Instructor Solutions Manual to Accompany Atkins' Physical Chemistry

ELEVENTH EDITION

Peter Bolgar
Haydn Lloyd
Aimee North
Vladimiras Oleinikovas
Stephanie Smith
and
James Keeler

Department of Chemistry
University of Cambridge
UK

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Preface

This manual provides detailed solutions to the (b) *Exercises* and the even-numbered *Discussion questions* and *Problems* from the 11th edition of *Atkins' Physical Chemistry*.

Conventions used is presenting the solutions

We have included page-specific references to equations, sections, figures and other features of the main text. Equation references are denoted [14B.3b–*595*], meaning eqn 14B.3b located on page 595 (the page number is given in italics). Other features are referred to by name, with a page number also given.

Generally speaking, the values of physical constants (from the first page of the main text) are used to 5 significant figures except in a few cases where higher precision is required. In line with the practice in the main text, intermediate results are simply truncated (not rounded) to three figures, with such truncation indicated by an ellipsis, as in 0.123...; the value is used in subsequent calculations to its full precision.

The final results of calculations, generally to be found in $\boxed{\text{a box}}$, are given to the precision warranted by the data provided. We have been rigorous in including units for all quantities so that the units of the final result can be tracked carefully. The relationships given on the back of the front cover are useful in resolving the units of more complex expressions, especially where electrical quantities are involved.

Some of the problems either require the use of mathematical software or are much easier with the aid of such a tool. In such cases we have used *Mathematica* (Wolfram Research, Inc.) in preparing these solutions, but there are no doubt other options available. Some of the *Discussion questions* relate directly to specific section of the main text in which case we have simply given a reference rather than repeating the material from the text.

Acknowledgements

In preparing this manual we have drawn on the equivalent volume prepared for the 10th edition of *Atkins' Physical Chemistry* by Charles Trapp, Marshall Cady, and Carmen Giunta. In particular, the solutions which use quantum chemical calculations or molecular modelling software, and some of the solutions to the *Discussion questions*, have been quoted directly from the solutions manual for the 10th edition, without significant modification. More generally, we have benefited from the ability to refer to the earlier volume and acknowledge, with thanks, the influence that its authors have had on the present work.

This manual has been prepared by the authors using the LaTeX typesetting system, in the implementation provided by MiKTeX (`miktex.org`); the vast majority of the figures and graphs have been generated using PGFPlots. We are grateful to the community who maintain and develop these outstanding resources.

Finally, we are grateful to the editorial team at OUP, Jonathan Crowe and Roseanna Levermore, for their invaluable support in bringing this project to a conclusion.

Errors and omissions

In such a complex undertaking some errors will no doubt have crept in, despite the authors' best efforts. Readers who identify any errors or omissions are invited to pass them on to us by email to `pchem@ch.cam.ac.uk`.

1

The properties of gases

1A The perfect gas

Answers to discussion questions

D1A.2 The partial pressure of gas J, p_J, in a mixture of gases is given by [1A.6–9], $p_J = x_J p$, where p is the total pressure and x_J is the mole fraction of J.

If the gases are perfect, the partial pressure is also the pressure the gas would exert if it occupied on its own the same container as the mixture at the same temperature. This leads to Dalton's law, which is that the pressure of a mixture of gases is the sum of the pressures that each one would exert if it occupied the container alone.

Dalton's law is a limiting law because it holds exactly only in the limit that there are no interactions between the molecules, which for real gases will be in the limit of zero pressure.

Solutions to exercises

E1A.1(b) From inside the front cover the conversion between pressure units is: 1 atm ≡ 101.325 kPa ≡ 760 Torr.

(i) A pressure of 22.5 kPa is converted to atm as follows

$$22.5\ \text{kPa} \times \frac{1\ \text{atm}}{101.325\,\text{kPa}} = \boxed{0.222\ \text{atm}}$$

(ii) A pressure of 770 Torr is converted to Pa as follows

$$770\ \text{Torr} \times \frac{1\ \text{atm}}{760\ \text{Torr}} \times \frac{101.325\,\text{kPa}}{1\ \text{atm}} = 103\ \text{kPa} = \boxed{1.03 \times 10^5\ \text{Pa}}$$

E1A.2(b) The perfect gas law [1A.4–8], $pV = nRT$, is rearranged to give the pressure, $p = nRT/V$. The amount n is found by dividing the mass by the molar mass of Ar, 39.95 g mol^{-1}.

$$\begin{aligned} p &= \overbrace{\frac{(25\ \text{g})}{(39.95\ \text{g}\,\text{mol}^{-1})}}^{n} \frac{\left(8.3145 \times 10^{-2}\ \text{dm}^3\ \text{bar}\,\text{K}^{-1}\ \text{mol}^{-1}\right) \times (303.15\ \text{K})}{1.5\ \text{dm}^3} \\ &= 10.4\ \text{bar} \end{aligned}$$

So $\boxed{\text{no}}$, the sample would not exert a pressure of 2.0 bar, but $\boxed{10.4\ \text{bar}}$ if it were a perfect gas.

E1A.3(b) Because the temperature is constant (isothermal) Boyle's law applies, pV = const. Therefore the product pV is the same for the initial and final states

$$p_\mathrm{f} V_\mathrm{f} = p_\mathrm{i} V_\mathrm{i} \quad \text{hence} \quad p_\mathrm{i} = p_\mathrm{f} V_\mathrm{f}/V_\mathrm{i}$$

The initial volume is 1.80 $\mathrm{dm^3}$ greater than the final volume so $V_\mathrm{i} = 2.14+1.80 = 3.94\ \mathrm{dm^3}$.

$$p_\mathrm{i} = \frac{V_\mathrm{f}}{V_\mathrm{i}} \times p_\mathrm{f} = \frac{2.14\ \mathrm{dm^3}}{3.94\ \mathrm{dm^3}} \times (1.97\ \mathrm{bar}) = 1.07\ \mathrm{bar}$$

(i) The in initial pressure is $\boxed{1.07\ \mathrm{bar}}$

(ii) Because 1 atm is equivalent to 1.01325 bar and also to 760 Torr, the initial pressure expressed in Torr is

$$\frac{1\ \mathrm{atm}}{1.01325\ \mathrm{bar}} \times \frac{760\ \mathrm{Torr}}{1\ \mathrm{atm}} \times 1.07\ \mathrm{bar} = \boxed{803\ \mathrm{Torr}}$$

E1A.4(b) If the gas is assumed to be perfect, the equation of state is [1A.4–*8*], $pV = nRT$. In this case the volume and amount (in moles) of the gas are constant, so it follows that the pressure is proportional to the temperature: $p \propto T$. The ratio of the final and initial pressures is therefore equal to the ratio of the temperatures: $p_\mathrm{f}/p_\mathrm{i} = T_\mathrm{f}/T_\mathrm{i}$. Solving for the final pressure p_f (remember to use absolute temperatures) gives

$$\begin{aligned} p_\mathrm{f} &= \frac{T_\mathrm{f}}{T_\mathrm{i}} \times p_\mathrm{i} \\ &= \frac{(11+273.15)\ \mathrm{K}}{(23+273.15)\ \mathrm{K}} \times (125\ \mathrm{kPa}) = \boxed{120\ \mathrm{kPa}} \end{aligned}$$

E1A.5(b) The perfect gas law $pV = nRT$ is rearranged to give $n = pV/RT$.

$$\begin{aligned} n &= \frac{pV}{RT} \\ &= \frac{(1.00 \times 1.01325 \times 10^5\ \mathrm{Pa}) \times (4.00 \times 10^3\ \mathrm{m^3})}{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times ([20+273.15]\ \mathrm{K})} = \boxed{1.66... \times 10^5\ \mathrm{mol}} \end{aligned}$$

where $1\ \mathrm{J} = 1\ \mathrm{kg\,m^2\,s^{-2}}$ and $1\ \mathrm{Pa} = 1\ \mathrm{kg\,m^{-1}\,s^{-2}}$ have been used.

The molar mass of $\mathrm{CH_4}$ is $12.01 + 4 \times 1.0079 = 16.0416\ \mathrm{g\,mol^{-1}}$, so the mass of $\mathrm{CH_4}$ is $(1.66... \times 10^5\ \mathrm{mol}) \times (16.0416\ \mathrm{g\,mol^{-1}}) = 2.67 \times 10^6\ \mathrm{g}$ or $\boxed{2.67 \times 10^3\ \mathrm{kg.}}$

E1A.6(b) The vapour is assumed to be a perfect gas, so the gas law $pV = nRT$ applies. The task is to use this expression to relate the measured mass density to the molar mass.

First, the amount n is expressed as the mass m divided by the molar mass M to give $pV = (m/M)RT$; division of both sides by V gives $p = (m/V)(RT/M)$.

The quantity (m/V) is the mass density ρ, so $p = \rho RT/M$, which rearranges to $M = \rho RT/p$; this is the required relationship between M and the density.

$$M = \frac{\rho RT}{p} = \frac{(0.6388\ \text{kg m}^{-3}) \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times ([100 + 273.15]\ \text{K})}{16.0 \times 10^3\ \text{Pa}}$$
$$= 0.123...\ \text{kg mol}^{-1}$$

where $1\ \text{J} = 1\ \text{kg m}^2\ \text{s}^{-2}$ and $1\ \text{Pa} = 1\ \text{kg m}^{-1}\ \text{s}^{-2}$ have been used. The molar mass of P is $30.97\ \text{g mol}^{-1}$, so the number of P atoms in the molecules comprising the vapour is $(0.123... \times 10^3\ \text{g mol}^{-1})/(30.97\ \text{g mol}^{-1}) = 4.00$. The result is expected to be an integer, so the formula is likely to be $\boxed{P_4.}$

E1A.7(b) The vapour is assumed to be a perfect gas, so the gas law $pV = nRT$ applies; the task is to use this expression to relate the measured data to the mass m. This is done by expressing the amount n as m/M, where M is the the molar mass. With this substitution it follows that $m = MPV/RT$.

The partial pressure of water vapour is 0.53 times the saturated vapour pressure

$$m = \frac{MpV}{RT}$$
$$= \frac{(18.0158\ \text{g mol}^{-1}) \times (0.53 \times 0.0281 \times 10^5\ \text{Pa}) \times (250\ \text{m}^3)}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times ([23 + 273.15]\ \text{K})}$$
$$= 2.7 \times 10^3\ \text{g} = \boxed{2.7\ \text{kg}}$$

E1A.8(b) Once the total amount and the total pressure p_{tot} are known, the volume is found using the perfect gas law. The total amount in moles of the mixture of gases is

$$n_{\text{tot}} = n_{\text{CH}_4} + n_{\text{Ar}} + n_{\text{Ne}} = \frac{m_{\text{CH}_4}}{M_{\text{CH}_4}} + \frac{m_{\text{Ar}}}{M_{\text{Ar}}} + \frac{m_{\text{Ne}}}{M_{\text{Ne}}}$$
$$= \frac{0.320\ \text{g}}{(12.01 + 4 \times 1.0079)\ \text{g mol}^{-1}} + \frac{0.175\ \text{g}}{39.95\ \text{g mol}^{-1}} + \frac{0.225\ \text{g}}{20.18\ \text{g mol}^{-1}}$$
$$= 3.54... \times 10^{-2}\ \text{mol}$$

The mole fraction of neon is

$$x_{\text{Ne}} = \frac{n_{\text{Ne}}}{n_{\text{tot}}} = \frac{0.225\ \text{g}}{20.18\ \text{g mol}^{-1}} \times \frac{1}{3.54... \times 10^{-2}\ \text{mol}} = 0.314...$$

Because $p_{\text{Ne}} = x_{\text{Ne}} \times p_{\text{tot}}$ it follow that

$$p_{\text{tot}} = \frac{p_{\text{Ne}}}{x_{\text{Ne}}} = \frac{8.87\ \text{kPa}}{0.314...} = \boxed{28.2\ \text{kPa}}$$

The volume is calculated using the perfect gas equation with the known total pressure and total amount

$$V = \frac{nRT}{p} = \frac{(3.54... \times 10^{-2}\ \text{mol}) \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (300\ \text{K})}{28.2 \times 10^3\ \text{Pa}}$$
$$= 3.14 \times 10^{-3}\ \text{m}^3 = \boxed{3.14\ \text{dm}^3}$$

E1A.9(b) The vapour is assumed to be a perfect gas, so the gas law $pV = nRT$ applies. The task is to use this expression to relate the measured pressure and volume of a known mass of gas to the molar mass.

The amount n is expressed as the mass m divided by the molar mass M to give $pV = (m/M)RT$; this rearranges to $M = mRT/pV$ which is the required relationship. The pressure in Torr is converted to Pa by noting that 760 Torr is equivalent to 1 atm.

$$\begin{aligned} M &= \frac{mRT}{pV} \\ &= \frac{(33.5\times10^{-6}\,\text{kg})\times(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(298\,\text{K})}{(152\,\text{Torr}/760\,\text{Torr})\times(1.01325\times10^{5}\,\text{Pa})\times(250\times10^{-6}\,\text{m}^3)} \\ &= \boxed{0.0164\,\text{kg mol}^{-1}} \end{aligned}$$

The relationships $1\,\text{J} = 1\,\text{kg m}^2\,\text{s}^{-2}$ and $1\,\text{Pa} = 1\,\text{kg m}^{-1}\,\text{s}^{-2}$ have been used; note the conversion of the volume to m^3.

E1A.10(b) The idea here is that the volume will go to zero at absolute zero. The data given are the slope of the volume/temperature plot, together with one fixed point, so the equation of the straight line can be found, and then the required intercept. The equation of the line is

$$(V/\text{dm}^3) = (0.0741)\times(\theta/^\circ\text{C}) + (c/\text{dm}^3)$$

The fixed point given is that the volume at $\theta = 0\,^\circ\text{C}$ is $20.00\,\text{dm}^3$, so the constant c is equal to this volume

$$(V/\text{dm}^3) = (0.0741)\times(\theta/^\circ\text{C}) + 20.00$$

This is solved for $V = 0$ to give $(\theta/^\circ\text{C}) = (-20.00)/(0.0741) = -270$, hence $\boxed{\theta = -270\,^\circ\text{C}}$. This is the estimate of absolute zero.

E1A.11(b) (i) The mole fractions are

$$x_{H_2} = \frac{n_{H_2}}{n_{H_2}+n_{N_2}} = \frac{1.5\,\text{mol}}{1.5\,\text{mol}+2.5\,\text{mol}} = \boxed{\tfrac{3}{8}} \qquad x_{N_2} = 1 - x_{H_2} = \boxed{\tfrac{5}{8}}$$

(ii) The partial pressures are given by $p_i = x_i p_{\text{tot}}$. The total pressure is given by the perfect gas law: $p_{\text{tot}} = n_{\text{tot}}RT/V$

$$\begin{aligned} p_{H_2} = x_{H_2}p_{\text{tot}} &= \frac{3}{8}\times\frac{(4.0\,\text{mol})\times(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(273.15\,\text{K})}{22.4\times10^{-3}\,\text{m}^3} \\ &= \boxed{1.5\times10^5\,\text{Pa}} \\ p_{N_2} = x_{N_2}p_{\text{tot}} &= \frac{5}{8}\times\frac{(4.0\,\text{mol})\times(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(273.15\,\text{K})}{22.4\times10^{-3}\,\text{m}^3} \\ &= \boxed{2.5\times10^5\,\text{Pa}} \end{aligned}$$

Expressed in atmospheres these are 1.5 atm and 2.5 atm, respectively.

(iii) The total pressure is

$$\frac{(3.0\ \text{mol})\times(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(273.15\ \text{K})}{22.4\times10^{-3}\ \text{m}^3}=\boxed{4.0\times10^5\ \text{Pa}}$$

or 4.0 atm.

Alternatively, note that 1 mol at STP occupies a volume of 22.4 dm^3 which is the stated volume. As there are a total of 4.0 mol present the (total) pressure must therefore be 4.0 atm.

Solutions to problems

P1A.2 Perfect gas behaviour indicates that $pV \propto T$, where T is the absolute temperature. In terms of the temperature θ in °N, T is written $T=\theta+\theta_0$, where θ_0 is the absolute temperature of zero on the °N scale. The proportionality is made an equality by inserting a constant

$$pV=\alpha(\theta+\theta_0)$$

The two data points given are expressed as the following two equations:

$$28=\alpha(0+\theta_0)\qquad 40=\alpha(100+\theta_0)$$

These are solved simultaneously to give $\theta_0 = 233$ K. This means that 0 °N corresponds to an absolute temperature of 233 K. It follows that, on the °N scale, absolute zero is $\boxed{-233\ {}^\circ\text{N.}}$

P1A.4 At absolute zero the volume will go to zero so the temperature corresponding to absolute zero θ_0 is found by solving

$$0=V_0(1+\alpha\theta_0)\qquad\text{hence}\qquad\theta_0=-1/\alpha$$

The quantity α varies with pressure, and what is required is its value in the limit that the pressure goes to zero, because in this limit perfect gas behaviour is achieved. A plot of α against pressure, Fig. 1.1, reveals a gentle curve which fits well to a polynomial of order 2.

The equation of the fitted line is

$$(10^3\,\alpha)/{}^\circ\text{C}^{-1}=4.5000\times10^{-9}\times(p/\text{Torr})^2+7.5870\times10^{-6}\times(p/\text{Torr})+3.6635$$

The intercept at $p=0$ gives the low pressure limit of α as $3.6635\times10^{-3}\ {}^\circ\text{C}^{-1}$, and hence

$$\theta_0=-1/\alpha=-1/(3.6635\times10^{-3}\ {}^\circ\text{C}^{-1})=\boxed{-273.96\ {}^\circ\text{C}}$$

P1A.6 For a given setting of the pivot, the balance point is reached for a given density of gas, because it is the density which affects the buoyancy of the bulb. The density of the gas depends on its pressure and its molar mass: the greater the molar mass, the higher the density for a given pressure.

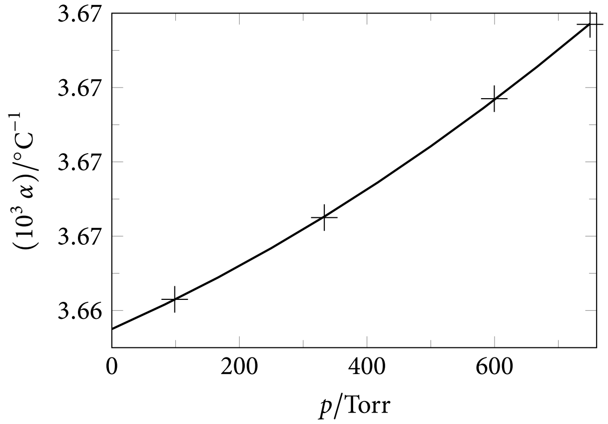


Figure 1.1

The exact relationship is derived for a perfect gas by starting with $pV = nRT$. The amount in moles is $n = m/M$, where M is the molar mass and m is the mass of the gas. It follows that $pV = (m/M)(RT)$ which rearranges to $pM = (m/V)(RT)$. The quantity m/V is the mass density ρ, and hence $pM = \rho RT$.

If the first gas has molar mass M_1 and balances the pivot at pressure p_1, and likewise M_2 and p_2 for the second gas, then because the densities must be the same it follows that (at fixed temperature)

$$p_1M_1 = p_2M_2 \qquad \text{hence} \qquad M_1 = \frac{p_2M_2}{p_1}$$

For the first experiment

$$M_1 = \frac{p_2M_2}{p_1} = \frac{(423.22\ \mathrm{Torr}) \times (70.014\ \mathrm{g\,mol^{-1}})}{(327.10\ \mathrm{Torr})} = 90.588\ \mathrm{g\,mol^{-1}}$$

For the second experiment

$$M_1 = \frac{p_2M_2}{p_1} = \frac{(427.22\ \mathrm{Torr}) \times (70.014\ \mathrm{g\,mol^{-1}})}{(293.22\ \mathrm{Torr})} = 102.01\ \mathrm{g\,mol^{-1}}$$

If the gases are behaving ideally, the two experiments should give the same molar mass – which evidently they do not. Because the lower pressure is closer to ideality, the second experiment is perhaps to be preferred, but high precision is not justified in quoting the result for the molar mass as $\boxed{102\ \mathrm{g\,mol^{-1}}}$.

The compounds CH_2FCF_3 and CHF_2CHF_2 have molar masses close to this value.

P1A.8 The stoichiometric equation for the production of NH_3 is $3\,H_2 + N_2 \longrightarrow 2\,NH_3$. Conversion of all of the H_2 (2 moles) to ammonia results in the formation of $\frac{4}{3}$ mol of NH_3 and consumes $\frac{2}{3}$ mol of N_2. After the reaction is complete the amounts are therefore

$$n_{H_2} = 0 \qquad n_{N_2} = 1 - \frac{2}{3} = \frac{1}{3}\text{ mol} \qquad n_{NH_3} = \frac{4}{3}\text{ mol}$$

The total amount is $\frac{1}{3} + \frac{4}{3} = \frac{5}{3}$ mol, from which the total pressure is calculated using the perfect gas law

$$p = \frac{nRT}{V} = \frac{(\frac{5}{3}\text{ mol}) \times (8.3145\text{ J K}^{-1}\text{ mol}^{-1}) \times (273.15\text{ K})}{22.4 \times 10^{-3}\text{ m}^3} = \boxed{1.69 \times 10^5\text{ Pa}}$$

The partial pressures are calculated from the mole fractions and the total pressure

$$p_{N_2} = x_{N_2}p = \frac{n_{N_2}}{n_{\text{tot}}}p = \frac{1/3\text{ mol}}{5/3\text{ mol}} \times (1.69... \times 10^5\text{ Pa}) = \boxed{0.338 \times 10^5\text{ Pa}}$$

$$p_{NH_3} = x_{NH_3}p = \frac{n_{NH_3}}{n_{\text{tot}}}p = \frac{4/3\text{ mol}}{5/3\text{ mol}} \times (1.69... \times 10^5\text{ Pa}) = \boxed{1.35 \times 10^5\text{ Pa}}$$

P1A.10 It is useful to recall that at STP 1 mol occupies a volume of 22.414 dm^3.

A concentration of 250 DU means that when all of the ozone in a column of cross-sectional area 1.00 dm^2 is compressed into a disc with the same cross-sectional area and at STP the thickness of the disc is 250/1000 cm. Expressed in dm, the thickness is therefore 2.50×10^{-2} dm, and so the volume of the disc is (thickness × area) = $(2.50 \times 10^{-2}\text{ dm}) \times (1.00\text{ dm}^2) = 2.50 \times 10^{-2}\text{ dm}^3$. The amount in moles of ozone is therefore

$$n_{O_3} = \frac{2.50 \times 10^{-2}\text{ dm}^3}{22.414\text{ dm}^3\text{ mol}^{-1}} = 1.11... \times 10^{-3}\text{ mol} = \boxed{1.12 \times 10^{-3}\text{ mol}}$$

The amount in moles corresponding to 100 DU is found by using a ratio

$$n_{O_3,100\text{ DU}} = \frac{100}{250} \times n_{O_3,250\text{ DU}} = \frac{100}{250} \times (1.11... \times 10^{-3}\text{ mol}) = \boxed{4.46 \times 10^{-3}\text{ mol}}$$

The volume of a column of cross-sectional area 1.00 dm^2 and height $(50-10) =$ 40 km is $(1.00 \times 10^{-2}\text{ m}^2) \times (40 \times 10^3\text{ m}) = 400\text{ m}^3$. If the amount in moles in this column is $1.11... \times 10^{-3}$ mol (corresponding to 250 DU) the concentration is

$$c_{O_3} = \frac{1.11... \times 10^{-3}\text{ mol}}{400\text{ m}^3} = 2.79 \times 10^{-6}\text{ mol m}^{-3}$$

or $\boxed{2.79 \times 10^{-9}\text{ mol dm}^{-3}}$. Using a ratio as before, the concentration corresponding to 100 DU is $(100/250) \times 2.79 \times 10^{-9}\text{ mol dm}^{-3} = \boxed{1.12 \times 10^{-9}\text{ mol dm}^{-3}}$.

P1A.12 (a) From the perfect gas law $pV = nRT$, the amount in moles is calculated using $n = pV/RT$; the volume of the balloon is $(4/3)\pi r^3$.

$$n = \frac{pV}{RT} = \frac{(1.01325 \times 10^5\text{ Pa}) \times (\frac{4}{3}\pi[3.0\text{ m}]^3)}{(8.3145\text{ J K}^{-1}\text{ mol}^{-1}) \times ([25 + 273.15]\text{ K})}$$
$$= 4.62... \times 10^3\text{ mol} = \boxed{4.6 \times 10^3\text{ mol}}$$

(b) The mass of the volume of air displaced by the balloon is

$$\text{mass} = \text{volume}\times\text{density} = (\tfrac{4}{3}\pi[3.0\,\text{m}]^3)\times(1.22\,\text{kg}\,\text{m}^{-3}) = 1.37...\times 10^2\,\text{kg}$$

The mass of the hydrogen in the balloon is

$$\begin{aligned}\text{mass} &= \text{amount in moles} \times \text{molar mass}\\ &= (4.62\ldots \times 10^3\,\text{mol}) \times (2 \times 1.0079 \times 10^{-3}\,\text{kg}\,\text{mol}^{-1}) = 9.31...\,\text{kg}\end{aligned}$$

The mass that can be lifted (the payload) is the difference between the displaced mass and the mass of the gas in the balloon (ignoring the mass of the material making up the balloon itself)

$$\text{payload} = (1.37... \times 10^2\,\text{kg}) - (9.31...\,\text{kg}) = \boxed{1.3 \times 10^2\,\text{kg}}$$

(c) If the gas is helium, the mass of the gas in the balloon is

$$(4.62\ldots \times 10^3\,\text{mol}) \times (4.00 \times 10^{-3}\,\text{kg}\,\text{mol}^{-1}) = 1.84... \times 10^1\,\text{kg}$$

and the payload is

$$\text{payload} = (1.37... \times 10^2\,\text{kg}) - (1.84... \times 10^1\,\text{kg}) = \boxed{1.2 \times 10^2\,\text{kg}}$$

P1A.14 To solve this problem it is necessary to assume that the *partial pressure* of each gas obeys a barometric formula in which the constant H depends on the identity of the gas

$$p_{N_2} = p_{0,N_2}\exp(-h/H_{N_2}) \qquad H_{N_2} = \frac{RT}{M_{N_2}g}$$

and likewise for O_2. The mole fractions of the two gases at sea level, and hence their partial pressures, are found from the mass composition at this level. Likewise, the mole fractions and partial pressures are found at the higher altitude from the stated mass composition.

Imagine 1000 g of atmosphere: at sea level this contains 800 g of N_2 and 200 g of O_2. The mole fractions are

$$x_{N_2} = \frac{(800\,\text{g})/(2 \times 14.01\,\text{g}\,\text{mol}^{-1})}{(800\,\text{g})/(2 \times 14.01\,\text{g}\,\text{mol}^{-1}) + (200\,\text{g})/(2 \times 16.00\,\text{g}\,\text{mol}^{-1})} = 0.820$$

Hence $x_{O_2} = 1 - x_{N_2} = 0.180$.

At the higher altitude the same mass of atmosphere contains 900 g of N_2 and 100 g of O_2. The mole fractions are

$$x'_{N_2} = \frac{(900\,\text{g})/(2 \times 14.01\,\text{g}\,\text{mol}^{-1})}{(900\,\text{g})/(2 \times 14.01\,\text{g}\,\text{mol}^{-1}) + (100\,\text{g})/(2 \times 16.00\,\text{g}\,\text{mol}^{-1})} = 0.911$$

Hence $x'_{O_2} = 1 - x'_{N_2} = 0.089$.

At altitude h the partial pressures of the two gases are

$$p_{N_2} = p_{0,N_2}\exp(-h/H_{N_2}) \qquad p_{O_2} = p_{0,O_2}\exp(-h/H_{O_2})$$

Taking the ratio of these two equations gives

$$\frac{p_{N_2}}{p_{O_2}} = \frac{p_{0,N_2}}{p_{0,O_2}}\exp(-h/H_{N_2} + h/H_{O_2})$$

The ratio of the partial pressures is the same as the ratio of the mole fractions

$$\frac{x'_{N_2}}{x'_{O_2}} = \frac{x_{N_2}}{x_{O_2}}\exp(-h/H_{N_2} + h/H_{O_2})$$

where x_{N_2} is the mole fraction at $h = 0$. This equation is rearranged to find h

$$\frac{x'_{N_2}}{x'_{O_2}}\frac{x_{O_2}}{x_{N_2}} = \exp(-h/H_{N_2} + h/H_{O_2})$$

$$\ln\left(\frac{x'_{N_2}}{x'_{O_2}}\frac{x_{O_2}}{x_{N_2}}\right) = -\frac{h}{H_{N_2}} + \frac{h}{H_{O_2}}$$

$$\ln\left(\frac{x'_{N_2}}{x'_{O_2}}\frac{x_{O_2}}{x_{N_2}}\right) = -\frac{hM_{N_2}g}{RT} + \frac{hM_{O_2}g}{RT}$$

$$\frac{RT}{g(M_{O_2} - M_{N_2})}\ln\left(\frac{x'_{N_2}}{x'_{O_2}}\frac{x_{O_2}}{x_{N_2}}\right) = h$$

Inserting the data gives

$$\begin{aligned} h &= \frac{RT}{g(M_{O_2} - M_{N_2})}\ln\left(\frac{x'_{N_2}}{x'_{O_2}}\frac{x_{O_2}}{x_{N_2}}\right) \\ &= \frac{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})([25 + 273.15]\,\mathrm{K})}{(9.807\,\mathrm{m\,s^{-2}}) \times [(2 \times 16.00 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}) - (2 \times 14.01 \times 10^{-3}\,\mathrm{kg\,mol^{-1}})]} \\ &\quad \times \ln\left(\frac{0.911}{0.0890}\frac{0.180}{0.820}\right) \\ &= 51.4...\,\mathrm{km} = \boxed{51\,\mathrm{km}} \end{aligned}$$

At this height the total pressure is found by summing the partial pressures at this height. The partial pressure at sea level is given by $p_{0,N_2} = x_{N_2}p_0$, so it follows that

$$p_{N_2} = x_{N_2}p_0\exp(-h/H_{N_2}) \quad p_{O_2} = x_{O_2}p_0\exp(-h/H_{O_2})$$

It is convenient to compute the scale heights H separately

$$\begin{aligned} H_{N_2} &= \frac{RT}{M_{N_2}g} = \frac{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})([25 + 273.15]\,\mathrm{K})}{(2 \times 14.01 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}) \times (9.807\,\mathrm{m\,s^{-2}})} \\ &= 9.02... \times 10^3\,\mathrm{m} \end{aligned}$$

$$\begin{aligned} H_{O_2} &= \frac{RT}{M_{O_2}g} = \frac{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})([25 + 273.15]\,\mathrm{K})}{(2 \times 16.00 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}) \times (9.807\,\mathrm{m\,s^{-2}})} \\ &= 7.90... \times 10^3\,\mathrm{m} \end{aligned}$$

The total pressure at height h is therefore

$$\begin{aligned} p &= x_{N_2} p_0 \exp(-h/H_{N_2}) + x_{O_2} p_0 \exp(-h/H_{O_2}) \\ &= (0.820 \times 1\ \text{atm}) \exp\left(-\frac{51.4... \times 10^3\ \text{m}}{9.02... \times 10^3\ \text{m}}\right) \\ &+ (0.180 \times 1\ \text{atm}) \exp\left(-\frac{51.4... \times 10^3\ \text{m}}{7.90... \times 10^3\ \text{m}}\right) \\ &= \boxed{0.0030\ \text{atm}} \end{aligned}$$

The calculation is incomplete as it assumes that composition is affected only by the mass and ignores the entropically driven mixing of gases. In fact, the composition of the atmosphere remains pretty much constant up to 100 km.

1B The kinetic model

Answer to discussion questions

D1B.2 The mean free path is given by [1B.14–*18*], $\lambda = kT/\sigma p$. 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 is the dependence on the size of the container and on the size of the molecules. 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 given 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 radius of the molecule).

Solutions to exercises

E1B.1(b) (i) The mean speed is given by [1B.9–*16*], $v_{\text{mean}} = (8RT/\pi M)^{1/2}$, so $v_{\text{mean}} \propto \sqrt{1/M}$. The ratio of the mean speeds therefore depends on the ratio of the molar masses

$$\frac{v_{\text{mean,He}}}{v_{\text{mean,Hg}}} = \left(\frac{M_{\text{Hg}}}{M_{\text{He}}}\right)^{1/2} = \left(\frac{200.59\ \text{g mol}^{-1}}{4.00\ \text{g mol}^{-1}}\right)^{1/2} = \boxed{7.08}$$

(ii) The mean translational kinetic energy $\langle E_k \rangle$ is given by $\frac{1}{2}m\langle v^2 \rangle$, where $\langle v^2 \rangle$ is the mean square speed, which is given by [1B.7–*15*], $\langle v^2 \rangle = 3RT/M$. The mean translational kinetic energy is therefore

$$\langle E_k \rangle = \frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}m\left(\frac{3RT}{M}\right)$$

The molar mass M is related to the mass m of one molecule by $M = mN_A$, where N_A is Avogadro's constant, and the gas constant can be written $R = kN_A$, hence

$$\langle E_k \rangle = \frac{1}{2}m\left(\frac{3RT}{M}\right) = \frac{1}{2}m\left(\frac{3kN_AT}{mN_A}\right) = \frac{3}{2}kT$$

The mean translational kinetic energy is therefore independent of the identity of the gas, and only depends on the temperature: it is the same for He and Hg.

This result is related to the principle of equipartition of energy: a molecule has three translational degrees of freedom (x, y, and z) each of which contributes $\frac{1}{2}kT$ to the average energy.

E1B.2(b) The rms speed is given by [1B.8–*15*], $v_{\text{rms}} = (3RT/M)^{1/2}$; $M_{CO_2} = 44.01\ \text{g mol}^{-1}$.

$$v_{\text{rms},CO_2} = \left(\frac{3RT}{M_{CO_2}}\right)^{1/2} = \left(\frac{3 \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (293.15\ \text{K})}{44.01 \times 10^{-3}\ \text{kg mol}^{-1}}\right)^{1/2}$$
$$= \boxed{408\ \text{m s}^{-1}}$$

where 1 J = 1 kg m^2 s^{-2} has been used. Note that the molar mass is in kg mol^{-1}.

$$v_{\text{rms},He} = \left(\frac{3 \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (293.15\ \text{K})}{4.00 \times 10^{-3}\ \text{kg mol}^{-1}}\right)^{1/2} = \boxed{1.35\ \text{km s}^{-1}}$$

E1B.3(b) The Maxwell–Boltzmann distribution of speeds, $f(v)$, is given by [1B.4–*14*]. The fraction of molecules with speeds between v_1 and v_2 is given by the integral

$$\int_{v_1}^{v_2} f(v)\,dv$$

If the range $v_2 - v_1 = \delta v$ is small, the integral is well-approximated by

$$f(v_{\text{mid}})\,\delta v$$

where v_{mid} is the mid-point of the velocity range: $v_{\text{mid}} = \frac{1}{2}(v_2 + v_1)$. In this exercise $v_{\text{mid}} = 402.5\ \text{m s}^{-1}$ and $\delta v = 5\ \text{m s}^{-1}$. $M_{CO_2} = 12.01 + 2 \times 16.00 = 44.01\ \text{g mol}^{-1}$.

$$\text{fraction} = f(v_{\text{mid}})\,\delta v = 4\pi \times \left(\frac{M}{2\pi RT}\right)^{3/2} v_{\text{mid}}^2 \exp\left(\frac{-Mv_{\text{mid}}^2}{2RT}\right)\delta v$$
$$= 4\pi \times \left(\frac{44.01 \times 10^{-3}\ \text{kg mol}^{-1}}{2\pi \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (400\ \text{K})}\right)^{3/2} \times (402.5\ \text{m s}^{-1})^2$$
$$\times \exp\left(\frac{-(44.01 \times 10^{-3}\ \text{kg mol}^{-1}) \times (402.5\ \text{m s}^{-1})^2}{2 \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (400\ \text{K})}\right) \times (5\ \text{m s}^{-1})$$
$$= \boxed{0.0107}$$

where 1 J = 1 kg m^2 s^{-2} has been used. Thus, 1.07% of molecules have velocities in this range.

E1B.4(b) The mean relative speed is given by [1B.11b–*16*], $v_{\text{rel}} = (8kT/\pi\mu)^{1/2}$, where $\mu = m_{\text{A}}m_{\text{B}}/(m_{\text{A}} + m_{\text{A}})$ is the effective mass. Multiplying top and bottom of the expression for v_{rel} by N_{A} and using $N_{\text{A}}k = R$ gives $v_{\text{rel}} = (8RT/\pi N_{\text{A}}\mu)^{1/2}$ in which $N_{\text{A}}\mu$ is the molar effective mass. For the relative motion of N_2 and O_2 this effective mass is

$$N_{\text{A}}\mu = \frac{M_{\text{N}_2}M_{\text{O}_2}}{M_{\text{N}_2} + M_{\text{O}_2}} = \frac{(2 \times 14.01\ \text{g mol}^{-1}) \times (2 \times 16.00\ \text{g mol}^{-1})}{(2 \times 14.01\ \text{g mol}^{-1}) + (2 \times 16.00\ \text{g mol}^{-1})} = 14.9\ldots\ \text{g mol}^{-1}$$

$$v_{\text{rel}} = \left(\frac{8RT}{\pi N_{\text{A}}\mu}\right)^{1/2} = \left(\frac{8 \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298.15\ \text{K})}{\pi \times (14.9\ldots \times 10^{-3}\ \text{kg mol}^{-1})}\right)^{1/2} = \boxed{650\ \text{m s}^{-1}}$$

E1B.5(b) The most probable speed is given by [1B.10–*16*], $v_{\text{mp}} = (2RT/M)^{1/2}$, the mean speed is given by [1B.9–*16*], $v_{\text{mean}} = (8RT/\pi M)^{1/2}$, and the mean relative speed between two molecules of the same mass is given by [1B.11a–*16*], $v_{\text{rel}} = \sqrt{2}v_{\text{mean}}$. $M_{\text{H}_2} = 2 \times 1.0079 = 2.0158\ \text{g mol}^{-1}$.

$$\begin{aligned}
v_{\text{mp}} &= \left(\frac{2RT}{M}\right)^{1/2} = \left(\frac{2 \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (293.15\ \text{K})}{2.0158 \times 10^{-3}\ \text{kg mol}^{-1}}\right)^{1/2} \\
&= \boxed{1.56 \times 10^3\ \text{m s}^{-1}} \\
v_{\text{mean}} &= \left(\frac{8RT}{\pi M}\right)^{1/2} = \left(\frac{8 \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (293.15\ \text{K})}{\pi \times (2.0158 \times 10^{-3}\ \text{kg mol}^{-1})}\right)^{1/2} \\
&= \boxed{1.75 \times 10^3\ \text{m s}^{-1}} \\
v_{\text{rel}} &= \sqrt{2}v_{\text{mean}} = \sqrt{2} \times (1.75 \times 10^3\ \text{m s}^{-1}) = \boxed{2.48 \times 10^3\ \text{m s}^{-1}}
\end{aligned}$$

E1B.6(b) The collision frequency is given by [1B.12b–*17*], $z = \sigma v_{\text{rel}}p/kT$, with the relative speed for two molecules of the same type given by [1B.11a–*16*], $v_{\text{rel}} = \sqrt{2}v_{\text{mean}}$. The mean speed is given by [1B.9–*16*], $v_{\text{mean}} = (8RT/\pi M)^{1/2}$. From the *Resource section* the collision cross-section σ is 0.40 nm^2.

$$\begin{aligned}
z = \frac{\sigma v_{\text{rel}}p}{kT} &= \frac{\sigma p}{kT} \times \sqrt{2} \times \left(\frac{8RT}{\pi M}\right)^{1/2} \\
&= \frac{(0.40 \times 10^{-18}\ \text{m}^2) \times (1.01325 \times 10^5\ \text{Pa})}{(1.3806 \times 10^{-23}\ \text{J K}^{-1}) \times (298.15\ \text{K})} \times \sqrt{2} \\
&\qquad \times \left(\frac{8 \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298.15\ \text{K})}{\pi \times (2 \times 16.00 \times 10^{-3}\ \text{kg mol}^{-1})}\right)^{1/2} \\
&= \boxed{6.2 \times 10^9\ \text{s}^{-1}}
\end{aligned}$$

where 1 J = 1 kg m^2 s^{-2} and 1 Pa = 1 kg m^{-1} s^{-2} have been used. Note the conversion of the collision cross-section σ to m^2: 1 nm^2 = $(1 \times 10^{-9})^2$ m^2 = 1×10^{-18} m^2.

