belongs to Group 14.

E18C.3(a) Three unpaired spins

E18C.4(a) $-6.4\times10^{-5}\ \text{cm}^3\,\text{mol}^{-1} = -6.4\times10^{-11}\ \text{m}^3\ \text{mol}^{-1}$

E18C.5(a) 4.326 , 5

E18C.6(a) $+1.6\times10^{-8}\ \text{m}^3\ \text{mol}^{-1}$

Topic 18D

E18D.1(a) 3.54 eV

Chapter 19

Topic 19A

E19A.1(a) $7.6\times10^{-3}\ \text{J K}^{-1}\ \text{m}^{-1}\ \text{s}^{-1}$

E19A.2(a) (i) $D = 1.5\ \text{m}^2\ \text{s}^{-1}$, $J_z/N_A = -61\ \text{mol m}^{-2}\ \text{s}^{-1}$ (ii) $D = 1.5\times10^{-5}\ \text{m}^2\ \text{s}^{-1}$, $J_z/N_A = -6.1\times10^{-4}\ \text{mol m}^{-2}\ \text{s}^{-1}$ (iii) $D = 1.5\times10^{-7}\ \text{m}^2\ \text{s}^{-1}$, $J_z/N_A = -6.1\times10^{-6}\ \text{mol m}^{-2}\ \text{s}^{-1}$

E19A.3(a) $-0.078\ \text{J m}^{-2}\ \text{s}^{-1}$

E19A.4(a)	0.0795 nm^2
E19A.5(a)	$10\overline{3}$ W
E19A.6(a)	0.201 nm^2
E19A.7(a)	(i) $\eta = 178\ \mu\mathrm{P}$ (ii) $\eta = 186\ \mu\mathrm{P}$ (iii) $\eta = 342\ \mu\mathrm{P}$
E19A.8(a)	1.9×10^{20}
E19A.9(a)	104 mg
E19A.10(a)	2.15×10^{3} Pa
E19A.11(a)	42.4 g mol^{-1}
E19A.12(a)	1.3 days

Topic 19B

E19B.1(a)	16.8 J mol^{-1}
E19B.2(a)	$7.63\times10^{-3}\ \mathrm{S\ m^2\ mol^{-1}}$
E19B.3(a)	$283\ \mu\mathrm{m\ s^{-1}}$
E19B.4(a)	$13.87\ \mathrm{mS\ m^2\ mol^{-1}}$
E19B.5(a)	$4.01\times10^{-8}\ \mathrm{m^2\ V^{-1}\ s^{-1}}$, $5.19\times10^{-8}\ \mathrm{m^2\ V^{-1}\ s^{-1}}$, $7.62\times10^{-8}\ \mathrm{m^2\ V^{-1}\ s^{-1}}$
E19B.6(a)	420 pm
E19B.7(a)	$1.90\times10^{-9}\ \mathrm{m^2\ s^{-1}}$

Topic 19C

E19C.1(a)	6.2×10^{3} s
E19C.2(a)	(i) 0.00 mol dm^{-3} (ii) 0.0121 mol dm^{-3}
E19C.3(a)	25 kN mol^{-1}, ∞
E19C.4(a)	67.5 kN mol^{-1}
E19C.5(a)	1.3×10^{3} s
E19C.6(a)	0.42 nm

E19C.7(a) 27.3 ps

E19C.8(a) 113 μm , 56 μm

Chapter 20

Topic 20A

E20A.1(a) No change in pressure

E20A.2(a) $8.1\ \mathrm{mol\ dm^{-3}\ s^{-1}}$, $2.7\ \mathrm{mol\ dm^{-3}\ s^{-1}}$, $2.7\ \mathrm{mol\ dm^{-3}\ s^{-1}}$, $5.4\ \mathrm{mol\ dm^{-3}\ s^{-1}}$

E20A.3(a) $1.3\overline{5}\ \mathrm{mol\,dm^{-3}\ s^{-1}}$, $4.0\overline{5}\ \mathrm{mol\ dm^{-3}\ s^{-1}}$, $2.7\ \mathrm{mol\ dm^{-3}\ s^{-1}}$, $1.3\overline{5}\ \mathrm{mol\,dm^{-3}\ s^{-1}}$

E20A.4(a) $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$, (i) $k_r[\mathrm{A}][\mathrm{B}]$ (ii) $3k_r[\mathrm{A}][\mathrm{B}]$

E20A.5(a) $\frac{1}{2}k_r[\mathrm{A}][\mathrm{B}][\mathrm{C}]$, $\mathrm{dm^6\ mol^{-2}\ s^{-1}}$

E20A.6(a) (i) $[k_r] = \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, $[k_r] = \mathrm{dm^6\ mol^{-2}\ s^{-1}}$ (ii) $[k_r] = \mathrm{kPa^{-1}\ s^{-1}}$, $[k_r] = \mathrm{kPa^{-2}\ s^{-1}}$

Topic 20B

E20B.1(a) $n = 2$

E20B.2(a) $1.03\times10^4\ \mathrm{s}$, (i) 498 Torr (ii) 461 Torr

E20B.3(a) (i) $0.098\ \mathrm{mol\,dm^{-3}}$ (ii) $0.050\ \mathrm{mol\,dm^{-3}}$

E20B.4(a) $1.11\times10^5\ \mathrm{s}$, 1.28 days

Topic 20C

E20C.1(a) $7.1\times10^5\ \mathrm{s^{-1}}$, $1.28\times10^4\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$

Topic 20D

E20D.1(a) $1.08\times10^5\ \mathrm{J\ mol^{-1}} = 108\ \mathrm{kJ\ mol^{-1}}$, $6.50\times10^{15}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, $6.50\times10^{15}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$

E20D.2(a) $35\ \mathrm{kJ\,mol^{-1}}$

Topic 20E

E20E.1(a) (i) $k_2K^{1/2}[A_2]^{1/2}[B]$ (ii) $\frac{k_2{}^2[B]^2}{4k_1'}\left(\sqrt{1+\frac{16k_1'k_1[A_2]}{k_2{}^2[B]^2}}-1\right)$, $k_2K^{1/2}[A_2]^{1/2}[B]$, $2k_1[A_2]$

E20E.2(a) –3 kJ mol^{-1}

Topic 20F

E20F.1(a) 1.9×10^{-6} Pa^{-1} s^{-1}, 1.9 MPa^{-1} s^{-1}

E20F.2(a) 251, 0.996

E20F.3(a) 0.125

Topic 20G

E20G.1(a) 3.3×10^{18}

E20G.2(a) 0.56 mol dm^{-3}

Topic 20H

E20H.1(a) $\frac{k_bK[AH]^2[B]}{[BH^+]}$

E20H.2(a) 1.50 mmol dm^{-3} s^{-1}

E20H.3(a) 2.0×10^{-5} mol dm^{-3}

Chapter 21

Topic 21A

E21A.1(a) 1.13×10^{10} s^{-1}, 1.62×10^{35} s^{-1} m^{-3}, 1.7%

E21A.2(a) (i) 1.04×10^{-3}, 0.069 (ii) 1.19×10^{-15}, 1.57×10^{-6}

E21A.3(a) (i) 22%, 3% (ii) 170%, 16%

E21A.4(a) 1.03×10^{-5} m^3 mol^{-1} s^{-1}, 1.03×10^{-2} dm^3 mol^{-1} s^{-1}

E21A.5(a) $0.79\ \text{nm}^2$, 1.16×10^{-3}

E21A.6(a) 0.73

E21A.7(a) 5.1×10^{-7}

Topic 21B

E21B.1(a) $4.\overline{5}\times10^{7}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}$, $4.\overline{5}\times10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$