E1B.7(b) From inside the front cover 760 Torr is equilvant to 1 atm, which is 1.01325×10^5 Pa. Therefore a pressure of 1 nTorr is expressed in Pa as

$$1\ \text{nTorr} = (1 \times 10^{-9}\ \text{Torr}) \times \frac{1\ \text{atm}}{760\ \text{Torr}} \times \frac{1.01325 \times 10^5\ \text{Pa}}{1\ \text{atm}} = 1.33... \times 10^{-7}\ \text{Pa}$$

The mean speed is given by [1B.9–*16*], $v_{\text{mean}} = (8RT/\pi M)^{1/2}$. The collision frequency is given by [1B.12b–*17*], $z = \sigma v_{\text{rel}} p/kT$, with the relative speed for two molecules of the same type given by [1B.11a–*16*], $v_{\text{rel}} = \sqrt{2}v_{\text{mean}}$. The mean free path is given by [1B.14–*18*], $\lambda = kT/\sigma p$

(i) The mean speed is calculated as

$$v_{\text{mean}} = \left(\frac{8RT}{\pi M}\right)^{1/2} = \left(\frac{8 \times (8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (298.15\,\text{K})}{\pi \times (2 \times 14.01 \times 10^{-3}\,\text{kg}\,\text{mol}^{-1})}\right)^{1/2} = \boxed{475\ \text{m}\,\text{s}^{-1}}$$

(ii) The collision cross-section σ is calculated from the collision diameter d as $\sigma = \pi d^2 = \pi \times (395 \times 10^{-9}\ \text{m})^2 = 4.90... \times 10^{-19}\ \text{m}^2$. With this value the mean free path is calculated as

$$\lambda = \frac{kT}{\sigma p} = \frac{(1.3806 \times 10^{-23}\,\text{J}\,\text{K}^{-1}) \times (298.15\,\text{K})}{(4.90... \times 10^{-19}\ \text{m}^2) \times (1.33... \times 10^{-7}\ \text{Pa})} = \boxed{6.30 \times 10^4\ \text{m}}$$

where $1\ \text{J} = 1\ \text{kg}\,\text{m}^2\,\text{s}^{-2}$ and $1\ \text{Pa} = 1\ \text{kg}\,\text{m}^{-1}\,\text{s}^{-2}$ have been used. The mean free path is 63 km, a distance very much greater than the dimensions of the apparatus.

(iii) The collision rate is calculated as

$$\begin{aligned} z = \frac{\sigma v_{\text{rel}} p}{kT} &= \frac{\sigma p}{kT} \times \sqrt{2} \times \left(\frac{8RT}{\pi M}\right)^{1/2} \\ &= \frac{(4.90 \times 10^{-19}\ \text{m}^2) \times (1.33... \times 10^{-7}\ \text{Pa})}{(1.3806 \times 10^{-23}\,\text{J}\,\text{K}^{-1}) \times (298.15\,\text{K})} \times \sqrt{2} \\ &\qquad \times \left(\frac{8 \times (8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (298.15\,\text{K})}{\pi \times (2 \times 14.01 \times 10^{-3}\,\text{kg}\,\text{mol}^{-1})}\right)^{1/2} \\ &= \boxed{1.07 \times 10^{-2}\ \text{s}^{-1}} \end{aligned}$$

An alternative for the calculation of z is to use [1B.13–*18*], $\lambda = v_{\text{rel}}/z$, rearranged to $z = v_{\text{rel}}/\lambda$

$$z = \frac{v_{\text{rel}}}{\lambda} = \frac{\sqrt{2}v_{\text{mean}}}{\lambda} = \frac{\sqrt{2} \times (475\ \text{m}\,\text{s}^{-1})}{6.30 \times 10^4\ \text{m}} = \boxed{1.07 \times 10^{-2}\ \text{s}^{-1}}$$

As expected for such a low pressure, collisions are very infrequent, occuring about once every 100 s.

E1B.8(b) The collision cross section σ is written in terms of a diameter as $\sigma = \pi d^2$, hence $d = \sqrt{\sigma/\pi}$

$$d = \sqrt{\sigma/\pi} = \sqrt{(0.36 \times 10^{-18}\ \mathrm{m}^2)/\pi} = 3.38... \times 10^{-10}\ \mathrm{m}$$

The mean free path is given by [1B.14–*18*], $\lambda = kT/\sigma p$. This is rearranged to give the pressure p with λ equal to 10 times the estimate for the diameter of the atoms

$$p = \frac{kT}{\sigma(10d)} = \frac{(1.3806 \times 10^{-23}\ \mathrm{J\,K^{-1}}) \times (298.15\ \mathrm{K})}{(0.36 \times 10^{-18}\ \mathrm{m}^2) \times 10 \times (3.38... \times 10^{-10}\ \mathrm{m})} = \boxed{3.4 \times 10^{6}\ \mathrm{Pa}}$$

E1B.9(b) The mean free path is given by [1B.14–*18*], $\lambda = kT/\sigma p$.

$$\lambda = \frac{kT}{\sigma p} = \frac{(1.3806 \times 10^{-23}\ \mathrm{J\,K^{-1}}) \times (217\ \mathrm{K})}{(0.43 \times 10^{-18}\ \mathrm{m}^2) \times (12.1 \times 10^{3}\ \mathrm{Pa})} = \boxed{5.8 \times 10^{-7}\ \mathrm{m} = 0.58\ \mu\mathrm{m}}$$

Solutions to problems

P1B.2 The Maxwell–Boltzmann distribution of speeds in one dimension (here x) is given by [1B.3–*13*]

$$f(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} \mathrm{e}^{-mv_x^2/2kT}$$

An analogous expression gives the distribution in the y direction, $f(v_y)$. The probability of finding a particle with velocity between v_x and $v_x + \mathrm{d}v_x$ is given by $f(v_x)\,\mathrm{d}v_x$, and similarly in the y direction. The overall probability of finding a particle with velocity between v_x and $v_x + \mathrm{d}v_x$, and between v_y and $v_y + \mathrm{d}v_y$, is therefore

$$\begin{aligned}
&\left[\left(\frac{m}{2\pi kT}\right)^{1/2} \mathrm{e}^{-mv_x^2/2kT}\right]\left[\left(\frac{m}{2\pi kT}\right)^{1/2} \mathrm{e}^{-mv_y^2/2kT}\right] \mathrm{d}v_x\mathrm{d}v_y \\
&= \left(\frac{m}{2\pi kT}\right) \mathrm{e}^{-m(v_x^2+v_y^2)/2kT}\,\mathrm{d}v_x\mathrm{d}v_y \\
&= \underbrace{\left(\frac{m}{2\pi kT}\right) \mathrm{e}^{-mv^2/2kT}}_{\mathrm{A}}\,\mathrm{d}v_x\mathrm{d}v_y
\end{aligned}$$

On the last line the speed v, given by $v^2 = v_x^2 + v_y^2$, is introduced.

As discussed in Section 1B.1(b) on page 13, the 'area element' $\mathrm{d}v_x\mathrm{d}v_y$ can be interpreted by imagining a velocity space with axes labelled (v_x, v_y). In this space, particles with speed v lie on a circle of radius v, so particles with speeds between v and $v + \mathrm{d}v$ lie in a ring of radius v and thickness $\mathrm{d}v$. Because the ring is very thin, its area is given by the circumference of the circle times the width: $2\pi v\,\mathrm{d}v$.

The *total* probability of a particle having speed v and $v+\mathrm{d}v$, $f(v)\mathrm{d}v$, is therefore found by multiplying the term A in the above expression, not by the area element $\mathrm{d}v_x\mathrm{d}v_y$ but by the area of the ring because this gives the total probability of having this range of speeds, regardless of direction

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

The distribution of speeds in two dimension is therefore

$$\boxed{f(v)\,\mathrm{d}v = \left(\frac{m}{kT}\right) v\mathrm{e}^{-mv^2/2kT}}$$

The average speed is found using [1B.6–*15*], $\langle v^n \rangle = \int_0^\infty v^n f(v)\,\mathrm{d}v$. In this case

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

The required integral is of the form of G.3 from the *Resource section*

$$\int_0^\infty x^2 \mathrm{e}^{-ax^2}\,\mathrm{d}x = \frac{1}{4}\left(\frac{\pi}{a^3}\right)^{1/2}$$

With $a = m/2kT$ the mean speed is

$$\langle v \rangle = \frac{1}{4}\left(\frac{m}{kT}\right)\left(\frac{\pi}{(m/2kT)^3}\right)^{1/2} = \boxed{\left(\frac{\pi kT}{2m}\right)^{1/2}}$$

P1B.4 The Maxwell–Boltzmann distribution of speeds in three dimensions is given by [1B.4–*14*]

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

with M the molar mass. The root mean square speed is given by [1B.8–*15*], $v_{\mathrm{rms}} = (3RT/M)^{1/2}$, and mean speed is given by [1B.9–*16*], $v_{\mathrm{mean}} = (8RT/\pi M)^{1/2}$. The required proportions are found by integrating $f(v)$ between the relevant limits for v.

(a) The fraction having speed greater than v_{rms} is given by

$$\int_{v_{\mathrm{rms}}}^\infty f(v)\,\mathrm{d}v$$

Mathematical software is used to evaluate the integral to give $\sqrt{6/\pi}\,\mathrm{e}^{3/2} + \mathrm{erfc}(\sqrt{3/2})$, where $\mathrm{erfc}(x)$ is the complementary error function, $\mathrm{erfc}(x) = 1 - \mathrm{erf}(x)$. The result is evaluated numerically to give 0.391, that is $\boxed{39\%}$ of molecules have speeds greater than the root mean square speed.

(b) The remaining fraction, $1 - 0.391 = 0.608$, have speeds smaller than v_{rms}. Thus $\boxed{61\%}$ of molecules have speeds smaller than the root mean square speed.

(c) The integral is as in (a), but with lower limit v_{mean}. Mathematical software gives the result $4/\pi\mathrm{e}^{-4/\pi} + \mathrm{erfc}(2/\sqrt{\pi})$. The result is evaluated numerically to give 0.467, that is $\boxed{47\%}$ of molecules have speeds greater than the mean speed, and so $\boxed{53\%}$ of molecules have speeds smaller than the mean speed.

P1B.6 The Maxwell–Boltzmann distribution of speeds in three dimensions is given by [1B.4–*14*]

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

with M the molar mass. The mean of v^n is found using [1B.6–*15*], $\langle v^n\rangle=\int_0^\infty v^n f(v)\,\mathrm{d}v$. The required integral is therefore

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

For the case where $n+2$ is odd, integral G.7 from the *Resource section* is used

$$\int_0^\infty x^{2m+1}\mathrm{e}^{-ax^2}\,\mathrm{d}x=\frac{m!}{2a^{m+1}}\qquad m=1,\ 2,\ 3,\ \ldots$$

The relationship between m and n is found by noting that for $n=1,\ 3,\ 5,\ \ldots$, m will be $1,\ 2,\ 3,\ \ldots$ (note that these generate only the odd values of $n+2$). It therefore follows that $m=\frac{1}{2}(n+1)$ and $m+1=\frac{1}{2}(n+3)$. These substitutions, along with $a=M/2RT$ allow the integral to be evaluated.

$$\begin{aligned}\langle v^n\rangle&=4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_0^\infty v^{n+2}\mathrm{e}^{-Mv^2/2RT}\,\mathrm{d}v\\&=4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\frac{1}{2}\,\frac{[\frac{1}{2}(n+1)]!}{(M/2RT)^{\frac{1}{2}(n+3)}}\\&=2\pi\left(\frac{1}{\pi}\right)^{3/2}\left(\frac{M}{2RT}\right)^{3/2}\left(\frac{M}{2RT}\right)^{-\frac{1}{2}(n+3)}[\tfrac{1}{2}(n+1)]!\\&=2\left(\frac{1}{\pi}\right)^{1/2}\left(\frac{2RT}{M}\right)^{\frac{1}{2}n}[\tfrac{1}{2}(n+1)]!\qquad\text{odd }n\end{aligned}$$

Hence

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

For the case where $n+2$ is even, integral G.8 from the *Resource section* is used

$$\int_0^\infty x^{2m}\mathrm{e}^{-ax^2}\,\mathrm{d}x=\frac{(2m-1)!!}{2^{m+1}a^m}\left(\frac{\pi}{a}\right)^{1/2}\qquad m=1,\ 2,\ 3,\ \ldots$$

where $(2m-1)!!=(2m-1)\times(2m-3)\times(2m-5)\times\ldots 1$ or 2.

The relationship between m and n is found by noting that for $n=2,\ 4,\ 6,\ \ldots$, m will be $2,\ 3,\ 4,\ \ldots$ (note that these generate only the even values of $n+2$). It therefore follows that $m=\frac{1}{2}(n+2)$, $m+1=\frac{1}{2}(n+4)$ and $(2m-1)=(n+1)$.

These substitutions, along with $a = M/2RT$ allow the integral to be evaluated.

$$\begin{aligned}
\langle v^n \rangle &= 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \int_0^\infty v^{n+2} \mathrm{e}^{-Mv^2/2RT}\,\mathrm{d}v \\
&= 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \frac{(2m-1)!!}{2^{m+1}a^m} \left(\frac{\pi}{a}\right)^{1/2} \\
&= 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \frac{(n+1)!!}{2^{\frac{1}{2}(n+4)}(M/2RT)^{\frac{1}{2}(n+2)}} \left(\frac{\pi}{(M/2RT)}\right)^{1/2} \\
&= \left(\frac{1}{2}\right)^{n/2} \left(\frac{M}{2RT}\right)^{3/2} \left(\frac{M}{2RT}\right)^{-\frac{1}{2}(n+2)} \left(\frac{M}{2RT}\right)^{-1/2} (n+1)!! \\
&= \left(\frac{1}{2}\right)^{n/2} \left(\frac{2RT}{M}\right)^{n/2} (n+1)!! \\
&= \left(\frac{RT}{M}\right)^{n/2} (n+1)!! \qquad \text{even } n
\end{aligned}$$

Hence

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

Mathematical software gives a solution for both even and odd n

$$\begin{aligned}
\langle v^n \rangle &= \int_0^\infty v^n f(v)\,\mathrm{d}v = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \int_0^\infty v^{n+2} \mathrm{e}^{-Mv^2/2RT}\,\mathrm{d}v \\
&= \frac{1}{\sqrt{\pi}} 2^{(n+2)/2} \left(\frac{RT}{M}\right)^{n/2} \Gamma\left(\tfrac{1}{2}[n+3]\right)
\end{aligned}$$

where $\Gamma(x)$ is the Euler gamma function.

If the argument x is an integer then $\Gamma(x) = (x-1)!$. This will be the case for odd n, in which case

$$\langle v^n \rangle = \frac{1}{\sqrt{\pi}} 2^{(n+2)/2} \left(\frac{RT}{M}\right)^{n/2} \left(\tfrac{1}{2}[n+1]\right)! \qquad \text{odd } n$$

which is the same result as found above.

If the argument of the Gamma function is an odd multiple of $\frac{1}{2}$ (that is $\frac{1}{2}m$, with $m = 1, 3, 5, \ldots$) then

$$\Gamma\left(\tfrac{1}{2}m\right) = \frac{(m-2)!!\sqrt{\pi}}{2^{(m-1)/2}}$$

This will be the case for even n, in which case

$$\begin{aligned}
\langle v^n \rangle &= \frac{1}{\sqrt{\pi}} 2^{(n+2)/2} \left(\frac{RT}{M}\right)^{n/2} \frac{(n+3-2)!!\sqrt{\pi}}{2^{(n+3-1)/2}} \\
&= \frac{1}{\sqrt{\pi}} 2^{(n+2)/2} \left(\frac{RT}{M}\right)^{n/2} \frac{(n+1)!!\sqrt{\pi}}{2^{(n+2)/2}} \\
&= \left(\frac{RT}{M}\right)^{n/2} (n+1)!! \qquad \text{even } n
\end{aligned}$$

which again is the same result as above.

P1B.8 The Maxwell–Boltzmann distribution of speeds in three dimensions is given by [1B.4–*14*]

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

with M the molar mass, here taken to be $0.1\,\text{kg}\,\text{mol}^{-1}$. Plots of $f(v)$ are shown in Fig. 1.2.

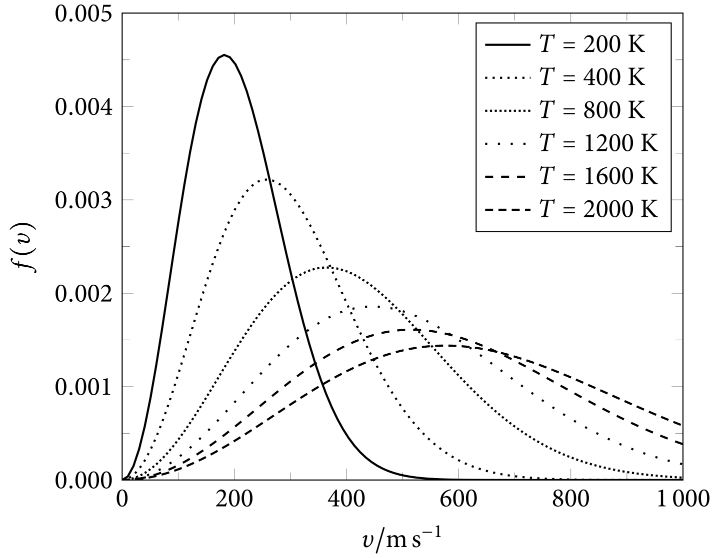


Figure 1.2

P1B.10 The Maxwell–Boltzmann distribution of speeds in three dimensions is given by [1B.4–*14*]

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

The speed at which this function is a maximum is found by setting the derivative $\mathrm{d}f(v)/\mathrm{d}v$ equal to zero. The derivative is found using the product rule and the chain rule

$$\frac{\mathrm{d}f(v)}{\mathrm{d}v} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\left[2ve^{-Mv^2/2RT} + v^2\left(\frac{-2Mv}{2RT}\right)e^{-Mv^2/2RT}\right]$$

The derivative is set to zero and factors of $e^{-Mv^2/2RT}$ and v are identified to give

$$4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} \times e^{-Mv^2/2RT} \times v \times \left[2 - v^2\left(\frac{M}{RT}\right)\right] = 0$$

The solution when $v = 0$ is not a maximum, and the solution $e^{-Mv^2/2RT} = 0$ corresponds to the asymptotic behave at large speeds. This leaves the maximum to be given by

$$2 - v_{\max}^2 \left(\frac{M}{RT}\right) = 0 \qquad \text{hence} \qquad \boxed{v_{\max} = \left(\frac{2RT}{M}\right)^{1/2}}$$

That this is a maximum can be verified by inspecting a plot of $f(v)$.

1C Real gases

Answer to discussion questions

D1C.2 The critical constants represent the state of a system at which the distinction between the liquid and vapour phases disappears. This situation is usually described 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.

D1C.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

E1C.1(b) The van der Waals equation of state in terms of the volume is given by [1C.5a–23], $p = nRT/(V-b) - an^2/V^2$. The parameters a and b for H_2S are given in the *Resource section* as $a = 4.484\ \text{atm dm}^6\ \text{mol}^{-2}$ and $b = 4.34 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1}$. With these units it is convenient to use $R = 8.2057 \times 10^{-2}\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}$. The pressure is computed by substituting in the relevant data.

(i) $T = 273.15\ \text{K}$, $V = 22.414\ \text{dm}^3$, $n = 1.0\ \text{mol}$

$$\begin{aligned} p &= \frac{nRT}{V - nb} - \frac{an^2}{V^2} \\ &= \frac{(1.0\ \text{mol}) \times (8.2057 \times 10^{-2}\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}) \times (273.15\ \text{K})}{(22.414\ \text{dm}^3) - (1.0\ \text{mol}) \times (4.34 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1})} \\ &\quad - \frac{(4.484\ \text{atm dm}^6\ \text{mol}^{-2}) \times (1.0\ \text{mol})^2}{(22.414\ \text{dm}^3)^2} = \boxed{0.99\ \text{atm}} \end{aligned}$$

(ii) $T = 500\ \text{K}$, $V = 150\ \text{cm}^3 = 0.150\ \text{dm}^3$, $n = 1.0\ \text{mol}$

$$\begin{aligned} p &= \frac{nRT}{V - nb} - \frac{an^2}{V^2} \\ &= \frac{(1.0\ \text{mol}) \times (8.2057 \times 10^{-2}\ \text{dm}^3\ \text{atm}\ \text{K}^{-1}\ \text{mol}^{-1}) \times (500\ \text{K})}{(0.150\ \text{dm}^3) - (1.0\ \text{mol}) \times (4.34 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1})} \\ &\quad - \frac{(4.484\ \text{atm}\ \text{dm}^6\ \text{mol}^{-2}) \times (1.0\ \text{mol})^2}{(0.150\ \text{dm}^3)^2} = \boxed{1.9 \times 10^2\ \text{atm}} \end{aligned}$$

E1C.2(b) Recall that $1\ \text{atm} = 1.01325 \times 10^5\ \text{Pa}$, $1\ \text{dm}^6 = 10^{-6}\ \text{m}^6$, and $1\ \text{Pa} = 1\ \text{kg}\ \text{m}^{-1}\ \text{s}^{-2}$

$$\begin{aligned} a &= (1.32\ \text{atm}\ \text{dm}^6\ \text{mol}^{-2}) \times \frac{1.01325 \times 10^5\ \text{Pa}}{1\ \text{atm}} \times \frac{10^{-6}\ \text{m}^6}{1\ \text{dm}^6} = 0.134\ \text{Pa}\ \text{m}^6\ \text{mol}^{-2} \\ &= 0.134\ \text{kg}\ \text{m}^{-1}\ \text{s}^{-2}\ \text{m}^6\ \text{mol}^{-2} = \boxed{0.134\ \text{kg}\ \text{m}^5\ \text{s}^{-2}\ \text{mol}^{-2}} \end{aligned}$$

$$b = (0.0436\ \text{dm}^3\ \text{mol}^{-1}) \times \frac{10^{-3}\ \text{m}^3}{1\ \text{dm}^3} = \boxed{4.36 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1}}$$

E1C.3(b) The compression factor Z is defined in [1C.1–*20*] as $Z = V_\text{m}/V_\text{m}^\circ$, where V_m° is the molar volume of a perfect gas under the same conditions. This volume is computed from the equation of state for a perfect gas, [1A.4–*8*], as $V_\text{m}^\circ = RT/p$, hence $Z = pV_\text{m}/RT$ [1C.2–*20*].

(i) If V_m is 12% larger than the molar volume of a perfect gas, it follows that $V_\text{m} = V_\text{m}^\circ(1 + 0.12) = 1.12V_\text{m}^\circ$. The compression factor is then computed directly as

$$Z = \frac{V_\text{m}}{V_\text{m}^\circ} = \frac{1.12 \times V_\text{m}^\circ}{V_\text{m}^\circ} = \boxed{1.12}$$

(ii) From [1C.2–*20*] it follows that $V_\text{m} = ZRT/p$

$$\begin{aligned} V_\text{m} &= \frac{ZRT}{p} = \frac{1.12 \times (8.2057 \times 10^{-2}\ \text{dm}^3\ \text{atm}\ \text{K}^{-1}\ \text{mol}^{-1}) \times (350\ \text{K})}{12\ \text{atm}} \\ &= \boxed{2.7\ \text{dm}^3\ \text{mol}^{-1}} \end{aligned}$$

Because $Z > 1$, implying that $V_\text{m} > V_\text{m}^\circ$, repulsive forces are dominant.

E1C.4(b) (i) The molar volume is computed from the equation of state for a perfect gas, [1A.4–*8*], as $V_\text{m} = RT/p$

$$V_\text{m} = \frac{RT}{p} = \frac{(8.3145\ \text{J}\ \text{K}^{-1}\ \text{mol}^{-1}) \times ([25 + 273.15]\ \text{K})}{200 \times 10^5\ \text{Pa}} = 1.24\times10^{-4}\ \text{m}^3\ \text{mol}^{-1}$$

hence $\boxed{V_\text{m} = 0.124\ \text{dm}^3\ \text{mol}^{-1}.}$

(ii) The van der Waals equation of state in terms of the molar volume is given by [1C.5b–*24*], $p = RT/(V_m - b) - a/V_m^2$. This equation is a cubic in V_m, as is seem by multiplying both sides by $(V_m - b)V_m^2$ and then gathering the terms together

$$pV_m^3 - V_m^2(pb + RT) + aV_m - ab = 0$$

The values of the constants are given, as is the pressure and temperature. Given the units of the quoted values of a and b it is convenient to convert the pressure of 200 bar (200×10^5 Pa) to atm, $p = (200 \times 10^5\ \text{Pa}) \times (1\ \text{atm})/(1.01325 \times 10^5\ \text{Pa}) = 197.4\ \text{atm}$, and to use $R = 8.2057 \times 10^{-2}\ \text{dm}^3\ \text{atm}\ \text{K}^{-1}\ \text{mol}^{-1}$. Inserting all of these values gives the polynomial

$$197.4V_m^3 - 30.762V_m^2 + 1.364V_m - 0.04351 = 0$$

The roots of this polynomial are found numerically using Mathematical software and of these roots only $\boxed{V_m = 0.112\ \text{dm}^3\ \text{mol}^{-1}}$ is a physically plausible value for the molar volume (the other roots are complex). This molar volume is smaller than the molar volume of the corresponding perfect gas by about 10%.

An alternative approach is to approximate the term a/V_m^2 as $a/(V_m^\circ)^2$ and then rearrange the van der Waals equation to give a simpler expression for V_m

$$p = \frac{RT}{(V_m - b)} - \frac{a}{(V_m^\circ)^2} \qquad \text{hence} \qquad V_m = \frac{RT}{p + [a/(V_m^\circ)^2]} + b$$

$$\begin{aligned} V_m &= \frac{RT}{p + [a/(V_m^\circ)^2]} + b \\ &= \frac{(8.2057 \times 10^{-2}\ \text{dm}^3\ \text{atm}\ \text{K}^{-1}\ \text{mol}^{-1}) \times (298.15\ \text{K})}{(197.4\ \text{atm}) + [(1.364\ \text{atm}\ \text{dm}^6\ \text{mol}^{-2})/(0.124\ \text{dm}^3\ \text{mol}^{-1})^2]} \\ &\quad + 3.19 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1} = 0.117\ \text{dm}^3\ \text{mol}^{-1} \end{aligned}$$

This approximate value for V_m is then used in place of V_m° and the whole process repeated. After a few iterations the value of V_m settles as $0.112\ \text{dm}^3\ \text{mol}^{-1}$, which is the same as the value found by solving the cubic.

E1C.5(b) (i) The compression factor Z is given in terms of the molar volume and pressure by [1C.2–*20*], $Z = pV_m/RT$, hence $V_m = ZRT/p$. The volume occupied by n mol is therefore $V = nV_m = nZRT/p$

$$\begin{aligned} V &= \frac{nZRT}{p} \\ &= \frac{(8.2 \times 10^{-3}\ \text{mol}) \times (0.86) \times (8.2057 \times 10^{-2}\ \text{dm}^3\ \text{atm}\ \text{K}^{-1}\ \text{mol}^{-1}) \times (300\ \text{K})}{20\ \text{atm}} \\ &= \boxed{8.7 \times 10^{-3}\ \text{dm}^3} = \boxed{8.7\ \text{cm}^3} \end{aligned}$$

(ii) The virial expansion in terms of V_m is given by [1C.3b–*21*], $pV_m = RT(1 + B/V_m + \ldots)$. The relationship in [1C.2–*20*], $Z = pV_m/RT$, is used to rewrite the term pV_m as ZRT. If only the first two terms of the expansion are retained it follows that

$$ZRT = RT\left(1 + \frac{B}{V_m}\right) \quad \text{hence} \quad Z = \left(1 + \frac{B}{V_m}\right)$$

and therefore $B = V_m(Z-1)$. The relationship $V_m = ZRT/p$ is used to give

$$\begin{aligned} B &= V_m(Z-1) = \frac{ZRT}{p}(Z-1) \\ &= \frac{(0.86)\times(8.2057\times10^{-2}\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1})\times(300\,\text{K})}{20\,\text{atm}}\times(0.86-1) \\ &= \boxed{-0.15\,\text{dm}^3\,\text{mol}^{-1}} \end{aligned}$$

E1C.6(b) The relation between the critical constants and the van der Waals parameters is given by [1C.6–*26*]

$$V_c = 3b \quad p_c = \frac{a}{27b^2} \quad T_c = \frac{8a}{27Rb}$$

All three critical constants are given, so the problem is over-determined: any pair of the these expressions is sufficient to find values of a and b. It is convenient to use $R = 8.2057\times10^{-2}\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}$ and volumes in units of dm^3.

If the expressions for V_c and p_c are used, a and b are found in the following way

$$V_c = 3b \quad \text{hence} \quad b = V_c/3 = (0.148\,\text{dm}^3\,\text{mol}^{-1})/3 = 0.0493\,\text{dm}^3\,\text{mol}^{-1}$$

$$\begin{aligned} p_c &= \frac{a}{27b^2} = \frac{a}{27(V_c/3)^2} \quad \text{hence} \quad a = 27(V_c/3)^2 p_c \\ a &= 27(V_c/3)^2 p_c = 27([0.148\,\text{dm}^3\,\text{mol}^{-1}]/3)^2\times(48.2\,\text{atm}) \\ &= 3.17\,\text{atm}\,\text{dm}^6\,\text{mol}^{-2} \end{aligned}$$

There are three possible ways of choosing two of the expressions with which to find a and b, and each choice gives a different value. For a the values are 3.17, 5.50, and 4.17, giving an average of $\boxed{4.28\,\text{atm}\,\text{dm}^6\,\text{mol}^{-2}}$. For b the values are 0.0493, 0.0650, and 0.0493, giving an average of $\boxed{0.0546\,\text{dm}^3\,\text{mol}^{-1}}$.

In Section 1C.2(a) on page 23 it is argued that $b = 4V_{\text{molec}}N_A$, where V_{molec} is the volume occupied by one molecule. This volume is written in terms of the radius r as $4\pi r^3/3$ so it follows that $r = (3b/16\pi N_A)^{1/3}$.

$$r = \left(\frac{3b}{16\pi N_A}\right)^{1/3} = \left(\frac{3\times(0.0546\,\text{dm}^3\,\text{mol}^{-1})}{16\pi\times(6.0221\times10^{23}\,\text{mol}^{-1})}\right)^{1/3} = 1.76\times10^{-9}\,\text{dm} = \boxed{176\,\text{pm}}$$

E1C.7(b) (i) In Section 1C.1(b) on page 20 it is explained that at the Boyle temperature $Z = 1$ and $\mathrm{d}Z/\mathrm{d}p = 0$; this latter condition corresponds to the second virial coefficient, B or B', being zero. The task is to find the relationship between the van der Waals parameters and the virial coefficients, and the starting point for this are the expressions for the product pV_m is each case ([1C.5b–*24*] and [1C.3b–*21*])

$$\text{van der Waals:}\ \ p = \frac{RT}{(V_\mathrm{m}-b)} - \frac{a}{V_\mathrm{m}^2} \quad \text{hence} \quad pV_\mathrm{m} = \frac{RTV_\mathrm{m}}{(V_\mathrm{m}-b)} - \frac{a}{V_\mathrm{m}}$$

$$\text{virial:}\ \ \mathrm{m} = RT\left(1+\frac{B}{V_\mathrm{m}}\right)$$

The van der Waals expression for pV_m is rewritten by dividing the denominator and numerator of the first fraction by V_m

$$pV_\mathrm{m} = \frac{RT}{(1-b/V_\mathrm{m})} - \frac{a}{V_\mathrm{m}}$$

The dimensionless parameter b/V_m is likely to be $\ll 1$, so the approximation $(1-x)^{-1} \approx 1+x$ is used to give

$$pV_\mathrm{m} = RT(1+b/V_\mathrm{m}) - \frac{a}{V_\mathrm{m}} = RT\left[1+\frac{1}{V_\mathrm{m}}\left(b-\frac{a}{RT}\right)\right]$$

Comparison of this expression with the virial expansion shows that

$$B = b - \frac{a}{RT}$$

It therefore follows that the Boyle temperature, when $B = 0$, is $T_\mathrm{b} = a/Rb$. For the van der Waals parameters from the *Resource section*

$$\begin{aligned} T_\mathrm{b} &= \frac{a}{Rb} = \frac{4.484\ \mathrm{atm\,dm^6\,mol^{-2}}}{(8.2057\times10^{-2}\ \mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}})\times(4.34\times10^{-2}\ \mathrm{dm^3\,mol^{-1}})} \\ &= \boxed{1.26\times10^3\ \mathrm{K}} \end{aligned}$$

(ii) In Section 1C.2(a) on page 23 it is argued that $b = 4V_\mathrm{molec}N_\mathrm{A}$, where V_molec is the volume occupied by one molecule. This volume is written in terms of the radius r as $4\pi r^3/3$ so it follows that $r = (3b/16\pi N_\mathrm{A})^{1/3}$.

$$\begin{aligned} r &= \left(\frac{3b}{16\pi N_\mathrm{A}}\right)^{1/3} = \left(\frac{3\times(4.34\times10^{-2}\ \mathrm{dm^3\,mol^{-1}})}{16\pi\times(6.0221\times10^{23}\ \mathrm{mol^{-1}})}\right)^{1/3} \\ &= 1.63\times10^{-9}\ \mathrm{dm} = \boxed{163\ \mathrm{pm}} \end{aligned}$$

E1C.8(b) The reduced variables are defined in terms of the critical constants in [1C.8–*26*]

$$V_\mathrm{r} = V_\mathrm{m}/V_\mathrm{c} \quad p_\mathrm{r} = p/p_\mathrm{c} \quad T_\mathrm{r} = T/T_\mathrm{c}$$

If the reduced pressure is the same for two gases (1) and (2) it follows that

$$\frac{p^{(1)}}{p_c^{(1)}} = \frac{p^{(2)}}{p_c^{(2)}} \quad \text{hence} \quad p^{(2)} = \frac{p^{(1)}}{p_c^{(1)}} \times p_c^{(2)}$$

and similarly

$$T^{(2)} = \frac{T^{(1)}}{T_c^{(1)}} \times T_c^{(2)}$$

These relationships are used to find the pressure and temperature of gas (2) corresponding to a particular state of gas (1); it is necessary to know the critical constants of both gases.

(i) From the tables in the *Resource section*, for N_2 $p_c = 33.54$ atm, $T_c = 126.3$ K, and for H_2O $p_c = 218.3$ atm, $T_c = 647.4$ K. Taking gas (1) as N_2 and gas (2) as H_2O, the pressure and temperature of H_2O corresponding to $p^{(N_2)} = 1.0$ atm and $T^{(N_2)} = 298.15$ K is calculated as

$$p^{(H_2O)} = \frac{p^{(N_2)}}{p_c^{(N_2)}} \times p_c^{(H_2O)} = \frac{1.0\text{ atm}}{33.54\text{ atm}} \times (218.3\text{ atm}) = \boxed{6.5\text{ atm}}$$

$$T^{(H_2O)} = \frac{T^{(N_2)}}{T_c^{(N_2)}} \times T_c^{(H_2O)} = \frac{298.15\text{ K}}{126.3\text{ K}} \times (647.4\text{ K}) = \boxed{1.5 \times 10^3\text{ K}}$$

(ii) For CO_2 $p_c = 72.9$ atm, $T_c = 304.2$ K.

$$p^{(CO_2)} = \frac{p^{(N_2)}}{p_c^{(N_2)}} \times p_c^{(CO_2)} = \frac{1.0\text{ atm}}{33.54\text{ atm}} \times (72.9\text{ atm}) = \boxed{2.2\text{ atm}}$$

$$T^{(CO_2)} = \frac{T^{(N_2)}}{T_c^{(N_2)}} \times T_c^{(CO_2)} = \frac{298.15\text{ K}}{126.3\text{ K}} \times (304.2\text{ K}) = \boxed{7.2 \times 10^2\text{ K}}$$

(iii) For Ar $p_c = 48.0$ atm, $T_c = 150.7$ K.

$$p^{(Ar)} = \frac{p^{(N_2)}}{p_c^{(N_2)}} \times p_c^{(Ar)} = \frac{1.0\text{ atm}}{33.54\text{ atm}} \times (48.0\text{ atm}) = \boxed{1.4\text{ atm}}$$

$$T^{(Ar)} = \frac{T^{(N_2)}}{T_c^{(N_2)}} \times T_c^{(Ar)} = \frac{298.15\text{ K}}{126.3\text{ K}} \times (150.7\text{ K}) = \boxed{3.6 \times 10^2\text{ K}}$$

E1C.9(b) The van der Waals equation of state in terms of the molar volume is given by [1C.5b–*24*], $p = RT/(V_m - b) - a/V_m^2$. This relationship is rearranged to find b

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad \text{hence} \quad p + \frac{a}{V_m^2} = \frac{RT}{V_m - b}$$

$$\text{hence} \quad \frac{pV_m^2 + a}{V_m^2} = \frac{RT}{V_m - b} \quad \text{hence} \quad \frac{V_m^2}{pV_m^2 + a} = \frac{V_m - b}{RT}$$

$$\text{hence} \quad b = V_m - \frac{RTV_m^2}{pV_m^2 + a}$$

With the data given

$$b = V_{\mathrm{m}} - \frac{RTV_{\mathrm{m}}^2}{pV_{\mathrm{m}}^2 + a} = (4.00 \times 10^{-4}\ \mathrm{m^3\,mol^{-1}})$$
$$- \frac{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (288\ \mathrm{K}) \times (4.00 \times 10^{-4}\ \mathrm{m^3\,mol^{-1}})^2}{(4.0 \times 10^6\ \mathrm{Pa}) \times (4.00 \times 10^{-4}\ \mathrm{m^3\,mol^{-1}})^2 + (0.76\ \mathrm{m^6\,Pa\,mol^{-2}})}$$
$$= \boxed{1.3 \times 10^{-4}\ \mathrm{m^3\,mol^{-1}}}$$

where $1\ \mathrm{Pa} = 1\ \mathrm{kg\,m^{-1}\,s^{-2}}$ and $1\ \mathrm{J} = 1\ \mathrm{kg\,m^2\,s^{-2}}$ have been used.

The compression factor Z is defined in [1C.1–*20*] as $Z = V_{\mathrm{m}}/V_{\mathrm{m}}^{\circ}$, where V_{m}° is the molar volume of a perfect gas under the same conditions. This volume is computed from the equation of state for a perfect gas, [1A.4–*8*], as $V_{\mathrm{m}}^{\circ} = RT/p$, hence $Z = pV_{\mathrm{m}}/RT$, [1C.2–*20*]. With the data given

$$Z = \frac{pV_{\mathrm{m}}}{RT} = \frac{(4.0 \times 10^6\ \mathrm{Pa}) \times (4.00 \times 10^{-4}\ \mathrm{m^3\,mol^{-1}})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (288\ \mathrm{K})} = \boxed{0.67}$$

Solutions to problems

P1C.2 (a) Using the perfect gas law, $pV = nRT$, the molar volume is calculate as

$$V_{\mathrm{m}} = \frac{RT}{p} = \frac{(8.2057 \times 10^{-2}\ \mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}) \times (350\ \mathrm{K})}{2.30\ \mathrm{atm}} = \boxed{12.5\ \mathrm{dm^3\,mol^{-1}}}$$

(b) The van der Waals equation of state in terms of the molar volume is given by [1C.5b–*24*], $p = RT/(V_{\mathrm{m}} - b) - a/V_{\mathrm{m}}^2$; the term a/V_{m}^2 is due to attractive interactions.

This equation is a cubic in V_{m} which can be solved numerically. A simpler approach is to approximate a/V_{m}^2 as $a/(V_{\mathrm{m}}^{\circ})^2$, where V_{m}° is the molar volume of a perfect gas under the prevailing conditions. The van der Waals equation is then rearranged to give a simpler expression for V_{m}

$$p = \frac{RT}{(V_{\mathrm{m}} - b)} - \frac{a}{(V_{\mathrm{m}}^{\circ})^2} \qquad \text{hence} \qquad V_{\mathrm{m}} = \frac{RT}{p + [a/(V_{\mathrm{m}}^{\circ})^2]} + b$$

The van der Waals constants for $\mathrm{Cl_2}$ are $a = 6.260\ \mathrm{atm\,dm^6\,mol^{-2}}$ and $b = 5.42 \times 10^{-2}\ \mathrm{dm^3\,mol^{-1}}$. With these values, the first approximation to the molar volume is calculated as

$$V_{\mathrm{m}} = \frac{(8.2057 \times 10^{-2}\ \mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}) \times (350\ \mathrm{K})}{(2.30\ \mathrm{atm}) + [(6.260\ \mathrm{atm\,dm^6\,mol^{-2}})/(12.5\ \mathrm{dm^3\,mol^{-1}})^2]}$$
$$+ 5.42 \times 10^{-2}\ \mathrm{dm^3\,mol^{-1}} = 12.3\ \mathrm{dm^3\,mol^{-1}}$$

This approximate value for V_{m} is then used in place of V_{m}° and the process repeated, to give $\boxed{V_{\mathrm{m}} = 12.3\ \mathrm{dm^3\,mol^{-1}}}$ – the same value. The process has converged (to this level of precision).

P1C.4 The van der Waals equation in terms of the molar volume is given by [1C.5b–*24*], $p = RT/(V_m - b) - a/V_m^2$. Multiplication of both sides by V_m gives

$$pV_m = \frac{RTV_m}{(V_m - b)} - \frac{a}{V_m}$$

Division of the numerator and denominator of the first fraction by V_m, and then taking a factor of RT on the right gives the required expression

$$pV_m = RT\left(\frac{1}{(1 - b/V_m)} - \frac{a}{RTV_m}\right) \qquad (1.1)$$

The approximation $(1 - x)^{-1} \approx 1 + x$ is the used to write $1/(1 - b/V_m)$ as $(1 + b/V_m)$ to give

$$pV_m = RT\left(1 + \frac{b}{V_m}\right) - \frac{a}{V_m} \quad \text{hence} \quad pV_m = RT\left[1 + \frac{1}{V_m}\left(b - \frac{a}{RT}\right)\right]$$

The virial equation in terms of the molar volume is given by [1C.3b–*21*]

$$pV_m = RT\left(1 + \frac{B}{V_m} + \dots\right)$$

Comparison of this equation with eqn 1.1 shows that $B = b - a/RT$, as required.

The value of the second virial coefficient at the critical temperature of 126.3 K is found from the given van der Waals parameters as

$$\begin{aligned} B &= b - \frac{a}{RT} \\ &= (0.0391\ \text{dm}^3\ \text{mol}^{-1}) - \frac{1.390\ \text{atm}\ \text{dm}^6\ \text{mol}^{-2}}{(8.2057 \times 10^{-2}\ \text{dm}^3\ \text{atm}\ \text{K}^{-1}\ \text{mol}^{-1}) \times (126.3\ \text{K})} \\ &= -0.0950...\ \text{dm}^3\ \text{mol}^{-1} \end{aligned}$$

With this value for B, the molar volume is computed using the virial equation and with the approximation that the molar volume or the right-hand side of the expression can be replaced by the molar volume of a perfect gas, V_m°, under the same conditions

$$V_m = \frac{RT}{p}\left(1 + \frac{B}{V_m}\right) \approx \frac{RT}{p}\left(1 + \frac{B}{V_m^\circ}\right) = \frac{RT}{p}\left(1 + \frac{B}{RT/p}\right)$$

$$\begin{aligned} \text{hence } V_m &= \frac{RT}{p} + B \\ &= \frac{(8.2057 \times 10^{-2}\ \text{dm}^3\ \text{atm}\ \text{K}^{-1}\ \text{mol}^{-1}) \times (126.3\ \text{K})}{10\ \text{atm}} - 0.0950...\ \text{dm}^3\ \text{mol}^{-1} \\ &= 0.941... = \boxed{0.94\ \text{dm}^3\ \text{mol}^{-1}} \end{aligned}$$

Repeating the calculation at the Boyle temperature, 327.2 K, gives $B = -0.0126...\ \text{dm}^3\ \text{mol}^{-1}$ and $V_m = 2.67...\ \text{dm}^3\ \text{mol}^{-1}$ hence $\boxed{V_m = 2.7\ \text{dm}^3\ \text{mol}^{-1}}$.

How close a gas under particular conditions is to perfect behaviour is assessed by computing the compression factor Z, given by [1C.2–*20*], $Z = pV_m/RT$. At 126.3 K

$$Z = \frac{pV_m}{RT} = \frac{(10\ \text{atm}) \times (0.941...\ \text{dm}^3\ \text{mol}^{-1})}{(8.2057 \times 10^{-2}\ \text{dm}^3\ \text{atm}\ \text{K}^{-1}\ \text{mol}^{-1}) \times (126.3\ \text{K})} = 0.91$$

and at 327.2 K

$$Z = \frac{pV_m}{RT} = \frac{(10\ \text{atm}) \times (2.67...\ \text{dm}^3\ \text{mol}^{-1})}{(8.2057 \times 10^{-2}\ \text{dm}^3\ \text{atm}\ \text{K}^{-1}\ \text{mol}^{-1}) \times (327.2\ \text{K})} = 1.00$$

The latter conditions give $Z = 1$, as expected at the Boyle temperature, whereas in the former case Z differs significantly from 1. The gas is closer to perfect behaviour at the Boyle temperature that at the critical temperature.

P1C.6 The molar volume for a perfect gas is computed from $V_m = RT/p$

$$V_m = \frac{RT}{p} = \frac{(8.2057 \times 10^{-2}\ \text{dm}^3\ \text{atm}\ \text{K}^{-1}\ \text{mol}^{-1}) \times (400\ \text{K})}{3\ \text{atm}} = 10.941\ \text{dm}^3\ \text{mol}^{-1}$$

The van der Waals equation of state in terms of the molar volume is given by [1C.5b–*24*], $p = RT/(V_m - b) - a/V_m^2$. This equation is a cubic in V_m, as is seen by multiplying both sides by $(V_m - b)V_m^2$ and then gathering the terms together

$$pV_m^3 - V_m^2(pb + RT) + aV_m - ab = 0$$

Inserting the values of the van der Waals constants, $a = 1.337\ \text{atm}\ \text{dm}^6\ \text{mol}^{-2}$ and $b = 3.20 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1}$, and the stated temperature and pressure gives the polynomial

$$3V^3 - 32.919V_m^2 + 1.337V_m - 0.042784 = 0$$

The roots of this polynomial are found numerically using mathematical software and of these roots only $V_m = 10.932\ \text{dm}^3\ \text{mol}^{-1}$ is a physically plausible value for the molar volume.

The difference between the molar volume and that of a perfect gas is expressed in terms of the fraction

$$\frac{V_m - V_m^\circ}{V_m^\circ} = \frac{(10.932\ \text{dm}^3\ \text{mol}^{-1}) - (10.941\ \text{dm}^3\ \text{mol}^{-1})}{10.941\ \text{dm}^3\ \text{mol}^{-1}} = -8.2 \times 10^{-4}$$

The difference between the molar volumes is therefore $\boxed{-0.082\%}$ of the molar volume of the perfect gas.

P1C.8 According to Table 1C.4 on page 25, for the Berthelot equation of state the critical constants are given by

$$p_c = \frac{1}{12}\left(\frac{2aR}{3b^3}\right)^{1/2} \qquad V_c = 3b \qquad T_c = \frac{2}{3}\left(\frac{2a}{3bR}\right)^{1/2}$$

The first step is to rewrite the bracket in the expression for T_c so that it matches the bracket in the expression for p_c

$$T_c = \frac{2}{3}\underbrace{\left(\frac{2a}{3bR}\right)^{1/2} \times \left(\frac{R^2}{b^2}\right)^{1/2}}_{\text{combine}} \times \left(\frac{b^2}{R^2}\right)^{1/2} = \frac{2}{3}\underbrace{\left(\frac{2aR}{3b^3}\right)^{1/2}}_{\text{A}} \times \left(\frac{b^2}{R^2}\right)^{1/2}$$

Term A is recognised as being $12p_c$. The next step is to rewrite b in terms of V_c, $b = V_c/3$, and then substitute this into the previous expression.

$$T_c = \frac{2}{3}(12p_c) \times \left(\frac{b^2}{R^2}\right)^{1/2} = \frac{2}{3}(12p_c) \times \left(\frac{(V_c/3)^2}{R^2}\right)^{1/2} = \frac{2}{3} \times 12 \times \frac{1}{3} \times \frac{p_c V_c}{R}$$

Tidying up the fractions gives $\boxed{T_c = (8/3)p_c V_c/R}$.

The critical temperature for this gas is therefore

$$T_c = \frac{8}{3} \times \frac{p_c V_c}{R} = \frac{8}{3} \times \frac{(40\ \text{atm}) \times (160 \times 10^{-3}\ \text{dm}^3\ \text{mol}^{-1})}{8.2057 \times 10^{-2}\ \text{dm}^3\ \text{atm}\ \text{K}^{-1}\ \text{mol}^{-1}} = \boxed{208\ \text{K}}$$

In the Berthelot equation of state the parameter b is still interpreted as an excluded volume in the same way as in the van der Waals equation. In Section 1C.2(a) on page 23 it is argued that $b = 4V_{\text{molec}}N_A$, where V_{molec} is the volume occupied by one molecule. This volume is written in terms of the radius r as $4\pi r^3/3$ so it follows that $r = (3b/16\pi N_A)^{1/3}$. Because $V_c = 3b$ this can be rewritten $r = (V_c/16\pi N_A)^{1/3}$

$$\begin{aligned} r &= \left(\frac{V_c}{16\pi N_A}\right)^{1/3} = \left(\frac{160 \times 10^{-3}\ \text{dm}^3\ \text{mol}^{-1}}{16\pi \times (6.0221 \times 10^{23}\ \text{mol}^{-1})}\right)^{1/3} \\ &= 1.74 \times 10^{-9}\ \text{dm} = \boxed{174\ \text{pm}} \end{aligned}$$

P1C.10 The virial equation (up to the second term) in terms of the molar volume is given by [1C.3b–*21*]

$$pV_m = RT\left(1 + \frac{B}{V_m}\right)$$

Division of each side by p gives

$$V_m = \frac{RT}{p}\left(1 + \frac{B}{V_m}\right)$$

The quantity RT/p is recognised as the molar volume of a perfect gas, V_m°, so it follows that

$$V_m = V_m^\circ\left(1 + \frac{B}{V_m}\right) \quad \text{hence} \quad \frac{V_m}{V_m^\circ} = Z = \left(1 + \frac{B}{V_m}\right)$$

In *Problem* P1C.4 it is shown that B is related to the van der Waals constants by $B = b - a/RT$; using this, the compression factor is given by

$$Z = \left(1 + \frac{b - a/RT}{V_m}\right)$$

It follows that

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

P1C.12 The starting point are the two equations

$$-\frac{RT}{(V_\mathrm{m}-b)^2} + \frac{2a}{V_\mathrm{m}^3} = 0 \qquad \frac{2RT}{(V_\mathrm{m}-b)^3} - \frac{6a}{V_\mathrm{m}^4} = 0$$

To eliminate a between these equations the first is multiplied by $3/V_\mathrm{m}$ and then they are added together to give

$$-\frac{3RT}{V_\mathrm{m}(V_\mathrm{m}-b)^2} + \frac{2RT}{(V_\mathrm{m}-b)^3} = 0$$

The term RT cancels, and the fractions are eliminated by multiplying through by $V_\mathrm{m}(V_\mathrm{m}-b)^3$ to give

$$-3(V_\mathrm{m}-b) + 2V_\mathrm{m} = 0$$

from which it follows that $\boxed{V_\mathrm{m} = 3b}$ at the critical point.

This expression for V_m is then used in the first equation

$$-\frac{RT}{(V_\mathrm{m}-b)^2} + \frac{2a}{V_\mathrm{m}^3} = 0 \quad \text{becomes} \quad -\frac{RT}{(2b)^2} + \frac{2a}{(3b)^3} = 0$$

Multiplication through by $4 \times 27 \times b^3$ eliminates the fractions to give

$$-27RTb + 8a = 0$$

from which it follows that $\boxed{T = 8a/27Rb}$ at the critical point.

To find the pressure at the critical point these values of V_m and T are substituted into the van der Waals equation in terms of the molar volume, [1C.5b–*24*]

$$\begin{aligned} p &= \frac{RT}{(V_\mathrm{m}-b)} - \frac{a}{V_\mathrm{m}^2} \\ &= \frac{8a}{27Rb}\frac{R}{2b} - \frac{a}{(3b)^2} = \frac{8a}{54b^2} - \frac{a}{9b^2} = \frac{a}{27b^2} \end{aligned}$$

The pressure at the critical point is therefore given by $\boxed{p = a/27b^2}$.

P1C.14 The virial equation in terms of the molar volume, [1C.3b–*21*], is

$$pV_\mathrm{m} = RT\left(1 + \frac{B}{V_\mathrm{m}} + \frac{C}{V_\mathrm{m}^2} + \dots\right) \tag{1.2}$$

The virial equation in terms of the pressure, [1C.3a–*21*], is

$$pV_\mathrm{m} = RT\left(1 + B'p + C'p^2 + \dots\right) \tag{1.3}$$

Equation 1.2 is rewritten to give an expresion for the pressure

$$p = \frac{RT}{V_\mathrm{m}}\left(1 + \frac{B}{V_\mathrm{m}} + \frac{C}{V_\mathrm{m}^2} + \ldots\right)$$

This expression for p is substituted into the right-hand side of eqn 1.3 to give

$$\begin{aligned} pV_\mathrm{m} &= RT\left(1 + B'p + C'p^2 + \ldots\right) \\ &= RT\left(1 + \frac{B'RT}{V_\mathrm{m}}\left(1 + \frac{B}{V_\mathrm{m}} + \frac{C}{V_\mathrm{m}^2} + \ldots\right) + \frac{C'R^2T^2}{V_\mathrm{m}^2}\left(1 + \frac{B}{V_\mathrm{m}} + \frac{C}{V_\mathrm{m}^2} + \ldots\right)^2 + \ldots\right) \end{aligned} \tag{1.4}$$

On the right there is only one term in $1/V_\mathrm{m}$

$$\frac{B'R^2T^2}{V_\mathrm{m}}$$

This is identified with the term in $1/V_\mathrm{m}$ on the right-hand side of eqn 1.2

$$\frac{B'R^2T^2}{V_\mathrm{m}} = \frac{BRT}{V_\mathrm{m}} \qquad \text{hence} \qquad \boxed{B = B'RT}$$

There are two terms in $1/V_\mathrm{m}^2$ on the right-hand side of eqn 1.4

$$\frac{B'BR^2T^2}{V_\mathrm{m}^2} + \frac{C'R^3T^3}{V_\mathrm{m}^2}$$

These are identified with the term in $1/V_\mathrm{m}^2$ on the right-hand side of eqn 1.2

$$\frac{B'BR^2T^2}{V_\mathrm{m}^2} + \frac{C'R^3T^3}{V_\mathrm{m}^2} = \frac{CRT}{V_\mathrm{m}^2} \qquad \text{hence} \qquad B'BRT + C'R^2T^2 = C$$

With the substitution $B = B'RT$, the relationship is $\boxed{C = R^2T^2[(B')^2 + C']}$.

P1C.16 The given equation of state is multiplied through by V_m^2 to give

$$pV_\mathrm{m}^2 = RTV_\mathrm{m} + (a + bT)$$

The partial differential with respect to T of both sides of the equation is then computed, being careful to remember that V_m is a function of T so, for example, the term RTV_m must be differentiated using the product rule. Calculating the derivative is essentially an application of the chain rule.

$$2pV_\mathrm{m}\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p = RT\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p + RV_\mathrm{m} + b$$

This equation is then rearranged by collecting the terms in $\partial V_\mathrm{m}/\partial T$ together

$$\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p (2pV_\mathrm{m} - RT) = RV_\mathrm{m} + b \quad \text{hence} \quad \boxed{\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p = \frac{RV_\mathrm{m} + b}{2pV_\mathrm{m} - RT}}$$

P1C.18 In Section 1C.2(b) on page 24 it is explained that critical behaviour is associated with oscillations in the isotherms predicted by a particular equation of state. In particular, at the critical point a minimum and a maximum in the isotherm coincide at the same pressure and volume, thus creating a point of inflexion. This is the critical isotherm, and is at the critical temperature.

A gas which shows critical behaviour can be liquefied by the application of pressure alone, provided the temperature is below the critical temperature.

An equation of state should predict that, as the volume decreases eventually the pressure increases without limit. For gas A, in the limit $b/V_m \gg 1$ the equation of state becomes $pV_m^2 = bRT$, which has the correct behaviour. As the volume increases, the expectation is that the perfect gas law will be regained, and for gas A the limit $b/V_m \ll 1$ gives $pV_m = RT$, as expected. For gas B in the limit $V_m \gg b$ the perfect gas law results, but in the opposite limit, $V_m \ll b$, the equation of state becomes $-pb = RT$, implying that the pressure reaches a constant value of $-RT/b$ which is problematic for positive b.

For there to be (at least) two extrema in the plots of V_m against p, the derivative dV_m/dT must have two roots – that is, values at which it is = 0. This implies that the expression for the derivative must be a quadratic in V_m, and therefore that the expression for V_m must be a cubic in V_m. It is evident that neither of the proposed equations of state are cubic in V_m, and so neither is expected to show critical behaviour.

P1C.20 In *Brief Illustration* 1C.5 the reduced pressure is 0.48 and the reduced temperature is 1.33; the critical constants for NH_3 are given in the *Resource section* as $p_c = 111.3$ atm and $T_c = 405.5$ K. The pressure and temperature for the same state as argon are therefore

$$p = 0.48 \times (111.3 \text{ atm}) = \boxed{53.42 \text{ atm}} \qquad T = 1.22 \times (405.5 \text{ K}) = \boxed{494.7 \text{ K}}$$

P1C.22 The equation of state for a perfect gas, [1A.4–*8*], is $pV = nRT$, and the van der Waals equation of state in terms of the volume is given by [1C.5a–*23*], $p = nRT/(V-b)-an^2/V^2$. From the *Resource section* the van der Waals parameters for CO_2 are $a = 3.610$ atm dm^6 mol^{-2} and $b = 4.29 \times 10^{-2}$ dm^3 mol^{-1}.

Plots of p against V, Fig. 1.3, show only minor deviations between a van der Waals gas and a perfect gas under these conditions. Plotting p against $1/V$ gives a straight line for the perfect gas, and as in seen in Fig. 1.4 the deviations for the van der Waals gas are minor.

P1C.24 The van der Waals equation in terms of the molar volume is given by [1C.5b–*24*], $p = RT/(V_m - b) - a/V_m^2$, and the compression factor Z is given by [1C.2–*20*], $Z = pV_m/RT$, hence

$$Z = \frac{V_m}{RT}\left(\frac{RT}{V_m - b} - \frac{a}{V_m^2}\right) = \frac{V_m}{V_m - b} - \frac{a}{RTV_m} \qquad (1.5)$$

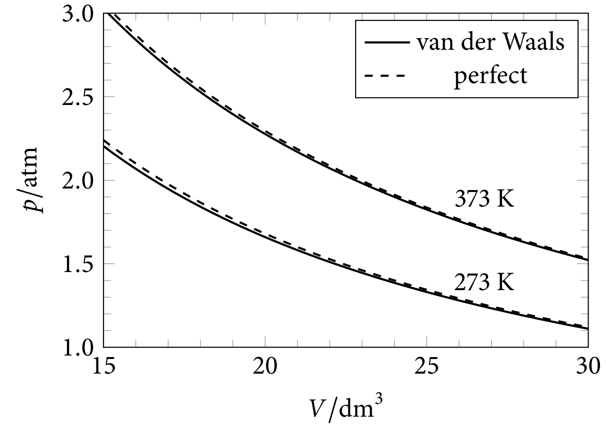


Figure 1.3

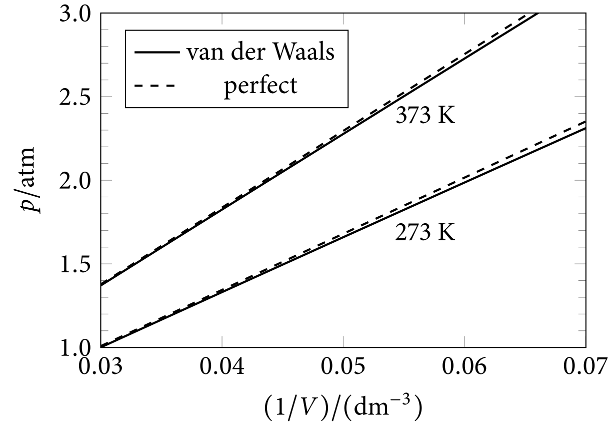


Figure 1.4

To find the turning points in Z as a function of V_{m} the derivative $\text{d}Z/\text{d}V_{\text{m}}$ is set to zero. In computing the derivative, write the first term as $V_{\text{m}}(V_{\text{m}}-b)^{-1}$ and recognise the the need to use the product rule

$$\frac{\text{d}Z}{\text{d}V_{\text{m}}}=\frac{-V_{\text{m}}}{(V_{\text{m}}-b)^2}+\frac{1}{V_{\text{m}}-b}+\frac{a}{RTV_{\text{m}}^2}=0$$

$$\text{hence}\quad V_{\text{m}}^2(a-bRT)-2abV_{\text{m}}+ab^2=0$$

To go to the second line the equation is multiplied through by $RTV_{\text{m}}^2(V_{\text{m}}-b)^2$. The resulting quadratic in V_{m} is solved in the usual way

$$V_{\text{m}}=\frac{1}{2(a-bRT)}\left[2ab\pm\left(4a^2b^2-4ab^2(a-bRT)\right)^{1/2}\right]$$

$$\text{hence}\quad V_{\text{m}}=\frac{b}{1-bRT/a}\left[1\pm\left(\frac{bRT}{a}\right)^{1/2}\right]$$

The positions of the turning points depend on the van der Waals parameters as well as the temperature. The predictions of these equation are best explored by inserting some typical values.

For N_2, $a = 1.352\ \mathrm{atm\,dm^6\,mol^{-2}}$ and $b = 0.0387\ \mathrm{dm^3\,mol^{-1}}$. At 298 K the two extrema occur at $V_m = 0.237\ \mathrm{dm^3\,mol^{-1}}$ and $V_m = 0.0211\ \mathrm{dm^3\,mol^{-1}}$; using these values in eqn 1.5 gives compression factors of 0.962 and −3.82. The latter value is physically unreasonable, but the former is acceptable and for this value the pressure is calculated as 99.3 atm.

For Ne $a = 0.205\ \mathrm{atm\,dm^6\,mol^{-2}}$ and $b = 0.0167\ \mathrm{dm^3\,mol^{-1}}$. At 298 K one of the extrema occurs at a negative value of V_m and the other occurs at $6.92 \times 10^{-3}\ \mathrm{dm^3\,mol^{-1}}$. However, this latter value gives a negative value of Z, which is not acceptable. Therefore, there are no physically plausible conditions under which Z is a minimum for Ne at 298 K.

Answers to integrated activities

I1.2 According to the equipartition theorem (*The chemist's toolkit* 7 in Topic 2A), each quadratic contribution to the energy of a molecule contributes $\frac{1}{2}kT$ to the average energy per molecule. Translational kinetic energy is a quadratic term, and because translation is possible in three dimensions, the quoted energy density of $0.15\ \mathrm{J\,cm^{-3}}$ is the result of three such contributions.

The rotation of a molecule about an axis is also a quadratic contribution to the energy, and in general three such contributions are expected corresponding to rotation about three mutually perpendicular axes. However, linear molecules, such as diatomics, do not show rotation about their long axes, so there are only two contributions. The contribution of rotation to the energy density will therefore be $\frac{2}{3}$ of that due to translation

$$\text{total energy denisty} = \overbrace{(0.15\ \mathrm{J\,cm^{-3}})}^{\text{trans.}} + \overbrace{\tfrac{2}{3} \times (0.15\ \mathrm{J\,cm^{-3}})}^{\text{rot.}} = \boxed{0.25\ \mathrm{J\,cm^{-3}}}$$

2

Internal energy

2A Internal energy

Answers to discussion questions

D2A.2 Work is done when a body is moves against an opposing force. For an infinitesimal displacement in the x-direction, dx, against a force F along that direction the work done by the body is $F\,\mathrm{d}x$.

When the energy of a system changes as a result of a temperature difference between the system and its surroundings, the resulting energy transfer from the hotter to the cooler body is described as heat. In thermodynamic terms, both heat and work cause the internal energy of an object to change: if heat 'flows in' the internal energy of the body rises, if the body 'does work', its internal energy decreases.

If the internal energy of an object increases, this is interpreted in molecular terms as the molecules moving up to higher energy levels. If the molecules drop down to lower levels the resulting energy is available as heat or work.

D2A.4 A reversible gas expansion is one in which the direction of the process can be reversed by an infinitesimal change in the external pressure. This is achieved if the external pressure is altered so that it is only ever infinitesimally different from the pressure of the gas which is expanding or contracting. In other words, the external pressure must always match the pressure of the expanding/contracting gas.

Solutions to exercises

E2A.1(b) *The chemist's toolkit* 7 in Topic 2A gives an explanation of the equipartition theorem. The molar internal energy is given by

$$U_\mathrm{m} = \tfrac{1}{2} \times \left(\nu_\mathrm{t} + \nu_\mathrm{r} + 2\nu_\mathrm{v}\right) \times RT$$

where ν_t is the number of translational degrees of freedom, ν_r is the number of rotational degrees of freedom and ν_v is the number of vibrational degrees of freedom. As each gas molecule can move independently along the x, y and z axis, the number of translational degrees of freedom is three. All the listed molecules have three degrees of rotational freedom and none of them is expected to have any vibrational modes which are significantly excited at room temperature. Therefore, at room temperature, ozone, ethane and sulfur dioxide are all expected to have an approximate molar internal energy of

$$U_m = \tfrac{1}{2}\times(3+2+0)\times RT = 3\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298.15\,\mathrm{K}) = \boxed{7.4\,\mathrm{kJ\,mol^{-1}}}$$

E2A.2(b) A state function is a property with a value that depends only on the current state of the system and is independent of how the state has been prepared. Volume, internal energy and density are all state functions.

E2A.3(b) The system is expanding against a constant external pressure, hence the expansion work is given by [2A.6–*40*], $w = -p_{ex}\Delta V$. The change in volume is the cross-sectional area times the linear displacement

$$\Delta V = (75\ \mathrm{cm^2}) \times (25\ \mathrm{cm}) = 1875\ \mathrm{cm^3} = 1.87... \times 10^{-3}\ \mathrm{m^3}$$

The external pressure is 150 kPa = 1.50×10^5 Pa, therefore the expansion work is

$$w = -(1.50 \times 10^5\ \mathrm{Pa}) \times (1.87... \times 10^{-3}\ \mathrm{m^3}) = \boxed{-281\ \mathrm{J}}$$

Note that the volume is expressed in $\mathrm{m^3}$. The relationships 1 Pa = 1 $\mathrm{kg\,m^{-1}\,s^{-2}}$ and 1 J = 1 $\mathrm{kg\,m^2\,s^{-2}}$ are used to verify the units of the result.

E2A.4(b) For all cases $\Delta U = 0$, because the internal energy of a perfect gas depends on the temperature alone.

(i) The work of reversible isothermal expansion of a perfect gas is given by [2A.9–*41*]

$$\begin{aligned} w &= -nRT\ln\left(\frac{V_f}{V_i}\right) \\ &= -(2.00\ \mathrm{mol}) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (273.15\ \mathrm{K}) \times \ln\left(\frac{20.0\ \mathrm{dm^3}}{5.0\ \mathrm{dm^3}}\right) \\ &= -6.3 \times 10^3\ \mathrm{J} = \boxed{-6.3\ \mathrm{kJ}} \end{aligned}$$

Note that the temperature is expressed in K in the above equation. Using the First Law of thermodynamics, [2A.2–*38*], gives

$$q = \Delta U - w = 0 - (-2.68\ \mathrm{kJ}) = \boxed{+2.68\ \ \mathrm{kJ}}$$

(ii) The final pressure of the expanding gas is found using the perfect gas law, [1A.4–*8*]

$$\begin{aligned} p_f &= \frac{nRT}{V_f} = \frac{(2.00\ \mathrm{mol}) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (273.15\ \mathrm{K})}{(20.0 \times 10^{-3}\ \mathrm{m^3})} \\ &= 2.27... \times 10^5\ \mathrm{Pa} \end{aligned}$$

This pressure equals the constant external pressure against which the gas is expanding, therefore the work of expansion is

$$\begin{aligned} w &= -p_{\text{ex}} \times \Delta V = (2.27... \times 10^5\ \text{Pa}) \times (20.0 \times 10^{-3}\ \text{m}^3 - 5.0 \times 10^{-3}\ \text{m}^3) \\ &= -3.41 \times 10^3\ \text{J} = \boxed{-3.41\ \text{kJ}} \end{aligned}$$

and hence $q = \boxed{+3.41\ \text{kJ}}$

(iii) Free expansion is expansion against zero force, so $\boxed{w = 0}$ and therefore $\boxed{q = 0}$ as well.

E2A.5(b) For a perfect gas at constant volume $p_\text{i}/T_\text{i} = p_\text{f}/T_\text{f}$ therefore,

$$p_\text{f} = p_\text{i} \times \frac{T_\text{f}}{T_\text{i}} = (111\ \text{kPa}) \times \left(\frac{356\ \text{K}}{277\ \text{K}}\right) = \boxed{143\ \text{kPa}}$$

The change in internal energy at constant volume is given by [2A.15b–*45*]

$$\begin{aligned} \Delta U &= nC_{V,\text{m}}\Delta T = (2.00\ \text{mol}) \times \left(\frac{5}{2} \times 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}\right) \times (356\ \text{K} - 277\ \text{K}) \\ &= +3.28 \times 10^3\ \text{J} = \boxed{+3.28\ \text{kJ}} \end{aligned}$$

The volume of the gas is constant, so the work of expansion is zero, $\boxed{w = 0}$. The First Law of thermodynamics gives $q = \Delta U - w = +3.28\ \text{kJ} - 0 = \boxed{+3.28\ \text{kJ}}$.

E2A.6(b) (i) The work of expansion against constant external pressure is given by [2A.6–*40*], $w = -p_{\text{ex}}\Delta V = -(7.7\ \text{kPa}) \times (2.5\ \text{dm}^3) = \boxed{-19\ \text{J}}$.

(ii) The work done in a reversible, isothermal expansion is given by [2A.9–*41*] $w = -nRT\ln(V_\text{f}/V_\text{i})$. The amount in moles of argon is

$$\begin{aligned} n &= \frac{m}{M} = \frac{(6.56\ \text{g})}{(39.95\ \text{g mol}^{-1})} = 0.164...\ \text{mol} \\ w &= -(0.164...\ \text{mol}) \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (305\ \text{K}) \\ &\quad \times \ln\left(\frac{[18.5 + 2.5]\ \text{dm}^3}{18.5\ \text{dm}^3}\right) = \boxed{-53\ \text{J}} \end{aligned}$$

Note that the modulus of the work done in a reversible expansion is greater than the work for expansion against constant external pressure because the latter is an irreversible process.

Solutions to problems

P2A.2 The First Law of thermodynamics states that $\Delta U = q + w$. Work is done on the electric heater, so $w = +1$ kJ. Heat is transferred to the surroundings, so $q = -1$ kJ. Therefore overall

$$\Delta U = q + w = (-1\ \text{kJ}) + (1\ \text{kJ}) = \boxed{0}$$

P2A.4 (a) $n = x/l = (90\ \text{nm})/(45\ \text{nm}) = 2.0$ therefore $\nu = n/N = 2.0/200 = 0.01$

$$F = \frac{kT}{2l}\ln\left(\frac{1+\nu}{1-\nu}\right)$$

$$= \frac{(1.3806\times10^{-23}\ \text{J K}^{-1})\times(298.15\ \text{K})}{(2\times45\times10^{-9}\ \text{m})}\times\ln\left(\frac{1+0.01}{1-0.01}\right) = \boxed{9.1\times10^{-16}\ \text{N}}$$

(b) The equation to be plotted is $F/\text{N} = 4.57\times10^{-14}\ln[(1+\nu)/(1-\nu)]$; this is shown in Fig. 2.1.

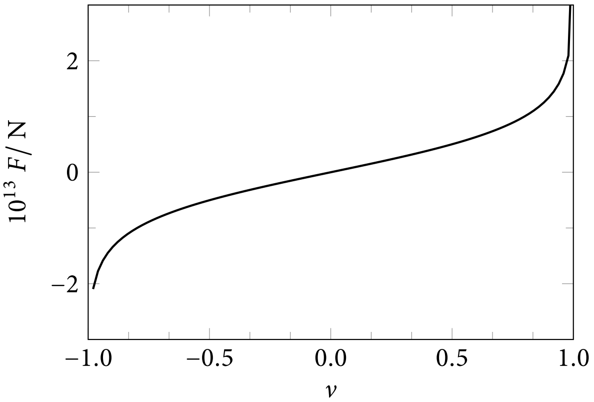


Figure 2.1

The natural logarithm can be expanded using the Taylor series as $\ln(1+\nu) \approx \nu + \nu^2/2! + \nu^3/3! + ...$, which, for $\nu << 1$, can be approximated as $\ln(1+\nu)\approx\nu$, and similarly, $\ln(1-\nu)\approx-\nu$. Therefore,

$$F = \frac{kT}{2l}[\ln(1+\nu)-\ln(1-\nu)] \approx \frac{kT}{2l}[\nu-(-\nu)] = \frac{\nu kT}{l}$$

Because $\nu = n/N$, it follows that

$$F = \frac{\nu kT}{l} = \frac{nkT}{Nl}$$

Hooke's law predicts $F = \text{const}\times x$, that is the restoring force is directly proportional to the displacement. Using $n = x/l$, the expression for the force obtained in part (a) is rewritten as

$$\frac{nkT}{Nl} = \frac{kTx}{Nl^2} \equiv \text{const}\times x$$

Therefore Hooke's law applies and kT/Nl^2 is the force constant.

(c)

$$\text{d}w = F\,\text{d}x = \frac{kT}{2l}\ln\left(\frac{1+\nu}{1-\nu}\right)\text{d}x = \frac{kT}{2l}\ln\left(\frac{1+\nu}{1-\nu}\right)(Nl\,\text{d}\nu)$$

$$= \frac{NkT}{2}\ln\left(\frac{1+\nu}{1-\nu}\right)\text{d}\nu$$

Integrating both sides and using $\int \ln(1 \pm x)\,dx = (x \pm 1)\ln(1 \pm x) - x$ gives

$$\begin{aligned}\int dw &= \frac{NkT}{2}\int_0^{V_f} \ln\left(\frac{1+\nu}{1-\nu}\right) d\nu \\ w &= \frac{NkT}{2}[(\nu+1)\ln(1+\nu)+\nu-(\nu-1)\ln(1-\nu)-\nu]_0^{\nu_f} \\ &= \frac{NkT}{2}\left[\ln(1+\nu)(1-\nu)+\nu\ln\left(\frac{1+\nu}{1-\nu}\right)\right]_0^{\nu_f} \\ &= \frac{NkT}{2}\left[\ln(1+\nu_f)(1-\nu_f)+\nu_f\ln\left(\frac{1+\nu_f}{1-\nu_f}\right)\right]\end{aligned}$$

P2A.6 The expansion work is given by [2A.6–*40*], $dw = -p_{ex}dV$. For a reversible expansion p_{ex} is always equal to the pressure of the gas so

$$dw = -p_{gas}dV = -\left(\frac{nRT}{V} - \frac{n^2a}{V^2}\right)dV$$

Integrating both sides gives

$$\begin{aligned}w &= \int_{V_i}^{V_f} -\left(\frac{nRT}{V} - \frac{n^2a}{V^2}\right)dV \\ &= \left[-nRT\ln V - \frac{n^2a}{V}\right]_{V_i}^{V_f} = -nRT\ln\left(\frac{V_f}{V_i}\right) - n^2a\left(\frac{1}{V_f} - \frac{1}{V_i}\right)\end{aligned}$$

The work done on the surroundings is the opposite of the work done on the gas.

$$w_{surr} = nRT\ln\left(\frac{V_f}{V_i}\right) + n^2a\left(\frac{1}{V_f} - \frac{1}{V_i}\right)$$

The first term is identical to the work done on the surroundings by a perfect gas expanding under reversible isothermal conditions. $V_f > V_i$, therefore $n^2a(1/V_f - 1/V_i)$ is negative, so the overall work done on the surroundings by the gas is smaller than it would be for a perfect gas. The attraction between the gas molecules has to be overcome when expanding, meaning that less energy is available as work.

P2A.8 Decomposition of 1.0 mol of calcium carbonate liberates 1.0 mol of carbon dioxide. In either case the expansion is against constant external atmospheric pressure, $p_{ex} = 1.0\text{ atm} = 1.01325 \times 10^5\text{ Pa}$. The final volume of the expanding gas is found using the perfect gas equation, $V = nRT/p_{ex}$. The change in volume of the solid is negligible compared to the change in volume due to the formation of the gas, therefore the overall change in volume of the system is $\Delta V = V$. The work against constant external pressure is

$$\begin{aligned}w &= -p_{ex}\Delta V = -p_{ex} \times \frac{nRT}{p_{ex}} = -nRT = -(1.0\text{ mol}) \times (8.3145\text{ J K}^{-1}\text{ mol}^{-1}) \\ &\times ([800 + 273.15]\text{ K}) = -8.9 \times 10^3\text{ J} = \boxed{-8.9\text{ kJ}}\end{aligned}$$

P2A.10 The reduced pressure of a van der Waals gas is given by [1C.9–*26*]

$$p_\mathrm{r} = \frac{8T_\mathrm{r}n}{3V_\mathrm{r}-1} - \frac{3n}{V_\mathrm{r}^2}$$

The reduced volume, pressure and temperature are given in terms of the van der Waals parameters in [1C.7–*26*] and [1C.8–*26*], $V_\mathrm{m,r} = V_\mathrm{m}/V_\mathrm{c} = V_\mathrm{m}/(3b)$, $p_\mathrm{r} = p/p_\mathrm{c} = 27b^2p/a$ and $T_\mathrm{r} = T/T_\mathrm{c} = 27RbT/8a$. In *Problem* P2A.7 the work done during the isothermal reversible expansion of a van der Waals gas is found as

$$w = -nRT\ln\left(\frac{V_\mathrm{f}-nb}{V_\mathrm{i}-nb}\right) - n^2a\left(\frac{1}{V_\mathrm{f}} - \frac{1}{V_\mathrm{i}}\right)$$

This expression is first rewritten in term of the molar volume and then in terms of the reduced volume, temperature and pressure.

$$\begin{aligned}
w &= -nRT\ln\left(\frac{nV_\mathrm{m,f}-nb}{nV_\mathrm{m,i}-nb}\right) - n^2a\left(\frac{1}{nV_\mathrm{m,f}} - \frac{1}{nV_\mathrm{m,i}}\right)\\
&= -nRT\ln\left(\frac{V_\mathrm{m,f}-b}{V_\mathrm{m,i}-b}\right) - na\left(\frac{1}{V_\mathrm{m,f}} - \frac{1}{V_\mathrm{m,i}}\right)\\
&= -nR\left(\frac{8a}{27Rb}\right)T_\mathrm{r}\ln\left(\frac{3bV_\mathrm{r,f}-b}{3bV_\mathrm{r,i}-b}\right) - na\left(\frac{1}{3bV_\mathrm{r,f}} - \frac{1}{3bV_\mathrm{r,i}}\right)\\
&= -n\left(\frac{8a}{27b}\right)T_\mathrm{r}\ln\left(\frac{3V_\mathrm{r,f}-1}{3V_\mathrm{r,i}-1}\right) - \frac{na}{3b}\left(\frac{1}{V_\mathrm{r,f}} - \frac{1}{V_\mathrm{r,i}}\right)
\end{aligned}$$

The reduced work is defined as $w_\mathrm{r} = (3b/a)w$, with this it follows that

$$w_\mathrm{r} = -n\left(\frac{8}{9}\right)T_\mathrm{r}\ln\left(\frac{3V_\mathrm{r,f}-1}{3V_\mathrm{r,i}-1}\right) - n\left(\frac{1}{V_\mathrm{r,f}} - \frac{1}{V_\mathrm{r,i}}\right)$$

For expansion along the critical isotherm from $V_\mathrm{m,i} = V_\mathrm{c}$ to $V_\mathrm{m,f} = xV_\mathrm{c}$. It follows that $V_\mathrm{r,i} = V_\mathrm{m,i}/V_\mathrm{c} = V_\mathrm{c}/V_\mathrm{c} = 1$ and $V_\mathrm{r,f} = V_\mathrm{m,f}/V_\mathrm{c} = xV_\mathrm{c}/V_\mathrm{c} = x$. Along the critical isotherm $T_\mathrm{c} = 1$, therefore w_r is

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

2B Enthalpy

Answers to discussion questions

D2B.2 If a substance is heated at constant volume all of the energy as heat is transformed into internal energy of the substance. If the same process is carried out under conditions of constant pressure some of the energy as heat will be used to expand the substance against the external pressure and so less of the energy as heat is transformed into internal energy. This effect is largest for gases whose volumes change much more rapidly with temperature than do solids or liquids.

The temperature of a substance is related to its internal energy, and therefore as energy as heat is supplied the temperature increases. For a given amount of energy as heat this increase in internal energy is smaller for the constant-pressure case than for the constant-volume case. Therefore the rise in temperate is smaller for the constant-pressure process, and this implies that the heat capacity is greater.

Solutions to exercises

E2B.1(b) The heat transferred under constant pressure equals the change in enthalpy of the system, [2B.2b–*47*], $q_\mathrm{p} = \Delta H$. The relationship between the change in enthalpy, change in temperature and the heat capacity is given by [2B.6b–*49*]

$$C_{p,\mathrm{m}} = \frac{\Delta H}{n\Delta T} = \frac{(178\,\mathrm{J})}{(1.9\,\mathrm{mol})\times(1.78\,\mathrm{K})} = 52.6...\,\mathrm{J\,K\,mol^{-1}} = \boxed{53\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

For a perfect gas $C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = R$, [2B.9–*49*], therefore

$$C_{V,\mathrm{m}} = C_{p,\mathrm{m}} - R = (52.6...\,\mathrm{J\,K^{-1}\,mol^{-1}}) - (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) = \boxed{44\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

E2B.2(b) There is no change in the number of gaseous species on going from reactants to products, therefore $\Delta n_\mathrm{g} = 0$ and $\Delta H_\mathrm{m} = \Delta U_\mathrm{m}$.