E21B.2(a) (i) $6.61\times10^{6}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}$, $6.61\times10^{9}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ (ii) $3.0\times10^{7}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}$, $3.0\times10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$

E21B.3(a) $8.0\times10^{6}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}$, $8.0\times10^{9}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$, $4.2\times10^{-8}\ \text{s}$

E21B.4(a) $1.81\times10^{8}\ \text{mol dm}^{-3}\ \text{s}^{-1}$

Topic 21C

E21C.1(a) $+69.7\ \text{kJ mol}^{-1}$, $-25\ \text{J K}^{-1}\ \text{mol}^{-1}$

E21C.2(a) $+73.4\ \text{kJ mol}^{-1}$, $+71.9\ \text{kJ mol}^{-1}$

E21C.3(a) $-91\ \text{J K}^{-1}\ \text{mol}^{-1}$

E21C.4(a) $-74\ \text{J K}^{-1}\ \text{mol}^{-1}$

E21C.5(a) (i) $-46\ \text{J K}^{-1}\ \text{mol}^{-1}$ (ii) $+5.0\ \text{kJ mol}^{-1}$ (iii) $+18.7\ \text{kJ mol}^{-1}$

E21C.6(a) $7.1\ \text{dm}^6\ \text{mol}^{-2}\ \text{min}^{-1}$

Topic 21D

E21D.1(a) Reactant is high in translational energy and low in vibrational energy, product is high in vibrational energy and relatively lower in translational energy

Topic 21E

E21E.1(a) $4\times10^{-21}\ \text{J}$, $2\ \text{kJ mol}^{-1}$

E21E.2(a) $12.\overline{5}\ \text{nm}^{-1}$

Topic 21F

E21F.1(a) 0.138 V

E21F.2(a) 2.82 mA cm^{-2}

E21F.3(a) Increases, factor of 50

E21F.4(a) (i) 1.7×10^{-4} A cm^{-2} (ii) 1.7×10^{-4} A cm^{-2}

E21F.5(a) (i) 0.31 mA cm^{-2} (ii) 5.44 mA cm^{-2} (iii) -2×10^{42} mA cm^{-2}

E21F.6(a) $4.9\times10^{15}\ \text{cm}^{-2}\ \text{s}^{-1}$, $1.6\times10^{16}\ \text{cm}^{-2}\ \text{s}^{-1}$, $3.1\times10^{7}\ \text{cm}^{-2}\ \text{s}^{-1}$, 3.9 s^{-1}, 12 s^{-1}, 2.4×10^{-8} s^{-1}

E21F.7(a) (i) $33\ \Omega$ (ii) $3.3\times10^{10}\ \Omega$

E21F.8(a) One can (barely) deposit zinc

Chapter 22

Topic 22A

22A.1(a) (i) $1.4\times10^{14}\ \text{cm}^{-2}\ \text{s}^{-1}$ (ii) $3.1\times10^{13}\ \text{cm}^{-2}\ \text{s}^{-1}$

22A.2(a) 0.13 bar

Topic 22B

E22B.1(a) $33.6\,\text{cm}^3$

E22B.2(a) Chemisorption , 50 s

E22B.3(a) 0.83 , 0.36

E22B.4(a) (i) 0.24 kPa (ii) 25 kPa

E22B.5(a) 15 kPa

E22B.6(a) $-12.\overline{4}\ \text{kJ mol}^{-1}$

E22B.7(a) $65\overline{1}\ \text{kJ mol}^{-1}$ (i) 1.6×10^{97} min (ii) 2.8×10^{-6} min

E22B.8(a) $61\overline{1}\ \text{kJ mol}^{-1}$

E22B.9(a) (i) 9.1 ps , 0.60 ps (ii) 4.1×10^{6} s , 6.6 μs

E22B.10(a) Zeroth-order , first-order

Topic 22C

E22C.1(a) 12 m^2

Solutions to odd-numbered problems

Chapter 1

Topic 1A

P1A.1	–233°N
P1A.3	-272.95°C
P1A.5	(a) 0.0245 kPa (b) 9.14 kPa (c) 0.0245 kPa
P1A.7	2.8×10^8 dm^3 = 2.8×10^5 m^3, 4.1×10^8 dm^3 = 4.1×10^5 m^3
P1A.9	(a) 1.7×10^{-5} (b) 0.72
P1A.13	51 km, 0.0029 atm

Topic 1B

P1B.3	$\left(\frac{2RT}{M}\right)^{1/2}$
P1B.5	$0.47\langle v_x \rangle_{\text{initial}}$
P1B.7	$n^2 e^{3(1-n^2)/2}$, 5.53×10^{-5}, 2.71×10^{-9}
P1B.9	(a) 11.2 km s^{-1} (b) 5.04 km s^{-1}

Topic 1C

P1C.1	(a) $12.5\ \text{dm}^3\ \text{mol}^{-1}$ (b) $12.3\ \text{dm}^3\ \text{mol}^{-1}$
P1C.3	(a) $0.941\,\text{dm}^3\,\text{mol}^{-1}$ (b) $2.69\ \text{dm}^3\,\text{mol}^{-1}$, $2.67\ \text{dm}^3\ \text{mol}^{-1}$ (c) $5.11\,\text{dm}^3\,\text{mol}^{-1}$, inversion temperature
P1C.5	(a) $0.1353\,\text{dm}^3\,\text{mol}^{-1}$ (b) 0.6957 (c) 0.7158
P1C.7	$59.4\,\text{cm}^3\,\text{mol}^{-1}$, $5.649\,\text{dm}^6\,\text{atm}\,\text{mol}^{-2}$, $21\ \text{atm}$
P1C.9	$B = b - \frac{a}{RT}$, $C = b^2$, 34.6 cm^3 mol^{-1}, $1.26\,\text{dm}^6\,\text{atm}\,\text{mol}^{-2}$
P1C.11	$\frac{3C}{B}$, $\frac{B^2}{3RC}$, $\frac{B^3}{27C^2}$, $\frac{1}{3}$

P1C.13	$0.0866\,\text{atm}^{-1}$, $2.12\,\text{dm}^3\,\text{mol}^{-1}$
P1C.17	0.011
P1C.21	$\dfrac{b\left\{1 \pm (bRT/a)^{1/2}\right\}}{1 - bRT/a}$