E2B.3(b) (i) The heat capacity can be expressed as $C_p = a + bT$ where $a = 20.17\,\mathrm{J\,K^{-1}}$ and $b = 0.3665\,\mathrm{J\,K^{-2}}$. Integrating the relationship $\mathrm{d}H = C_p\mathrm{d}T$ on both sides gives

$$\int_{T_1}^{T_2}\mathrm{d}H = \int_{T_1}^{T_2} C_p\mathrm{d}T = \int_{T_1}^{T_2}(a+bT)\mathrm{d}T = \left[aT + \tfrac{1}{2}bT^2\right]_{T_1}^{T_2}$$

$$\begin{aligned} H(T_2) - H(T_1) &= na(T_2 - T_1) + \frac{1}{2}nb(T_2^2 - T_1^2) \\ &= (20.17\,\mathrm{J\,K^{-1}})\times(373.15\,\mathrm{K} - 298.15\,\mathrm{K}) \\ &\quad + \tfrac{1}{2}\times(0.4001\,\mathrm{J\,K^{-2}})\times[(373.15\,\mathrm{K})^2 - (298.15\,\mathrm{K})^2] \\ &= +11.5...\,\mathrm{kJ} = \boxed{+11.6\,\mathrm{kJ}} \end{aligned}$$

Under constant pressure conditions $\Delta H = \boxed{q_\mathrm{p} = +11.6\,\mathrm{kJ}}$.
The work of expansion against constant pressure p_ex is given by [2A.6–*40*], $w = -p_\mathrm{ex}\Delta V = -p_\mathrm{ex}(V_\mathrm{f} - V_\mathrm{i})$. Assume that the gas is in mechanical equilibrium with its surroundings, therefore p_ex is the same as the pressure of the gas, p. The initial and final volumes are calculated from T_f and T_i by $V_\mathrm{f} = nRT_\mathrm{f}/p$ and $V_\mathrm{i} = nRT_\mathrm{i}/p$, therefore $V_\mathrm{f} - V_\mathrm{i} = (T_\mathrm{f} - T_\mathrm{i})nR/p$. Hence

$$\begin{aligned} w &= -p\times\frac{nR}{p}(T_\mathrm{f} - T_\mathrm{i}) = -nR\Delta T \\ &= -(1.00\,\mathrm{mol})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(373.15\,\mathrm{K} - 298.15\,\mathrm{K}) \\ &= -6.23...\times10^2\,\mathrm{J} = \boxed{-624\,\mathrm{J}} \end{aligned}$$

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

(ii) The energy and enthalpy of a perfect gas depends on the temperature alone, hence ΔH and ΔU is the same as above, $\boxed{\Delta H = \Delta U = +11.6\ \mathrm{kJ}}$. Under constant volume conditions there is no expansion work, $\boxed{w = 0}$, therefore the heat is equal to the change in internal energy, $q_V = \Delta U = \boxed{+11.0\ \mathrm{kJ}}$.

E2B.4(b) Under constant pressure $q_p = \Delta H$, therefore

$$\begin{aligned} q_p = \Delta H = nC_{p,\mathrm{m}}\Delta T &= (2.0\ \mathrm{mol}) \times (37.11\ \mathrm{J\,K\,mol^{-1}}) \times (277\ \mathrm{K} - 250\ \mathrm{K}) \\ &= 2.00...\ \mathrm{kJ} = \boxed{+2.0\ \mathrm{kJ}} \end{aligned}$$

The definition of enthalpy is given by [2B.1–*46*], $H = U + pV$. For a change at constant pressure, it follows that $\Delta H = \Delta U + p\Delta V$, where $\Delta V = V_\mathrm{f} - V_\mathrm{i}$. If the gas is assumed to be perfect, then $V_\mathrm{f} = nRT_\mathrm{f}/p$ and $V_\mathrm{i} = nRT_\mathrm{i}/p$, so $\Delta V = (T_\mathrm{f} - T_\mathrm{i})nR/p$. Hence $p\Delta V = nR(T_\mathrm{f} - T_\mathrm{i}) = nR\Delta T$.

$$\begin{aligned} \Delta U &= \Delta H - nR\Delta T \\ &= (2.0...\ \mathrm{kJ}) - (2.0\ \mathrm{mol}) \times (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (277\ \mathrm{K} - 250\ \mathrm{K}) \\ &= \boxed{+1.6\ \mathrm{kJ}} \end{aligned}$$

Solutions to problems

P2B.2 The volume of the room is $V = (5.5\ \mathrm{m}) \times (6.5\ \mathrm{m}) \times (3.0\ \mathrm{m}) = 107.25\ \mathrm{m^3}$. Using 1 atm = 1.01325×10^5 Pa, the amount in moles of gas in the room initially is

$$n = \frac{pV}{RT} = \frac{(1.01325 \times 10^5\ \mathrm{Pa}) \times (107.25\ \mathrm{m^3})}{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\ \mathrm{K})} = 4.38... \times 10^3\ \mathrm{mol}$$

Assuming that the heat is transferred under constant pressure

$$q_p = nC_{p,\mathrm{m}}\Delta T = (4.38... \times 10^3\ \mathrm{mol}) \times (21\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (10\ \mathrm{K}) = 9.21 \times 10^5\ \mathrm{J}$$

The time needed to transfer this heat is $\Delta t = (9.21... \times 10^5\ \mathrm{J})/(1500\ \mathrm{J\,s^{-1}}) = \boxed{6.1 \times 10^2\ \mathrm{s}}$.

P2B.4 Fitting the data set using a computer program to an expression in the form of $C^{\ominus}_{p,\mathrm{m}}(T) = a + bT + cT^{-2}$ yields $a = 28.8\ \mathrm{J\,K^{-1}\,mol^{-1}}$, $b = 2.79 \times 10^{-2}\ \mathrm{J\,K^{-2}\,mol^{-1}}$ and $c = -1.51 \times 10^5\ \mathrm{J\,K\,mol^{-1}}$. Fitting the data set to an expression in the form of $C^{\ominus}_{p,\mathrm{m}}(T) = \alpha + \beta T + \gamma T^2$ yields $\alpha = 24.6\ \mathrm{J\,K^{-1}\,mol^{-1}}$, $\beta = 3.83 \times 10^{-2}\ \mathrm{J\,K^{-2}\,mol^{-1}}$ and $\gamma = -6.58 \times 10^{-6}\ \mathrm{J\,K^{-3}\,mol^{-1}}$. This second expression gives a slightly better fit to the data set than the first expression.

2C Thermochemistry

Answers to discussion questions

D2C.2 When a system is subjected to constant pressure conditions, and only expansion work can occur, the energy supplied as heat is the change in enthalpy of the system. Thus enthalpy changes in the system can be determined by measuring the amount of heat supplied under constant-pressure conditions.

A very simple example often encountered in elementary laboratory classes is a thermally insulated vessel (for example, a foam plastic coffee cup) left open to the atmosphere: the heat released in the reaction is determined by measuring the change in temperature of the contents.

For a combustion reaction a constant-pressure flame calorimeter (Section 2B.1(b) on page 47) may be used. In this apparatus a certain amount of substance burns in a supply of oxygen and the rise in temperature is monitored. More sophisticated methods include isothermal titration calorimetry and differential scanning calorimetry, both described in Section 2C.4 on page 56.

D2C.4 The main objection to the use of the term 'heat' to describe the energy change associated with a physical or chemical process is that heat is not a state function. The value of the heat therefore depends on the path chosen.

If, in fact, the processes being described takes place at constant pressure, the heat is equal to the enthalpy change. Because enthalpy is a state function, the heat measured under these circumstance is a property of the physical or chemical change itself, and not affected by the path taken, and so is a meaningful and useful quantity to discuss.

It is more appropriate to talk about the enthalpy change, the change in a state function, rather to talk about the heat which, because of an unstated restriction, just so happens to have the same value.

Solutions to exercises

E2C.1(b) Ethanol is vaporized at constant pressure, therefore $q = \Delta H$.

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

The work of expansion under constant pressure is given by [2A.6–*40*], $w = -p_{\text{ex}}\Delta V$. Note that $\Delta V = V_\text{f}$ because the final state (gas) has a much larger volume than the initial state (liquid). The perfect gas law is used to calculate V_f.

$$\begin{aligned} w &= -p_{\text{ex}}\Delta V = -p_{\text{ex}}(V_\text{f} - V_\text{i}) \approx -p_{\text{ex}}V_\text{f} = -p_{\text{ex}} \times \frac{nRT}{p_{\text{ex}}} = -nRT \\ &= -(1.75\ \text{mol}) \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (260\ \text{K}) = -3.78...\ \text{kJ} = \boxed{-3.78\ \text{kJ}} \end{aligned}$$

The First Law of thermodynamics [2A.2–*38*] gives

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

E2C.2(b) The chemical equation for combustion of phenol is $C_6H_6O(s) + 7\,O_2(g) \longrightarrow 6\,CO_2(g) + 3\,H_2O(l)$. The standard enthalpy of combustion is calculated using [2C.5a–*55*] and using values for the standard enthalpies of formation from Table 2C.7.

$$\begin{aligned}\Delta_c H^\ominus &= \sum_{\text{products}} \nu\Delta_f H^\ominus - \sum_{\text{reactants}} \nu\Delta_f H^\ominus \\ &= 6\Delta_f H^\ominus(CO_2,g) + 3\Delta_f H^\ominus(H_2O,l) - 7\Delta_f H^\ominus(O_2,g) - \Delta_f H^\ominus(C_6H_6O,s) \\ &= 6\times(-393.51\text{ kJ mol}^{-1}) + 3\times(-285.83\text{ kJ mol}^{-1}) \\ &\quad - 0 - (-165.0\text{ kJ mol}^{-1}) = \boxed{-3054\text{ kJ mol}^{-1}}\end{aligned}$$

E2C.3(b) The standard enthalpy of formation of HI(aq) is $\Delta_r H^\ominus$ for the reaction

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(g) \longrightarrow HI(aq)$$

Because HI is a strong acid, the reaction is effectively

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(g) \longrightarrow H^+(aq) + I^-(aq)$$

By definition, $\Delta_f H^\ominus(H^+,aq) = 0$, so $\Delta_r H^\ominus$ for this reaction is $\Delta_f H^\ominus(I^-,aq)$.

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

E2C.4(b) The equation for combustion of anthracene is $C_{14}H_{10}(s) + \frac{33}{2}O_2(g) \longrightarrow 14\,CO_2(g) + 5\,H_2O(l)$. In a bomb calorimeter the heat is at constant volume and is given by $q_V = n\Delta_c U^\ominus$. $\Delta_c U^\ominus$ is related to $\Delta_c H^\ominus$ by [2B.3–*48*], $\Delta_r H^\ominus = \Delta_r U^\ominus + \Delta n_g RT$, where Δn_g is the change in the amount of gas molecules in the reaction. In this case $\Delta n_g = 16.5\text{ mol} - 14\text{ mol} = -2.5\text{ mol}$, hence

$$\begin{aligned}\Delta_c U^\ominus &= \Delta_c H^\ominus - \Delta n_g RT \\ &= (-7.06...\times 10^6\text{ J}) - (-2.5\text{ mol})\times(8.3145\text{ J K}^{-1}\text{ mol}^{-1})\times(298\text{ K}) \\ &= -7.05...\times 10^3\text{ kJ mol}^{-1}\end{aligned}$$

The heat released in the bomb calorimeter on combustion of 2.25 mg of anthracene ($M = 178.219\text{ g mol}^{-1}$) is

$$q_V = n\Delta_c U^\ominus = \left(\frac{2.25\times 10^{-3}\text{ g}}{178.219\text{ g mol}^{-1}}\right)\times(-7.05...\times 10^3\text{ kJ mol}^{-1}) = -8.90...\times 10^{-2}\text{ kJ}$$

Therefore the calorimeter constant is

$$C = \frac{|q_V|}{\Delta T} = \frac{(8.90...\times 10^{-2}\text{ kJ})}{(1.75\text{ K})} = 5.08...\times 10^{-2}\text{ kJ K}^{-1} = \boxed{5.09\times 10^{-2}\text{ kJ K}^{-1}}$$

The chemical equation for combustion of phenol is $C_6H_6O(s) + 7\,O_2(g) \longrightarrow 6\,CO_2(g) + 3\,H_2O(l)$. Following the same logic as above, $\Delta_c H^\ominus = -3054\text{ kJ mol}^{-1}$,

$\Delta n_g = -1$ mol and $\Delta_c U^\ominus = -3.05... \times 10^3\ \text{kJ mol}^{-1}$. The heat released on combustion of 125 mg of phenol ($M = 94.10\ \text{g mol}^{-1}$) is

$$q_V = n\Delta_c U^\ominus = \left(\frac{0.125\ \text{g}}{94.1074\ \text{g mol}^{-1}}\right) \times (-3.05... \times 10^3\ \text{kJ mol}^{-1}) = -4.05...\ \text{kJ}$$

Therefore $\Delta T = |q_V|/C = (4.05...\ \text{kJ})/(5.08... \times 10^{-2}\text{kJ K}^{-1}) = \boxed{+79.6\ \text{K}}$

E2C.5(b) (i) Reaction(3) is reaction(2) − 2 × reaction(1), therefore

$$\begin{aligned}\Delta_r H^\ominus(3) &= \Delta_r H^\ominus(2) - 2\Delta_r H^\ominus(1)\\ &= (-483.64\ \text{kJ mol}^{-1}) - 2 \times (+52.96\ \text{kJ mol}^{-1})\\ &= \boxed{-589.56\ \text{kJ mol}^{-1}}\end{aligned}$$

The relationship between $\Delta_r H$ and $\Delta_r U$ is given by [2B.3–*48*], $\Delta_r H = \Delta_r U + \Delta n_g RT$ where Δn_g is the change in the amount of gas molecules in the reaction. For this reaction $\Delta n_g = 2\ \text{mol} + 2\ \text{mol} - 4\ \text{mol} - 1\ \text{mol} = -1\ \text{mol}$

$$\begin{aligned}\Delta_r U^\ominus &= \Delta_r H^\ominus - \Delta n_g RT\\ &= (-589.56 \times 10^3\ \text{J mol}^{-1})\\ &\quad - (-3.0\ \text{mol}) \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K}) = \boxed{-582\ \text{kJ mol}^{-1}}\end{aligned}$$

(ii) Reaction(1) represents the formation of 2 moles of HI(g) from its elements in their reference states, therefore the standard enthalpy of formation of HI(g) is

$$\Delta_f H^\ominus(\text{HI, g}) = \tfrac{1}{2}\Delta_r H^\ominus(1) = \tfrac{1}{2} \times (+52.96\ \text{kJ mol}^{-1}) = \boxed{+26.48\ \text{kJ mol}^{-1}}$$

Reaction(2) represents the formation of 2 moles of H_2O(g) from its elements in their reference states, therefore

$$\Delta_f H^\ominus(\text{H}_2\text{O, g}) = \tfrac{1}{2}\Delta_r H^\ominus(2) = \tfrac{1}{2}\times(-483.64\ \text{kJ mol}^{-1}) = \boxed{-241.82\ \text{kJ mol}^{-1}}$$

E2C.6(b) The relationship between $\Delta_r H$ and $\Delta_r U$ is given by [2B.3–*48*], $\Delta_r H = \Delta_r U + \Delta n_g RT$ where Δn_g is the change in the amount of gas molecules in the reaction. For this reaction $\Delta n_g = 14\ \text{mol} + 6\ \text{mol} - 15\ \text{mol} = +5\ \text{mol}$

$$\begin{aligned}\Delta_r H^\ominus &= \Delta_r U^\ominus + \Delta n_g RT\\ &= (-772.7 \times 10^3\ \text{J mol}^{-1}) + (+5.0\ \text{mol}) \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K})\\ &= \boxed{-760.3\ \text{kJ mol}^{-1}}\end{aligned}$$

E2C.7(b) The following reactions are used to construct a thermodynamic cycle which gives the standard enthalpy of hydrogenation of ethyne to ethene.

	reaction	$\Delta_r H^\ominus/\mathrm{kJ\,mol^{-1}}$
(1)	$C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l)$	−1300
(2)	$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$	−1411
(3)	$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$	−285.83
(4)	$C_2H_2(g) + H_2(g) \longrightarrow C_2H_4(g)$	$\Delta_r H^\ominus(4)$

$$\begin{aligned}\Delta_r H^\ominus(4) &= \Delta_r H^\ominus(1) + \Delta_r H^\ominus(3) - \Delta_r H^\ominus(2)\\ &= (-1300\,\mathrm{kJ\,mol^{-1}}) + (-285.83\,\mathrm{kJ\,mol^{-1}}) - (-1411\,\mathrm{kJ\,mol^{-1}})\\ &= \boxed{-174.83\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

The relationship between $\Delta_r H$ and $\Delta_r U$ is given by [2B.3–*48*], $\Delta_r H = \Delta_r U + \Delta n_g RT$ where Δn_g is the change in the amount of gas molecules in the reaction. For this reaction $\Delta n_g = 1\text{ mol} - 1\text{ mol} - 1\text{ mol} = -1\text{ mol}$

$$\begin{aligned}\Delta_r U^\ominus(298\text{ K}) &= \Delta_r H^\ominus(298\text{ K}) - \Delta n_g RT\\ &= (-174.83\times10^3\,\mathrm{J\,mol^{-1}}) - (-1.0\text{ mol})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\\ &\quad\times(298\text{ K}) = \boxed{-172\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

The difference of the molar heat capacities of products and reactants is calculated using [2C.7b–*55*] and the corresponding heat capacity data from the *Resource section*

$$\begin{aligned}\Delta_r C_p^\ominus &= \sum_{\text{products}} \nu C_{p,\mathrm{m}}^\ominus - \sum_{\text{reactants}} \nu C_{p,\mathrm{m}}^\ominus\\ &= C_{p,\mathrm{m}}^\ominus(C_2H_4,g) - C_{p,\mathrm{m}}^\ominus(C_2H_2,g) - C_{p,\mathrm{m}}^\ominus(H_2,g)\\ &= (43.56\,\mathrm{J\,K^{-1}\,mol^{-1}}) - (43.93\,\mathrm{J\,K^{-1}\,mol^{-1}}) - (28.824\,\mathrm{J\,K^{-1}\,mol^{-1}})\\ &= -29.1...\,\mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

It is assumed that all heat capacities are constant over the temperature range of interest, therefore the integrated form of Kirchhoff's Law is applicable, [2C.7d–*56*]

$$\begin{aligned}\Delta_r H^\ominus(427\text{ K}) &= \Delta_r H^\ominus(298\text{ K}) + \Delta T\Delta_r C_p^\ominus\\ &= (-174.83\times10^3\,\mathrm{J\,mol^{-1}})\\ &\quad + (427\text{ K} - 298\text{ K})\times(-29.1...\,\mathrm{J\,K^{-1}\,mol^{-1}}) = \boxed{-179\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

E2C.8(b) The reaction equation $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$ represents the formation of $NH_3(g)$ from its elements in their reference states, therefore $\Delta_r H^\ominus(298\,\mathrm{K}) = \Delta_f H^\ominus(NH_3,g) = -46.11\,\mathrm{kJ\,mol^{-1}}$. The variation of standard reaction enthalpy with temperature is given by Kirchhoff's Law, [2C.7a–*55*]

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\ominus\,\mathrm{d}T$$

The difference of the molar heat capacities of products and reactants is given by [2C.7b–*55*]

$$\begin{aligned}\Delta_r C_p^\ominus &= \sum_{\text{products}} \nu C_{p,m}^\ominus - \sum_{\text{reactants}} \nu C_{p,m}^\ominus \\ &= C_{p,m}^\ominus(\mathrm{NH_3,g}) - \tfrac{3}{2}C_{p,m}^\ominus(\mathrm{H_2,g}) - \tfrac{1}{2}C_{p,m}^\ominus(\mathrm{N_2,g})\end{aligned}$$

The heat capacities in Table 2B.1 are expressed in the form of $C_{p,m}^\ominus = a + bT + c/T^2$ therefore $\Delta_r C_p^\ominus = \Delta a + \Delta bT + \Delta c/T^2$ where $\Delta a = a(\mathrm{NH_3,g}) - \frac{3}{2}a(\mathrm{H_2,g}) - \frac{1}{2}a(\mathrm{N_2,g})$ and likewise for Δb and Δc.

$$\begin{aligned}\Delta a &= (29.75\ \mathrm{J\,K^{-1}\,mol^{-1}}) - \tfrac{3}{2}\times(27.28\ \mathrm{J\,K^{-1}\,mol^{-1}}) - \tfrac{1}{2}\times(28.58\ \mathrm{J\,K^{-1}\,mol^{-1}}) \\ &= -25.46\ \mathrm{J\,K^{-1}\,mol^{-1}} \\ \Delta b &= (25.1\times10^{-3}\ \mathrm{J\,K^{-2}\,mol^{-1}}) - \tfrac{3}{2}\times(3.26\times10^{-3}\ \mathrm{J\,K^{-2}\,mol^{-1}}) \\ &\quad - \tfrac{1}{2}\times(3.77\times10^{-3}\ \mathrm{J\,K^{-2}\,mol^{-1}}) = +18.325\times10^{-3}\ \mathrm{J\,K^{-2}\,mol^{-1}} \\ \Delta c &= (-1.55\times10^{5}\ \mathrm{J\,K\,mol^{-1}}) - \tfrac{3}{2}\times(0.50\times10^{5}\ \mathrm{J\,K\,mol^{-1}}) \\ &\quad - \tfrac{1}{2}\times(-0.50\times10^{5}\ \mathrm{J\,K\,mol^{-1}}) = -2.05\times10^{5}\ \mathrm{J\,K\,mol^{-1}}\end{aligned}$$

Integrating Kirchhoff's Law gives

$$\begin{aligned}\Delta_r H^\ominus(T_2) &= \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2}\left(\Delta a + \Delta bT + \frac{\Delta c}{T^2}\right)\mathrm{d}T \\ &= \Delta_r H^\ominus(T_1) + \Delta a(T_2 - T_1) + \tfrac{1}{2}\Delta b(T_2^2 - T_1^2) - \Delta c\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\ &= (-46.11\times10^{3}\ \mathrm{J\,mol^{-1}}) + (-25.46\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(750\ \mathrm{K} - 298\ \mathrm{K}) \\ &\quad + \tfrac{1}{2}\times(+18.325\times10^{-3}\ \mathrm{J\,K^{-2}\,mol^{-1}})\times[(750\ \mathrm{K})^2 - (298\ \mathrm{K})^2] \\ &\quad - (-2.05\times10^{5}\ \mathrm{J\,K\,mol^{-1}})\times\left(\frac{1}{750\ \mathrm{K}} - \frac{1}{298\ \mathrm{K}}\right) \\ &= \boxed{-53.7\ \mathrm{kJ\,mol^{-1}}}\end{aligned}$$

Solutions to problems

P2C.2 The combustion equation for octane is $\mathrm{C_8H_{18}(l) + 12.5\,O_2(g) \longrightarrow 8\,CO_2(g) + 9\,H_2O(l)}$. The standard enthalpy of combustion of octane is given in Table 2C.6 as $-5471\ \mathrm{kJ\,mol^{-1}}$. The amount in moles in $1.0\ \mathrm{dm^3}$ octane is

$$n = \frac{m}{M} = \frac{\rho V}{M} = \frac{(0.703\ \mathrm{g\,cm^{-3}})\times(1.0\times10^{3}\ \mathrm{cm^3})}{(114.2222\ \mathrm{g\,mol^{-1}})} = 6.15...\ \mathrm{mol}$$

The heat is

$$q_\mathrm{p} = n\Delta_c H^\ominus = (6.15...\ \mathrm{mol})\times(-5471\ \mathrm{kJ\,mol^{-1}}) = \boxed{3.4\times10^{4}\ \mathrm{kJ}}$$

P2C.4 $\Delta_f H^\ominus(\mathrm{B_2H_6,g})$ is the standard enthalpy change of $\mathrm{2\,B(s) + 3\,H_2(g) \longrightarrow B_2H_6(g)}$. This reaction is 3 × reaction(3) + reaction(2) − reaction(1) = reaction(4), and so

$$\Delta_f H^\ominus(B_2H_6,g) = 3\Delta_r H^\ominus(3) + \Delta_r H^\ominus(2) - \Delta_r H^\ominus(1)$$
$$\Delta_f H^\ominus(B_2H_6,g) = 3\times(-241.8\ \text{kJ mol}^{-1}) + (-2368\ \text{kJ mol}^{-1}) - (-1941\ \text{kJ mol}^{-1})$$
$$= \boxed{-1152.4\ \text{kJ mol}^{-1}}$$

P2C.6 The relationship between $\Delta_r H$ and $\Delta_r U$ is given by [2B.3–*48*], $\Delta_r H = \Delta_r U + \Delta n_g RT$ where Δn_g is the change in the amount of gas molecules in the reaction. For this reaction $\Delta n_g = 2\ \text{mol} - 0\ \text{mol} = +2\ \text{mol}$

$$\begin{aligned}\Delta_r H^\ominus &= \Delta_r U^\ominus + \Delta n_g RT\\ &= (+8.0\times10^3\ \text{J mol}^{-1}) + (2.0\ \text{mol})\times(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(583\ \text{K})\\ &= 17.6...\ \text{kJ mol}^{-1} = \boxed{+18\ \text{kJ mol}^{-1}}\end{aligned}$$

Applying [2C.5a–*55*] to this reaction gives

$$\Delta_r H^\ominus = 2\Delta_f H^\ominus(C_6H_6,g) + \Delta_f H^\ominus(\text{Cr},s) - \Delta_f H^\ominus(\text{Cr}(C_6H_6)_2,s)$$

The standard enthalpies of formation of elements in their reference states are zero at *all* temperatures, therefore $\Delta_f H^\ominus(\text{Cr},s,583\ \text{K}) = \Delta_f H^\ominus(\text{Cr},s,298\ \text{K}) = 0$. $\Delta_f H^\ominus(C_6H_6,g,298\ \text{K})$ is equal to $\Delta_r H^\ominus$ of the reaction $6\,\text{C}(s) + 3\,H_2(g) \longrightarrow C_6H_6(g)$ at 298 K. The difference of the molar heat capacities of products and reactants of this reaction is calculated using [2C.7b–*55*] and data from Table 2C.7

$$\begin{aligned}\Delta_r C_p^\ominus &= \sum_{\text{products}} \nu C_{p,\text{m}}^\ominus - \sum_{\text{reactants}} \nu C_{p,\text{m}}^\ominus\\ &= C_{p,\text{m}}^\ominus(C_6H_6,g) - 3C_{p,\text{m}}^\ominus(H_2,g) - 6C_{p,\text{m}}^\ominus(\text{graphite},s)\\ &= (81.67\ \text{J K}^{-1}\ \text{mol}^{-1}) - 3\times(28.824\ \text{J K}^{-1}\ \text{mol}^{-1}) - 6\times(8.527\ \text{J K}^{-1}\ \text{mol}^{-1})\\ &= -55.9...\ \text{J K}^{-1}\ \text{mol}^{-1}\end{aligned}$$

Assuming that $\Delta_r C_p^\ominus$ is independent of temperature in the given range, using data from Table 2C.6 and applying Kirchhoff's Law [2C.7d–*56*] gives

$$\begin{aligned}\Delta_f H^\ominus(C_6H_6,g,583\ \text{K}) &= \Delta_r H^\ominus(583\ \text{K}) + \Delta_r H^\ominus(298\ \text{K}) + \Delta T\Delta_r C_p^\ominus\\ &= (+82.93\times10^3\ \text{J mol}^{-1}) + (583\ \text{K} - 298\ \text{K})\\ &\quad\times(-55.9...\ \text{J K}^{-1}\ \text{mol}^{-1}) = +66.9...\ \text{kJ mol}^{-1}\end{aligned}$$

Therefore the standard enthalpy of formation of the chromium complex at 583 K is

$$\begin{aligned}\Delta_f H^\ominus(\text{Cr}(C_6H_6)_2,s,583\ \text{K}) &= 2\Delta_f H^\ominus(C_6H_6,g,583\ \text{K}) + \Delta_f H^\ominus(\text{Cr},s) - \Delta_r H^\ominus\\ &= 2\times(+66.9...\ \text{kJ mol}^{-1}) + 0 - (+17.6...\ \text{kJ mol}^{-1})\\ &= \boxed{+116\ \text{kJ mol}^{-1}}\end{aligned}$$

P2C.8 (a) Using [2C.5a–*55*] and the values for the standard enthalpies of formation given in the problem

$$\begin{aligned}\Delta_r H^\ominus &= \sum_{\text{products}} \nu\Delta_f H^\ominus - \sum_{\text{reactants}} \nu\Delta_f H^\ominus\\ &= \Delta_f H^\ominus(\text{SiH}_2,\text{g}) + \Delta_f H^\ominus(\text{H}_2,\text{g}) - \Delta_f H^\ominus(\text{SiH}_4,\text{g})\\ &= (+274\ \text{kJ mol}^{-1}) + 0 - (+34.3\ \text{kJ mol}^{-1}) = \boxed{+239.7\ \text{kJ mol}^{-1}}\end{aligned}$$

(b) Similarly to part (a)

$$\begin{aligned}\Delta_r H^\ominus &= \Delta_f H^\ominus(\text{SiH}_2,\text{g}) + \Delta_f H^\ominus(\text{SiH}_4,\text{g}) - \Delta_f H^\ominus(\text{Si}_2\text{H}_6,\text{g})\\ &= (+274\ \text{kJ mol}^{-1}) + (+34.3\ \text{kJ mol}^{-1}) - (+80.3\ \text{kJ mol}^{-1})\\ &= \boxed{+228.0\ \text{kJ mol}^{-1}}\end{aligned}$$

P2C.10 The enthalpy change is found using [2C.9–*57*], $\Delta H = \int_{T_1}^{T_2} C_{p,\text{ex}}\,\text{d}T$, where $C_{p,\text{ex}}$ is the excess heat capacity reported by the instrument. The integral is the area under the trace, which is estimated to be 230 mJ: this is the estimate for ΔH.

From the data given the amount in moles in the sample volume of 0.80 cm^3 is $(0.80\ \text{cm}^3) \times (2.17 \times 10^{-3}\ \text{g cm}^{-3})/(14.3 \times 10^3\ \text{g mol}^{-1}) = 1.21... \times 10^{-7}$ mol. The molar enthalpy of unfolding is therefore

$$\Delta H_\text{m} = (230 \times 10^{-3}\ \text{J})/(1.21... \times 10^{-7}\ \text{mol}) = \boxed{1.9 \times 10^3\ \text{kJ mol}^{-1}}$$

2D State functions and exact differentials

Answers to discussion questions

D2D.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.4 on page 64, 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

E2D.1(b) The molar volume of a perfect gas at 298 K is calculated as

$$V_\text{m} = \frac{RT}{p} = \frac{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K})}{(1.00\ \text{bar}) \times [(10^5\ \text{Pa})/(1.00\ \text{bar})]} = 2.47... \times 10^{-2}\ \text{m}^3\ \text{mol}^{-1}$$

The van der Waals parameter a of sulfur dioxide is found in Table 1C.3, and needs to be converted to SI units

$$a = (6.775\ \mathrm{dm^6\,atm\,mol^{-2}}) \times \left(\frac{10^{-6}\ \mathrm{m^6}}{1\ \mathrm{dm^6}}\right) \times \left(\frac{1.01325\times10^5\ \mathrm{Pa}}{1\ \mathrm{atm}}\right)$$
$$= 0.686...\ \mathrm{m^6\,Pa\,mol^{-2}}$$

Therefore the internal pressure is

$$\pi_T = \frac{a}{V_\mathrm{m}^2} = \frac{(0.686...\ \mathrm{m^6\,Pa\,mol^{-2}})}{(2.47...\times10^{-2}\ \mathrm{m^3\,mol^{-1}})^2} = \boxed{1.12\times10^3\ \mathrm{Pa}}$$

E2D.2(b) The internal energy of a closed system of constant composition is a function of temperature and volume. For a change in V and T, $\mathrm{d}U$ is given by [2D.5–*61*], $\mathrm{d}U = \pi_T\mathrm{d}V + C_V\mathrm{d}T$. At constant temperature, this reduces to $\mathrm{d}U = \pi_T\mathrm{d}V$. Substituting in the given expression for π_T for a van der Waals gas and using molar quantities

$$\mathrm{d}U_\mathrm{m} = \frac{a}{V_\mathrm{m}^2}\mathrm{d}V_\mathrm{m}$$

This expression is integrated between $V_\mathrm{m,i}$ and $V_\mathrm{m,f}$ to give

$$\int_{V_\mathrm{m,i}}^{V_\mathrm{m,f}} \mathrm{d}U_\mathrm{m} = \int_{V_\mathrm{m,i}}^{V_\mathrm{m,f}} \frac{a}{V_\mathrm{m}^2}\mathrm{d}V_\mathrm{m}$$

hence

$$\Delta U_\mathrm{m} = -\left.\frac{a}{V_\mathrm{m}^2}\right|_{V_\mathrm{m,i}}^{V_\mathrm{m,f}} = -a\left(\frac{1}{V_\mathrm{m,f}} - \frac{1}{V_\mathrm{m,i}}\right)$$

The van der Waals parameter a for argon is found in Table 1C.3, and needs to be converted to SI units

$$a = (1.337\ \mathrm{dm^6\,atm\,mol^{-2}}) \times \left(\frac{10^{-6}\ \mathrm{m^6}}{1\ \mathrm{dm^6}}\right) \times \left(\frac{1.01325\times10^5\ \mathrm{Pa}}{1\ \mathrm{atm}}\right)$$
$$= 0.135...\ \mathrm{m^6\,Pa\,mol^{-2}}$$

$$\Delta U_\mathrm{m} = -(0.135...\ \mathrm{m^6\,Pa\,mol^{-2}})\left(\frac{1}{30.00\times10^{-3}\ \mathrm{m^3\,mol^{-1}}} - \frac{1}{1.00\times10^{-3}\ \mathrm{m^3\,mol^{-1}}}\right)$$
$$= +1.30...\times10^2\ \mathrm{J\,mol^{-1}} = \boxed{+131\ \mathrm{J\,mol^{-1}}}$$

The work done by an expanding gas is given by [2A.5a–*39*], $\mathrm{d}w = -p_\mathrm{ex}\mathrm{d}V$. For a reversible expansion p_ex is the pressure of the gas, hence

$$w = -\int p\mathrm{d}V_\mathrm{m}$$

Substituting in the expression for the pressure of a van der Waals gas, [1C.5b–*24*]

$$w = -\int \frac{RT}{V_\mathrm{m}-b} - \frac{a}{V_\mathrm{m}^2}\,\mathrm{d}V_\mathrm{m} = -\int \frac{RT}{V_\mathrm{m}-b}\mathrm{d}V_\mathrm{m} + \int \frac{a}{V_\mathrm{m}^2}\mathrm{d}V_\mathrm{m}$$
$$= -\int \frac{RT}{V_\mathrm{m}-b}\mathrm{d}V_\mathrm{m} + \Delta U_\mathrm{m}$$

The second term is identified as ΔU_m from the above. According to the First Law, $\Delta U = q + w$, the first term in the expression above must be $-q$, therefore

$$q = \int_{V_\mathrm{m,i}}^{V_\mathrm{m,f}} \frac{RT}{V_\mathrm{m} - b}\,\mathrm{d}V_\mathrm{m} = RT\ln(V_\mathrm{m} - b)\big|_{V_\mathrm{m,i}}^{V_\mathrm{m,f}} = RT\ln\left(\frac{V_\mathrm{m,f} - b}{V_\mathrm{m,i} - b}\right)$$

$$= (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K}) \times \ln\left(\frac{30.00\,\mathrm{dm^3} - 3.20 \times 10^{-2}\,\mathrm{dm^3}}{1.00\,\mathrm{dm^3} - 3.20 \times 10^{-2}\,\mathrm{dm^3}}\right)$$

$$= +8.50... \times 10^3\,\mathrm{J\,mol^{-1}} = \boxed{+8.51\,\mathrm{kJ\,mol^{-1}}}$$

where the value for b is taken from the Resource section. From the First Law the work done is $w = -q + \Delta U_\mathrm{m}$, hence

$$w = -q + \Delta U_\mathrm{m} = -8.50... \times 10^3\,\mathrm{J\,mol^{-1}} + 1.30... \times 10^2\,\mathrm{J\,mol^{-1}} = \boxed{-8.37\,\mathrm{kJ\,mol^{-1}}}$$

E2D.3(b) The volume of the liquid can be written as

$$V = V'(a + bT + cT^2)$$

where $a = 0.77$, $b = 3.7 \times 10^{-4}\,\mathrm{K^{-1}}$ and $c = 1.52 \times 10^{-6}\,\mathrm{K^{-2}}$. The expansion coefficient is defined in [2D.6–62] as $\alpha = (1/V)(\partial V/\partial T)_p$. The derivative with respect to T is

$$\left(\frac{\partial V}{\partial T}\right)_p = V'(b + 2cT)$$

Therefore

$$\alpha = \frac{1}{V'(a + bT + cT^2)} \times [V'(b + 2cT)] = \frac{b + 2cT}{a + bT + cT^2}$$

Evaluating this expression at 310 K gives

$$\alpha_{310} = \frac{(3.7 \times 10^{-4}\,\mathrm{K^{-1}}) + 2 \times (1.52 \times 10^{-6}\,\mathrm{K^{-2}}) \times (310\,\mathrm{K})}{(0.77) + (3.7 \times 10^{-4}\,\mathrm{K^{-1}}) \times (310\,\mathrm{K}) + (1.52 \times 10^{-6}\,\mathrm{K^{-2}}) \times (310\,\mathrm{K})^2}$$

$$= \boxed{+1.3 \times 10^{-3}\,\mathrm{K^{-1}}}$$

E2D.4(b) The isothermal compressibility is defined in [2D.7–62], $\kappa_T = -(1/V)(\partial V/\partial p)_T$, therefore at constant temperature $\mathrm{d}V/V = -\kappa_T\mathrm{d}p$. This question is concerned with changes in density, so the next step is to rewrite the volume in terms of the density, ρ. If the mass is m, $V = m/\rho$, and therefore $\mathrm{d}V = (-m/\rho^2)\mathrm{d}\rho$. Therefore

$$\frac{\mathrm{d}V}{V} = \frac{1}{V}\left(-\frac{m}{\rho^2}\mathrm{d}\rho\right) = -\left(\frac{\rho}{m}\right)\left(\frac{m}{\rho^2}\right)\mathrm{d}\rho = -\frac{1}{\rho}\mathrm{d}\rho$$

It therefore follows that

$$\frac{\mathrm{d}\rho}{\rho} = \kappa_T\mathrm{d}p \quad \text{and hence} \quad \mathrm{d}p = \frac{1}{\kappa_T\rho}\mathrm{d}\rho$$

This expression gives the relationship between the change in pressure and the change in density. Approximating $\mathrm{d}\rho$ by $\delta\rho$ and $\mathrm{d}p$ by δp for sufficiently small changes gives

$$\delta p = \frac{1}{\kappa_T} \times \frac{\delta\rho}{\rho} = \left(\frac{1}{2.21 \times 10^{-6}\ \mathrm{atm}^{-1}}\right) \times (1.0 \times 10^{-3}) = \boxed{+4.5 \times 10^{2}\ \mathrm{atm}}$$

E2D.5(b) The difference $C_{p,\mathrm{m}} - C_{V,\mathrm{m}}$ is given by [2D.11–*63*], $C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = \alpha^2 T V_\mathrm{m}/\kappa_T$. In this expression the molar volume is found from the mass density ρ and the molar mass M by $V_\mathrm{m} = M/\rho$. The values of α and κ are available in the *Resource section*, as is the mass density.

$$\begin{aligned} C_{p,\mathrm{m}} - C_{V,\mathrm{m}} &= \frac{\alpha^2 T V_\mathrm{m}}{\kappa_T} = \frac{\alpha^2 T M}{\kappa_T \rho} \\ &= \frac{(11.2 \times 10^{-4}\ \mathrm{K}^{-1})^2 \times (298\ \mathrm{K}) \times (46.0674\ \mathrm{g\,mol}^{-1})}{[(76.8 \times 10^{-6}\ \mathrm{bar}) \times (1\ \mathrm{bar}/10^5\ \mathrm{Pa})] \times (0.789 \times 10^6\ \mathrm{g\,m}^{-3})} \\ &= \boxed{+28.4\ \mathrm{J\,K}^{-1}\,\mathrm{mol}^{-1}} \end{aligned}$$

The units are $\mathrm{K}^{-1}\,\mathrm{Pa\,m}^3\,\mathrm{mol}^{-1} = \mathrm{K}^{-1}\,(\mathrm{N\,m}^{-2})\,\mathrm{m}^3\,\mathrm{mol}^{-1} = \mathrm{K}^{-1}\,\mathrm{N\,m\,mol}^{-1}$ $= \mathrm{J\,K}^{-1}\,\mathrm{mol}^{-1}$

Solutions to problems

P2D.2 The pressure p is a function of T and V, therefore according to the Euler chain relation and the reciprocal identity

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

Substituting this into the expression given for $C_p - C_V$ gives

$$\begin{aligned} C_p - C_V &= T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p = -T\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial V}{\partial T}\right)_p \\ &= -\frac{T(\partial V/\partial T)_p^2}{(\partial V/\partial p)_T} \end{aligned}$$

For a perfect gas $pV = nRT$, therefore

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

It follows that

$$C_p - C_V = -\frac{T(nR/p)^2}{(-nRT/p^2)} = nR$$

which is the expected result quoted in [2B.9–*49*].

P2D.4 Rearranging the van der Waals equation of state to give T as a function of p and V gives

$$T = \frac{p(V-nb)}{nR} + \frac{na(V-nb)}{V^2R}$$

The partial differentials are

$$\left(\frac{\partial T}{\partial p}\right)_V = \frac{V-nb}{nR} \quad \text{and} \quad \left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V-nb}$$

As expected, these two partial differentials are the reciprocals of each other.

$$\left(\frac{\partial T}{\partial p}\right)_V = \frac{1}{(\partial p/\partial T)_V}$$

P2D.6 From the perfect gas law, [1A.4–8], $pV = nRT$. Writing $n = m/M$, where m is the mass, it follows that

$$pV = \frac{m}{M}RT \quad \text{and hence} \quad \frac{RT}{M} = \frac{pV}{m}$$

The mass density, ρ is $\rho = m/V$, therefore $(RT/M) = \rho/p$.

$$c_s = \left(\frac{\gamma RT}{M}\right)^{1/2} = \left(\frac{\gamma p}{\rho}\right)^{1/2}$$

For argon, a monoatomic gas, $C_{V,\mathrm{m}} = \frac{3}{2}R$ and $C_{p,\mathrm{m}} = \frac{5}{2}R$ therefore $\gamma = C_{p,\mathrm{m}}/C_{V,\mathrm{m}} = 5/3$.

$$c_s = \left(\frac{\frac{5}{3} \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298.15\,\mathrm{K})}{(39.95 \times 10^{-3}\,\mathrm{kg\,mol^{-1}})}\right)^{1/2} = \boxed{322\,\mathrm{m\,s^{-1}}}$$

P2D.8 In *How is that done?* 2D.1 on page 63 is is shown that

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

An expression for $(\partial H/\partial p)_T$ is developed as follows

$$\begin{aligned}
\left(\frac{\partial H}{\partial p}\right)_T &= \left(\frac{\partial H}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T \quad [\text{change of variable}]\\
&= \left(\frac{\partial (U+pV)}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T \quad [\text{definition of } H]\\
&= \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T + \left(\frac{\partial (pV)}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T\\
&= \left\{T\left(\frac{\partial p}{\partial T}\right)_V - p\right\}\left(\frac{\partial V}{\partial p}\right)_T + \left(\frac{\partial (pV)}{\partial p}\right)_T \left[\quad \text{equation for } \left(\frac{\partial U}{\partial V}\right)_T\right]\\
&= T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial p}\right)_T - p\left(\frac{\partial V}{\partial p}\right)_T + V + p\left(\frac{\partial V}{\partial p}\right)_T\\
&= T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial p}\right)_T + V = \frac{-T}{(\partial T/\partial V)_p} + V \quad [\text{chain relation}]\\
&= -T\left(\frac{\partial V}{\partial T}\right)_p + V \quad [\text{reciprocal identity}]
\end{aligned}$$

With this result

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

In order to compute the partial derivative $(\partial V/\partial T)_p$ it is convenient to take the van der Waals equation and re-express it in the form of a virial expansion

$$p = \frac{RT}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}^2} = \frac{RT}{V_\mathrm{m}}\left(\frac{1}{1 - b/V_\mathrm{m}} - \frac{a}{RTV_\mathrm{m}}\right)$$

Assuming $b/V_\mathrm{m} \ll 1$, the first fraction can be approximated using $(1 - x)^{-1} \approx 1 + x$

$$\begin{aligned}
p &= \frac{RT}{V_\mathrm{m}}\left(1 + \frac{b}{V_\mathrm{m}} - \frac{a}{RTV_\mathrm{m}}\right)\\
\text{hence } V_\mathrm{m} &= \frac{RT}{p}\left(1 + \frac{b}{V_\mathrm{m}} - \frac{a}{RTV_\mathrm{m}}\right) = RT\left(\frac{1}{p} + \frac{b}{pV_\mathrm{m}} - \frac{a}{RTpV_\mathrm{m}}\right)
\end{aligned}$$

Within the parentheses the perfect gas equation is used to approximate $pV_\mathrm{m} = RT$

$$V_\mathrm{m} = RT\left(\frac{1}{p} + \frac{b}{RT} - \frac{a}{R^2T^2}\right) = \frac{RT}{p} + b - \frac{a}{RT}$$

It is now straightforward to compute the required partial derivative

$$\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p = \frac{R}{p} + \frac{a}{RT^2}$$

Using this in the expression above for μ and switching to molar quantities

$$\mu = \frac{1}{C_{p,\mathrm{m}}}\left(T\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p - V_\mathrm{m}\right) = \frac{1}{C_{p,\mathrm{m}}}\left(T\left[\frac{R}{p}+\frac{a}{RT^2}\right]-V_\mathrm{m}\right)$$

The above expression for V_m is used once more

$$\begin{aligned}\mu &= \frac{1}{C_{p,\mathrm{m}}}\left(T\left[\frac{R}{p}+\frac{a}{RT^2}\right]-\left\{\frac{RT}{p}+b-\frac{a}{RT}\right\}\right)\\ &= \frac{1}{C_{p,\mathrm{m}}}\left(\frac{RT}{p}+\frac{a}{RT}-\frac{RT}{p}-b+\frac{a}{RT}\right)\\ &= \frac{1}{C_{p,\mathrm{m}}}\left(\frac{2a}{RT}-b\right)\end{aligned}$$

which is the required result.

2E Adiabatic changes

Answers to discussion questions

D2E.2 In an adiabatic expansion the system does work but as no energy as heat is permitted to enter the system, the internal energy of the system falls and so consequently does the temperature. From the First Law, $\Delta U = w$ because $q = 0$. However, the change in internal energy is also related to the temperature change and the heat capacity: $\Delta U = C_V \Delta T$. Equating these two expressions for ΔU gives $w = C_V\Delta T$, or $\mathrm{d}w = C_V \mathrm{d}T$ for an infinitesimal change.

For a reversible expansion, the work is $\mathrm{d}w = -p\mathrm{d}V$. Equating these two expressions for the work gives $-p\mathrm{d}V = C_V\mathrm{d}T$. This equation is the point from which the relationships between pressure, volume and temperature for a reversible adiabatic expansion are found: the heat capacity comes into the final expressions via this route.

In words, the key thing here is that in an adiabatic process there is a change in temperature, so it is not surprising that the properties of such a process are related to the heat capacity because this quantity relates the energy and the temperature rise.

Solutions to exercises

E2E.1(b) Carbon dioxide is a linear polyatomic molecule which has three degrees of translational and two degrees of rotational freedom. From the equipartition theorem

$$C_{V,\mathrm{m}} = \tfrac{1}{2}\times(\nu_\mathrm{t}+\nu_\mathrm{r}+2\nu_\mathrm{v})\times R$$

where ν_t is the number of translational degrees of freedom, ν_r is the number of rotational degrees of freedom and ν_v is the number of vibrational degrees of freedom.

(i) *Without any vibrational contribution:* $C_{V,\mathrm{m}} = \frac{1}{2} \times (3+2+0) \times R = \frac{5}{2}R$. For a perfect gas, [2B.9–*49*], $C_{p,\mathrm{m}} = C_{V,\mathrm{m}} + R$, therefore

$$\gamma = \frac{C_{V,\mathrm{m}} + R}{C_{V,\mathrm{m}}} = \frac{\frac{5}{2}R + R}{\frac{5}{2}R} = \frac{7}{5} \approx 1.40$$

(ii) *With the vibrational contribution:* The number of vibrational modes is $\nu_\mathrm{v} = 3N - 5$ for a linear molecule, where N is the number of atoms in the molecule. Therefore $\nu_\mathrm{v} = 3N - 5 = 4$. This gives $C_{V,\mathrm{m}} = \frac{1}{2} \times (3 + 2 + 2 \times 4) \times R = \frac{13}{2}R$ and thus $C_{p,\mathrm{m}} = \frac{15}{2}R$ and so $\gamma = 15/13 \approx 1.15$.

The experimental value of γ for carbon dioxide is

$$\gamma = \frac{C_{p,\mathrm{m}}}{C_{V,\mathrm{m}}} = \frac{C_{p,\mathrm{m}}}{C_{p,\mathrm{m}} - R} = \frac{(37.11\,\mathrm{J\,K^{-1}\,mol^{-1}})}{(37.11\,\mathrm{J\,K^{-1}\,mol^{-1}}) - (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})} = 1.29$$

which is somewhat closer to the value expected if vibration is neglected, but does not match that value closely. This indicates that vibrations may be contributing somewhat - for example the lower frequency bending modes.

E2E.2(b) For a reversible adiabatic expansion the initial and final states are related by [2E.2a–*68*], $(T_\mathrm{f}/T_\mathrm{i}) = (V_\mathrm{i}/V_\mathrm{f})^{1/c}$, where $c = C_{V,\mathrm{m}}/R$. For a perfect gas $C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = R$, [2B.9–*49*], so $c = (C_{p,\mathrm{m}} - R)/R$. Using the value of $C_{p,\mathrm{m}}$ from the *Resource section* gives

$$c = \frac{(37.11\,\mathrm{J\,K^{-1}\,mol^{-1}}) - (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})} = 3.463$$

Therefore

$$T_\mathrm{f} = T_\mathrm{i}\left(\frac{V_\mathrm{i}}{V_\mathrm{f}}\right)^{\frac{1}{c}} = (298.15\,\mathrm{K}) \times \left(\frac{500\,\mathrm{cm^3}}{2.00 \times 10^3\,\mathrm{cm^3}}\right)^{\frac{1}{3.463}} = \boxed{200\,\mathrm{K}}$$

E2E.3(b) For a reversible adiabatic expansion the initial and final states are related by [2E.3–*68*], $p_\mathrm{i}V_\mathrm{i}^\gamma = p_\mathrm{f}V_\mathrm{f}^\gamma$, where γ is the ratio of heat capacities, $\gamma = C_{p,\mathrm{m}}/C_{V,\mathrm{m}}$. The initial volume of the sample is

$$V_\mathrm{i} = \frac{nRT}{p} = \frac{(2.5\,\mathrm{mol}) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (325\,\mathrm{K})}{(2.40 \times 10^5\,\mathrm{Pa})} = 2.81... \times 10^{-2}\,\mathrm{m^3}$$
$$= 28.1...\,\mathrm{dm^3}$$

For a perfect gas $C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = R$, hence

$$\gamma = \frac{C_{p,\mathrm{m}}}{C_{V,\mathrm{m}}} = \frac{C_{p,\mathrm{m}}}{C_{p,\mathrm{m}} - R} = \frac{(20.8\,\mathrm{J\,K^{-1}\,mol^{-1}})}{(20.8\,\mathrm{J\,K^{-1}\,mol^{-1}}) - (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})} = 1.66...$$

The final volume is given by

$$V_\mathrm{f} = (28.1...\,\mathrm{dm^3}) \times (2.40 \times 10^5\,\mathrm{Pa}/1.50 \times 10^5\,\mathrm{Pa})^{1/1.66...} = 37.3...\,\mathrm{dm^3} = \boxed{37\,\mathrm{dm^3}}$$

The initial and final states are also related by $(T_f/T_i) = (V_i/V_f)^{1/c}$ where $c = C_{V,m}/R$. For this gas

$$c = \frac{(20.8\,\mathrm{J\,K^{-1}\,mol^{-1}}) - (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})} = 1.50...$$

and hence

$$T_f = T_i\left(\frac{V_i}{V_f}\right)^{1/c} = (325\,\mathrm{K}) \times \left(\frac{28.1...\,\mathrm{dm^3}}{37.3\,\mathrm{dm^3}}\right)^{1/1.50...} = 2.69... \times 10^2\,\mathrm{K} = \boxed{269\,\mathrm{K}}$$

The work done by a perfect gas during adiabatic expansion is given by [2E.1–*67*]

$$\begin{aligned} w_{ad} &= C_V\Delta T = nC_{V,m}(T_f - T_i) = n(C_{p,m} - R)(T_f - T_i) \\ &= (2.5\,\mathrm{mol}) \times [(20.8\,\mathrm{J\,K^{-1}\,mol^{-1}}) - (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})] \\ &\quad \times (2.69... \times 10^2\,\mathrm{K} - 325\,\mathrm{K}) = \boxed{-1.7\,\mathrm{kJ}} \end{aligned}$$

E2E.4(b) The work done in a reversible adiabatic expansion is given by [2E.1–*67*], $w_{ad} = C_V\Delta T$. The task is to find ΔT. The initial and final states in a reversible adiabatic expansion are related by [2E.2b–*68*], $V_iT_i^c = V_fT_f^c$, where $c = C_{V,m}/R$. If the gas is assumed to be perfect, $C_{p,m} - C_{V,m} = R$ [2B.9–*49*], and so

$$c = \frac{C_{V,m}}{R} = \frac{C_{p,m} - R}{R} = \frac{(29.125\,\mathrm{J\,K^{-1}\,mol^{-1}}) - (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})} = 2.50...$$

The temperature change is given by

$$\Delta T = T_f - T_i = T_i\left(\frac{V_i}{V_f}\right)^{1/c} - T_i = T_i\left[\left(\frac{V_i}{V_f}\right)^{1/c} - 1\right]$$

Therefore the work done is

$$\begin{aligned} w_{ad} &= C_V\Delta T = nC_{V,m}\Delta T = nC_{V,m}T_i\left[\left(\frac{V_i}{V_f}\right)^{1/c} - 1\right] \\ &= n(C_{p,m} - R)T_i\left[\left(\frac{V_i}{V_f}\right)^{1/c} - 1\right] \\ &= \left(\frac{3.12\,\mathrm{g}}{28.02\,\mathrm{g\,mol^{-1}}}\right) \times [(29.125\,\mathrm{J\,K^{-1}\,mol^{-1}}) \\ &\quad - (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})] \times (296.15\,\mathrm{K}) \times \left[\left(\frac{400\,\mathrm{cm^3}}{2.00 \times 10^3\,\mathrm{cm^3}}\right)^{1/2.50...} - 1\right] \\ &= \boxed{-325\,\mathrm{J}} \end{aligned}$$

E2E.5(b) The initial and final states in a reversible adiabatic expansion are related by [2E.3–*68*], $p_iV_i^{\gamma} = p_fV_f^{\gamma}$, therefore

$$p_f = p_i\left(\frac{V_i}{V_f}\right)^{\gamma} = (97.3\,\mathrm{Torr}) \times \left(\frac{400\,\mathrm{cm^3}}{5.0 \times 10^3\,\mathrm{cm^3}}\right)^{1.3} = \boxed{3.6\,\mathrm{Torr}}$$

Solutions to problems

P2E.2 In a reversible adiabatic expansion the initial and final states are related by [2E.2a–*68*], $(T_f/T_i) = (V_i/V_f)^{1/c}$ where $c = C_{V,m}/R$. Taking the logarithm of both sides and using the relationship $\ln x^a = a \ln x$ gives

$$\ln\left(\frac{T_f}{T_i}\right) = \frac{1}{c}\ln\left(\frac{V_i}{V_f}\right)$$

It follows that

$$c = \frac{\ln(V_i/V_f)}{\ln(T_i/T_f)} = \frac{\ln(1/2)}{\ln(248.44\ \mathrm{K}/298.15\ \mathrm{K})} = 3.80...$$

$C_{V,m}$ is calculated from c as follows

$$C_{V,m} = cR = (3.80...) \times (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) = 31.5...\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

Likewise, the initial and final states are related by [2E.3–*68*], $p_i V_i^{\gamma} = p_f V_f^{\gamma}$, where $\gamma = C_{p,m}/C_{V,m}$. It follows that $\ln(p_i/p_f) = \gamma \ln(V_f/V_i)$, hence

$$\gamma = \frac{\ln(p_f/p_i)}{\ln(V_i/V_f)} = \frac{\ln(81.840\ \mathrm{kPa}/202.94\ \mathrm{kPa})}{\ln(1/2)} = 1.31...$$

Hence

$$C_{p,m} = C_{V,m}\gamma = (31.5...\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (1.31...) = \boxed{41.397\ \mathrm{J\,K^{-1}\,mol^{-1}}}$$

Integrated activities

I2.2 (a) The table below displays computed enthalpies of formation (semi-empirical, PM3 level, PC Spartan Pro$^{\mathrm{TM}}$), enthalpies of combustion based on them (and on experimental enthalpies of formation of H_2O(l), −285.83 kJ mol^{-1}, and CO_2(g), −393.51 kJ mol^{-1}), experimental enthalpies of combustion (from the *Resource section*), and the relative error in the enthalpy of combustion.

compound	$\Delta_f H^{\ominus}/\mathrm{kJ\,mol^{-1}}$	$\Delta_c H^{\ominus}/\mathrm{kJ\,mol^{-1}}$ (calc.)	$\Delta_c H^{\ominus}/\mathrm{kJ\,mol^{-1}}$ (expt.)	% error
CH_4(g)	−54.45	−910.7	−890	2.33
C_2H_6(g)	−75.88	−1568.6	−1560	0.55
C_3H_8(g)	−98.84	−2225.0	−2220	0.23
C_4H_{10}(g)	−121.6	−2881.6	−2878	0.12
C_5H_{12}(g)	−142.1	−3540.4	−3537	0.10

The combustion reactions can be expressed as

$$C_nH_{2n+2}(g) + \tfrac{1}{2}(3n+1)O_2(g) \longrightarrow n\,CO_2(g) + (n+1)H_2O(l)$$

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

$$\Delta_c H^\ominus = n\Delta_f H^\ominus(\mathrm{CO_2}) + (n+1)\Delta_f H^\ominus(\mathrm{H_2O}) - \Delta_f H^\ominus(\mathrm{C}_n\mathrm{H}_{2n+2})$$

The % error is defined as

$$\%\ \text{error} = \frac{\Delta_c H^\ominus(\text{calc.}) - \Delta_c H^\ominus(\text{expt.})}{\Delta_c H^\ominus(\text{expt.})} \times 100\%$$

(b) The errors are shown in the table above. It is evident that the agreement is quite good.

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

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

it follows by taking logarithms that

$$\ln|\Delta_c H^\ominus| = \ln k + n\ln[M/(\mathrm{g\,mol^{-1}})]$$

A plot of $\ln|\Delta_c H^\ominus|$ against $\ln[M/(\mathrm{g\,mol^{-1}})]$ is expected to be a straight line with slope n and y-intercept $\ln|k|$; see Fig. 2.2.

compound	$M/$ $\mathrm{g\,mol^{-1}}$	$\Delta_c H^\ominus/$ $\mathrm{kJ\,mol^{-1}}$	$\ln[M/(\mathrm{g\,mol^{-1}})]$	$\ln\lvert\Delta_c H^\ominus/(\mathrm{kJ\,mol^{-1}})\rvert$
$\mathrm{CH_4(g)}$	16.04	−910.72	2.775	6.814
$\mathrm{C_2H_6(g)}$	30.07	−1568.6	3.404	7.358
$\mathrm{C_3H_8(g)}$	44.10	−2225.0	3.786	7.708
$\mathrm{C_4H_{10}(g)}$	58.12	−2881.6	4.063	7.966
$\mathrm{C_5H_{12}(g)}$	72.15	−3540.4	4.279	8.172

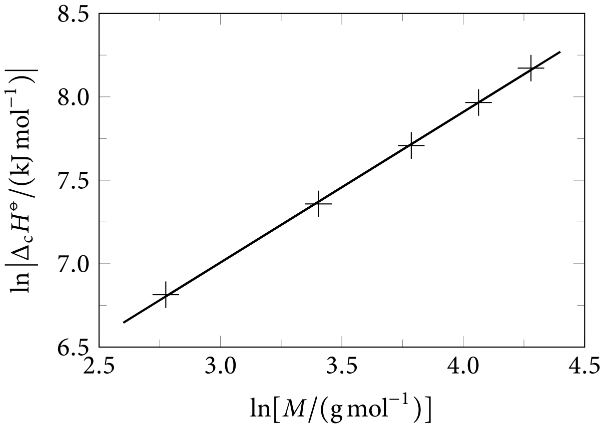


Figure 2.2

The data are a good fit to the line

$$\ln|\Delta_c H^\ominus/(\mathrm{kJ\,mol^{-1}})| = 0.90 \times (\ln[M/(\mathrm{g\,mol^{-1}})]) + 4.30$$

The data from these compounds support the proposed relationship, with the parameters $\boxed{n = 0.90}$ and $k = -\mathrm{e}^{4.30}\ \mathrm{kJ\,mol^{-1}}\ (\mathrm{g\,mol^{-1}})^{-0.9}$, which is $\boxed{k = -73.7\ \mathrm{kJ\,mol^{-1}}\ (\mathrm{g\,mol^{-1}})^{-0.9}}$.

I2.4 The change in reaction enthalpy with respect to temperature is described by Kirchhoff's Law, [2C.7a–*55*]. Assuming that the heat capacities are independent of temperature, the integrated form of Kirchoff's Law is applicable and is given by [2C.7d–*56*]

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + (T_2 - T_1)\Delta_r C_p^\ominus$$

If $\Delta_r C_p^\ominus$ is negative, then the reaction enthalpy will decrease with increasing temperature, whereas if $\Delta_r C_p^\ominus$ is positive, then the reaction enthalpy will increase with increasing temperature.

(a)

$$\begin{aligned}\Delta_r C_p^\ominus &= \sum_{\text{products}} \nu C_{p,\mathrm{m}}^\ominus - \sum_{\text{reactants}} \nu C_{p,\mathrm{m}}^\ominus\\ &= 2C_{p,\mathrm{m}}^\ominus(\mathrm{H_2O,l}) - C_{p,\mathrm{m}}^\ominus(\mathrm{O_2,g}) - 2C_{p,\mathrm{m}}^\ominus(\mathrm{H_2,g})\\ &= 2\times(9R) - \left(\tfrac{7}{2}R\right) - 2\times\left(\tfrac{7}{2}R\right) = +7\tfrac{1}{2}R\end{aligned}$$

$\Delta_r C_p^\ominus$ is positive, therefore the standard reaction enthalpy of reaction will increase with increasing temperature.

(b)

$$\begin{aligned}\Delta_r C_p^\ominus &= C_{p,\mathrm{m}}^\ominus(\mathrm{CO_2,g}) + 2C_{p,\mathrm{m}}^\ominus(\mathrm{H_2O,l}) - 2C_{p,\mathrm{m}}^\ominus(\mathrm{O_2,g}) - C_{p,\mathrm{m}}^\ominus(\mathrm{CH_4,g})\\ &= \left(\tfrac{7}{2}R\right) + 2\times(9R) - 2\times\left(\tfrac{7}{2}R\right) - (4R) = +10\tfrac{1}{2}R\end{aligned}$$

$\Delta_r C_p^\ominus$ is positive, therefore the standard reaction enthalpy of reaction will increase with increasing temperature.

I2.6 (a) From the equipartition principle (*The chemist's toolkit* 7 in Topic 2A), and assuming that only translational and rotational levels contribute, the constant volume heat capacity of a gas of diatomic molecules is $C_{V,\mathrm{m}} = \tfrac{5}{2}R$. For a perfect gas $C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = R$, [2B.9–*49*], therefore $C_{p,\mathrm{m}} = C_{V,\mathrm{m}} + R = \tfrac{7}{2}R$ and so $\gamma = C_{p,\mathrm{m}}/C_{V,\mathrm{m}} = \tfrac{7}{5}$. It follows that

$$c_\mathrm{s} = \left(\frac{\gamma RT}{M}\right)^{1/2} = \left(\frac{7RT}{5M}\right)^{1/2}$$

(b) A linear triatomic has the same number of translational and rotational modes of motion (three translational, two rotational) as a diatomic, so the calculation is the same as in (a).

(c) A gas of non-linear triatomic molecules has one extra mode of rotational motion when compared to a linear triatomic, so the constant volume heat capacity is $C_{V,\mathrm{m}} = 3R$. Because $C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = R$ it follows that $C_{p,\mathrm{m}} = C_{V,\mathrm{m}} + R = 4R$ and so $\gamma = C_{p,\mathrm{m}}/C_{V,\mathrm{m}} = \frac{4}{3}$.

$$c_\mathrm{s} = \left(\frac{\gamma RT}{M}\right)^{1/2} = \left(\frac{4RT}{3M}\right)^{1/2}$$

The air is mostly composed of diatomic and linear triatomic molecules, N_2, O_2 and CO_2, hence $\gamma \approx \frac{7}{5}$. The average molecular weight of air is approximately $29.0\ \mathrm{g\,mol^{-1}}$, therefore

$$c_\mathrm{s} = \left(\frac{7RT}{5M}\right)^{1/2} = \left(\frac{7\times(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(298.15\ \mathrm{K})}{5\times(29.0\times10^{-3}\ \mathrm{kg\,mol^{-1}})}\right)^{1/2} = \boxed{346\ \mathrm{m\,s^{-1}}}$$

3

The second and third laws

3A Entropy

Answers to discussion questions

D3A.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. For a perfect gas this entropy change of such an expansion is derived in Section 3A.2(a) on page 80 as $\Delta S = nR\ln(V_f/V_i)$. The entropy change 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 $S = k\ln\mathcal{W}$, where $\mathcal{W}$ 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.

Solutions to exercises

E3A.1(b) For the process to be spontaneous it must be irreversible and obey the Clausius inequality [3A.12–*86*] implying that $\Delta S_{\text{tot}} = \Delta S + \Delta S_{\text{sur}} > 0$. In this case, $\Delta S_{\text{tot}} = 105\ \text{J K}^{-1} + (-95\ \text{J K}^{-1}) = +10\ \text{J K}^{-1}$, the total entropy increases and thus the process is $\boxed{\text{spontaneous}}$.

E3A.2(b) The thermodynamic definition of entropy is [3A.1a–*80*], $\mathrm{d}S = \mathrm{d}q_{\text{rev}}/T$ or for a finite change at constant temperature $\Delta S = q_{\text{rev}}/T$. The transfer of heat is specified as being reversible, which can often be assumed for a large enough metal block, therefore $q_{\text{rev}} = 250$ kJ.

(i)

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{250\ \text{kJ}}{(273.15\ \text{K} + 20\ \text{K})} = 0.853\ \text{kJ} = \boxed{+853\ \text{J}}$$

(ii)

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{250\ \text{kJ}}{(273.15\ \text{K} + 100\ \text{K})} = 0.670\ \text{kJ} = \boxed{+670\ \text{J}}$$

E3A.3(b) As explained in Section 3A.2(a) on page 80 the change in entropy for an isothermal expansion of a gas is calculated using

$$\begin{aligned}\Delta S &= nR\ln\left(\frac{V_\text{f}}{V_\text{i}}\right) = \frac{m}{M}R\ln\left(\frac{V_\text{f}}{V_\text{i}}\right)\\ &= \left(\frac{4.00\ \text{g}}{28.02\ \text{g}\,\text{mol}^{-1}}\right) \times (8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) \times \ln\left(\frac{750\ \text{cm}^3}{500\ \text{cm}^3}\right)\\ &= \boxed{+0.481\ \text{J}\,\text{K}^{-1}}.\end{aligned}$$

E3A.4(b) The change in entropy for an isothermal expansion of a gas is $\Delta S = nR\ln(V_\text{f}/V_\text{i})$ as explained in Section 3A.2(a) on page 80.

(i) Isothermal reversible expansion

$$\begin{aligned}\Delta S &= \left(\frac{14\ \text{g}}{28.02\ \text{g}\,\text{mol}^{-1}}\right) \times (8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) \times \ln\left(\frac{4.60\ \text{dm}^3}{1.20\ \text{dm}^3}\right)\\ &= \boxed{+0.81\ \text{J}\,\text{K}^{-1}}.\end{aligned}$$

Because the process is reversible $\Delta S_\text{tot} = \boxed{0}$.
Because $\Delta S_\text{tot} = \Delta S + \Delta S_\text{sur}$

$$\Delta S_\text{sur} = \Delta S_\text{tot} - \Delta S = \boxed{-0.81\ \text{J}\,\text{K}^{-1}}.$$

(ii) Isothermal irreversible expansion against $p_\text{ex} = 0$ Because entropy is a state function and the initial and final states of the system are the same as in (a), ΔS is the same.

$$\Delta S = \boxed{+0.81\ \text{J}\,\text{K}^{-1}}.$$

Expansion against an external pressure of 0 does no work, and for an isothermal process of an ideal gas $\Delta U = 0$. From the First Law if follows that $q = 0$ and therefore $\Delta S_\text{sur} = \boxed{0}$.

$$\Delta S_\text{tot} = \Delta S + \Delta S_\text{sur} = \boxed{+0.81\ \text{J}\,\text{K}^{-1}}.$$

(iii) Adiabatic reversible expansion For an adiabatic expansion there is no heat flowing to or from the surroundings, thus $\Delta S_\text{sur} = \boxed{0}$. For a reversible process $\Delta S_\text{tot} = \boxed{0}$, therefore it follows that $\Delta S = \boxed{0}$ as well.

E3A.5(b) The efficiency is defined in [3A.7–*84*], $\eta = |w|/|q_h|$, and for a Carnot cycle efficiency is given by [3A.9–*84*], $\eta = 1 - (T_c/T_h)$. These two are combined and rearranged into an expression for the temperature of the hot source

$$|w|/|q_h| = 1 - (T_c/T_h)$$

$$\text{hence} \qquad T_h = \frac{T_c}{1 - |w|/|q_h|} = \frac{(273.15\text{ K} + 0\text{ K})}{1 - |3.00\text{ kJ}|/|-10.00\text{ kJ}|} = \boxed{390\text{ K}}.$$

E3A.6(b) The efficiency of a Carnot cycle is given by [3A.9–*84*], $\eta = 1 - (T_c/T_h)$. This is rearranged to give an expression for the temperature of the cold sink

$$T_c = (1 - \eta) \times T_h = (1 - 0.10) \times (273.15\text{ K} + 40\text{ K}) = \boxed{282\text{ K}}.$$

Note that the temperature must be in kelvins.

Solutions to problems

P3A.2 (a) The final volume of the gas at 1.00 bar and 300 K temperature is found using the perfect gas law [1A.4–*8*]:

$$\begin{aligned} V_f &= \frac{nRT}{p} \\ &= \frac{(0.10\text{ mol}) \times (8.3145 \times 10^{-2}\text{ dm}^3\text{ bar K}^{-1}\text{ mol}^{-1}) \times (300\text{ K})}{1.00\text{ bar}} \\ &= 2.49...\text{ dm}^3 = \boxed{2.5\text{ dm}^3}. \end{aligned}$$

(b) The expansion work against a constant external pressure is given by [2A.6–*40*], $w = -p_{ex}(V_f - V_i)$.

$$\begin{aligned} w &= -p_{ex}(V_f - V_i) \\ &= -(1.00 \times 10^5\text{ Pa}) \times \left(2.49... \times 10^{-3}\text{ m}^3 - 1.25 \times 10^{-3}\text{ m}^3\right) \\ &= -1.24... \times 10^2\text{ J} = \boxed{-1.2 \times 10^2\text{ J}}. \end{aligned}$$

The work will be in joules if the pressure is expressed in pascals and the volume in m^3.

(c) For an isothermal process of a perfect gas $\Delta U = 0$. The First Law [2A.2–*38*], $\Delta U = q + w$, is then used to find the heat

$$q = \Delta U - w = 0 - (-1.24... \times 10^2\text{ J}) = +1.24... \times 10^2\text{ J} = \boxed{+1.2 \times 10^2\text{ J}}.$$

As explained in Section 3A.2(a) on page 80 the change in entropy of an isothermal expansion of an ideal gas can be calculated from $\Delta S = nR\ln(V_f/V_i)$.

The entropy of the surroundings is given by [3A.2b–*81*], $\Delta S_{\text{sur}} = -q_{\text{rev}}/T$, and $q_{\text{sur}} = -q$. Therefore

$$\begin{aligned}\Delta S_{\text{tot}} &= \Delta S + \Delta S_{\text{sur}}\\ &= nR\ln\left(\frac{V_{\text{f}}}{V_{\text{i}}}\right) + \frac{-q}{T}\\ &= (0.10\ \text{mol}) \times (8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) \times \ln\left(\frac{2.49...\ \text{dm}^3}{1.25\ \text{dm}^3}\right)\\ &\quad + \frac{-(+1.24... \times 10^2\ \text{J})}{300\ \text{K}}\\ &= +0.159...\ \text{J}\,\text{K}^{-1} = \boxed{+0.16\,\text{J}\,\text{K}^{-1}}.\end{aligned}$$

P3A.4 The isotherms correspond to constant temperature, and the adiabats correspond to constant entropy. This implies that Stages 1 and 3 of the Carnot cycle are horizontal straight lines, whereas Stages 2 and 4 are vertical straight lines on the temperature–entropy diagram, as shown in Fig. 3.1.

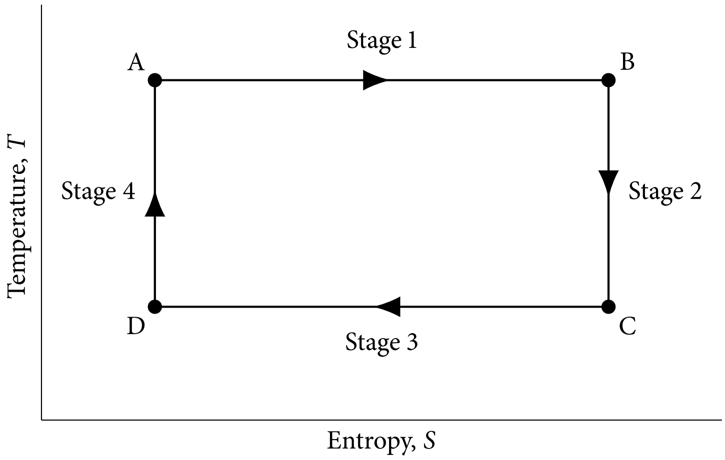


Figure 3.1

(a) The entropy change for a reversible isothermal expansion is given in Section 3A.2(a) on page 80 as $\Delta S = nR\ln(V_{\text{f}}/V_{\text{i}})$. Thus the entropy change for Stage 1 is $\Delta S_1 = nR\ln(V_{\text{B}}/V_{\text{A}})$ and for Stage 3 $\Delta S_3 = nR\ln(V_{\text{D}}/V_{\text{C}}) = -nR\ln(V_{\text{B}}/V_{\text{A}})$. The area enclosed by the Carnot cycle is is just that of a rectangle with sides $nR\ln(V_{\text{B}}/V_{\text{A}})$ and $(T_{\text{h}} - T_{\text{c}})$, thus

$$\oint T\text{d}S = \text{Area} = \boxed{nR(T_{\text{h}} - T_{\text{c}})\ln(V_{\text{B}}/V_{\text{A}})}.$$

(b) The amount of heat extracted from the hot source is $q_{\text{h}} = nRT_{\text{h}}\ln(V_{\text{B}}/V_{\text{A}})$ as explained in Section 3A.3(a) on page 82. The efficiency is defined in [3A.7–*84*], $\eta = |w|/|q_{\text{h}}|$, and for a Carnot cycle efficiency is given by

[3A.9–*84*], $\eta = 1 - (T_c/T_h)$. Equating them an expression for the net work is obtained

$$\begin{aligned} |w|/|q_h| &= 1 - (T_c/T_h) \\ \text{hence} \quad |w| &= q_h \times \left(1 - \frac{T_c}{T_h}\right) \\ &= nRT_h \ln\left(\frac{V_B}{V_A}\right) \times \left(1 - \frac{T_c}{T_h}\right) \\ &= \boxed{nR(T_h - T_c)\ln(V_B/V_A)}. \end{aligned}$$

(c) The area of the temperature–entropy diagram of a Carnot cycle is equal to the net work done in the cycle.

P3A.6 As shown in *Problem* P3A.5 for the process in which a heat pump extracts heat $q_c = -|q|$ from the cold source and deposits heat $q_h = |q| + |w|$ into the hot sink the overall change in entropy is

$$\Delta S = \frac{-|q|}{T_c} + \frac{|q| + |w|}{T_h}$$

For the process to be permissible by the Second Law the Clausius inequality [3A.12–*86*] must be satisfied

$$\frac{-|q|}{T_c} + \frac{|q| + |w|}{T_h} \geq 0$$

The minimum work corresponds to the equlity. This work is

$$|w| = |q| \times \left(\frac{T_h}{T_c} - 1\right)$$

If energy as work or heat is expended for a period of time Δt, the power is $(\text{energy})/\Delta t$. Thus dividing both sides of the above equation by Δt gives

$$\frac{|w|}{\Delta t} = \frac{|q|}{\Delta t} \times \left(\frac{T_h}{T_c} - 1\right)$$

$|w|/\Delta t$ is the power expended as work on the engine and $|q|/\Delta t$ is the power expended due to the heat transferred, therefore

$$\begin{aligned} P_{\text{work}} &= P_{\text{heat}} \times \left(\frac{T_h}{T_c} - 1\right) \\ &= 5\ \text{kW} \times \left(\frac{(273.15\ \text{K} + 18\ \text{K})}{(273.15\ \text{K} + 13\ \text{K})} - 1\right) \\ &= 0.0874...\ \text{kW} = \boxed{0.09\ \text{kW}}. \end{aligned}$$

3B Entropy changes accompanying specific processes

Answer to discussion question

Solutions to exercises

E3B.1(b) The entropy change of a phase transition is given by [3B.4–*89*], $\Delta_{\text{trs}}S = \Delta_{\text{trs}}H/T_{\text{trs}}$. As discussed in Section 3B.2 on page 89 because there is no hydrogen bonding in liquid cyclohexane it is safe to apply Trouton's rule. That is $\Delta_{\text{vap}}S^{\ominus} = +85\ \text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$. It follows that

$$\begin{aligned}\Delta_{\text{vap}}H^{\ominus} &= T_{\text{b}} \times \Delta_{\text{vap}}S^{\ominus}\\ &= (273.15\ \text{K} + 80.7\ \text{K}) \times (+85\ \text{J}\,\text{K}^{-1}\,\text{mol}^{-1})\\ &= 3.00... \times 10^{4}\ \text{J}\,\text{mol}^{-1} = \boxed{+30\ \text{kJ}\,\text{mol}^{-1}}.\end{aligned}$$

E3B.2(b) (i) The entropy change of a phase transition is given by [3B.4–*89*], $\Delta_{\text{trs}}S = \Delta_{\text{trs}}H/T_{\text{trs}}$. For vaporisation this becomes

$$\begin{aligned}\Delta_{\text{vap}}S^{\ominus} &= \frac{\Delta_{\text{vap}}H^{\ominus}}{T_{\text{b}}} = \frac{+35.27 \times 10^{3}\ \text{J}\,\text{mol}^{-1}}{(273.15\ \text{K} + 64.1\ \text{K})}\\ &= \boxed{+104.6\ \text{J}\,\text{K}^{-1}\,\text{mol}^{-1}}.\end{aligned}$$

(ii) Because the system at the transition temperature is at equilibrium, $\Delta S_{\text{tot}} = 0$, thus

$$\Delta S_{\text{sur}} = -\Delta_{\text{vap}}S^{\ominus} = \boxed{-104.6\ \text{J}\,\text{K}^{-1}\,\text{mol}^{-1}}.$$

E3B.3(b) The change in entropy with temperature is given by [3B.6–*90*],

$$\Delta S = S(T_{\text{f}}) - S(T_{\text{i}}) = \int_{T_{\text{i}}}^{T_{\text{f}}} C_{p}\frac{\text{d}T}{T}$$

Assuming that C_p is constant in the temperature range T_{i} to T_{f}, this becomes $\Delta S = C_p \ln(T_{\text{f}}/T_{\text{i}})$ as detailed in Section 3B.3 on page 90. Thus, the increase in the molar entropy of nitrogen gas is

$$\begin{aligned}\Delta S_{\text{m}} &= S_{\text{m}}(273\ \text{K}) - S_{\text{m}}(298\ \text{K}) = (29.125\ \text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) \times \ln\left(\frac{273\ \text{K}}{298\ \text{K}}\right)\\ &= \boxed{-2.55\ \text{J}\,\text{K}^{-1}\,\text{mol}^{-1}}.\end{aligned}$$

E3B.4(b) As explained in Section 3B.3 on page 90 the temperature variation of the entropy at constant volume is given by

$$\Delta S = S(T_{\text{f}}) - S(T_{\text{i}}) = \int_{T_{\text{i}}}^{T_{\text{f}}} C_{V}\frac{\text{d}T}{T}$$

Assuming that $C_V = \frac{3}{2}R$, the ideal gas limit, for the temperature range of interest, the molar entropy at 250 K is given by

$$\begin{aligned} S_\mathrm{m}(250\ \mathrm{K}) &= S_\mathrm{m}(298\ \mathrm{K}) + \int_{298\ \mathrm{K}}^{250\ \mathrm{K}} \tfrac{3}{2}R\frac{\mathrm{d}T}{T} \\ &= S_\mathrm{m}(298\ \mathrm{K}) + \tfrac{3}{2}R \times \ln\left(\frac{250\ \mathrm{K}}{298\ \mathrm{K}}\right) \\ &= (154.84\ \mathrm{J\,K^{-1}\,mol^{-1}}) \\ &\quad + (\tfrac{3}{2} \times 8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{250\ \mathrm{K}}{298\ \mathrm{K}}\right) \\ &= \boxed{153\ \mathrm{J\,K^{-1}\,mol^{-1}}}. \end{aligned}$$

E3B.5(b) Two identical blocks must come to their average temperature. Therefore the final temperature is

$$\begin{aligned} T_\mathrm{f} &= \tfrac{1}{2}(T_1 + T_2) = \tfrac{1}{2} \times (100\ ^\circ\mathrm{C} + 25\ ^\circ\mathrm{C}) \\ &= 62.5...\ ^\circ\mathrm{C} = 3.35... \times 10^2\ \mathrm{K} = \boxed{336\ \mathrm{K}}. \end{aligned}$$

Although the above result may seem self-evident, the more detailed explaination is as follows. The heat capacity at constant volume is defined in [2A.14–*43*], $C_V = (\partial U/\partial T)_V$. As shown in Section 2A.4(b) on page 43, if the heat capacity is constant, the internal energy changes linearly with the change in temperature. That is $\Delta U = C_V \Delta T = C_V(T_\mathrm{f} - T_\mathrm{i})$. For the two blocks at the initial temperatures of T_1 and T_2, the change in internal energy to reach the final temperature T_f is $\Delta U_1 = C_{V,1}(T_\mathrm{f} - T_1)$ and $\Delta U_2 = C_{V,2}(T_\mathrm{f} - T_2)$, respectively. The blocks of metal are made of the same substance and are of the same size, therefore $C_{V,1} = C_{V,2} = C_V$. Because the system is isolated the total change in internal energy is $\Delta U = \Delta U_1 + \Delta U_2 = 0$. This means that $\Delta U = C_V\left((T_\mathrm{f} - T_1) - (T_\mathrm{f} - T_2)\right) = C_V \times (2T_\mathrm{f} - (T_1 + T_2)) = 0$, which implies that the final temperature is $T_\mathrm{f} = \frac{1}{2}(T_1 + T_2)$, as stated above.