Chapter 2

Topic 2A

P2A.1	$-nRT\ \ln\left(\dfrac{V_2 - nb}{V_1 - nb}\right) - n^2 a\left(\dfrac{1}{V_2} - \dfrac{1}{V_1}\right)$
	(a) $-1.7\,\text{kJ}$ (b) $-1.8\,\text{kJ}$ (c) $-1.5\ \text{kJ}$
P2A.3	(a) -1.5kJ (b) -1.6kJ
P2A.5	$\frac{1}{2}k_{\text{F}}x_{\text{f}}{}^2$

Topic 2B

P2B.1	$62.2\ \text{kJ mol}^{-1}$
P2B.3	$w = 0$, $\Delta U = +2.35\ \text{kJ}$, $+3.03\ \text{kJ}$

Topic 2C

P2C.1	$-1270\ \text{kJ mol}^{-1}$
P2C.3	-67.44, $n = 0.9253$, $-6625.5\ \text{kJ mol}^{-1}$, 2.17 per cent
P2C.5	$-994.30\ \text{kJ mol}^{-1}$
P2C.7	$-802.31\ \text{kJ mol}^{-1}$
P2C.9	$+37\ \text{K}$, $4.09\ \text{kg}$

Topic 2D

P2D.1	$1.6\,\text{m}$, $0.80\,\text{m}$, $2.8\,\text{m}$
P2D.3	nR

P2D.5	$T=\left(\dfrac{p}{nR}\right)\times(V-nb)+\left(\dfrac{na}{RV^2}\right)\times(V-nb)$, $\left(\dfrac{\partial T}{\partial p}\right)_V=\dfrac{V-nb}{nR}$
P2D.7	$c_\mathrm{s}=\left(\dfrac{\gamma p}{\rho}\right)^{1/2}$, $322\ \mathrm{m\ s^{-1}}$
P2D.11	(a) $23.5\ \mathrm{K\ MPa^{-1}}$ (b) $14.0\ \mathrm{K\ MPa^{-1}}$

Topic 2E

P2E.1	$41.40\,\mathrm{J\,K^{-1}\,mol^{-1}}$

Chapter 3

Topic 3A

P3A.5	1.00 kJ, 8.4 kJ
P3A.7	$10.\overline{7}\,\mathrm{J\,K^{-1}\,mol^{-1}}$
P3A.9	*Path (a)* $-2.74\,\mathrm{kJ}$, 0 , $+2.74\,\mathrm{kJ}$, $+9.13\ \mathrm{J\,K^{-1}}$, 0 , $-9.13\,\mathrm{J\,K^{-1}}$ *Path (b)* $-1.66\ \mathrm{kJ}$, 0 , $+1.66\,\mathrm{kJ}$, $+9.13\ \mathrm{J\,K^{-1}}$, $-5.53\,\mathrm{J\,K^{-1}}$, $+3.60\,\mathrm{J\,K^{-1}}$
P3A.11	$nC_{p,\mathrm{m}}\ln\dfrac{T_\mathrm{f}}{T_\mathrm{h}}+nC_{p,\mathrm{m}}\ln\dfrac{T_\mathrm{f}}{T_\mathrm{c}}$, $+22.6\ \mathrm{J\,K^{-1}}$
P3A.13	$47\overline{7}\ \mathrm{J\,K^{-1}\ mol^{-1}}$

Topic 3B

P3B.1	(a) $200.7\ \mathrm{J\,K^{-1}\ mol^{-1}}$ (b) $232.0\ \mathrm{J\,K^{-1}\ mol^{-1}}$
P3B.3	$+41.16\ \mathrm{kJ\ mol^{-1}}$, $+42.08\ \mathrm{J\,K^{-1}\ mol^{-1}}$, $+40.84\ \mathrm{kJ\ mol^{-1}}$, $+41.08\ \mathrm{J\,K^{-1}\ mol^{-1}}$
P3B.5	$34.4\ \mathrm{kJ\ mol^{-1}}$, $243\ \mathrm{J\,K^{-1}\ mol^{-1}}$

Topic 3C

P3C.1	(a) $50.7\,\mathrm{J\,K^{-1}}$, $-11.5\,\mathrm{J\,K^{-1}}$ (b) $+3.46\ \mathrm{kJ}$, indeterminate (c) $3.46\times10^3\ \mathrm{J}$, indeterminate (d) $+39.2\ \mathrm{J\,K^{-1}}$, $-39.2\,\mathrm{J\,K^{-1}}$

P3C.3 (a) $+35\ \mathrm{J\ K^{-1}\ mol^{-1}}$ (b) $12\ \mathrm{W\ m^{-3}}$, $1.5\times10^{4}\ \mathrm{W\ m^{-3}}$ (c) $0.46\dfrac{\text{mol ATP}}{\text{mol glutamine}}$

Topic 3D

P3D.1 $-501\ \mathrm{kJ\,mol^{-1}}$

P3D.3 $-21\,\mathrm{kJ\,mol^{-1}}$

P3D.5 $\left(\dfrac{\partial V}{\partial S}\right)_p=\left(\dfrac{\partial T}{\partial p}\right)_S$, $\left(\dfrac{\partial S}{\partial V}\right)_T=\left(\dfrac{\partial p}{\partial T}\right)_V$

P3D.7 $C_p\mathrm{d}T-\alpha TV\,\mathrm{d}p$, $-\alpha TV\Delta p$, $-0.50\,\mathrm{kJ}$

Chapter 4

Topic 4B

P4B.1 $196.0\,\mathrm{K}$, $11.1\,\mathrm{Torr}$

P4B.3 (a) $+5.56\times10^{3}\,\mathrm{Pa\,K^{-1}}$ (b) 2.6 per cent

P4B.5 (a) $-1.63\ \mathrm{cm^{3}\ mol^{-1}}$ (b) $+30.1\ \mathrm{dm^{3}\ mol^{-1}}$ (c) $+6\times10^{2}\,\mathrm{J\,mol^{-1}}$

P4B.7 22°C

P4B.9 (a) 227.5°C (b) $+53\ \mathrm{kJ\ mol^{-1}}$

P4B.13 $9.8\,\mathrm{Torr}$

P4B.15 363 K

P4B.17 $\dfrac{\mathrm{d}p}{\mathrm{d}T}=\dfrac{\alpha_2-\alpha_1}{\kappa_{T,2}-\kappa_{T,1}}$, $\dfrac{\mathrm{d}p}{\mathrm{d}T}=\dfrac{C_{p,\mathrm{m}2}-C_{p,\mathrm{m}1}}{TV_\mathrm{m}(\alpha_2-\alpha_1)}$

Chapter 5

Topic 5A

P5A.1 $18.079-0.11482x^{3/2}$

P5A.3 $15.58\,\mathrm{kPa}$, $47.03\,\mathrm{kPa}$

P5A.5 $4.6\ \mathrm{cm^{3}}$

Topic 5B

P5B.3	109.0 $\text{cm}^3\ \text{mol}^{-1}$, 279.3 $\text{cm}^3\ \text{mol}^{-1}$
P5B.5	165 K, 0.99978, 19.89 g solute (100 g solvent)$^{-1}$, $-\Delta_{\text{fus}}H/R$
P5B.7	(a) (i) 2 (ii) 3 (b) (ii) 0.19, 0.82, 0.24 (c) $x_{\text{Pb}} = 0.19$, $x_{\text{Cu}} = 0.18$
P5B.9	$\dfrac{\Delta_{\text{fus}}H}{RT^2}$, $\ln x_{\text{A}} = \dfrac{-\Delta_{\text{fus}}H}{R}\times\left(\dfrac{1}{T}-\dfrac{1}{T^*}\right)$
P5B.11	$1.26\times10^5\ \text{g mol}^{-1}$, $1.23\times10^4\ \text{dm}^3\ \text{mol}^{-1}$
P5B.13	$x_{\text{A}} = x_{\text{B}} = 0.5$
P5B.15	$4.78\times10^4\ \text{dm}^3\ \text{mol}^{-1}$

Topic 5C

P5C.1	(b) 391.0 K (c) 0.532
P5C.7	(b) Ca_2Si and a Ca-rich liquid ($x_{\text{Si}} = 0.13$), 0.5 (c) 0.53, 0.67
P5C.9	$\dfrac{x_{\text{A}}p_{\text{A}}^*/p_{\text{B}}^*}{1+(p_{\text{A}}^*/p_{\text{B}}^*-1)x_{\text{A}}}$

Topic 5E

P5E.3	$\Pi = \phi[\text{B}]RT$

Chapter 6

Topic 6A

P6A.1	(a) $+4.48\ \text{kJ mol}^{-1}$ (b) 0.101 atm
P6A.3	0.007 mol H_2, 0.107 mol I_2, 0.786 mol HI
P6A.5	$\xi = 1-\left(\dfrac{1}{1+ap/p^{\ominus}}\right)^{1/2}$

Topic 6B

P6B.1	(a) 1.24×10^{-9} (b) 1.29×10^{-8} (c) 1.8×10^{-4}
P6B.3	$300.\ \text{kJ mol}^{-1}$
P6B.5	0.740, 5.71, $-103\ \text{kJ mol}^{-1}$
P6B.7	(a) 1.2×10^{8} (b) 2.7×10^{3}
P6B.9	$K_c(T)=K_c(T_{\text{ref}})\times\left(\frac{T_{\text{ref}}}{T}\right)^{\Delta\nu}\ \mathrm{e}^{\frac{\Delta_\mathrm{r}H^{\ominus}}{R}\times\left(\frac{1}{T_{\text{ref}}}-\frac{1}{T}\right)}$

Topic 6C

P6C.1	(a) $+1.23\ \text{V}$ (b) $+1.09\ \text{V}$
P6C.3	$+14.7\ \text{kJ mol}^{-1}$, $+18.8\ \text{kJ mol}^{-1}$

Topic 6D

P6D.1	$+0.26843\ \text{V}$

Chapter 7

Topic 7A

P7A.1	(a) $1.6\times10^{-33}\ \text{J m}^{-3}$ (b) $2.5\times10^{-4}\ \text{J m}^{-3}$
P7A.3	$\lambda_{\max}T\cong\tfrac{1}{5}hc/k$
P7A.5	$25\overline{5}\ \text{K}$ or $1\overline{8}\ {}^\circ\text{C}$, $11\ \mu\text{m}$, $\frac{c\mathcal{E}}{4}$
P7A.7	(a) $8\pi hc$, hc (b) $\left(\frac{4}{c}\right)\sigma_{\text{Wien}}T^{4}$
P7A.9	(a) $223\overline{1}\ \text{K}$, $\theta_\text{E}=0.0315$ (b) $343\ \text{K}$, $\theta_\text{E}=0.897$

Topic 7B

P7B.1	(a) $N=\left(\frac{2}{L}\right)^{1/2}$ (b) $N=\frac{1}{c(2\text{L})^{1/2}}$ (c) $N=\frac{1}{(\pi a^{3})^{1/2}}$ (d) $N=\frac{1}{(32\pi a^{5})^{1/2}}$
P7B.3	0.0183

P7B.5 (a) 9.0×10^{-6} (b) 1.2×10^{-6}

P7B.7 $x_{\max} = a$

Topic 7C

P7C.1 (a) $\left(-\dfrac{\hbar^2}{2m_e}\dfrac{d^2}{dx^2}-\dfrac{e^2}{4\pi\varepsilon_0 x}\right)\psi = E\psi$ (b) $\left(-\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2}\right)\psi = E\psi$ (c) $\left(-\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2}-cx\right)\psi = E\psi$

P7C.3 (a) Yes (b) Yes (c) No (d) No

P7C.5 (a) Yes, $-k^2$ (b) Yes (c) Yes (d) No

(i) (a) and (b) (ii) (c)

P7C.7 (a) $+k\hbar$ (b) 0 (c) 0

P7C.9 $\dfrac{1}{a}$

P7C.11 (a) (i) $N=\left(\pi a_0^3\right)^{-1/2}$ (ii) $N=\left(32\pi a_0^5\right)^{-1/2}$ (c) (i) $1.5a_0$, $4.5a_0^2$ (ii) $5a_0$, $30a_0^2$

P7C.15 $\left[\hat{x},\hat{p}_x\right]=\mathrm{i}\hbar$

Chapter 8

Topic 8A

P8A.1 1.24×10^{-39} J, 2.2×10^{9}, 1.8×10^{-30} J

P8A.3 (a) $\dfrac{L}{2}$, $\dfrac{L}{3^{1/2}}$ (b) $\dfrac{L}{2}$, $\left(\dfrac{L^2}{3}-\dfrac{1}{4(n\pi/L)^2}\right)^{1/2}$

P8A.5 1.2×10^{6}

P8A.7 (a) $T=|A_3|^2=A_3\times A_3^*=\dfrac{4k_1^2k_2^2}{(a^2+b^2)\sinh^2(k_2L)+b^2}$

where $a^2+b^2=(k_1^2+k_2^2)(k_2^2+k_3^2)$ and $b^2=k_2^2(k_1+k_3)^2$

Topic 8B

P8B.1 HI < HBr < HCl < NO < CO

P8B.5 $\frac{1}{2}\left(v+\frac{1}{2}\right)\hbar\omega$

Topic 8C

P8C.1 (a) $\pm 5.275\times 10^{-34}$ J s, 7.89×10^{-19} J (b) 5.2×10^{14} Hz

P8C.3 (a) $+\hbar$ (b) $-2\hbar$ (c) 0 (d) $\hbar\cos 2\chi$

(a) $\frac{\hbar^2}{2I}$ (b) $\frac{2\hbar^2}{I}$ (c) $\frac{\hbar^2}{2I}$ (d) $\frac{\hbar^2}{2I}$

P8C.5 0, 2.62, 7.86, 15.72

P8C.7 1

P8C.9 $\frac{\hbar}{\mathrm{i}}\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$, $\frac{\hbar}{\mathrm{i}}\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$, $\frac{\hbar}{\mathrm{i}}\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$, $-\frac{\hbar}{\mathrm{i}}\hat{l}_z$.