The temperature variation of the entropy at constant volume is given by [3B.7–*90*], $\Delta S = C_V \ln(T_\mathrm{f}/T_\mathrm{i})$, with C_p replaced by C_V. Expressed with the specific heat $C_{V,\mathrm{s}} = C_V/m$ it becomes

$$\Delta S = mC_{V,\mathrm{s}} \ln\left(\frac{T_\mathrm{f}}{T_\mathrm{i}}\right)$$

Note that for a solid the internal energy does not change significantly with the volume or pressure, thus it can be assumed that $C_V = C_p = C$. The entropy change for each block is found using this expression

$$\begin{aligned}\Delta S_1 &= mC_{V,\mathrm{s}}\ln\left(\frac{T_\mathrm{f}}{T_1}\right)\\ &= (1.00\times10^4\ \mathrm{g})\times(0.449\ \mathrm{J\,K^{-1}\,g^{-1}})\times\ln\left(\frac{3.35...\times10^2\ \mathrm{K}}{100\ \mathrm{K}+273.15\ \mathrm{K}}\right)\\ &= -4.75...\times10^2\ \mathrm{J\,K^{-1}} = \boxed{-476\ \mathrm{J\,K^{-1}}}.\\ \Delta S_2 &= mC_{V,\mathrm{s}}\ln\left(\frac{T_\mathrm{f}}{T_2}\right)\\ &= (1.00\times10^4\ \mathrm{g})\times(0.449\ \mathrm{J\,K^{-1}\,g^{-1}})\times\ln\left(\frac{3.35...\times10^2\ \mathrm{K}}{25\ \mathrm{K}+273.15\ \mathrm{K}}\right)\\ &= 5.31...\times10^2\ \mathrm{J\,K^{-1}} = \boxed{+532\ \mathrm{J\,K^{-1}}}.\end{aligned}$$

The total change in entropy is

$$\begin{aligned}\Delta S_\mathrm{tot} &= \Delta S_1+\Delta S_2 = (-4.75...\times10^2\ \mathrm{J\,K^{-1}})+(5.31...\times10^2\ \mathrm{J\,K^{-1}})\\ &= 0.563...\times10^2\ \mathrm{J\,K^{-1}} = \boxed{+56\ \mathrm{J\,K^{-1}}}.\end{aligned}$$

Because $\Delta S_\mathrm{tot} > 0$ the process is spontaneous, in accord with experience.

E3B.6(b) Because entropy is a state function, ΔS between the initial and final states is the same irrespective of the path taken. Thus the overall process can be broken down into steps that are easier to evaluate. First consider heating the initial system at constant pressure to the final temperature. The variation of entropy with temperature at constant pressure is given by [3B.7–*90*], $S(T_\mathrm{f}) = S(T_\mathrm{i}) + C_p\ln(T_\mathrm{f}/T_\mathrm{i})$. Thus the change in entropy, $\Delta S = S(T_\mathrm{f}) - S(T_\mathrm{i})$, of this step is

$$\Delta S_1 = C_p\ln\left(\frac{T_\mathrm{f}}{T_\mathrm{i}}\right) = nC_{p,\mathrm{m}}\ln\left(\frac{T_\mathrm{f}}{T_\mathrm{i}}\right)$$

Next consider an isothermal change in pressure. As explained in Section 3A.2(a) on page 80 the change in entropy of an isothermal expansion of an ideal gas is given by $\Delta S = nR\ln(V_\mathrm{f}/V_\mathrm{i})$. Because for a fixed amount of gas at fixed temperature $p \propto (1/V)$ an equivalent expression for this entropy change is

$$\Delta S_2 = nR\ln\left(\frac{p_\mathrm{i}}{p_\mathrm{f}}\right)$$

Therefore the overall entropy change for the system is

$$\begin{aligned}\Delta S &= \Delta S_1+\Delta S_2 = nC_{p,\mathrm{m}}\ln\left(\frac{T_\mathrm{f}}{T_\mathrm{i}}\right)+nR\ln\left(\frac{p_\mathrm{i}}{p_\mathrm{f}}\right)\\ &= (2.00\ \mathrm{mol})\times\left(\frac{7}{2}\times8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}\right)\times\ln\left(\frac{273.15\ \mathrm{K}+135\ \mathrm{K}}{273.15\ \mathrm{K}+25\ \mathrm{K}}\right)\\ &\quad+(2.00\ \mathrm{mol})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times\ln\left(\frac{1.50\ \mathrm{atm}}{7.00\ \mathrm{atm}}\right)\\ &= (+18.2...\ \mathrm{J\,K^{-1}})+(-25.6...\ \mathrm{J\,K^{-1}}) = \boxed{-7.3\ \mathrm{J\,K^{-1}}}.\end{aligned}$$

E3B.7(b) Because entropy is a state function, ΔS between the initial and final states is the same irrespective of the path taken. Thus the overall process can be broken down into steps that are easier to evaluate. First consider heating the ice at constant pressure from the initial temperature to the melting point, T_m. The variation of entropy with temperature at constant pressure is given by [3B.7–*90*], $S(T_f) = S(T_i) + C_p \ln(T_f/T_i)$. Thus the change in entropy, $\Delta S = S(T_f) - S(T_i)$, for this step is

$$\Delta S_1 = C_p \ln\left(\frac{T_m}{T_i}\right) = nC_{p,m}(H_2O(s)) \ln\left(\frac{T_m}{T_i}\right)$$

Next consider the phase transition from solid to liquid at the melting temperature. The entropy change of a phase transition is given by [3B.4–*89*], $\Delta_{trs}S = \Delta_{trs}H/T_{trs}$, thus

$$\Delta S_2 = n\frac{\Delta_{fus}H_m^\ominus}{T_m}$$

Then the liquid is heated to the boiling temperature, T_b. In analogy to the first step

$$\Delta S_3 = nC_{p,m}(H_2O(l)) \ln\left(\frac{T_b}{T_m}\right)$$

The next phase transition is from liquid to gas

$$\Delta S_4 = n\frac{\Delta_{vap}H_m^\ominus}{T_b}$$

Finally, the vapour is heated from T_b to T_f

$$\Delta S_5 = nC_{p,m}(H_2O(g)) \ln\left(\frac{T_f}{T_b}\right)$$

Therefore the overall entropy change for the system is

$$\begin{aligned}\Delta S &= \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5\\ &= nC_{p,\mathrm{m}}(\mathrm{H_2O(s)})\ln\left(\frac{T_\mathrm{m}}{T_\mathrm{i}}\right) + n\frac{\Delta_\mathrm{fus}H^\ominus_\mathrm{m}}{T_\mathrm{m}} + nC_{p,\mathrm{m}}(\mathrm{H_2O(l)})\ln\left(\frac{T_\mathrm{b}}{T_\mathrm{m}}\right)\\ &\quad + n\frac{\Delta_\mathrm{vap}H^\ominus_\mathrm{m}}{T_\mathrm{b}} + nC_{p,\mathrm{m}}(\mathrm{H_2O(g)})\ln\left(\frac{T_\mathrm{f}}{T_\mathrm{b}}\right)\\ &= \frac{15.0\ \mathrm{g}}{18.02\ \mathrm{g\,mol^{-1}}} \times (37.6\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{273.15\ \mathrm{K}}{273.15\ \mathrm{K} - 12.0\ \mathrm{K}}\right)\\ &\quad + \frac{15.0\ \mathrm{g}}{18.02\ \mathrm{g\,mol^{-1}}} \times \frac{6.01\times10^3\ \mathrm{J\,mol^{-1}}}{273.15\ \mathrm{K}}\\ &\quad + \frac{15.0\ \mathrm{g}}{18.02\ \mathrm{g\,mol^{-1}}} \times (75.3\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{273.15\ \mathrm{K} + 100.0\ \mathrm{K}}{273.15\ \mathrm{K}}\right)\\ &\quad + \frac{15.0\ \mathrm{g}}{18.02\ \mathrm{g\,mol^{-1}}} \times \frac{40.7\times10^3\ \mathrm{J\,mol^{-1}}}{273.15\ \mathrm{K} + 100.0\ \mathrm{K}}\\ &\quad + \frac{15.0\ \mathrm{g}}{18.02\ \mathrm{g\,mol^{-1}}} \times (33.6\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{273.15\ \mathrm{K} + 105.0\ \mathrm{K}}{273.15\ \mathrm{K} + 100.0\ \mathrm{K}}\right)\\ &= (+1.40...\ \mathrm{J\,K^{-1}}) + (+18.3...\ \mathrm{J\,K^{-1}}) + (+19.5...\ \mathrm{J\,K^{-1}})\\ &\quad + (+90.7...\ \mathrm{J\,K^{-1}}) + (0.372...\ \mathrm{J\,K^{-1}})\\ &= \boxed{+130.4\ \mathrm{J\,K^{-1}}}.\end{aligned}$$

Solutions to problems

P3B.2 Because entropy is a state function, ΔS between the initial and final states is the same irrespective of the path taken. Thus the overall process can be broken down into steps that are easier to evaluate.

First consider cooling the water at constant pressure to from the initial temperature T to that of freezing, T_f. Entropy variation with temperature at constant pressure is given by [3B.7–*90*], $S(T_\mathrm{final}) = S(T_\mathrm{initial}) + C_p \ln(T_\mathrm{final}/T_\mathrm{initial})$. Thus the change in entropy, $\Delta S = S(T_\mathrm{final}) - S(T_\mathrm{initial})$, of this step is

$$\Delta S_1 = C_p \ln\left(\frac{T_\mathrm{f}}{T}\right) = nC_{p,\mathrm{m}}(\mathrm{H_2O(l)})\ln\left(\frac{T_\mathrm{f}}{T}\right)$$

Next consider the phase transition from liquid to solid at the freezing temperature; note that freezing is just the opposite of fusion, thus $\Delta H_2 = n(-\Delta_\mathrm{fus}H^\ominus_\mathrm{m})$. The entropy change of a phase transition is given by [3B.4–*89*], $\Delta_\mathrm{trs}S = \Delta_\mathrm{trs}H/T_\mathrm{trs}$, thus

$$\Delta S_2 = \frac{\Delta H_2}{T_\mathrm{f}} = n\frac{-\Delta_\mathrm{fus}H^\ominus_\mathrm{m}}{T_\mathrm{f}}$$

The ice is then heated to the final temperature, T. In analogy to the first step

$$\Delta S_3 = nC_{p,\mathrm{m}}(\mathrm{H_2O(s)})\ln\left(\frac{T}{T_\mathrm{f}}\right)$$

Therefore the overall entropy change for the system is

$$\begin{aligned}
\Delta S &= \Delta S_1 + \Delta S_2 + \Delta S_3 \\
&= nC_{p,\mathrm{m}}(\mathrm{H_2O(l)})\ln\left(\frac{T_\mathrm{f}}{T}\right) + n\frac{-\Delta_\mathrm{fus}H^\ominus_\mathrm{m}}{T_\mathrm{f}} + nC_{p,\mathrm{m}}(\mathrm{H_2O(s)})\ln\left(\frac{T}{T_\mathrm{f}}\right) \\
&= (1.00\ \mathrm{mol}) \times (75.3\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{273.15\ \mathrm{K}}{273.15\ \mathrm{K} + 5.00\ \mathrm{K}}\right) \\
&\quad + (1.00\ \mathrm{mol}) \times \frac{-6.01 \times 10^3\ \mathrm{J\,mol^{-1}}}{273.15\ \mathrm{K}} \\
&\quad + (1.00\ \mathrm{mol}) \times (37.6\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{273.15\ \mathrm{K} + 5.00\ \mathrm{K}}{273.15\ \mathrm{K}}\right) \\
&= (-1.36...\ \mathrm{J\,K^{-1}}) + (-22.0...\ \mathrm{J\,K^{-1}}) + (+0.682...\ \mathrm{J\,K^{-1}}) \\
&= -22.6...\ \mathrm{J\,K^{-1}}.
\end{aligned}$$

Consider the enthalphy change for the same path. The variation of the enthalpy with temperature at constant pressure is given by [2B.6b–*49*], $\Delta H = C_p \Delta T$. Thus for the first and third steps, respectively

$$\Delta H_1 = nC_{p,\mathrm{m}}(\mathrm{H_2O(l)})(T_\mathrm{f} - T) \quad \text{and} \quad \Delta H_3 = nC_{p,\mathrm{m}}(\mathrm{H_2O(s)})(T - T_\mathrm{f})$$

Therefore the overall enthalpy change for the system is

$$\begin{aligned}
\Delta H &= \Delta H_1 + \Delta H_2 + \Delta H_3 \\
&= nC_{p,\mathrm{m}}(\mathrm{H_2O(l)})(T_\mathrm{f} - T) + n(-\Delta_\mathrm{fus}H^\ominus_\mathrm{m}) + nC_{p,\mathrm{m}}(\mathrm{H_2O(s)})(T - T_\mathrm{f}) \\
&= (1.00\ \mathrm{mol}) \times (75.3\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (-5.00\ \mathrm{K}) \\
&\quad + (1.00\ \mathrm{mol}) \times (-6.01 \times 10^3\ \mathrm{J\,mol^{-1}}) \\
&\quad + (1.00\ \mathrm{mol}) \times (37.6\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (+5.00\ \mathrm{K}) \\
&= (-3.76... \times 10^2\ \mathrm{J}) + (-6.01... \times 10^3\ \mathrm{J}) + (+1.88... \times 10^2\ \mathrm{J}) \\
&= -6.19... \times 10^3\ \mathrm{J}
\end{aligned}$$

At constant pressure the heat released by the system is the enthalpy change of the system, $q = \Delta H$. Because $q_\mathrm{sur} = -q$, the entropy change of the surroundings is

$$\begin{aligned}
\Delta S_\mathrm{sur} &= \frac{-q}{T} = \frac{-(-6.19... \times 10^3\ \mathrm{J})}{273.15\ \mathrm{K} + 5.00\ \mathrm{K}} \\
&= +22.2...\ \mathrm{J\,K^{-1}}
\end{aligned}$$

Therefore the total entropy change is

$$\begin{aligned}
\Delta S_\mathrm{tot} &= \Delta S + \Delta S_\mathrm{sur} = (-22.6...\ \mathrm{J\,K^{-1}}) + (+22.2...\ \mathrm{J\,K^{-1}}) \\
&= -0.401...\ \mathrm{J\,K^{-1}} = \boxed{-0.4\ \mathrm{J\,K^{-1}}}.
\end{aligned}$$

Because the change in the total entropy is negative, the Second Law implies that the process is $\boxed{\text{not spontaneous}}$.

P3B.4 Consider heating nitrogen at constant pressure to from the initial to final temperatures. The variation of the entropy with temperature is given by [3B.6–*90*], $S(T_f) = S(T_i) + \int_{T_i}^{T_f}(C_p/T)\mathrm{d}T$. The constant-pressure molar heat capacity is given as a function of temperature of a form $C_{p,\mathrm{m}} = a + bT$, with $a = +28.58\,\mathrm{J\,K^{-1}\,mol^{-1}}$ and $b = +3.77\times10^{-3}\,\mathrm{J\,K^{-2}\,mol^{-1}}$. Thus the molar entropy at $T_f = 373$ K is

$$\begin{aligned}
S_\mathrm{m}^\ominus(373\,\mathrm{K}) &= S_\mathrm{m}^\ominus(298\,\mathrm{K}) + \int_{298\,\mathrm{K}}^{373\,\mathrm{K}} (C_{p,\mathrm{m}}/T)\,\mathrm{d}T\\
&= S_\mathrm{m}^\ominus(298\,\mathrm{K}) + \int_{298\,\mathrm{K}}^{373\,\mathrm{K}} \frac{a+bT}{T}\,\mathrm{d}T\\
&= S_\mathrm{m}^\ominus(298\,\mathrm{K}) + a\times\int_{298\,\mathrm{K}}^{373\,\mathrm{K}} \frac{1}{T}\,\mathrm{d}T + b\times\int_{298\,\mathrm{K}}^{373\,\mathrm{K}} \mathrm{d}T\\
&= S_\mathrm{m}^\ominus(298\,\mathrm{K}) + a\times\ln\left(\frac{373\,\mathrm{K}}{298\,\mathrm{K}}\right) + b\times(373\,\mathrm{K} - 298\,\mathrm{K})\\
&= (191.6\,\mathrm{J\,K^{-1}\,mol^{-1}}) + (+28.58\,\mathrm{J\,K^{-1}\,mol^{-1}})\times\ln\left(\frac{373\,\mathrm{K}}{298\,\mathrm{K}}\right)\\
&\quad + (+3.77\times10^{-3}\,\mathrm{J\,K^{-2}\,mol^{-1}})\times(373\,\mathrm{K} - 298\,\mathrm{K})\\
&= (191.6\,\mathrm{J\,K^{-1}\,mol^{-1}})\\
&\quad + (6.41...\,\mathrm{J\,K^{-1}\,mol^{-1}}) + (0.282...\,\mathrm{J\,K^{-1}\,mol^{-1}})\\
&= \boxed{+198.3\,\mathrm{J\,K^{-1}\,mol^{-1}}}.
\end{aligned}$$

When the heat capacity is instead assumed to be temperature independent, $C_{p,\mathrm{m}} = 29.13\,\mathrm{J\,K^{-1}\,mol^{-1}}$, the result is

$$\begin{aligned}
S_\mathrm{m}^\ominus(373\,\mathrm{K}) &= S_\mathrm{m}^\ominus(298\,\mathrm{K}) + \int_{298\,\mathrm{K}}^{373\,\mathrm{K}} (C_{p,\mathrm{m}}/T)\,\mathrm{d}T\\
&= S_\mathrm{m}^\ominus(298\,\mathrm{K}) + C_{p,\mathrm{m}}\times\ln\left(\frac{373\,\mathrm{K}}{298\,\mathrm{K}}\right)\\
&= (191.6\,\mathrm{J\,K^{-1}\,mol^{-1}}) + (+29.13\,\mathrm{J\,K^{-1}\,mol^{-1}})\times\ln\left(\frac{373\,\mathrm{K}}{298\,\mathrm{K}}\right)\\
&= (191.6\,\mathrm{J\,K^{-1}\,mol^{-1}}) + (6.53...\,\mathrm{J\,K^{-1}\,mol^{-1}})\\
&= \boxed{+198.1\,\mathrm{J\,K^{-1}\,mol^{-1}}}.
\end{aligned}$$

The difference between the results is relatively small (≈ 0.1 %). This is because the temperature variation of the heat capacity over this range is relatively small.

P3B.6 (a) Rearranging Newton's law gives

$$\frac{\mathrm{d}T}{T - T_\mathrm{sur}} = -\alpha\mathrm{d}t$$

Integrating both sides give

$$\ln(T - T_\mathrm{sur}) = -\alpha t + D$$

where D is an integration constant that is determinded applying the boundary conditions $T = T_i$ at $t = 0$. Hence, $D = \ln(T_i - T_{\text{sur}})$, and therefore

$$\boxed{\ln\left(\frac{T - T_{\text{sur}}}{T_i - T_{\text{sur}}}\right) = -\alpha t}.$$

(b) The above equation is rearranged to give an expression for T

$$T = T_{\text{sur}} + (T_i - T_{\text{sur}}) \times e^{-\alpha t}$$

Given that $S(T) - S(T_i) = C\ln(T/T_i)$, it follows that

$$\begin{aligned} S(t) = S(T(t)) &= S(T_i) + C\ln\left(\frac{T(t)}{T_i}\right) \\ &= \boxed{S(T_i) + C\ln\left(\frac{T_{\text{sur}} + (T_i - T_{\text{sur}}) \times e^{-\alpha t}}{T_i}\right)}. \end{aligned}$$

P3B.8 (a) Because enthalpy is a state function, ΔH between the initial and final states is the same irrespective of the path taken. Thus the overall process can be broken down into steps that are easier to evaluate. First consider condensation of vapour. Given that all the vapour turns to liquid water, the heat released is the opposite of that of vaporization

$$\Delta H_1 = n(-\Delta_{\text{vap}}H^{\ominus}).$$

The newly formed liquid water is initially at the boiling point. The next step is the water cooling from the boiling to final temperatures. The enthalpy change associated with a temperature change is given by [2B.6b–*49*], $\Delta H = C_p\Delta T$. Thus

$$\Delta H_2 = C_p\Delta T = nC_{p,\text{m}}(\text{H}_2\text{O(l)})(T_f - T_b)$$

The final step is for the metal block to come to thermal equilibrium with the water

$$\Delta H_3 = C_p\Delta T = \frac{m}{M}C_{p,\text{m}}(\text{Cu(s)})(T_f - T_i)$$

where T_i is the initial temperature of the block.

Because the system is insulated there is no overall change in the enthalpy of the system as a whole, $\Delta H_{\text{sys}} = \Delta H_1 + \Delta H_2 + \Delta H_3 = 0$. Putting together the expresssions of enthalpy change at each step gives

$$n(-\Delta_{\text{vap}}H^{\ominus}) + nC_{p,\text{m}}(\text{H}_2\text{O(l)})(T_f - T_b) + \frac{m}{M}C_{p,\text{m}}(\text{Cu(s)})(T_f - T_i) = 0$$

Hence

$$\begin{aligned} T_f\times\left(nC_{p,\text{m}}(\text{H}_2\text{O(l)}) + \frac{m}{M}C_{p,\text{m}}(\text{Cu(s)})\right) &= \\ = n\Delta_{\text{vap}}H^{\ominus} + nC_{p,\text{m}}(\text{H}_2\text{O(l)}) \times T_b &+ \frac{m}{M}C_{p,\text{m}}(\text{Cu(s)}) \times T_i \end{aligned}$$

Thus the final temperature is given by

$$T_\mathrm{f} = \frac{n\Delta_\mathrm{vap}H^\ominus + nC_{p,\mathrm{m}}(\mathrm{H_2O(l)}) \times T_\mathrm{b} + (m/M)C_{p,\mathrm{m}}(\mathrm{Cu(s)}) \times T_\mathrm{i}}{nC_{p,\mathrm{m}}(\mathrm{H_2O(l)}) + (m/M)C_{p,\mathrm{m}}(\mathrm{Cu(s)})}$$

For convenience the numerator and denominator is estimated separately

$$\begin{aligned}\text{numerator} &= (1.00\ \mathrm{mol}) \times (4.07 \times 10^4\ \mathrm{J\,mol^{-1}}) \\ &\quad + (1.00\ \mathrm{mol}) \times (75.3\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (373.15\ \mathrm{K}) \\ &\quad + \left(\frac{2.00 \times 10^3\ \mathrm{g}}{63.55\ \mathrm{g\,mol^{-1}}}\right) \times (24.44\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (273.15\ \mathrm{K}) \\ &= +2.78... \times 10^5\ \mathrm{J\,mol^{-1}}\end{aligned}$$

$$\begin{aligned}\text{denominator} &= (1.00\ \mathrm{mol}) \times (75.3\ \mathrm{J\,K^{-1}\,mol^{-1}}) \\ &\quad + \left(\frac{2.00 \times 10^3\ \mathrm{g}}{63.55\ \mathrm{g\,mol^{-1}}}\right) \times (24.44\ \mathrm{J\,K^{-1}\,mol^{-1}}) \\ &= +8.44... \times 10^2\ \mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

Hence

$$T_\mathrm{f} = \frac{+2.78... \times 10^5\ \mathrm{J\,mol^{-1}}}{+8.44... \times 10^2\ \mathrm{J\,K^{-1}\,mol^{-1}}} = 3.30... \times 10^2\ \mathrm{K} = \boxed{330\ \mathrm{K}}.$$

(b) The net heat transferred to the metal block is

$$\begin{aligned}\Delta H_3 &= \frac{m}{M}C_{p,\mathrm{m}}(\mathrm{Cu(s)})(T_\mathrm{f} - T_\mathrm{i}) \\ &= \frac{2.00 \times 10^3\ \mathrm{g}}{63.55\ \mathrm{g\,mol^{-1}}} \times (24.44\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (3.30... \times 10^2\ \mathrm{K} - 273.15\ \mathrm{K}) \\ &= +4.39... \times 10^4\ \mathrm{J} = \boxed{+43.9\ \mathrm{kJ}}.\end{aligned}$$

(c) The entropy change of a phase transition is given by [3B.4–*89*], $\Delta_\mathrm{trs}S = \Delta_\mathrm{trs}H/T_\mathrm{trs}$. Thus the entropy of the condensation step is

$$\begin{aligned}\Delta S_1 &= \frac{\Delta H_1}{T_\mathrm{b}} = \frac{n(-\Delta_\mathrm{vap}H^\ominus)}{T_\mathrm{b}} \\ &= \frac{(1.00\ \mathrm{mol}) \times (-4.07 \times 10^4\ \mathrm{J\,mol^{-1}})}{373.15\ \mathrm{K}} \\ &= -1.09... \times 10^2\ \mathrm{J\,K^{-1}}\end{aligned}$$

The temperature dependence of the entropy at constant pressure is given by [3B.7–*90*], $\Delta S = nC_{p,\mathrm{m}} \ln(T_\mathrm{f}/T_\mathrm{i})$. Thus, the changes in entropy for the second and third steps are, respectively

$$\begin{aligned}\Delta S_2 &= nC_{p,\mathrm{m}}(\mathrm{H_2O(l)}) \ln\left(\frac{T_\mathrm{f}}{T_\mathrm{b}}\right) \\ &= (1.00\ \mathrm{mol}) \times (75.3\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{3.30... \times 10^2\ \mathrm{K}}{373.15\ \mathrm{K}}\right) \\ &= -9.19...\ \mathrm{J\,K^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta S_3 &= \frac{m}{M}C_{p,\mathrm{m}}(\mathrm{Cu(s)})\ln\left(\frac{T_\mathrm{f}}{T_\mathrm{i}}\right)\\ &= \frac{2.00\times10^3\ \mathrm{g}}{63.55\ \mathrm{g\,mol^{-1}}}\times(24.44\ \mathrm{J\,K^{-1}\,mol^{-1}})\times\ln\left(\frac{3.30...\times10^2\ \mathrm{K}}{273.15\ \mathrm{K}}\right)\\ &= +1.46...\times10^2\ \mathrm{J\,K^{-1}}\end{aligned}$$

The overall entropy change for water is

$$\Delta S_1+\Delta S_2 = (-1.09...\times10^2\ \mathrm{J\,K^{-1}})+(-9.19...\ \mathrm{J\,K^{-1}}) = \boxed{-118\ \mathrm{J\,K^{-1}}}.$$

The entropy change change for copper block is $\Delta S_3 = \boxed{+146\ \mathrm{J\,K^{-1}}}$.
The total entropy change is therefore

$$\begin{aligned}\Delta S_\mathrm{tot} &= \Delta S_1+\Delta S_2+\Delta S_3\\ &= (-1.09...\times10^2\ \mathrm{J\,K^{-1}})+(-9.19...\ \mathrm{J\,K^{-1}})+(+1.46...\times10^2\ \mathrm{J\,K^{-1}})\\ &= +27.8...\ \mathrm{J\,K^{-1}} = \boxed{+28\ \mathrm{J\,K^{-1}}}.\end{aligned}$$

P3B.10 (a) Because the working substance is assumed to be a perfect gas, its internal energy depends on temperature only. DU as a function of temperature is given by [2A.15b–*45*], $\Delta U = C_V\Delta T$. Because the steps 1 and 3 are adiabatic, $q_1 = \boxed{0}$ and $q_3 = \boxed{0}$. Thus, from the First Law, $\Delta U = q + w$, the work done in these steps is equal to the change in internal energy

$$\begin{aligned}w_1 &= \Delta U_1 = C_V(T_\mathrm{B}-T_\mathrm{A}) = \boxed{nC_{V,\mathrm{m}}(T_\mathrm{B}-T_\mathrm{A})}.\\ w_3 &= \Delta U_3 = C_V(T_\mathrm{D}-T_\mathrm{C}) = \boxed{nC_{V,\mathrm{m}}(T_\mathrm{D}-T_\mathrm{C})}.\end{aligned}$$

Because the steps 2 and 4 are at constant volume, no work is done: $w_2 = \boxed{0}$ and $w_4 = \boxed{0}$. Thus, from the First Law, $\Delta U = q + w$, the heat in these steps is equal to the change in internal energy

$$\begin{aligned}q_2 &= \Delta U_2 = C_V(T_\mathrm{C}-T_\mathrm{B}) = \boxed{nC_{V,\mathrm{m}}(T_\mathrm{C}-T_\mathrm{B})}.\\ q_4 &= \Delta U_4 = C_V(T_\mathrm{A}-T_\mathrm{D}) = \boxed{nC_{V,\mathrm{m}}(T_\mathrm{A}-T_\mathrm{D})}.\end{aligned}$$

(b) The efficiency is defined as $\eta = |w_\mathrm{cycle}|/|q_2|$, thus

$$\begin{aligned}\eta &= \frac{|w_\mathrm{cycle}|}{|q_2|} = \frac{|w_1+w_3|}{|q_2|}\\ &= \frac{nC_{V,\mathrm{m}}\times|(T_\mathrm{B}-T_\mathrm{A})+(T_\mathrm{D}-T_\mathrm{C})|}{nC_{V,\mathrm{m}}\times|T_\mathrm{C}-T_\mathrm{B}|}\\ &= \frac{|(T_\mathrm{D}-T_\mathrm{A})-(T_\mathrm{C}-T_\mathrm{B})|}{|T_\mathrm{C}-T_\mathrm{B}|}\\ &= \left|\frac{T_\mathrm{D}-T_\mathrm{A}}{T_\mathrm{C}-T_\mathrm{B}}-1\right| = \boxed{\left|1-\frac{T_\mathrm{D}-T_\mathrm{A}}{T_\mathrm{C}-T_\mathrm{B}}\right|}.\end{aligned}$$

(c) For a reversible adiabatic expansion in step 1: $V_A T_A{}^c = V_B T_B{}^c$. This is rearranged to give a ratio of temperatures

$$\frac{T_A}{T_B} = \left(\frac{V_B}{V_A}\right)^{1/c}$$

Similarly, in step 3: $V_C T_C{}^c = V_D T_D{}^c$, and noting that $V_A = V_D$ and $V_B = V_C$, the temperature ratio is

$$\frac{T_D}{T_C} = \left(\frac{V_C}{V_D}\right)^{1/c} = \left(\frac{V_B}{V_A}\right)^{1/c} = \frac{T_A}{T_B}$$

Using this to write $T_D = (T_C T_A)/T_B$ and then substituting this into the above expression for the efficiency gives

$$\begin{aligned}\eta &= \left|1 - \frac{(T_C T_A/T_B) - T_A}{T_C - T_B}\right| = \left|1 - \frac{(T_A/T_B)(T_C - T_B)}{T_C - T_B}\right| \\ &= \left|1 - \frac{T_A}{T_B}\right| = \left|1 - \left(\frac{V_B}{V_A}\right)^{1/c}\right| = \boxed{1 - \left(\frac{V_B}{V_A}\right)^{1/c}}.\end{aligned}$$

In the last step it becomes apparent that the modulo is redundant because $V_B < V_A$ and $c = C_{V,m}/R$ is positive.

(d) Because the steps 1 and 3 are adiabatic, no heat is exchanged between the system and the surroundings, therefore $\Delta S_1 = \Delta S_{\text{sur},1} = \boxed{0}$ and $\Delta S_3 = \Delta S_{\text{sur},3} = \boxed{0}$. As explained in Section 3B.3 on page 90 the variation of the entropy with temperature at constant volume is given by $\Delta S = C_V \ln(T_f/T_i)$. Thus, the entropy changes for the steps 2 and 4 are, respectively

$$\Delta S_2 = C_V \ln\left(\frac{T_C}{T_B}\right) = \boxed{nC_{V,m} \ln\left(\frac{T_C}{T_B}\right)}.$$

$$\Delta S_4 = C_V \ln\left(\frac{T_A}{T_D}\right) = \boxed{nC_{V,m} \ln\left(\frac{T_A}{T_D}\right)}.$$

Because the processes during these steps are reversible, the total change in entropy is zero, $\Delta S_{\text{tot}} = \Delta S + \Delta S_{\text{sur}} = 0$. Therefore, the entropy change of the surroundings for each process is, respectively, $\Delta S_{\text{sur},2} = -\Delta S_2 = \boxed{-nC_{V,m} \ln(T_C/T_B)}$ and $\Delta S_{\text{sur},4} = -\Delta S_4 = \boxed{-nC_{V,m} \ln(T_A/T_D)}$.

(e) Given $C_{V,m} = \frac{5}{2}R$ and $V_A = 10V_B$, the efficiency of the cycle is

$$\eta = 1 - \left(\frac{V_B}{10V_B}\right)^{R/C_{V,m}} = 1 - \left(\frac{1}{10}\right)^{2/5} = 0.601... = \boxed{60.2\%}.$$

It is given that $p_C/p_B = 5$ and $V_B = V_C$. In this constant volume process the perfect gas law, $pV = nRT$, implies that $p \propto T$, therefore $T_C/T_B = p_C/p_B$. It is shown above that $T_D/T_C = T_A/T_B$, so it also follows that $T_A/T_D = T_B/T_C = 1/5$. Therefore the entropy changes in steps 2 and 4 are, respectively

$$\begin{aligned}\Delta S_2 &= n\left(\tfrac{5}{2}R\right)\ln(5)\\ &= (1.00\,\text{mol}) \times \left(\tfrac{5}{2} \times \left(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}\right) \times \ln(5)\right.\\ &= \boxed{+33.5\,\text{J}\,\text{K}^{-1}}.\\ \Delta S_4 &= n\left(\tfrac{5}{2}R\right)\ln(1/5)\\ &= (1.00\,\text{mol}) \times \left(\tfrac{5}{2} \times \left(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}\right) \times \ln(1/5)\right.\\ &= \boxed{-33.5\,\text{J}\,\text{K}^{-1}}.\end{aligned}$$

The entropy of the surroundings during these steps are thus, respectively, $\Delta S_{\text{sur}2} = \boxed{-33.5\,\text{J}\,\text{K}^{-1}}$ and $\Delta S_{\text{sur}4} = \boxed{+33.5\,\text{J}\,\text{K}^{-1}}$. Finally, for the steps 1 and 3 the entropy changes are always zero: $\Delta S_1 = \Delta S_{\text{sur},1} = \boxed{0}$ and $\Delta S_3 = \Delta S_{\text{sur},3} = \boxed{0}$.

P3B.12 The entropy dependence on temperature is given by [3B.6–*90*], $S(T_\text{f}) = S(T_\text{i}) + \int_{T_\text{i}}^{T_\text{f}}(C_p/T)\text{d}T$. The empirical expression for the constant-pressure molar heat capacity is given by [2B.7–*49*], $C_{p,\text{m}} = a + bT + c/T^2$. Using this, the expression for the molar entropy variation becomes

$$\begin{aligned}S_\text{m}(T_\text{f}) &= S_\text{m}(T_\text{i}) + \int_{T_\text{i}}^{T_\text{f}} \frac{a + bT + c/T^2}{T}\,\text{d}T\\ &= S_\text{m}(T_\text{i}) + a\int_{T_\text{i}}^{T_\text{f}}\frac{\text{d}T}{T} + b\int_{T_\text{i}}^{T_\text{f}}\text{d}T + c\int_{T_\text{i}}^{T_\text{f}}\frac{\text{d}T}{T^3}\\ &= S_\text{m}(T_\text{i}) + a\ln\left(\frac{T_\text{f}}{T_\text{i}}\right) + b(T_\text{f} - T_\text{i}) - \frac{c}{2}\left(\frac{1}{T_\text{f}^2} - \frac{1}{T_\text{i}^2}\right)\end{aligned}$$

Therefore, using the data given in the *Resource section*, and given $S_\text{m}^\ominus(298\,\text{K}) = 192.45\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$, it follows that

(a) $T_\text{f} = 100\,^\circ\text{C}$

$$\begin{aligned}S_\text{m}(373\,\text{K}) &= (192.45\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})\\ &\quad + (29.75\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) \times \ln\left(\frac{373.15\,\text{K}}{298\,\text{K}}\right)\\ &\quad + (25.1 \times 10^{-3}\,\text{J}\,\text{K}^{-2}\,\text{mol}^{-1}) \times (373.15\,\text{K} - 298\,\text{K})\\ &\quad - \frac{-1.55 \times 10^5\,\text{J}\,\text{K}\,\text{mol}^{-1}}{2} \times \left(\frac{1}{(373.15\,\text{K})^2} - \frac{1}{(298\,\text{K})^2}\right)\\ &= (192.45\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) + (+6.69...\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})\\ &\quad + (+1.88...\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) - (+0.316...\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})\\ &= \boxed{+200.71\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}}.\end{aligned}$$

(b) $T_f = 500\ °\mathrm{C}$

$$\begin{aligned}S_m(773\ \mathrm{K}) &= (192.45\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &\quad+ (29.75\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{773.15\ \mathrm{K}}{298\ \mathrm{K}}\right)\\ &\quad+ (25.1\times10^{-3}\ \mathrm{J\,K^{-2}\,mol^{-1}}) \times (773.15\ \mathrm{K} - 298\ \mathrm{K})\\ &\quad- \frac{-1.55\times10^{5}\ \mathrm{J\,K\,mol^{-1}}}{2} \times \left(\frac{1}{(773.15\ \mathrm{K})^2} - \frac{1}{(298\ \mathrm{K})^2}\right)\\ &= (192.45\ \mathrm{J\,K^{-1}\,mol^{-1}}) + (+28.3...\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &\quad+ (+11.9...\ \mathrm{J\,K^{-1}\,mol^{-1}}) - (+0.743...\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &= \boxed{+232.00\ \mathrm{J\,K^{-1}\,mol^{-1}}}.\end{aligned}$$

3C The measurement of entropy

Answer to discussion question

Solutions to exercises

E3C.1(b) Assuming that the Debye extrapolation is valid, the constant-pressure molar heat capacity is $C_{p,m}(T) = aT^3$. The temperature dependence of the entropy is given by [3C.1a–92], $S(T_2) = S(T_1) = \int_{T_1}^{T_2}(C_{p,m}/T)\mathrm{d}T$. For a given temperature T the change in molar entropy from zero temperature is therefore

$$\begin{aligned}S_m(T) - S_m(0) &= \int_0^T \frac{C_{p,m}}{T'}\,\mathrm{d}T' = \int_0^T \frac{aT'^3}{T'}\,\mathrm{d}T'\\ &= a\int_0^T T'^2\mathrm{d}T' = \frac{a}{3}T^3\end{aligned}$$

Hence

$$\begin{aligned}S_m(10\ \mathrm{K}) - S_m(0) &= \frac{1.956\times10^{-4}\ \mathrm{J\,K^{-4}\,mol^{-1}}}{3} \times (10\ \mathrm{K})^3\\ &= \boxed{6.5\times10^{-2}\ \mathrm{J\,K^{-1}\,mol^{-1}}}.\end{aligned}$$

E3C.2(b) The standard reaction entropy is given by [3C.3b–94], $\Delta_r S^\ominus = \sum_J \nu_J S_m^\ominus(J)$, where ν_J are the signed stoichiometric numbers.