Chapter 9

Topic 9A

P9A.1 $\pm 106\,\mathrm{pm}$

P9A.3 (b) $\rho_{\mathrm{node}}=3+\sqrt{3}$ and $\rho_{\mathrm{node}}=3-\sqrt{3}$, $\rho_{\mathrm{node}}=0$ and $\rho_{\mathrm{node}}=4$, $\rho_{\mathrm{node}}=0$ (c) $\langle r\rangle_{3\mathrm{s}}=\frac{27a_0}{2}$

P9A.7 (a) $\frac{Z}{a_0}$ (b) $\frac{Z}{4a_0}$ (c) $\frac{Z}{4a_0}$ (d) $\frac{Z}{a_0}$

P9A.11 $60957.4\,\mathrm{cm}^{-1}$, $60954.7\,\mathrm{cm}^{-1}$, $329170\,\mathrm{cm}^{-1}$, $329155\,\mathrm{cm}^{-1}$

Topic 9B

P9B.1 $0.420\,\mathrm{pm}$

Topic 9C

P9C.1 $n_2\to 6$

P9C.3 $\tilde{R}_{\mathrm{Li}^{2+}} = 987663\,\mathrm{cm}^{-1}$, $137175\,\mathrm{cm}^{-1}$, $185187\,\mathrm{cm}^{-1}$, $122.5\ \mathrm{eV}$

P9C.5 ${}^2\mathrm{P}_{1/2}$ and ${}^2\mathrm{P}_{3/2}$, ${}^2\mathrm{D}_{3/2}$ and ${}^2\mathrm{D}_{5/2}$, ${}^2\mathrm{D}_{3/2}$

P9C.7 $3.3429\times10^{-27}\ \mathrm{kg}$, 1.000272

P9C.9 (a) $0.9\ \mathrm{cm}^{-1}$ (b) small

P9C.11 (a) $2kT$ (b) $23.8\ \mathrm{T\ m}^{-1}$

Chapter 10

Topic 10A

P10A.1 $\dfrac{Z^{3/2}\mathrm{e}^{-\rho/2}}{(24\pi)^{1/2}a^{3/2}}\left(\dfrac{2-\rho}{2}+\dfrac{\rho\sin\theta}{8^{1/2}}\times(-\cos\phi+3^{1/2}\sin\phi)\right)$, 120°

Topic 10B

P10B.1 $1.87\times10^{6}\ \mathrm{J\ mol^{-1}} = 1.87\ \mathrm{MJ\ mol^{-1}}$

P10B.3 $E_{\mathrm{H1s}}-\dfrac{j+k}{1+S}+\dfrac{j_0}{R}$, $E_{\mathrm{H1s}}-\dfrac{j-k}{1-S}+\dfrac{j_0}{R}$

P10B.5 (b) $2.5a_0 = 1.3\times10^{-10}$ m, $-0.555j_0/a_0 = -15.1$ eV, $-0.565j_0/a_0 = -15.4$ eV, $0.055j_0/a_0 = 1.5$ eV, $0.065j_0/a_0 = 1.8$ eV

Topic 10C

P10C.1 $2.1a_0$

P10C.3 (c) $\pi/4$ or $3\pi/4$

Topic 10D

P10D.1 $\dfrac{\alpha_\mathrm{A}+\alpha_\mathrm{B}-2\beta S}{2(1-S^2)}\pm\dfrac{\alpha_\mathrm{A}-\alpha_\mathrm{B}}{2(1-S^2)}\left(1+\dfrac{4(\beta+\alpha_\mathrm{A}S)(\beta+\alpha_\mathrm{B}S)}{(\alpha_\mathrm{A}-\alpha_\mathrm{B})^2}\right)^{1/2}$, $\dfrac{\alpha_\mathrm{A}-\beta S}{1-S^2}+\dfrac{(\beta+\alpha_\mathrm{A}S)(\beta+\alpha_\mathrm{B}S)}{(\alpha_\mathrm{A}-\alpha_\mathrm{B})(1-S^2)}$, $\dfrac{\alpha_\mathrm{B}-\beta S}{1-S^2}-\dfrac{(\beta+\alpha_\mathrm{A}S)(\beta+\alpha_\mathrm{B}S)}{(\alpha_\mathrm{A}-\alpha_\mathrm{B})(1-S^2)}$

P10D.3 (i) $E/\mathrm{eV} = -10.7, -8.7$, and -6.6 (ii) $E/\mathrm{eV} = -10.8, -8.9$, and -6.9

Topic 10E

P10E.1 $E = \alpha_{\mathrm{O}},\ \dfrac{1}{2}\left(\alpha_{\mathrm{O}} + \alpha_{\mathrm{C}} \pm (\alpha_{\mathrm{O}} - \alpha_{\mathrm{C}})\sqrt{1 + \dfrac{12\beta^2}{(\alpha_{\mathrm{O}} - \alpha_{\mathrm{C}})^2}}\right),$

$$(\alpha_{\mathrm{O}} - \alpha_{\mathrm{C}})\left(\sqrt{1 + \frac{12\beta^2}{(\alpha_{\mathrm{O}} - \alpha_{\mathrm{C}})^2}} - \sqrt{1 + \frac{4\beta^2}{(\alpha_{\mathrm{O}} - \alpha_{\mathrm{C}})^2}}\right),\ \frac{4\beta^2}{\alpha_{\mathrm{O}} - \alpha_{\mathrm{C}}}$$

P10E.7 Standard potential increases as the LUMO decreases

P10E.13 (b) 26780 cm^{-1}

Chapter 11

Topic 11A

P11A.1 (a) $D_{3\mathrm{d}}$ (b) $D_{3\mathrm{d}}$, $C_{2\mathrm{v}}$ (c) $D_{2\mathrm{h}}$ (d) D_3 (e) $D_{4\mathrm{d}}$

P11A.3 S_4 , C_2 , S_4

Topic 11B

P11B.1 *trans*-CHCl=CHCl

P11B.3 $\Gamma = 3\mathrm{A}_1 + \mathrm{B}_1 + 2\mathrm{B}_2$

P11B.7 $+1$ or $-1,\ +1,\ -1$

P11B.9 (a) $2\mathrm{A}_1 + \mathrm{A}_2 + 2\mathrm{B}_1 + 2\mathrm{B}_2$ (b) $\mathrm{A}_1 + 3\mathrm{E}$ (c) $\mathrm{A}_1 + \mathrm{T}_1 + \mathrm{T}_2$ (d) $\mathrm{A}_{2\mathrm{u}} + \mathrm{T}_{1\mathrm{u}} + \mathrm{T}_{2\mathrm{u}}$

Topic 11C

P11C.1 $\mathrm{A}_1 + \mathrm{T}_2$, s and p, $(\mathrm{d}_{xy}, \mathrm{d}_{yz}, \mathrm{d}_{zx})$

Chapter 12

Topic 12A

P12A.1 4.4×10^3

P12A.3 $A = \varepsilon'[\mathrm{J}]_0\left(1-\mathrm{e}^{-L/\lambda}\right)$, $A = \varepsilon'[\mathrm{J}]_0$

P12A.7 $\frac{1}{2}\left(\frac{\pi}{\ln 2}\right)^{1/2}\varepsilon_{\max}\Delta\tilde{\nu}_{1/2}$, $5.7\times10^{4}\ \mathrm{dm^3\ mol^{-1}\ cm^{-2}}$

P12A.9 (a) receding, $1.128\times10^{-3}\ c = 3.381\times10^{5}\ \mathrm{m\ s^{-1}}$

P12A.11 $2\left(kT/mc^2\right)^{1/2}$

Topic 12B

P12B.1 $m_{\mathrm{eff}}R^2$

Topic 12C

P12C.1 596 GHz, 19.9 $\mathrm{cm^{-1}}$, 0.503 mm, $9.941\ \mathrm{cm^{-1}}$

P12C.3 $128.393\,\mathrm{pm}$, $128.13\,\mathrm{pm}$, slightly different

P12C.5 $116.28\ \mathrm{pm}$, $155.97\ \mathrm{pm}$

P12C.7 $14.35\ \mathrm{m^{-1}}$, 26, 15

P12C.9 $\left(\frac{kT}{2hc\tilde{B}}\right)^{1/2}-\frac{1}{2}$, 30, $\left(\frac{kT}{hc\tilde{B}}\right)^{1/2}-\frac{1}{2}$, 6

Topic 12D

P12D.1 $k_{\mathrm{f}} = 2Da^2.$

P12D.3 $142.81\,\mathrm{cm^{-1}}$, $3.36\ \mathrm{eV}$, $93.8\,\mathrm{N\,m^{-1}}$

P12D.7 $2\tilde{D}_{\mathrm{e}}/\tilde{\nu}-\tfrac{1}{2}$

P12D.9 $112.83\ \mathrm{pm}$, $123.52\ \mathrm{pm}$

P12D.11 $\tilde{B}_0 = 10.433\ \mathrm{cm^{-1}}$, $\tilde{B}_1 = 10.126\ \mathrm{cm^{-1}}$

P12D.13 $\left\langle x^2\right\rangle = \frac{1}{k_{\mathrm{f}}}(v+½)\hbar\omega.$, rotational constant B decreases, B decreases with increased anharmonicity

P12D.15 (a) $2143.26\ \text{cm}^{-1}$ (b) $12.8195\,\text{kJ mol}^{-1}$ (c) $1.85563\times10^{3}\,\text{N m}^{-1}$ (d) 1.91cm^{-1} (e) $113\ \text{pm}$

Topic 12E

P12E.1 (a) Cannot undergo simple harmonic motion

P12E.3 (a) $C_{3\text{v}}$ (b) nine (c) $3\text{A}_1+3\text{E}$ (d) all modes are infrared active (e) all modes are Raman active

Chapter 13

Topic 13A

P13A.1 $^2\Sigma_\text{g}^+ \leftarrow {}^2\Sigma_\text{u}^+$ is allowed

P13A.3 $6808.2\ \text{cm}^{-1}$ or $0.84411\ \text{eV}$, $5.08\ \text{eV}$

Topic 13C

P13C.1 $4\times10^{-10}\ \text{s}$ or $0.4\ \text{ns}$

Chapter 14

Topic 14A

P14A.1 $10.3\ \text{T}$, 2.42×10^{-5}, β, $\left(m_I=-\tfrac{1}{2}\right)$

Topic 14B

P14B.1 $29\ \mu\text{T m}^{-1}$

P14B.3 Both fit the data equally well.

P14B.5 $\cos\phi = B/4C$

Topic 14C

P14C.1 $400\times10^{6}\ \text{Hz}\pm8\,\text{Hz}$, $0.29\,\text{s}$

P14C.5 $\left(\frac{1}{2}\right)\frac{a\tau}{1+(\omega_0-\omega)^2\tau^2}$

P14C.7 158 pm

P14C.9 0.58 mT

Topic 14D

P14D.1 2.8×10^{13} Hz

P14D.3 6.9 mT , 2.1mT

Chapter 15

Topic 15A

P15A.1 {2, 2, 0, 1, 0, 0}, {2, 1, 2, 0, 0, 0}

P15A.7 $\mathrm{e}^{-Mgh/RT}$, 0.363 , 0.57

Topic 15B

P15B.3 (a) (i) 5.00 (ii) 6.26 (b) 1.00 , 0.80, 6.58×10^{-11} , 0.122

P15B.5 1.209 , 3.004

P15B.7 (a) 1.049 (b) 1.548 , 0.953 , 0.645 , 0.044 , 0.230 , 0.002 , 0.083

P15B.9 (a) 660.6 (b) 4.26×10^{4}

Topic 15C

P15C.3 (a) 104 K (b) $1+a$

Topic 15E

P15E.1 0.351, 0.079, 0.029

P15E.3 4.2 J K^{-1} mol^{-1}

P15E.5 28, 258 J mol^{-1} K^{-1}

P15E.7	(a) $nRT\left(\frac{\dot{q}}{q}\right)$, $nR\left\{\frac{\ddot{q}}{q}-\left(\frac{\dot{q}}{q}\right)^2\right\}$, $nR\left(\frac{\dot{q}}{q}+\ln\frac{\mathrm{e}q}{N}\right)$ (b) $5.41\ \mathrm{J\ K^{-1}\ mol^{-1}}$
P15E.11	$191\ \mathrm{J\ K^{-1}\ mol^{-1}}$
P15E.17	(a) $87.55\,\mathrm{K}$, $6330\,\mathrm{K}$ (b) and (c) $2\alpha C_{V,\mathrm{m}}(\mathrm{H})+(1-\alpha)C_{V,\mathrm{m}}(\mathrm{H_2})$, $\frac{kT_i\left(\Lambda_{\mathrm{H}_2 i}\right)^3\mathrm{e}^{-(D/RT_i)}}{p^{\ominus}q_i^{\mathrm{V}}q_i^{\mathrm{R}}\left(\Lambda_{\mathrm{H}i}\right)^6}$, $1.5R,\ 2.5R+\left[\frac{\theta^{\mathrm{V}}}{T_i}\times\frac{\mathrm{e}^{-(\theta^{\mathrm{V}}/2T_i)}}{1-\mathrm{e}^{\theta^{\mathrm{V}}/T_i}}\right]^2R$
P15E.19	$9.57\times10^{-15}\ \mathrm{J\ K^{-1}}$

Topic 15F

P15F.3	$100\ \mathrm{T}$
P15F.5	$45.76\,\mathrm{kJ\,mol^{-1}}$

Chapter 16

Topic 16A

P16A.1	(a) 0 (b) $0.7\ \mathrm{D}$ (c) $0.4\ \mathrm{D}$
P16A.5	$1.00\ \mu\mathrm{D}$
P16A.7	$1.2\times10^{-23}\ \mathrm{cm^3}$, $0.86\ \mathrm{D}$
P16A.9	$2.24\times10^{-24}\ \mathrm{cm^3}$, $1.58\ \mathrm{D}$, $5.66\,\mathrm{cm^3\ mol^{-1}}$
P16A.11	$68.8\ \mathrm{cm^3\ mol^{-1}}$, 4.40 , 2.10 , $8.14\ \mathrm{cm^3\ mol^{-1}}$, 1.76 , 1.33
P16A.13	Increase in the relative permittivity.