(i)

$$\begin{aligned}\Delta_r S^\ominus &= S_m^\ominus(\mathrm{Zn^{2+}},(\mathrm{aq})) + S_m^\ominus(\mathrm{Cu},(\mathrm{s})) - S_m^\ominus(\mathrm{Zn},(\mathrm{s})) - S_m^\ominus(\mathrm{Cu^{2+}},(\mathrm{aq}))\\ &= (-112.1\ \mathrm{J\,K^{-1}\,mol^{-1}}) + (33.150\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &\quad- (41.63\ \mathrm{J\,K^{-1}\,mol^{-1}}) - (-99.6\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &= \boxed{-21.0\ \mathrm{J\,K^{-1}\,mol^{-1}}}.\end{aligned}$$

(ii)

$$\begin{aligned}\Delta_r S^\ominus &= 12S_m^\ominus(\mathrm{CO_2,(g)}) + 11S_m^\ominus(\mathrm{H_2O,(l)}) - S_m^\ominus(\mathrm{sucrose,(s)}) - 12S_m^\ominus(\mathrm{O_2,(g)})\\ &= 12\times(213.74\,\mathrm{J\,K^{-1}\,mol^{-1}}) + 11\times(69.91\,\mathrm{J\,K^{-1}\,mol^{-1}})\\ &\quad -(360.2\,\mathrm{J\,K^{-1}\,mol^{-1}}) - 12\times(205.138\,\mathrm{J\,K^{-1}\,mol^{-1}})\\ &= \boxed{+512.0\,\mathrm{J\,K^{-1}\,mol^{-1}}}.\end{aligned}$$

E3C.3(b) Consider chemical equation

$$\mathrm{N_2(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{N_2O(g)}$$

Standard reaction entropy is given by [3C.3b–*94*], $\Delta_r S^\ominus = \sum_J \nu_J S_m^\ominus(J)$, where ν_J are singed stoichiometric coefficients for a given reaction equation. Therefore, using data from the *Resource section*

$$\begin{aligned}\Delta_r S^\ominus &= nS_m^\ominus(\mathrm{N_2O,(g)}) - \tfrac{1}{2}nS_m^\ominus(\mathrm{O_2,(g)}) - nS_m^\ominus(\mathrm{N_2,(g)})\\ &= (1.00\,\mathrm{mol})\times(219.85\,\mathrm{J\,K^{-1}\,mol^{-1}})\\ &\quad -\left(\tfrac{1}{2}\times 1.00\,\mathrm{mol}\right)\times(205.138\,\mathrm{J\,K^{-1}\,mol^{-1}})\\ &\quad -(1.00\,\mathrm{mol})\times(191.61\,\mathrm{J\,K^{-1}\,mol^{-1}})\\ &= \boxed{-74.33\,\mathrm{J\,K^{-1}}}.\end{aligned}$$

Solutions to problems

P3C.2 Consider the process of determining the calorimetric entropy from zero to the temperature of interest. Assuming that the Debye extrapolation is valid, the constant-pressure molar heat capacity at the lowest temperatures is of a form $C_{p,m}(T) = aT^3$. The temperature dependence of the entropy is given by [3C.1a–*92*], $S(T_2) = S(T_1) = \int_{T_1}^{T_2}(C_{p,m}/T)\mathrm{d}T$. Thus for a given (low) temperature T the change in molar entropy from zero is

$$\begin{aligned}S_m(T) - S_m(0) &= \int_0^T \frac{C_{p,m}}{T'}\,\mathrm{d}T' = \int_0^T \frac{aT'^3}{T'}\,\mathrm{d}T'\\ &= a\int_0^T T'^2\mathrm{d}T' = \frac{a}{3}T^3 = \tfrac{1}{3}C_{p,m}(T)\end{aligned}$$

Hence

$$S_m^\ominus(10\ \mathrm{K}) - S_m^\ominus(0) = \tfrac{1}{3}\times(4.64\,\mathrm{J\,K^{-1}\,mol^{-1}}) = 1.54...\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

The increase in entropy on raising the temperature to the melting point is $S_m^\ominus(234.4\,\mathrm{K}) - S_m^\ominus(10\ \mathrm{K}) = 57.74\,\mathrm{J\,K^{-1}\,mol^{-1}}$. The entropy change of a phase transition is given by [3C.1b–*92*], $\Delta_{trs}S(T_{trs}) = \Delta_{trs}H(T_{trs})/T_{trs}$. Thus

$$\Delta_{fus}S_m^\ominus(234.4\,\mathrm{K}) = \frac{2322\,\mathrm{J\,mol^{-1}}}{234.4\,\mathrm{K}} = 9.90...\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

Further raising the temperature to 298 K gives an increase in the entropy of $S_\mathrm{m}^\ominus(298\ \mathrm{K}) - S_\mathrm{m}^\ominus(234.4\ \mathrm{K}) = 6.85\ \mathrm{J\,K^{-1}\,mol^{-1}}$.

Further raising the temperature to the boiling point, the entropy increases by $S_\mathrm{m}^\ominus(343.9\ \mathrm{K}) - S_\mathrm{m}^\ominus(234.4\ \mathrm{K}) = 10.83\ \mathrm{J\,K^{-1}\,mol^{-1}}$. Finally, the contribution of the second phase transition is

$$\begin{aligned}\Delta_\mathrm{vap}S_\mathrm{m}^\ominus(343.9\ \mathrm{K}) &= \frac{\Delta_\mathrm{vap}H_\mathrm{m}^\ominus}{T_\mathrm{b}} = \frac{6.050\times10^4\ \mathrm{J\,mol^{-1}}}{343.9\ \mathrm{K}}\\ &= 1.75...\times10^2\ \mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

The Third-Law standard molar entropy at 298 K is the sum of the above contributions.

$$\begin{aligned}S_\mathrm{m}^\ominus(298\ \mathrm{K}) - S_\mathrm{m}^\ominus(0) &= (1.54...\ \mathrm{J\,K^{-1}\,mol^{-1}}) + (57.74\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &\quad + (9.90...\ \mathrm{J\,K^{-1}\,mol^{-1}}) + (10.83\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &\quad + (1.75...\times10^2\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &= \boxed{256.0\ \mathrm{J\,K^{-1}\,mol^{-1}}}.\end{aligned}$$

P3C.4 Assuming that the Debye extrapolation is valid, the constant-pressure molar heat capacity is of a form $C_{p,\mathrm{m}}(T) = aT^3$. The temperature dependence of the entropy is given by [3C.1a–*92*], $S(T_2) = S(T_1) = \int_{T_1}^{T_2}(C_{p,\mathrm{m}}/T)\mathrm{d}T$. Thus for a given (low) temperature T the change in the molar entropy from zero is

$$\begin{aligned}S_\mathrm{m}(T) - S_\mathrm{m}(0) &= \int_0^T \frac{C_{p,\mathrm{m}}}{T'}\,\mathrm{d}T' = \int_0^T \frac{aT'^3}{T'}\,\mathrm{d}T'\\ &= a\int_0^T T'^2\mathrm{d}T' = \frac{a}{3}T^3 = \tfrac{1}{3}C_{p,\mathrm{m}}(T)\end{aligned}$$

Hence

$$S_\mathrm{m}^\ominus(10\ \mathrm{K}) - S_\mathrm{m}^\ominus(0) = \tfrac{1}{3}\times(2.09\ \mathrm{J\,K^{-1}\,mol^{-1}}) = 0.696...\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

The change in entropy is determined calorimetrically by measuring the area under a plot of $(C_{p,\mathrm{m}}/T)$ against T, as shown in Fig. 3.2.

T/K	$C_{p,\mathrm{m}}/(\mathrm{J\,K^{-1}\,mol^{-1}})$	$(C_{p,\mathrm{m}}/T)/(\mathrm{J\,K^{-2}\,mol^{-1}})$
10	2.09	0.2090
20	14.43	0.7215
30	36.44	1.2147
40	62.55	1.5638
50	87.03	1.7406
60	111.0	1.8500
70	131.4	1.8771
80	149.4	1.8675
90	165.3	1.8367
100	179.6	1.7960
110	192.8	1.7527
150	237.6	1.5840
160	247.3	1.5456
170	256.5	1.5088
180	265.1	1.4728
190	273.0	1.4368
200	280.3	1.4015

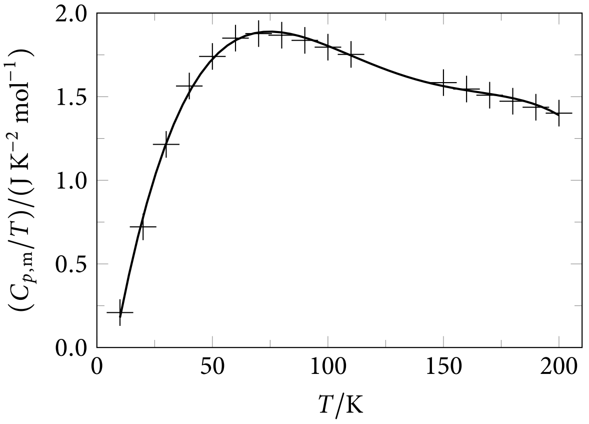


Figure 3.2

The plot fits well to a polynomial of order 4. Define $y = (C_{p,\mathrm{m}}/T)/(\mathrm{J\,K^{-2}\,mol^{-1}})$ and $x = T/\mathrm{K}$, so that the fitted function is expressed

$$y = c_4x^4 + c_3x^3 + c_2x^2 + c_1x + c_0$$

where the best fitted coefficients c_i are

c_i	10 K to 200 K
c_4	-1.0380×10^{-8}
c_3	$+5.7041 \times 10^{-6}$
c_2	-1.1263×10^{-3}
c_1	$+9.0159 \times 10^{-2}$
c_0	-6.1544×10^{-1}

The integral of the fitted functions over the range x_i to x_f is

$$\begin{aligned} I &= \int_{x_\mathrm{i}}^{x_\mathrm{f}} c_4x^4 + c_3x^3 + c_2x^2 + c_1x + c_0\,\mathrm{d}x \\ &= \frac{c_4}{5}\left(x_\mathrm{f}^5 - x_\mathrm{i}^5\right) + \frac{c_3}{4}\left(x_\mathrm{f}^4 - x_\mathrm{i}^4\right) + \frac{c_2}{3}\left(x_\mathrm{f}^3 - x_\mathrm{i}^3\right) \\ &\quad + \frac{c_1}{2}\left(x_\mathrm{f}^2 - x_\mathrm{i}^2\right) + c_0\left(x_\mathrm{f} - x_\mathrm{i}\right) \end{aligned}$$

Using the appropriate coefficients and limits the integral gives

$$S_\mathrm{m}^\ominus(30\ \mathrm{K}) - S_\mathrm{m}^\ominus(10\ \mathrm{K}) = 2.96... \times 10^2\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

The standard Third-Law molar entropy at 200 K is the sum of the both contributions.

$$\begin{aligned} S_\mathrm{m}^\ominus(200\ \mathrm{K}) - S_\mathrm{m}^\ominus(0) &= \left(S_\mathrm{m}^\ominus(200\ \mathrm{K}) - S_\mathrm{m}^\ominus(10\ \mathrm{K})\right) \\ &\quad + \left(S_\mathrm{m}^\ominus(10\ \mathrm{K}) - S_\mathrm{m}^\ominus(0)\right) \\ &= \left(2.96... \times 10^2\ \mathrm{J\,K^{-1}\,mol^{-1}}\right) \\ &\quad + \left(0.696...\ \mathrm{J\,K^{-1}}\right) \\ &= \boxed{297\ \mathrm{J\,K^{-1}\,mol^{-1}}}. \end{aligned}$$

For entropy at 100 K, the above integral in needs to be calculated to the required limit. Therefore

$$S_\mathrm{m}^\ominus(100\ \mathrm{K}) - S_\mathrm{m}^\ominus(10\ \mathrm{K}) = 1.37... \times 10^2\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

The other contribution is the same as before. Hence the molar entropy at 100 K is

$$\begin{aligned} S_\mathrm{m}^\ominus(100\ \mathrm{K}) - S_\mathrm{m}^\ominus(0) &= \left(0.696...\ \mathrm{J\,K^{-1}\,mol^{-1}}\right) + \left(1.37... \times 10^2\ \mathrm{J\,K^{-1}\,mol^{-1}}\right) \\ &= \boxed{138\ \mathrm{J\,K^{-1}\,mol^{-1}}}. \end{aligned}$$

P3C.6 The standard reaction entropy is given by [3C.3b–*94*], $\Delta_\mathrm{r}S^\ominus = \sum_\mathrm{J} \nu_\mathrm{J} S_\mathrm{m}^\ominus(\mathrm{J})$, where ν_J are the signed stoichiometric numbers.

$$\begin{aligned} \Delta_\mathrm{r}S^\ominus(298\ \mathrm{K}) &= S_\mathrm{m}^\ominus(\mathrm{NH_3},(\mathrm{g})) - \tfrac{1}{2}S_\mathrm{m}^\ominus(\mathrm{N_2},(\mathrm{g})) - \tfrac{3}{2}S_\mathrm{m}^\ominus(\mathrm{H_2},(\mathrm{g})) \\ &= \left(192.45\ \mathrm{J\,K^{-1}\,mol^{-1}}\right) - \tfrac{1}{2} \times \left(191.61\ \mathrm{J\,K^{-1}\,mol^{-1}}\right) \\ &\quad - \tfrac{3}{2} \times \left(130.684\ \mathrm{J\,K^{-1}\,mol^{-1}}\right) \\ &= -99.38...\ \mathrm{J\,K^{-1}\,mol^{-1}} = \boxed{-99.38\ \mathrm{J\,K^{-1}\,mol^{-1}}}. \end{aligned}$$

The standard reaction enthalpy is given by [2C.5b–*55*], $\Delta_r H^\ominus = \sum_J \nu_J \Delta_f H^\ominus(J)$. Thus

$$\begin{aligned}\Delta_r H^\ominus(298\ \mathrm{K}) &= \Delta_f H^{\ominus\ominus}(\mathrm{NH_3,(g)}) - \tfrac{1}{2}\Delta_f H^{\ominus\ominus}(\mathrm{H_2O,(g)}) - \tfrac{3}{2}\Delta_f H^{\ominus\ominus}(\mathrm{H_2,(g)})\\ &= (-46.11\ \mathrm{kJ\,mol^{-1}}) - \tfrac{1}{2}\times 0 - \tfrac{3}{2}\times 0 = \boxed{-46.11\ \mathrm{kJ\,mol^{-1}}}.\end{aligned}$$

The temperature dependence of the reaction entropy is given by [3C.5a–*95*], $\Delta_r S^\ominus(T_2) = \Delta_r S^\ominus(T_1) + \int_{T_1}^{T_2}(\Delta_r C_p^\ominus/T)\mathrm{d}T$. Similarly, the enthalpy dependence on temperature is given by Kirchhoff's law [2C.7a–*55*], $\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2}\Delta_r C_p^\ominus \mathrm{d}T$. The quantity $\Delta_r C_p^\ominus$ is defined in [3C.5b–*95*], $\Delta_r C_p^\ominus = \sum_J \nu_J C_{p,\mathrm{m}}^\ominus(J)$. For the reaction at 298 K

$$\begin{aligned}\Delta_r C_p^\ominus &= C_{p,\mathrm{m}}^\ominus(\mathrm{NH_3,(g)}) - \tfrac{1}{2}C_{p,\mathrm{m}}^\ominus(\mathrm{N_2,(g)}) - \tfrac{3}{2}C_{p,\mathrm{m}}^\ominus(\mathrm{H_2,(g)})\\ &= (35.06\ \mathrm{J\,K^{-1}\,mol^{-1}}) - \tfrac{1}{2}\times(29.125\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &\quad - \tfrac{3}{2}\times(28.824\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &= -22.7...\ \mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

Assuming that $\Delta_r C_p^\ominus$ is constant over the temperature range, the standard entropy and enthalpy changes of the reaction are given, respectively, by [3C.5b–*95*], $\Delta_r S^\ominus(T_2) = \Delta_r S^\ominus(T_1) + \Delta_r C_p^\ominus \ln(T_2/T_1)$, and [2C.7d–*56*], $\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \Delta_r C_p^\ominus(T_2 - T_1)$.

$$\begin{aligned}\Delta_r S^\ominus(500\ \mathrm{K}) &= \Delta_r S^\ominus(298\ \mathrm{K}) + \Delta_r C_p^\ominus \times \ln\left(\frac{500\ \mathrm{K}}{298\ \mathrm{K}}\right)\\ &= (-99.38...\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &\quad + (-22.7...\ \mathrm{J\,K^{-1}\,mol^{-1}})\times\ln\left(\frac{500}{298}\right)\\ &= \boxed{+111.15\ \mathrm{J\,K^{-1}\,mol^{-1}}}.\end{aligned}$$

$$\begin{aligned}\Delta_r H^\ominus(500\ \mathrm{K}) &= \Delta_r H^\ominus(298\ \mathrm{K}) + \Delta_r C_p^\ominus \times (500\ \mathrm{K} - 298\ \mathrm{K})\\ &= (-46.11\times 10^3\ \mathrm{J\,mol^{-1}})\\ &\quad + (-22.7...\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(202\ \mathrm{K})\\ &= \boxed{-50.70\ \mathrm{kJ\,mol^{-1}}}.\end{aligned}$$

P3C.8 The change in entropy is determined calorimetrically by measuring the area under a plot of $(C_{p,\mathrm{m}}/T)$ against T, as shown in Fig. 3.3.

T/K	$C_{p,\mathrm{m}}/(\mathrm{J\,K^{-1}\,mol^{-1}})$	$(C_{p,\mathrm{m}}/T)/(\mathrm{J\,K^{-2}\,mol^{-1}})$
100	23.00	0.2300
120	23.74	0.1978
140	24.25	0.1732
150	24.44	0.1629
160	24.61	0.1538
180	24.89	0.1383
200	25.11	0.1256

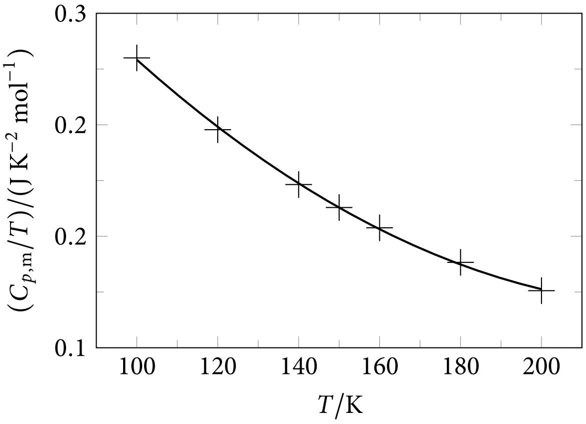


Figure 3.3

The plot is found to be well fitted by a polynomial of order 2. Define $y = (C_{p,\mathrm{m}}/T)/(\mathrm{J\,K^{-2}\,mol^{-1}})$ and $x = T/\mathrm{K}$, so that the fitted function is expressed

$$y = (5.9463\times10^{-6})x^2 - (2.8129\times10^{-3})x + 0.45100$$

The integral of the fitted functions over the range x_i to x_f is

$$\begin{aligned} I = \int_{y(x_\mathrm{i})}^{y(x_\mathrm{f})} y\,\mathrm{d}y = {} & \frac{5.9463\times10^{-6}}{3}\left(x_\mathrm{f}{}^3 - x_\mathrm{i}{}^3\right) \\ & - \frac{2.8129\times10^{-3}}{2}\left(x_\mathrm{f}{}^2 - x_\mathrm{i}{}^2\right) + (0.45100)\left(x_\mathrm{f} - x_\mathrm{i}\right) \end{aligned}$$

Evaluating this integral over the range of x of 100 to 200 gives

$$S_\mathrm{m}^\ominus(200\ \mathrm{K}) - S_\mathrm{m}^\ominus(100\ \mathrm{K}) = 16.7...\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

Given $S_\mathrm{m}^\ominus(100\ \mathrm{K})$ the entropy at 200 K is

$$\begin{aligned} S_\mathrm{m}^\ominus(200\ \mathrm{K}) &= S_\mathrm{m}^\ominus(100\ \mathrm{K}) + \left(S_\mathrm{m}^\ominus(200\ \mathrm{K}) - S_\mathrm{m}^\ominus(100\ \mathrm{K})\right) \\ &= (29.79\ \mathrm{J\,K^{-1}\,mol^{-1}}) + (16.7...\ \mathrm{J\,K^{-1}\,mol^{-1}}) \\ &= \boxed{46.57\ \mathrm{J\,K^{-1}\,mol^{-1}}}. \end{aligned}$$

Assuming the heat capacity to be constant over the temperature range of interest, the change in entropy as a function of temperature is given by [3B.7–*90*], $S(T_f) = S(T_i) + C_p \ln(T_f/T_i)$. Therefore

$$S_m^{\ominus}(200\,\text{K}) = (29.79\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) + (24.44\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) \times \ln\left(\frac{200\,\text{K}}{100\,\text{K}}\right)$$

$$= \boxed{46.73\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}}.$$

The difference is slight as expected because $C_{p,m}$ does not vary significantly in the given temperature range.

P3C.10 The temperature dependence of the entropy is given by [3C.1a–*92*], $S(T_2) = S(T_1) = \int_{T_1}^{T_2}(C_{p,m}/T)\mathrm{d}T$. Given that the heat capacity at the lowest temperatures is the sum of the Debye, aT^3, and electronic, bT, contributions, the molar heat capacity is $C_{p,m}(T) = aT^3 + bT$. Therefore, the molar entropy from zero as a function of temperature is given by

$$\begin{aligned} S_m(T) - S_m(0) &= \int_0^T \frac{C_{p,m}}{T'}\,\mathrm{d}T' = \int_0^T \frac{aT'^3 + bT'}{T'}\,\mathrm{d}T' \\ &= \frac{a}{3}T^3 + bT \end{aligned}$$

Setting the contributions to the entropy corresponding to each term to be equal gives

$$\frac{a}{3}T^3 = bT$$

$$\text{hence} \quad T = \sqrt{\frac{3b}{a}}$$

Therefore this temperature is

$$T = \sqrt{\frac{3 \times 1.38 \times 10^{-3}\,\text{J}\,\text{K}^{-2}\,\text{mol}^{-1}}{0.507 \times 10^{-3}\,\text{J}\text{K}^{-4}\text{mol}^{-1}}} = \boxed{2.86\,\text{K}}.$$

Because the Debye term in the entropy expression has a cubic dependence on T, as the temperature increases it will dominate over the linear electronic term. Thus, $\boxed{\text{the Debye contribution}}$.

3D Concentrating on the system

Answers to discussion questions

D3D.2 As is discussed in detail in Topic 3D the criteria for spontaneity at constant volume and temperature is expressed in terms of the Helmholtz energy, $\mathrm{d}A \le 0$, and at constant pressure and temperature in terms of the Gibbs energy, $\mathrm{d}G \le 0$.

Both the Helmholtz and Gibbs energies refer to properties of the system alone. However, because of the way they are defined these quantities effectively allow the entropy change of the system plus surroundings to be evaluated. For example, at constant volume and temperature the change in the Helmholtz energy is expressed in terms of the internal energy change and the entropy change of the *system*: $\mathrm{d}A = \mathrm{d}U - T\mathrm{d}S$. If this expression is divided by $-T$ to give $-\mathrm{d}A/T = -\mathrm{d}U/T + \mathrm{d}S$ the two terms on the right can bothe be identified as entropy changes.

The first term, $-\mathrm{d}U/T$, is equal to the entropy change of the surroundings because $\mathrm{d}q_{\mathrm{sur}} = -\mathrm{d}q$, and at constant volume $\mathrm{d}q = \mathrm{d}U$. The second term is the entropy change of the system. Thus the sum of the two is the total entropy change, which the Second Law shows must be positive in a spontaneous process. Therefore, the change in the Helmholtz energy is an indicator of the total entropy change, even though the former refers only to the system. Similar considerations can be applied to the Gibbs energy.

It is also possible to express the criterion for spontaneity in terms of the change in H, U or S for the system. For example, as shown in Topic 3D, $\mathrm{d}S_{U,V} \geq 0$. However, the variables which are being held constant (here U and V) do not correspond to such easily realizable conditions such as constant temperature and volume (or pressure) so such criteria are less applicable to chemical systems.

Solutions to exercises

E3D.1(b) The standard reaction Gibbs energy is given by [3D.9–*100*], $\Delta_{\mathrm{r}}G^{\ominus} = \Delta_{\mathrm{r}}H^{\ominus} - T\Delta_{\mathrm{r}}S^{\ominus}$. The standard reaction enthalpy is given in terms of the enthalpies of formation by [2C.5b–*55*], $\Delta_{\mathrm{r}}H^{\ominus} = \sum_{\mathrm{J}} \nu_{\mathrm{J}}\Delta_{\mathrm{f}}H^{\ominus}(\mathrm{J})$, where ν_{J} are the signed stoichiometric numbers.

(i)

$$\begin{aligned}\Delta_{\mathrm{r}}H^{\ominus} &= \Delta_{\mathrm{f}}H^{\ominus}(\mathrm{Zn}^{2+},(\mathrm{aq})) + \Delta_{\mathrm{f}}H^{\ominus}(\mathrm{Cu},(\mathrm{s})) \\ &\quad - \Delta_{\mathrm{f}}H^{\ominus}(\mathrm{Zn},(\mathrm{s})) - \Delta_{\mathrm{f}}H^{\ominus}(\mathrm{Cu}^{2+},(\mathrm{aq})) \\ &= (-153.89\ \mathrm{kJ\,mol^{-1}}) + 0 - 0 - (+64.77\ \mathrm{kJ\,mol^{-1}}) \\ &= \boxed{-218.66\ \mathrm{kJ\,mol^{-1}}}.\end{aligned}$$

Given the result for the previous execise, $\Delta_{\mathrm{r}}S^{\ominus} = -21.0\ \mathrm{J\,K^{-1}\,mol^{-1}}$.

$$\begin{aligned}\Delta_{\mathrm{r}}G^{\ominus} &= (-218.66\ \mathrm{kJ\,mol^{-1}}) - (298.15\ \mathrm{K}) \times (-0.0210\ \mathrm{kJ\,K^{-1}\,mol^{-1}}) \\ &= \boxed{-212.40\ \mathrm{kJ\,mol^{-1}}}.\end{aligned}$$

(ii)

$$\begin{aligned}\Delta_{\mathrm{r}}H^{\ominus} &= 12\Delta_{\mathrm{f}}H^{\ominus}(\mathrm{CO_2},(\mathrm{g})) + 11\Delta_{\mathrm{f}}H^{\ominus}(\mathrm{H_2O},(\mathrm{l})) \\ &\quad - \Delta_{\mathrm{f}}H^{\ominus}(\mathrm{sucrose},(\mathrm{s})) - 12\Delta_{\mathrm{f}}H^{\ominus}(\mathrm{O_2},(\mathrm{g})) \\ &= 12 \times (-393.51\ \mathrm{kJ\,mol^{-1}}) + 11 \times (-285.83\ \mathrm{kJ\,mol^{-1}}) \\ &\quad - (-2222\ \mathrm{kJ\,mol^{-1}}) - 12 \times 0 \\ &= -5644.25\ \mathrm{kJ\,mol^{-1}} = \boxed{-5644\ \mathrm{kJ\,mol^{-1}}}.\end{aligned}$$

Given the result for the previous execise, $\Delta_r S^\ominus = +512.0\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

$$\begin{aligned}\Delta_r G^\ominus &= (-5644.25\,\mathrm{kJ\,mol^{-1}}) - (298.15\,\mathrm{K}) \times (+0.5120\,\mathrm{kJ\,K^{-1}\,mol^{-1}})\\ &= \boxed{-5797\,\mathrm{kJ\,mol^{-1}}}.\end{aligned}$$

E3D.2(b) The standard reaction entropy is given by [3C.3b–*94*], $\Delta_r S^\ominus = \sum_J \nu_J S^\ominus_m(J)$, where ν_J are the signed stoichiometric numbers.

$$\begin{aligned}\Delta_r S^\ominus &= S^\ominus_m(CH_3CH_2COOH,(l)) - S^\ominus_m(CO,(g)) - S^\ominus_m(CH_3CH_2OH,(l))\\ &= (191\,\mathrm{J\,K^{-1}\,mol^{-1}}) - (197.67\,\mathrm{J\,K^{-1}\,mol^{-1}}) - (160.7\,\mathrm{J\,K^{-1}\,mol^{-1}})\\ &= -167...\,\mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

The standard reaction enthalpy is given by [2C.5b–*55*], $\Delta_r H^\ominus = \sum_J \nu_J \Delta_f H^\ominus(J)$.

$$\begin{aligned}\Delta_r H^\ominus &= \Delta_f H^\ominus(CH_3CH_2COOH,(l)) - \Delta_f H^\ominus(CO,(g))\\ &\quad - \Delta_f H^\ominus(CH_3CH_2OH,(l))\\ &= (-510\,\mathrm{kJ\,mol^{-1}}) - (-110.53\,\mathrm{kJ\,mol^{-1}}) - (-277.69\,\mathrm{kJ\,mol^{-1}})\\ &= -121...\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

The standard reaction Gibbs energy is given by [3D.9–*100*], $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$.

$$\begin{aligned}\Delta_r G^\ominus &= (-121...\,\mathrm{J\,K^{-1}\,mol^{-1}}) - (298.15\,\mathrm{K}) \times (-0.167...\,\mathrm{kJ\,K^{-1}\,mol^{-1}})\\ &= \boxed{-72\,\mathrm{kJ\,mol^{-1}}}.\end{aligned}$$

E3D.3(b) The maximum non-expansion work is equal to the Gibbs free energy as explained in Section 3D.1(e) on page 100. The standard reaction Gibbs energy is given by [3D.10b–*101*], $\Delta_r G^\ominus = \sum_J \nu_J \Delta_f G^\ominus(J)$, where ν_J are the signed stoichiometric numbers. For the reaction $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$

$$\begin{aligned}\Delta_r G^\ominus &= 3\Delta_f G^\ominus(CO_2,(g)) + 4\Delta_f G^\ominus(H_2O,(l)) - \Delta_f H^\ominus(C_3H_8,(g))\\ &\quad - 5\Delta_f H^\ominus(O_2,(g))\\ &= 3 \times (-394.36\,\mathrm{kJ\,mol^{-1}}) + 4 \times (-237.13\,\mathrm{kJ\,mol^{-1}})\\ &\quad - (-23.49\,\mathrm{kJ\,mol^{-1}}) - 5 \times 0\\ &= -2108.11\,\mathrm{kJ\,mol^{-1}}.\end{aligned}$$

Therefore, the $|w_{\mathrm{add,max}}| = |\Delta_r G^\ominus| = \boxed{2108.11\,\mathrm{kJ\,mol^{-1}}}$.

E3D.4(b) The standard reaction Gibbs energy is given by [3D.10b–*101*], $\Delta_r G^\ominus = \sum_J \nu_J \Delta_f G^\ominus(J)$, where ν_J are the signed stoichiometric numbers.

(i)

$$\begin{aligned}\Delta_r G^\ominus &= \Delta_f G^\ominus(\mathrm{Zn^{2+}},(\mathrm{aq})) + \Delta_f G^\ominus(\mathrm{Cu},(\mathrm{s}))\\ &\quad - \Delta_f G^\ominus(\mathrm{Zn},(\mathrm{s})) - \Delta_f G^\ominus(\mathrm{Cu^{2+}},(\mathrm{aq}))\\ &= (-147.06\ \mathrm{kJ\,mol^{-1}}) + 0 - 0 - (+65.49\ \mathrm{kJ\,mol^{-1}})\\ &= \boxed{-212.55\ \mathrm{kJ\,mol^{-1}}}.\end{aligned}$$

(ii)

$$\begin{aligned}\Delta_r G^\ominus &= 12\Delta_f G^\ominus(\mathrm{CO_2},(\mathrm{g})) + 11\Delta_f G^\ominus(\mathrm{H_2O},(\mathrm{l}))\\ &\quad - \Delta_f G^\ominus(\mathrm{sucrose},(\mathrm{s})) - 12\Delta_f G^\ominus(\mathrm{O_2},(\mathrm{g}))\\ &= 12\times(-394.36\ \mathrm{kJ\,mol^{-1}}) + 11\times(-237.13\ \mathrm{kJ\,mol^{-1}})\\ &\quad - (-1543\ \mathrm{kJ\,mol^{-1}}) - 12\times 0\\ &= \boxed{-5798\ \mathrm{kJ\,mol^{-1}}}.\end{aligned}$$

E3D.5(b) Consider the reaction

$$\mathrm{NH_2CH_2COOH(s)} + \tfrac{9}{2}\mathrm{O_2(g)} \longrightarrow 2\mathrm{CO_2(g)} + \tfrac{5}{2}\mathrm{H_2O(l)} + \tfrac{1}{2}\mathrm{N_2(g)}$$

The standard reaction enthalpy is given by [2C.5b–*55*], $\Delta_r H^\ominus = \sum_J \nu_J \Delta_f H^\ominus(J)$, where ν_J are the signed stoichiometric numbers.

$$\begin{aligned}\Delta_r H^\ominus &= 2\Delta_f H^\ominus(\mathrm{CO_2},(\mathrm{g})) + \tfrac{5}{2}\Delta_f H^\ominus(\mathrm{H_2O},(\mathrm{l})) + \tfrac{1}{2}\Delta_f H^\ominus(\mathrm{N_2},(\mathrm{g}))\\ &\quad - \Delta_f H^\ominus(\mathrm{NH_2CH_2COOH},(\mathrm{s})) - \tfrac{9}{2}\Delta_f H^\ominus(\mathrm{O_2},(\mathrm{g}))\end{aligned}$$

when rearranged this gives

$$\begin{aligned}\Delta_f H^\ominus(\mathrm{NH_2CH_2COOH},(\mathrm{s})) &= 2\Delta_f H^\ominus(\mathrm{CO_2},(\mathrm{g})) + \tfrac{5}{2}\Delta_f H^\ominus(\mathrm{H_2O},(\mathrm{l}))\\ &\quad + \tfrac{1}{2}\Delta_f H^\ominus(\mathrm{N_2},(\mathrm{g})) - \tfrac{9}{2}\Delta_f H^\ominus(\mathrm{O_2},(\mathrm{g})) - \Delta_r H^\ominus\\ &= 2\times(-393.51\ \mathrm{kJ}) + \tfrac{5}{2}\times(-285.83\ \mathrm{kJ}) + \tfrac{1}{2}\times 0\\ &\quad - \tfrac{9}{2}\times 0 - (-969\ \mathrm{kJ\,mol^{-1}})\\ &= -5.32...\times 10^2\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

The standard reaction entropy is given by [3C.3b–*94*], $\Delta_r S^\ominus = \sum_J \nu_J S_m^\ominus(J)$. Therefore, for the formation of the compound

$$\begin{aligned}\Delta_f S^\ominus(\mathrm{NH_2CH_2COOH},(\mathrm{s})) &= S_m^\ominus(\mathrm{NH_2CH_2COOH},(\mathrm{s})) - 2S_m^\ominus(\mathrm{C},(\mathrm{s}))\\ &\quad - \tfrac{5}{2}S_m^\ominus(\mathrm{H_2},(\mathrm{g})) - S_m^\ominus(\mathrm{O_2},(\mathrm{g})) - \tfrac{1}{2}S_m^\ominus(\mathrm{N_2},(\mathrm{g}))\\ &= (103.5\ \mathrm{J\,K^{-1}\,mol^{-1}}) - 2(5.740\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &\quad - \tfrac{5}{2}(130.684\ \mathrm{J\,K^{-1}\,mol^{-1}}) - (205.138\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &\quad - \tfrac{1}{2}(191.61\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &= -5.35...\times 10^2\ \mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

The standard reaction Gibbs energy is defined in [3D.9–*100*], $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$, thus

$$\begin{aligned}\Delta_f G^\ominus(\mathrm{CH_3COOC_2H_5},(\mathrm{l})) &= (-5.32... \times 10^2\ \mathrm{kJ\,mol^{-1}}) \\ &\quad - (298.15\ \mathrm{K})(-0.535...\ \mathrm{kJ\,K^{-1}\,mol^{-1}}) \\ &= \boxed{-373\ \mathrm{kJ\,mol^{-1}}}.\end{aligned}$$

Solutions to problems

P3D.2 (a) The standard reaction Gibbs energy is defined in [3D.9–*100*], $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$. This is rearranged to give the reaction entropy change

$$\begin{aligned}\Delta_r S^\ominus &= \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T} \\ &= \frac{(-20\times 10^3\ \mathrm{J\,mol^{-1}}) - (-31\times 10^3\ \mathrm{J\,mol^{-1}})}{310\ \mathrm{K}} = \boxed{+35\ \mathrm{J\,K^{-1}\,mol^{-1}}}.\end{aligned}$$

(b) The number of moles that are hydrolysed each second is $n = N/N_A$. Thus the amount of non-expansion work that is done $|w_{\text{non-exp}}| = (N/N_A)|\Delta_r G^\ominus|$. Assuming that the cell is spherical, its volume is given by $\frac{4}{3}\pi r^3$. The power density is the work that is done in a time interval for a unit volume. Therefore

$$\begin{aligned}\text{Power density} &= \frac{(N/N_A)|\Delta_r G^\ominus|}{\frac{4}{3}\pi r^3} \\ &= \frac{(1.0\times 10^6)/(6.0221\times 10^{23}\ \mathrm{mol^{-1}}) \times |-31\times 10^3\ \mathrm{J\,mol^{-1}}|}{\frac{4}{3}\pi(10\times 10^{-6})^3} \\ &= \boxed{12\ \mathrm{W\,m^{-3}}}.\end{aligned}$$

For a computer battery it is

$$\text{Power density (battery)} = \frac{15\ \mathrm{W}}{100\times 10^{-6}\ \mathrm{m^3}} = 1.5\times 10^5\ \mathrm{W\,m^{-3}}$$

Thus the power density of the cell is much smaller.

(c) The non-expansion work needed to produce 1 mol of glutamine is given 14.2 kJ. Thus

$$n = \frac{|w_{\text{non-exp}}|}{|\Delta_r G^\ominus|} = \frac{14.2\ \mathrm{kJ}}{31\ \mathrm{kJ\,mol^{-1}}} = \boxed{0.46\ \mathrm{mol}}.$$

P3D.4 The standard reaction Gibbs energy is given by [3D.9–*100*], $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$. The standard reaction entropy is [2C.5b–*55*], $\Delta_r S^\ominus = \sum_J \nu_J S_m^\ominus(J)$, where ν_J are the signed stoichiometric numbers. Therefore

$$\begin{aligned}\Delta_r S_1^\ominus &= S_m^\ominus(\mathrm{Na^+},(\mathrm{g})) + S_m^\ominus(\mathrm{Cl^-},(\mathrm{g})) - S_m^\ominus(\mathrm{NaCl},(\mathrm{s})) \\ &= (148\ \mathrm{J\,K^{-1}\,mol^{-1}}) + (154\ \mathrm{J\,K^{-1}\,mol^{-1}}) - (72.1\ \mathrm{J\,K^{-1}\,mol^{-1}}) \\ &= 229.9\ \mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

And so

$$\begin{aligned}\Delta_r G_1^\ominus &= (787\ \mathrm{kJ\,mol^{-1}}) - (298\ \mathrm{K}) \times (0.2299\ \mathrm{kJ\,K^{-1}\,mol^{-1}})\\ &= +7.18... \times 10^2\ \mathrm{kJ\,mol^{-1}} = \boxed{+718\ \mathrm{kJ\,mol^{-1}}}.\end{aligned}$$

For the second step $\Delta_r G_2^\ominus = \Delta_{\mathrm{solv}} G^\ominus(\mathrm{Na^+}) + \Delta_{\mathrm{solv}} G^\ominus(\mathrm{Cl^-})$. The Gibbs energy of solvation in water is given by Born equation [3D.12b–*103*], $\Delta_{\mathrm{solv}} G^\ominus = -(z_\mathrm{i}{}^2/[r_\mathrm{i}/\mathrm{pm}]) \times 6.86 \times 10^4\ \mathrm{kJ\,mol^{-1}}$, thus

$$\begin{aligned}\Delta_r G_2^\ominus &= -\left(\frac{(+1)^2}{[r(\mathrm{Na^+})/\mathrm{pm}]} + \frac{(-1)^2}{[r(\mathrm{Cl^-})/\mathrm{pm}]}\right) \times 6.86 \times 10^4\ \mathrm{kJ\,mol^{-1}}\\ &= -\left(\frac{1}{170} + \frac{1}{211}\right) \times 6.86 \times 10^4\ \mathrm{kJ\,mol^{-1}} = -7.28... \times 10^2\ \mathrm{kJ\,mol^{-1}}\\ &= \boxed{-729\ \mathrm{kJ\,mol^{-1}}}\end{aligned}$$

Therefore the total Gibbs energy change of the process

$$\begin{aligned}\Delta_r G^\ominus &= \Delta_r G_1^\ominus + \Delta_r G_2^\ominus = (+7.18... \times 10^2\ \mathrm{kJ\,mol^{-1}}) + (-7.28... \times 10^2\ \mathrm{kJ\,mol^{-1}})\\ &= \boxed{-10\ \mathrm{kJ\,mol^{-1}}}.\end{aligned}$$

The change in negative implying that the process is spontaneous.

P3D.6 As hinted, the entropy is related to Gibbs energy as $S = -(\partial G/\partial T)_p$. Because the Born equation [3D.12a–*103*], $\Delta_{\mathrm{solv}} G^\ominus = -[(z_\mathrm{i}{}^2 e^2 N_\mathrm{A})/(8\pi\varepsilon_0 r_\mathrm{i})] \times [1 - (1/\varepsilon_\mathrm{r})]$, does not have an explicit dependence on temperature. Thus the entropy contribution is neglected by this model, $\Delta_{\mathrm{solv}} S^\ominus = \boxed{0}$. The standard reaction Gibbs energy is given by [3D.9–*100*], $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$. Therefore

$$\Delta_{\mathrm{solv}} H^\ominus = \boxed{\Delta_{\mathrm{solv}} G^\ominus = -\frac{z_\mathrm{i}{}^2 e^2 N_\mathrm{A}}{8\pi\varepsilon_0 r_\mathrm{i}} \times \left(1 - \frac{1}{\varepsilon_\mathrm{r}}\right)}.$$

The model is derived considering only the net work needed to transfer a charged ion from vacuum to a given medium. This implicitly assumes no heat exchange during the process hence resulting in zero entropy contribution.

3E Combining the First and Second Laws

Answer to discussion questions

D3E.2 The relation $(\partial G/\partial p)_T = V$, combined with the fact that the volume is always positive, shows that the Gibbs function of a system increases as the pressure increases (at constant temperature).