Topic 16B

P16B.1	$1.9\ \mathrm{nm}$
P16B.3	$-1.8\times10^{-27}\ \mathrm{J}=-1.1\times10^{-3}\ \mathrm{J\,mol^{-1}}$
P16B.5	$\frac{-6C}{r^7}$
P16B.7	(b) $r_\mathrm{e} = 1.3598\ r_0$, $A=1.8531$

Chapter 17

Topic 17A

P17A.1 (a) $\sqrt{2/5}\,a$, $0.046460\times\left\{\left(\upsilon_\mathrm{s}/\mathrm{cm^3\ g^{-1}}\right)\times\left(M/\mathrm{g\ mol^{-1}}\right)\right\}^{1/3}$, 1.96 nm

(b) $\sqrt{1/2}\,a$, $\sqrt{1/12}\,l$, 0.35 nm, 46 nm

P17A.3 Nl^2

P17A.5 (a) $\sqrt{1/2}\,a$, $a/2$ (b) $\sqrt{1/2}\,a$, $\sqrt{1/12}\,l$ (c) $\sqrt{2/5}\,a$

Topic 17B

P17B.1 $\dfrac{1}{2\pi l}\left(\dfrac{RT}{M}\right)^{1/2}$, 6.3 GHz

Topic 17D

P17D.1 $\bar{M}+\left(\dfrac{2\gamma}{\pi}\right)^{1/2}$

P17D.3 (a)

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

(b) 90°

P17D.5 3500 r.p.m.

P17D.7 $69\ \mathrm{kg\ mol^{-1}}$, 3.4 nm

P17D.9 $0.0716\ \mathrm{dm^3\ g^{-1}}$

P17D.11 $1.6\times10^5\ \mathrm{g\ mol^{-1}}$

Chapter 18

Topic 18A

P18A.1	$3.61\times10^5\ \mathrm{g\,mol^{-1}}$
P18A.3	$V=\left(3\sqrt{3}/2\right)a^2c$
P18A.5	$834\ \mathrm{pm}$, $606\ \mathrm{pm}$, $870\ \mathrm{pm}$
P18A.7	4
P18A.9	$\dfrac{1}{d^2}=\left(\dfrac{h}{a}\right)^2+\left(\dfrac{k}{b}\right)^2+\left(\dfrac{l}{c}\right)^2$
P18A.11	Simple (primitive) cubic lattice, a = 344 pm
P18A.13	$629\ \mathrm{pm}$, gave support
P18A.15	0
P18A.17	(a) 14.0°, 24.2°, 0.72°, 1.23° (b) R_{CCl} = 176 pm and R_{ClCl} = 289 pm

Topic 18B

P18B.1	0.340
P18B.3	$7.654\ \mathrm{g\ cm^{-3}}$
P18B.7	(a) 0.41421 (b) 0.73205

Topic 18C

P18C.1	μ, $\dfrac{3\lambda+2\mu}{3}$
P18C.3	$\lim\limits_{T\to0}P(E)=1$ when $E<\mu$, $\lim\limits_{T\to0}f(E)=0$ when $E>\mu$, $\left(3\mathcal{N}/8\pi\right)^{2/3}\left(h^2/2m_{\mathrm{e}}\right)$, 3.1 eV
P18C.5	0.736 eV
P18C.7	$0.127\times10^{-6}\ \mathrm{m^3\ mol^{-1}}$, $0.254\times10^{-6}\ \mathrm{m^3\ mol^{-1}}$, $0.423\times10^{-6}\ \mathrm{m^3\ mol^{-1}}$, $0.254\ \mathrm{cm^3\ mol^{-1}}$
P18C.9	0.41

Chapter 19

Topic 19A

P19A.1 (a) $\sigma = 0.602\ \text{nm}^2$, $d = (\sigma/\pi)^{1/2} = 438$ pm (b) $\sigma = 0.421\ \text{nm}^2$, $d = (\sigma/\pi)^{1/2} = 366$ pm

P19A.3 $2.37\times10^{17}\ \text{m}^2\ \text{s}^{-1}$, $2.85\ \text{J K}^{-1}\ \text{m}^{-1}\ \text{s}^{-1}$

P19A.5 (a) $1.7\times10^{14}\ \text{s}^{-1}$ (b) $1.1\times10^{16}\ \text{s}^{-1}$

Topic 19B

P19B.1 $10.2\ \text{kJ mol}^{-1}$

P19B.3 $12.78\ \text{mS m}^2\ \text{mol}^{-1}$, $2.57\ \text{mS m}^2\ (\text{mol dm}^{-1})^{-3/2}$

P19B.5 $12.6\ \text{mS m}^2\ \text{mol}^{-1}$, $6.66\ \text{mS m}^2\ (\text{mol dm}^{-1})^{-3/2}$ (a) $12.02\ \text{mS m}^2\ \text{mol}^{-1}$ (b) $120\ \text{mS m}^{-1}$ (c) $172\ \Omega$

P19B.7 0.83 nm

P19B.9 $9.3\ \text{kJ mol}^{-1}$

Topic 19C

P19C.1 (a) $12\ \text{kN mol}^{-1}$, $2.0\times10^{-20}\ \text{N molecule}^{-1}$ (b) $16.\overline{5}\ \text{kN mol}^{-1}$, $2.7\times10^{-20}\ \text{N molecule}^{-1}$

(c) $24.\overline{8}\ \text{kN mol}^{-1}$, $4.1\times10^{-20}\ \text{N molecule}^{-1}$

P19C.7 $\langle x^4\rangle^{1/4} / \langle x^2\rangle^{1/2} = 3^{1/4}$

P19C.9 (a) 0 (b) 0.0156 (c) 0.0537

P19C.11 $P = \left(\dfrac{2}{\pi N}\right)^{½} \text{e}^{-n^2/2N}$

Chapter 20

Topic 20A

P20A.1 Second order

P20A.3 (a) 1, 2, 3 (b) $2.2\times10^{9}\ \text{mol}^{-2}\ \text{dm}^6\ \text{s}^{-1}$

Topic 20B

P20B.3 Second-order, $k_\text{r} = 0.059\overline{4}\ \text{dm}^3\ \text{mol}^{-1}\ \text{min}^{-1}$, 2.94 g

P20B.5	$7.0\times10^{-5}\ \mathrm{s^{-1}}$, $7.3\times10^{-5}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$
P20B.7	$6\times10^{-14}\,\mathrm{mol\ dm^{-3}\ s^{-1}}$, $4.\overline{4}\times10^{8}\ \mathrm{s}=14\ \mathrm{yr}$
P20B.9	First-order, $5.84\times10^{-3}\ \mathrm{s^{-1}}$, $k_\mathrm{r}=2.92\times10^{-3}\ \mathrm{s^{-1}}$, first-order, $1.98\ \mathrm{min}$
P20B.11	$3.65\times10^{-3}\ \mathrm{min^{-1}}$, $190\ \mathrm{min}$, $274\ \mathrm{min}$
P20B.13	$2.37\times10^{7}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, $k_\mathrm{r}=1.18\times10^{7}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, $4.98\times10^{-3}\ \mathrm{s}$
P20B.15	First-order, third-order
P20B.17	$\left(\frac{1}{3A_0-2B_0}\right)\ln\left(\frac{(2x-A_0)B_0}{A_0(3x-B_0)}\right)$
P20B.19	$\frac{2^{n-1}-1}{\left(\frac{4}{3}\right)^{n-1}-1}$

Topic 20C

P20C.3	$\frac{k_\mathrm{r}'([\mathrm{A}]_0+[\mathrm{B}]_0)+(k_\mathrm{r}[\mathrm{A}]_0-k_\mathrm{r}'[\mathrm{B}]_0)\mathrm{e}^{-(k_\mathrm{r}+k_\mathrm{r}')t}}{k_\mathrm{r}+k_\mathrm{r}'}$, $\left(\frac{k_\mathrm{r}'}{k_\mathrm{r}+k_\mathrm{r}'}\right)\times([\mathrm{A}]_0+[\mathrm{B}]_0)$, $\left(\frac{k_\mathrm{r}}{k_\mathrm{r}+k_\mathrm{r}'}\right)\times([\mathrm{A}]_0+[\mathrm{B}]_0)$, $\frac{[\mathrm{B}]_\infty}{[\mathrm{A}]_\infty}=\frac{k_\mathrm{r}}{k_\mathrm{r}'}$
P20C.5	(a) (i) $8k_\mathrm{a}k_\mathrm{a}'[\mathrm{A}]_\mathrm{tot}+(k_\mathrm{a}')^2$ (c) $1.\overline{7}\times10^{7}\ \mathrm{s^{-1}}$, $2.\overline{7}\times10^{9}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, $1.\overline{6}\times10^{2}$

Topic 20D

P20D.3	$16.7\ \mathrm{kJ\ mol^{-1}}$, $1.14\times10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$
P20D.5	(a) $2.1\times10^{-16}\,\mathrm{mol\ dm^{-3}\ s^{-1}}$ (b) $4.3\times10^{11}\ \mathrm{kg}$ or 430 Tg

Topic 20E

P20E.1	Steady-state approximation
P20E.3	Steady-state intermediate
P20E.5	$k_\mathrm{r}K_1K_2[\mathrm{HCl}]^3[\mathrm{CH_3CH{=}CH_2}]$

Topic 20F

P20F.3	$\left(1+2k_\mathrm{r}t[\mathrm{A}]_0^2\right)^{1/2}$

Topic 20G

P20G.1	1.11
P20G.3	(a) 6.7 ns (b) $0.10\overline{5}$ ns^{-1}
P20G.5	$1.98\times10^{9}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$
P20G.7	3.5 nm

Topic 20H

P20H.1	$v=\dfrac{v_\mathrm{max}}{1+\dfrac{1}{K[\mathrm{S}]_0}}$ Rate law based on rapid pre-equilibrium approximation
P20H.5	2.31 μmol $\mathrm{dm^{-3}\ s^{-1}}$, 115 $\mathrm{s^{-1}}$, 115 $\mathrm{s^{-1}}$, 1.11 μmol $\mathrm{dm^{-3}}$, 104 $\mathrm{dm^3}$ $\mu\mathrm{mol^{-1}\ s^{-1}}$

Chapter 21

Topic 21A

P21A.1	(a) $4.3\overline{5}\times10^{-20}\ \mathrm{m^2}$ (b) 0.15
P21A.3	$1.7\times10^{11}\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$, 3.6 ns
P21A.5	$3.12\times10^{14}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, 193 kJ $\mathrm{mol^{-1}}$, $7.29\times10^{11}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, 175 kJ $\mathrm{mol^{-1}}$

Topic 21C

P21C.1	E_a = 86.0 kJ $\mathrm{mol^{-1}}$, +83.9 kJ $\mathrm{mol^{-1}}$, +19.6 J $\mathrm{K^{-1}\ mol^{-1}}$, +79.0 kJ $\mathrm{mol^{-1}}$
P21C.5	+60.44 kJ $\mathrm{mol^{-1}}$, +62.9 kJ $\mathrm{mol^{-1}}$, −181 J $\mathrm{K^{-1}\ mol^{-1}}$, +114.7 kJ $\mathrm{mol^{-1}}$

P21C.7 3×10^{7}

P21C.9 Two univalent ions of the same sign

P21C.11 (a) 0.06 (b) 0.89, 0.83

Topic 21D

P21D.1 $I = I_0 \mathrm{e}^{-\sigma \mathcal{N} L}$

Topic 21E

P21E.1 $k_\mathrm{r} \approx (k_\mathrm{AA} k_\mathrm{DD} K)^{1/2}$

P21E.3 1.15 eV

Topic 21F

P21F.1 0.78, 0.38

P21F.3 (a) -0.618 V

P21F.5 2.00×10^{-5} mA m^{-2}, 0.498, no

Chapter 22

Topic 22A

P22A.1 -76.9 kJ mol^{-1}, -348.1 kJ mol^{-1}, corner is the likely settling point

P22A.3 (a) 1.61×10^{15} cm^{-2} (b) 1.14×10^{15} cm^{-2} (c) 1.86×10^{15} cm^{-2}

Topic 22B

P22B.3 (a) 165, 13.1 cm^{3} (b) 263, 12.5 cm^{3}

P22B.5 5.78 mol kg^{-1}, 7.02 Pa^{-1}

P22B.7 -20.0 kJ mol^{-1}, -63.5 kJ mol^{-1}

P22B.9 (a) R values in the range 0.975 to 0.991 (b) 3.68×10^{-3}, -8.67 kJ mol^{-1}, 2.62×10^{-5} ppm^{-1}, $\Delta_\mathrm{b}H = -15.7$ kJ mol^{-1}

P22B.11 $0.138\ \mathrm{mg\ g^{-1}}$, 0.58

P22B.13 (a) $k = 0.2289$, $n = 0.6180$, $k = 0.2289$, $n = 0.6180$ (c) $k = 0.5227$, $n = 0.7273$

Topic 22C

P22C.1 $-\frac{k_r}{K}\frac{p_{\mathrm{NH_3}}}{p_{\mathrm{H_2}}}$, $k_c = \frac{p - p_0}{t} - \frac{p_0}{t}\ln\frac{p}{p_0}$, $k_c = 2.5\times10^{-3}\ \mathrm{kPa\ s^{-1}}$