Solutions to exercises

E3E.1(b) The Gibbs energy dependence on temperature for a perfect gas is given by [3E.14–*109*], $G_m(p_f) = G_m(p_i) + RT\ln(p_f/p_i)$. From the perfect gas law $p \propto (1/V)$. This allows rewriting the previous equation for the change in Gibbs energy due to isothermal gas expansion

$$\begin{aligned}\Delta G &= nRT\ln\left(\frac{V_i}{V_f}\right)\\ &= (6.0\times10^{-3}\ \text{mol})\times(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(298\ \text{K})\times\ln\left(\frac{52\ \text{cm}^3}{122\ \text{cm}^3}\right)\\ &= \boxed{-13\ \text{J}}.\end{aligned}$$

E3E.2(b) The variation of the Gibbs energy with pressure is given by [3E.8–*107*], $(\partial G/\partial T)_p = -S$. The change in entropy is thus

$$\begin{aligned}\Delta S = S_f - S_i &= -\left(\frac{\partial G_f}{\partial T}\right)_p + \left(\frac{\partial G_i}{\partial T}\right)_p = -\left(\frac{\partial(G_f-G_i)}{\partial T}\right)_p\\ &= -\left(\frac{\partial\Delta G}{\partial T}\right)_p = -\left(\frac{\partial[(-73.1\ \text{J}) + T\times(42.8\,\text{J K}^{-1})]}{\partial T}\right)_p\\ &= -(42.8\,\text{J K}^{-1}) = \boxed{-42.8\,\text{J K}^{-1}}.\end{aligned}$$

E3E.3(b) The Gibbs-Helmholtz relation for the change in Gibbs energy is given by [3E.11–*108*], $(\partial[\Delta G/T]/\partial T)_p = -\Delta H/T^2$. Expressing for the change in enthalpy gives

$$\begin{aligned}\Delta H &= -T^2\left(\frac{\partial[\Delta G/T]}{\partial T}\right)_p = -T^2\left(\frac{\partial[(-73.1\ \text{J})/T + (42.8\,\text{J K}^{-1})]}{\partial T}\right)_p\\ &= T^2\left(\frac{-73.1\ \text{J}}{T^2}\right) = \boxed{-73.1\ \text{J}}.\end{aligned}$$

E3E.4(b) The molar Gibbs energy dependence on pressure for an incompressible substance is given by [3E.13–*108*], $G_m(p_f) = G_m(p_i) + (p_f - p_i)V_m$. Assuming that the volume of liquid water changes little over the range of pressures considered

$$\begin{aligned}\Delta G &= n[G_m(p_f) - G_m(p_i)] = (p_f - p_i)nV_m = (p_f - p_i)V\\ &= [(500\times10^3\ \text{kPa}) - (100\times10^3\ \text{Pa})]\times(100\times10^{-6}\ \text{m}^3) = \boxed{+40.0\ \text{J}}.\end{aligned}$$

For the molar Gibbs energy

$$\begin{aligned}\Delta G_m &= \frac{\Delta G}{n} = \frac{\Delta G}{m/M} = \frac{M\Delta G}{\rho V}\\ &= \frac{(18.02\,\text{g mol}^{-1})\times(+40.0\ \text{J})}{(0.997\,\text{g cm}^{-3})\times(100\ \text{cm}^3)} = \boxed{+7.23\,\text{J mol}^{-1}}.\end{aligned}$$

E3E.5(b) As explained in Section 3E.2(c) on page 108, the change in Gibbs energy of a phase transition varies with pressure as $\Delta_{\rm trs}G_{\rm m}(p_{\rm f}) = \Delta_{\rm trs}G_{\rm m}(p_{\rm i})\int_{p_{\rm i}}^{p_{\rm f}} \Delta_{\rm trs}V_{\rm m}\,{\rm d}p$. Assuming that $\Delta_{\rm trs}V_{\rm m}$ changes little over the range of pressures considered

$$\begin{aligned}\Delta G_{\rm m} &= \Delta_{\rm trs}G_{\rm m}(p_{\rm f}) - \Delta_{\rm trs}G_{\rm m}(p_{\rm i}) = (p_{\rm f}-p_{\rm i})\Delta_{\rm trs}V_{\rm m}\\ &= [(5000\times10^5\ {\rm Pa})-(1\times10^5\ {\rm Pa})]\times(0.5\times10^{-6}\ {\rm m^3\,mol^{-1}})\\ &= \boxed{+2.5\times10^2\ {\rm J\,mol^{-1}}}.\end{aligned}$$

E3E.6(b) The Gibbs energy dependence on pressure for a perfect gas is given by [3E.14–*109*], $G_{\rm m}(p_{\rm f}) = G_{\rm m}(p_{\rm i}) + RT\ln(p_{\rm f}/p_{\rm i})$, thus

$$\begin{aligned}\Delta G_{\rm m} &= RT\ln\left(\frac{p_{\rm f}}{p_{\rm i}}\right)\\ &= (8.3145\ {\rm J\,K^{-1}\,mol^{-1}})\times(500\ {\rm K})\times\ln\left(\frac{100.0\ {\rm kPa}}{50.0\ {\rm kPa}}\right)\\ &= +2.88...\times10^3\ {\rm J\,mol^{-1}} = \boxed{+2.88\ {\rm kJ\,mol^{-1}}}.\end{aligned}$$

Solutions to problems

P3E.2 The standard reaction entropy is given by [3C.3b–*94*], $\Delta_{\rm r}G^\ominus = \sum_{\rm J}\nu_{\rm J}\Delta_{\rm f}G^\ominus({\rm J})$, where $\nu_{\rm J}$ are the signed stoichiometric numbers.

$$\begin{aligned}\Delta_{\rm r}G^\ominus(298\ {\rm K}) &= 2\Delta_{\rm f}G^\ominus({\rm NH_3\,(g)}) - \Delta_{\rm f}G^\ominus({\rm N_2\,(g)}) - 3\Delta_{\rm f}G^\ominus({\rm H_2\,(g)})\\ &= 2\times(-16.45\ {\rm kJ\,mol^{-1}}) - 0 - 3\times0\\ &= \boxed{-32.90\ {\rm kJ\,mol^{-1}}}.\end{aligned}$$

Similarly, the standard reaction enthalpy is [2C.5b–*55*], $\Delta_{\rm r}H^\ominus = \sum_{\rm J}\nu_{\rm J}\Delta_{\rm f}H^\ominus({\rm J})$.

$$\begin{aligned}\Delta_{\rm r}H^\ominus(298\ {\rm K}) &= 2\Delta_{\rm f}H^\ominus({\rm NH_3\,(g)}) - \Delta_{\rm f}H^\ominus({\rm N_2\,(g)}) - 3\Delta_{\rm f}H^\ominus({\rm H_2\,(g)})\\ &= 2\times(-46.11\ {\rm kJ\,mol^{-1}}) - 0 - 3\times0\\ &= \boxed{-92.22\ {\rm kJ\,mol^{-1}}}.\end{aligned}$$

The given expression for the reaction Gibbs energy dependence on temperature is rearranged for $\Delta G(T_2)$ and becomes

$$\Delta G(T_2) = \Delta G(T_1)\frac{T_2}{T_1} + \Delta H\left(1-\frac{T_2}{T_1}\right)$$

Hence at temperatures 500 K and 1000 K, respectively

$$\begin{aligned}\Delta G(500\ {\rm K}) &= (-32.90\ {\rm kJ\,mol^{-1}})\frac{500\ {\rm K}}{298\ {\rm K}} + (-92.22\ {\rm kJ\,mol^{-1}})\left(1-\frac{500\ {\rm K}}{298\ {\rm K}}\right)\\ &= \boxed{+7.31\ {\rm kJ\,mol^{-1}}}.\end{aligned}$$

$$\begin{aligned}\Delta G(1000\ {\rm K}) &= (-32.90\ {\rm kJ\,mol^{-1}})\frac{1000\ {\rm K}}{298\ {\rm K}} + (-92.22\ {\rm kJ\,mol^{-1}})\left(1-\frac{1000\ {\rm K}}{298\ {\rm K}}\right)\\ &= \boxed{+107\ {\rm kJ\,mol^{-1}}}.\end{aligned}$$

P3E.4 (a) $p = (RT)/V_\mathrm{m}$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\frac{RT}{V_\mathrm{m}}\right)_V = \frac{R}{V_\mathrm{m}}\left(\frac{\partial}{\partial T}T\right)_V = \boxed{\frac{R}{V_\mathrm{m}}}.$$

(b) $p = (RT)/(V_\mathrm{m} - b) - a/V_\mathrm{m}^2$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\left[\frac{RT}{V_\mathrm{m}-b} - \frac{a}{V_\mathrm{m}^2}\right]\right)_V$$
$$= \frac{R}{V_\mathrm{m}-b}\left(\frac{\partial}{\partial T}T\right)_V - 0 = \boxed{\frac{R}{V_\mathrm{m}-b}}.$$

(c) $p = (RT\mathrm{e}^{-a/(RTV_\mathrm{m})})/(V_\mathrm{m} - b)$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\frac{RT\mathrm{e}^{-a/(RTV_\mathrm{m})}}{V_\mathrm{m}-b}\right)_V$$
$$= \boxed{\left(1 + \frac{a}{RT^2V_\mathrm{m}}\right)\frac{R}{V_\mathrm{m}-b}\mathrm{e}^{-a/(RTV_\mathrm{m})}}.$$

The change in entropy for an isothermal expansion is

$$\Delta S = \int_{S(V_\mathrm{i})}^{S(V_\mathrm{f})} \mathrm{d}S = \int_{V_\mathrm{i}}^{V_\mathrm{f}} \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V$$

Comparing the $(\partial S/\partial V)_T$ for the perfect and van der Waals gases implies that the change in entropy due to expansion (i.e. positive change in V) is always larger for the van der Waals gases: $(\partial S/\partial V)_{T,\mathrm{vdW}} > (\partial S/\partial V)_{T,\mathrm{perfect}}$. This is because $R/(V_\mathrm{m} - b) > R/V_\mathrm{m}$ for the excluded volume constant b is positive. The result is expected as the relative volume expansion for the van der Waals gases is always slightly greater than that of the perfect gas due to the fixed finite excluded volume. Therefore, the entropy is expected to be more sensitive to the changes in volume, especially at the very small volume.

P3E.6 Using Maxwell's relation $(\partial S/\partial p)_T = -(\partial V/\partial T)_p$ and $(\partial S/\partial T)_p = C_p/T$ the given equation becomes

$$\mathrm{d}S = \left(\frac{\partial S}{\partial p}\right)_T \mathrm{d}p + \left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T = -\left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p + \frac{C_p}{T}\mathrm{d}T$$
$$= \frac{1}{T}\left(C_p\mathrm{d}T - \left[\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p\right]TV\mathrm{d}p\right)$$

The expansion coefficient is definded as $\alpha = (1/V)(\partial V/\partial T)_p$, therefore

$$T\mathrm{d}S = C_p\mathrm{d}T - \alpha TV\mathrm{d}p$$

The entropy change is defined in [3A.1a–*80*], $\mathrm{d}S = \mathrm{d}q_\mathrm{rev}/T$, hence $q_\mathrm{rev} = \int_\mathrm{i}^\mathrm{f} T\mathrm{d}S$. For an isothermal reversible process $q = q_\mathrm{rev}$ and $\mathrm{d}T = 0$. Therefore, assuming that V and α are constant for the range of pressures considered, the amount of heat transferred is

$$\begin{aligned} q &= \int_{S(p_\mathrm{i})}^{S(p_\mathrm{f})} \mathrm{d}S = \int_{p_\mathrm{i}}^{p_\mathrm{f}} -\alpha T V \,\mathrm{d}p = -\alpha T V(p_\mathrm{i} - p_\mathrm{f}) = -\alpha T V \Delta p \\ &= -(1.82\times 10^{4}\ \mathrm{K^{-1}}) \times (273.15\ \mathrm{K}) \times (100\times 10^{-6}\ \mathrm{m^3}) \times (1.0\times 10^{8}\ \mathrm{Pa}) \\ &= \boxed{-497\ \mathrm{J}}. \end{aligned}$$

P3E.8 The Gibbs-Helmholtz relation for the change in Gibbs energy is given by [3E.11–*108*], $(\partial[\Delta G/T]/\partial T)_p = -\Delta H/T^2$. Integrating the equation between the temperatures T_1 and T_2 and assuming that ΔH is temperature independent gives

$$\begin{aligned} \int_{T_1}^{T_2} \left(\frac{\partial}{\partial T}\frac{\Delta G(T)}{T}\right)_p \mathrm{d}T &= \Delta H \int_{T_1}^{T_2} -\frac{1}{T^2}\,\mathrm{d}T \\ \frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} &= \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \end{aligned}$$

This is rearranged for $\Delta G(T_2)$

$$\Delta_\mathrm{r} G^\ominus(T_2) = \Delta_\mathrm{r} G^\ominus(T_1)\frac{T_2}{T_1} + \Delta_\mathrm{r} H^\ominus\left(1 - \frac{T_2}{T_1}\right)$$

Hence for $n = 1$, $n = 2$ and $n = 3$, respectively

$$\begin{aligned} \Delta_\mathrm{r} G_1^\ominus(190\ \mathrm{K}) &= (46.2\ \mathrm{kJ\,mol^{-1}}) \times \frac{190\ \mathrm{K}}{220\ \mathrm{K}} \\ &\quad + (127\ \mathrm{kJ\,mol^{-1}}) \times \left(1 - \frac{190\ \mathrm{K}}{220\ \mathrm{K}}\right) \\ &= \boxed{+57.2\ \mathrm{kJ\,mol^{-1}}}. \end{aligned}$$

$$\begin{aligned} \Delta_\mathrm{r} G_2^\ominus(190\ \mathrm{K}) &= (69.4\ \mathrm{kJ\,mol^{-1}}) \times \frac{190\ \mathrm{K}}{220\ \mathrm{K}} \\ &\quad + (188\ \mathrm{kJ\,mol^{-1}}) \times \left(1 - \frac{190\ \mathrm{K}}{220\ \mathrm{K}}\right) \\ &= \boxed{+85.6\ \mathrm{kJ\,mol^{-1}}}. \end{aligned}$$

$$\begin{aligned} \Delta_\mathrm{r} G_3^\ominus(190\ \mathrm{K}) &= (93.2\ \mathrm{kJ\,mol^{-1}}) \times \frac{190\ \mathrm{K}}{220\ \mathrm{K}} \\ &\quad + (273\ \mathrm{kJ\,mol^{-1}}) \times \left(1 - \frac{190\ \mathrm{K}}{220\ \mathrm{K}}\right) \\ &= \boxed{+112.8\ \mathrm{kJ\,mol^{-1}}}. \end{aligned}$$

Answers to integrated activities

I3.2 The statistical definition of entropy is given by [3A.4–*81*], $S = k \ln \mathcal{W}$, where $\mathcal{W}$ is the number of microstates, the number of ways in which the molecules of a system can be distributed over the energy states for a specified total energy. As explained in Section 3A.2(a) on page 80 the molecular interpretation of helps to explain why, in the thermodynamic definition given by [3A.1a–*80*],$\mathrm{d}S = q_{\text{rev}}/T$, the entropy change depends inversely on the temperature. In a system at high temperature the molecules are spread out over a large number of energy states. Increasing the energy of the system by the transfer of heat makes more states accessible, but given that very many states are already occupied the proportionate change in $\mathcal{W}$ is small. In contrast, for a system at a low temperature fewer states are occupied, and so the transfer of the same energy results in a proportionately larger increase in the number of accessible states, and hence a larger increase in $\mathcal{W}$. This argument suggests that the change in entropy for a given transfer of energy as heat should be greater at low temperatures than at high, as in the thermodynamic definition. As discussed in Section 3C.2(a) on page 93, the statistical definition of entropy also justifies the Third Law of thermodynamics. The law states that the entropy of all perfect crystalline substances is zero at $T = 0$. At a molecular level the absence of thermal motion in a perfectly localized crystalline solid is interpreted as there is only one way to arrange the molecules like that. Thus, $\mathcal{W} = 1$ and from $S = k \ln \mathcal{W}$ it follows that $S = 0$ as stated by the law.

4

Physical transformations of pure substances

4A Phase diagrams of pure substances

Answers to discussion questions

D4A.2 Mathematically the change in chemical potential when the pressure is changed can be traced 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, which is the analogy for a compressible gas; however, it can transmit energy in the same way that a hydraulic fluid does. Furthermore, an incompressible system under pressure is under stress at a molecular level. Its bonds or intermolecular repulsive forces resist external forces without contraction.

D4A.4 Consider the phase diagram shown in Fig. 4A.4 on page 122 and imagine starting at a pressure and temperature somewhat above the critical point; only a single phase is present, which would be described as a supercritical fluid. Then proceed on an clockwise path centred on the critical point. Eventually the path will reach the liquid–vapour phase boundary, and if the traverse is stopped at this point the sample will be found to consist of liquid at the bottom of the tube with vapour above, and a visible meniscus. As the path is continued the system moves into the liquid phase (in principle the meniscus would rise up the tube and then disappear) and once more only one phase is present. Eventually the path takes the system above the critical point and back to the starting point.

The somewhat curious thing about this path is that it takes us from vapour to liquid via the usual process of condensation, but then returns the liquid to the vapour phase without crossing a phase boundary, and so with no visible boiling.

Solutions to exercises

E4A.1(b) In a phase diagram, a single phase is represented by an area, while a line represents a phase boundary where two phases coexist in equilibrium. Point *a* lies within an area and therefore only $\boxed{\text{one phase}}$ is present. Point *d* lies on the boundary between two areas, and therefore $\boxed{\text{two phases}}$ are present. Points *b* and *c* each lie at the intersection of three phase boundaries, so in each case $\boxed{\text{three phases}}$ are present.

E4A.2(b) The change in Gibbs energy when an infinitesimal amount dn of substance is moved from location 1 to location 2 is given by (Section 4A.1(c) on page 121)

$$\mathrm{d}G = (\mu_2 - \mu_1)\mathrm{d}n$$

Assuming that 0.15 mmol is a sufficiently small amount to be regarded as infinitesimal, the Gibbs energy change in this case is

$$\Delta G = (\mu_2 - \mu_1)\Delta n = (-8.3 \times 10^3\ \mathrm{J\,mol^{-1}}) \times (0.15 \times 10^{-3}\ \mathrm{mol}) = \boxed{-1.2\ \mathrm{J}}$$

E4A.3(b) Use the phase rule [4A.1–*124*], $F = C - P + 2$, with $C = 4$ (for four components). Rearranging for the number of phases gives

$$P = C - F + 2 = 4 - F + 2 = 6 - F$$

The number of variables that can be changed arbitrarily, F, cannot be smaller than zero so the maximum number of phases in this case is $\boxed{6}$.

E4A.4(b) Use the phase rule [4A.1–*124*], $F = C - P + 2$, with $C = 1$ (one component). Inserting $P = 2$ gives $F = 1 - 2 + 2 = 1$. The condition $P = 2$ therefore represents a $\boxed{\text{line}}$. A line has $F = 1$ because a variation in pressure determines the required variation in the temperature needed to stay on the line. $P = 2$ indicates that two phases are present, so this result confirms that a situation in which two phases are in equilibrium is represented by a line in a phase diagram.

E4A.5(b)
- (i) 100 K and 1 atm lies in the Ice I region of the phase diagram, so only $\boxed{\text{one phase}}$ (Ice I) will be present.
- (ii) 300 K and 10 atm lies in the liquid region, so only $\boxed{\text{one phase}}$ (liquid) will be present.
- (iii) 273.16 K and 611 Pa corresponds to the triple point of water. So $\boxed{\text{three phases}}$ (Ice I, liquid water, and gas) will be present.

Solutions to problems

P4A.2
- (a) At 200 K and 0.1 atm, the phase diagram indicates that CO_2 is a gas. On increasing the pressure, a point will be reached at which gas and solid are in equilibrium. Above this pressure only the solid form will exist.
- (b) 310 K is above the critical temperature so distinct liquid and gas phases do not exist. A single phase (a supercritical fluid) therefore exists at all pressures (except perhaps at extremely high pressures when a solid might be formed).
- (c) 216.8 K corresponds to the triple point of CO_2. Below 5.11 atm (the pressure corresponding to the triple point) CO_2 will exist as a gas. At 5.11 atm solid, liquid and gas phases will all be present in equilibrium. Above this pressure, the phase diagram shows that only the solid phase will be present.

P4A.4 A schematic phase diagram is shown in Fig 4.1. Note that in reality the phase boundaries may be curved rather than straight. There is one triple point which is marked with a dot.

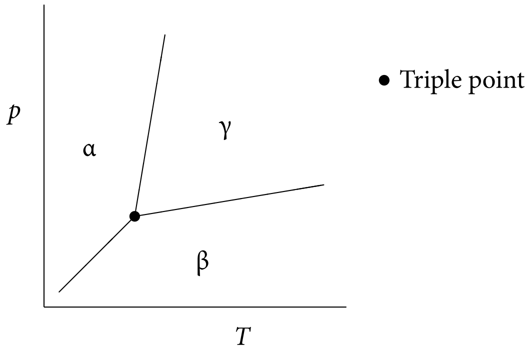


Figure 4.1

4B Thermodynamic aspects of phase transitions

Answers to discussion questions

D4B.2 Formally, the pressure derivative of the chemical potential is $(\partial\mu/\partial p)_T = V_m$. Because the molar volume is always positive, the slope of the change in chemical potential with respect to change in pressure is positive: that is, the chemical potential increases with increasing pressure.

Solutions to exercises

E4B.1(b) The variation of chemical potential with temperature is given by [4B.1a–*128*], $(\partial\mu/\partial T)_p = -S_m$. For a finite change this gives $\Delta\mu = -S_m\Delta T$.

$$\Delta\mu(\text{liquid}) = -(65\ \text{J K}^{-1}\,\text{mol}^{-1}) \times (-1.5\ \text{K}) = \boxed{+98\ \text{J mol}^{-1}}$$
$$\Delta\mu(\text{solid}) = -(43\ \text{J K}^{-1}\,\text{mol}^{-1}) \times (-1.5\ \text{K}) = \boxed{+65\ \text{J mol}^{-1}}$$

The chemical potential of the liquid rises by more than that of the solid. So if they were initially in equilibrium, the $\boxed{\text{solid}}$ will be the more stable phase at the lower temperature.

E4B.2(b) The variation of chemical potential with temperature is given by [4B.1a–*128*], $(\partial\mu/\partial T)_p = -S_m$. For a finite change this gives $\Delta\mu = -S_m\Delta T$, assuming that S_m is constant over the temperature range.

$$\Delta\mu = -(53\ \text{J K}^{-1}\,\text{mol}^{-1}) \times ([150 - 100]\ \text{K}) = \boxed{-2.7 \times 10^3\ \text{J mol}^{-1}}$$

E4B.3(b) The variation of chemical potential with pressure at constant temperature is given by [4B.1b–*128*], $(\partial\mu/\partial p)_T = V_m$. For a finite change, and assuming that V_m is constant over the pressure range, this gives $\Delta\mu = V_m\Delta p$. The molar volume V_m is given by M/ρ where M is the molar mass of benzene and ρ is the mass density.

$$\begin{aligned}\Delta\mu &= V_m\Delta p = (M/\rho)\Delta p\\ &= \frac{78.1074\times10^{-3}\ \mathrm{kg\,mol^{-1}}}{876.5\ \mathrm{kg\,m^{-3}}}\times([10\times10^6-100\times10^3]\ \mathrm{Pa})\\ &= \boxed{+8.8\times10^2\ \mathrm{J\,mol^{-1}}}\end{aligned}$$

Note that 1 Pa m^3 = 1 J.

E4B.4(b) The variation of vapour pressure with applied pressure is given by [4B.2–*130*], $p = p^* e^{V_m(l)\Delta p/RT}$. V_m is given by $V_m = M/\rho$ where M is the molar mass of naphthalene ($C_{10}H_8$, M = 128.1632 g mol^{-1}) and ρ is the mass density.

$$V_m = \frac{M}{\rho} = \frac{128.1632\ \mathrm{g\,mol^{-1}}}{1.16\times10^6\ \mathrm{g\,m^{-3}}} = 1.10...\times10^{-4}\ \mathrm{m^3\,mol^{-1}}$$

$$\begin{aligned}p &= (2.0\times10^3\ \mathrm{Pa})\times\exp\left(\frac{(1.10...\times10^{-4}\ \mathrm{m^3\,mol^{-1}})\times([15\times10^6-1\times10^5]\ \mathrm{Pa})}{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times([95+273.15]\ \mathrm{K})}\right)\\ &= 3420\ \mathrm{Pa} = \boxed{3.42\ \mathrm{kPa}}\end{aligned}$$

E4B.5(b) The relationship between pressure and temperature along the solid–liquid boundary is given by [4B.7–*132*], $p = p^* + (\Delta_{fus}H/T^*\Delta_{fus}V)(T-T^*)$, which is rearranged to give $\Delta_{fus}H$. In this case p^* = 1.00 atm, T^* = 427.15 K, p = 1.2 MPa and T = 429.26 K.

$$\begin{aligned}\Delta_{fus}H &= \frac{p-p^*}{T-T^*}T^*\Delta_{fus}V\\ &= \frac{(1.2\times10^6\ \mathrm{Pa})-[(1\ \mathrm{atm})\times(1.01325\times10^5\ \mathrm{Pa/1\ atm})]}{([429.26-427.15]\ \mathrm{K})}\times(427.15\ \mathrm{K})\\ &\quad\times([152.6-142.0]\times10^{-6}\ \mathrm{m^3\,mol^{-1}})\\ &= 2.36...\times10^3\ \mathrm{J\,mol^{-1}} = \boxed{2.4\ \mathrm{kJ\,mol^{-1}}}\end{aligned}$$

The entropy of transition is given by [3B.4–*89*], $\Delta_{fus}S = \Delta_{fus}H/T$, where T is the transition temperature. At the melting temperature the entropy of fusion is

$$\Delta_{fus}S = \frac{2.36...\times10^3\ \mathrm{J\,mol^{-1}}}{427.15\ \mathrm{K}} = \boxed{5.5\ \mathrm{J\,K^{-1}\,mol^{-1}}}$$

E4B.6(b) The integrated version of the Clausius–Clapeyron equation [4B.10–*133*] is given by $\ln(p/p^*) = -(\Delta_{vap}H/R)(1/T - 1/T^*)$. Rearranging for T gives

$$\begin{aligned}T &= \left(\frac{1}{T^*}-\frac{R}{\Delta_{vap}H}\ln\frac{p}{p^*}\right)^{-1}\\ &= \left(\frac{1}{[20.0+273.15]\ \mathrm{K}}-\frac{8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}}{32.7\times10^3\ \mathrm{J\,mol^{-1}}}\times\ln\frac{66.0\ \mathrm{kPa}}{58.0\ \mathrm{kPa}}\right)^{-1}\\ &= \boxed{296\ \mathrm{K}}\text{ or }\boxed{22.9\ ^\circ\mathrm{C}}\end{aligned}$$

E4B.7(b) The Clausius–Clapeyron equation [4B.9–*133*] is $\mathrm{d}\ln p/\mathrm{d}T = \Delta_{\text{vap}}H/RT^2$. This equation is rearranged for $\Delta_{\text{vap}}H$, and the expression for $\ln p$ is differentiated. It does not matter that the pressure is given in units of Torr because only the slope of $\ln p$ is required.

$$\Delta_{\text{vap}}H = RT^2\frac{\mathrm{d}\ln p}{\mathrm{d}T} = RT^2\frac{\mathrm{d}}{\mathrm{d}T}\left(18.361 - \frac{3036.8\,\mathrm{K}}{T}\right) = RT^2\left(\frac{3036.8\,\mathrm{K}}{T^2}\right)$$
$$= (3036.8\,\mathrm{K})R = (3036.8\,\mathrm{K}) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) = \boxed{25.249\,\mathrm{kJ\,mol^{-1}}}$$

E4B.8(b) (i) The Clausius–Clapeyron equation [4B.9–*133*] is $\mathrm{d}\ln p/\mathrm{d}T = \Delta_{\text{vap}}H/RT^2$. This equation is rearranged for $\Delta_{\text{vap}}H$, and the expression for $\ln p$ is differentiated, noting from inside the front cover that $\ln x = (\ln 10)\log x$. It does not matter that the pressure is given in units of Torr because only the slope of $\ln p$ is required.

$$\Delta_{\text{vap}}H = RT^2\frac{\mathrm{d}\ln p}{\mathrm{d}T} = RT^2\ln 10\frac{\mathrm{d}\log p}{\mathrm{d}T} = RT^2\ln 10\frac{\mathrm{d}}{\mathrm{d}T}\left(8.750 - \frac{1625\,\mathrm{K}}{T}\right)$$
$$= RT^2\ln 10\left(\frac{1625\,\mathrm{K}}{T^2}\right) = (1625\,\mathrm{K})R\ln 10$$
$$= (1625\,\mathrm{K}) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln 10 = \boxed{31.11\,\mathrm{kJ\,mol^{-1}}}$$

(ii) The normal boiling point refers to the temperature at which the vapour pressure is 1 atm which is 760 Torr. The given expression, $\log(p/\mathrm{Torr}) = 8.750 - (1625\mathrm{K})/T$ is rearranged for T and a pressure of 760 Torr is substituted into it to give

$$T = \frac{1625\,\mathrm{K}}{8.750 - \log(p/\mathrm{Torr})} = \frac{1625\,\mathrm{K}}{8.750 - \log 760} = \boxed{276.9\,\mathrm{K}} \text{ or } \boxed{3.720\,°\mathrm{C}}$$

Note that this temperature lies outside the range 15 °C to 35 °C for which the expression for $\log(p/\mathrm{Torr})$ is known to be valid, and is therefore an estimate.

E4B.9(b) The relationship between pressure and temperature along the solid–liquid boundary is given by [4B.7–*132*], $p = p^* + (\Delta_{\text{fus}}H/T^*\Delta_{\text{fus}}V)(T - T^*)$. The value of $\Delta_{\text{fus}}V$ is found using $V_{\mathrm{m}} = M/\rho$ where M is the molar mass and ρ is the mass density:

$$\Delta_{\text{fus}}V = V_{\mathrm{m}}(\mathrm{l}) - V_{\mathrm{m}}(\mathrm{s}) = \frac{M}{\rho(\mathrm{l})} - \frac{M}{\rho(\mathrm{s})}$$
$$= \frac{46.1\,\mathrm{g\,mol^{-1}}}{0.789 \times 10^6\,\mathrm{g\,m^{-3}}} - \frac{46.1\,\mathrm{g\,mol^{-1}}}{0.801 \times 10^6\,\mathrm{g\,m^{-3}}} = 8.75... \times 10^{-7}\,\mathrm{m^3\,mol^{-1}}$$

[4B.7–*132*] is then rearranged for T and the values substituted in to give

$$T = T^* + (p - p^*)\frac{T^*\Delta_{\text{fus}}V}{\Delta_{\text{fus}}H}$$
$$= ([-3.65 + 273.15]\,\mathrm{K}) + \left([100 \times 10^6 - 1 \times 10^5]\,\mathrm{Pa}\right)$$
$$\times \frac{([-3.65 + 273.15]\,\mathrm{K}) \times (8.75... \times 10^{-7}\,\mathrm{m^3})}{8.68 \times 10^3\,\mathrm{J\,mol^{-1}}} = \boxed{272\,\mathrm{K}} \text{ or } \boxed{-0.935\,°\mathrm{C}}$$

E4B.10(b) The integrated version of the Clausius–Clapeyron equation [4B.10–*133*] is given by $\ln(p/p^*) = -(\Delta_{\text{vap}}H/R)(1/T - 1/T^*)$. In this case $p^* = 1$ atm (corresponding to the normal boiling point, $T^* = 100\,^\circ\text{C}$) and $p = 1$ bar (corresponding to the standard boiling point). Rearranging for T and putting in the numbers gives

$$\begin{aligned} T &= \left(\frac{1}{T^*} - \frac{R}{\Delta_{\text{vap}}H}\ln\frac{p}{p^*}\right)^{-1} \\ &= \left(\frac{1}{[100 + 273.15]\,\text{K}} - \frac{8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}}{40.7 \times 10^3\,\text{J mol}^{-1}} \times \ln\frac{1 \times 10^5\,\text{Pa}}{1.01325 \times 10^5\,\text{Pa}}\right)^{-1} \\ &= 372.7...\,\text{K or } 99.6...\,^\circ\text{C} \end{aligned}$$

The standard boiling point is therefore lower than the normal boiling point by $373.15\,\text{K} - 372.7...\,\text{K} = \boxed{0.37\,\text{K}}$.

E4B.11(b) Using $1\,\text{W} = 1\,\text{J s}^{-1}$ and $1\,\text{ha} = 1 \times 10^4\,\text{m}^2$, the rate at which energy is absorbed is $(0.87\,\text{kW m}^{-2}) \times (1 \times 10^4\,\text{m}^2) = 8.7 \times 10^3\,\text{kJ s}^{-1}$. The rate of vaporization is then

$$\frac{\text{rate of energy absorption}}{\Delta_{\text{vap}}H} = \frac{8.7 \times 10^3\,\text{kJ s}^{-1}}{44\,\text{kJ mol}^{-1}} = 1.97... \times 10^2\,\text{mol s}^{-1}$$

Multiplication by the molar mass of water gives the rate of loss of water as $(1.97... \times 10^2\,\text{mol s}^{-1}) \times (18.0158\,\text{g mol}^{-1}) = \boxed{3.6\,\text{kg s}^{-1}}$.

E4B.12(b) Vapour pressure as a function of temperature is given by [4B.10–*133*], except that $\Delta_{\text{vap}}H$ is replaced by $\Delta_{\text{sub}}H$. Using the triple point values for p^* and T^* the partial pressure expected for ice at $-5\,^\circ\text{C}$ is

$$\begin{aligned} p &= p^* \exp\left(-\frac{\Delta_{\text{sub}}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right) \\ &= (611\,\text{Pa}) \times \exp\left(-\frac{51 \times 10^3\,\text{J mol}^{-1}}{8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}}\left(\frac{1}{[-5 + 273.15]\,\text{K}} - \frac{1}{273.16\,\text{K}}\right)\right) \\ &= \boxed{0.40\,\text{kPa}} \end{aligned}$$

This is less than the partial pressure of water in the atmosphere, so $\boxed{\text{yes}}$, the frost will sublime. A partial pressure of 0.40 kPa or more would be needed to ensure that the frost remains.

E4B.13(b) (i) Trouton's rule (Section 3B.2 on page 89) states that $\Delta_{\text{vap}}H/T \approx 85\,\text{J K}^{-1}\,\text{mol}^{-1}$ where T is the normal boiling point. Rearranging for $\Delta_{\text{vap}}H$ gives

$$\begin{aligned} \Delta_{\text{vap}}H &= (85\,\text{J K}^{-1}\,\text{mol}^{-1})T = (85\,\text{J K}^{-1}\,\text{mol}^{-1}) \times ([69.0 + 273.15]\,\text{K}) \\ &= 2.90... \times 10^4\,\text{J mol}^{-1} = \boxed{29\,\text{kJ mol}^{-1}} \end{aligned}$$

(ii) The variation of vapour pressure with temperature is given by [4B.10–*133*]:

$$p = p^* \exp\left(-\frac{\Delta_{\text{vap}}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right)$$

The values $T^* = 69.0\,°\text{C}$ and $p^* = 1\,\text{atm}$ or $1.01325 \times 10^5\,\text{Pa}$, are used, hence at 25°C

$$\begin{aligned} p &= (1.01325 \times 10^5\,\text{Pa}) \\ &\quad \times \exp\left(-\frac{2.90... \times 10^4\,\text{J mol}^{-1}}{8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}}\left(\frac{1}{(25 + 273.15)\,\text{K}} - \frac{1}{(69.0 + 273.15)\,\text{K}}\right)\right) \\ &= \boxed{22\,\text{kPa}} \end{aligned}$$

and at 60°C

$$\begin{aligned} p &= (1.01325 \times 10^5\,\text{Pa}) \\ &\quad \times \exp\left(-\frac{2.90... \times 10^4\,\text{J mol}^{-1}}{8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}}\left(\frac{1}{(60 + 273.15)\,\text{K}} - \frac{1}{(69.0 + 273.15)\,\text{K}}\right)\right) \\ &= \boxed{77\,\text{kPa}} \end{aligned}$$

E4B.14(b) The relationship between pressure and temperature along the solid–liquid boundary is given by [4B.7–*132*], $p = p^* + (\Delta_{\text{fus}}H/T^*\Delta_{\text{fus}}V)(T - T^*)$. The molar volume is $V_m = M/\rho$ where M is the molar mass and ρ is the mass density

$$\Delta_{\text{fus}}V = V_m(\text{l}) - V_m(\text{s}) = M/\rho(\text{l}) - M/\rho(\text{s})$$

This expression is inserted into [4B.7–*132*], which is then rearranged for T. T^*, p^*, and $\Delta_{\text{vap}}H$ are taken as the values corresponding to the normal melting point of ice, that is, 0 °C (273.15 K) and 1 atm (101.325 kPa). It is assumed that $\Delta_{\text{vap}}H$ is constant over the temperature range of interest.

$$\begin{aligned} T &= T^* + (p - p^*)\frac{T^*}{\Delta_{\text{fus}}H}\left(\frac{M}{\rho(\text{l})} - \frac{M}{\rho(\text{s})}\right) \\ &= (273.15\,\text{K}) + ([10 \times 10^6 - 1.01325 \times 10^5]\,\text{Pa}) \times \frac{273.15\,\text{K}}{6.008 \times 10^3\,\text{J mol}^{-1}} \\ &\quad \times \left(\frac{18.0158\,\text{g mol}^{-1}}{0.998 \times 10^6\,\text{g m}^{-3}} - \frac{18.0158\,\text{g mol}^{-1}}{0.915 \times 10^6\,\text{g m}^{-3}}\right) = \boxed{272\,\text{K}} \text{ or } \boxed{-0.74\,°\text{C}} \end{aligned}$$

Solutions to problems

P4B.2 At the triple point the vapour pressures of the solid and liquid are equal, so the two expressions for the vapour pressure are set equal

$$10.5916 - (1871.2\,\text{K})/T = 8.3186 - (1425.7\,\text{K})/T$$

This expression is rearranged to find T as

$$T = \frac{(1871.2 - 1425.7)\,\text{K}}{(10.5916 - 8.3186)} = 1.95... \times 10^2\,\text{K} = \boxed{196.00\,\text{K}}$$

This temperature is then substituted back into one of the expressions for the pressure

$$\log(p/\text{Torr}) = 10.5916 - \frac{1871.2\,\text{K}}{1.95... \times 10^2\,\text{K}} = 1.04...$$

and so $p = 10^{1.04...}$ Torr = $\boxed{11.079\ \text{Torr}}$.

P4B.4 (a) The temperature dependence of the vapour pressure is given by [4B.4a–*131*], $\mathrm{d}p/\mathrm{d}T = \Delta_{\text{vap}}S/\Delta_{\text{vap}}V$. The entropy change is written as $\Delta_{\text{vap}}H/T$ and $\Delta_{\text{vap}}V$ is $V_{\text{m}}(\text{g}) - V_{\text{m}}(\text{s})$.

$$\begin{aligned}\frac{\mathrm{d}p}{\mathrm{d}T} &= \frac{\Delta_{\text{vap}}H}{T(V_{\text{m}}(\text{g}) - V_{\text{m}}(\text{l}))}\\ &= \frac{14.4 \times 10^3\,\text{J mol}^{-1}}{(180\,\text{K}) \times ([14.5 \times 10^{-3} - 115 \times 10^{-6}]\,\text{m}^3\,\text{mol}^{-1})}\\ &= 5.56... \times 10^3\,\text{Pa K}^{-1} = \boxed{5.56\,\text{kPa K}^{-1}}\end{aligned}$$

1 Pa m^3 = 1 J has been used.

(b) The Clausius–Clapeyron equation, [4B.9–*133*], is $\mathrm{d}\ln p/\mathrm{d}T = \Delta_{\text{vap}}H/RT^2$. This is rewritten as $\mathrm{d}p/\mathrm{d}T = p\Delta_{\text{vap}}H/RT^2$ using $\mathrm{d}x/x = \mathrm{d}\ln x$.

$$\begin{aligned}\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{p\Delta_{\text{vap}}H}{RT^2} &= \frac{(1.01325 \times 10^5\,\text{Pa}) \times (14.4 \times 10^3\,\text{J mol}^{-1})}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (180\,\text{K})^2}\\ &= 5.41... \times 10^3\,\text{Pa K}^{-1} = \boxed{5.42\,\text{kPa K}^{-1}}\end{aligned}$$

The percentage error from the value in part (a) is

$$\frac{(5.56... - 5.41...) \times 10^3\,\text{Pa K}^{-1}}{5.56... \times 10^3\,\text{Pa K}^{-1}} \times 100\,\% = \boxed{2.61\,\%}$$

P4B.6 (a) From the variation of chemical potential with temperature (at constant pressure) [4B.1b–*128*], $(\partial\mu/\partial T)_p = V_{\text{m}}$, the slope of the chemical potential against pressure is equal to the molar volume. The difference in slope on either side of the normal freezing point of water is therefore

$$\left(\frac{\partial\mu(\text{l})}{\partial p}\right)_T - \left(\frac{\partial\mu(\text{s})}{\partial p}\right)_T = V_{\text{m}}(\text{l}) - V_{\text{m}}(\text{s}) = \Delta_{\text{fus}}V.$$

V_{m} is given by M/ρ, so the difference in slope is

$$\begin{aligned}\Delta_{\text{fus}}V = V_{\text{m}}(\text{l}) - V_{\text{m}}(\text{s}) &= \frac{M}{\rho(\text{l})} - \frac{M}{\rho(\text{s})}\\ &= \frac{18.0158\,\text{g mol}^{-1}}{1.000 \times 10^6\,\text{g m}^{-3}} - \frac{18.0158\,\text{g mol}^{-1}}{0.917 \times 10^6\,\text{g m}^{-3}}\\ &= -1.63... \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1} = \boxed{-1.63 \times 10^{-6}\,\text{J Pa}^{-1}\,\text{mol}^{-1}}\end{aligned}$$

where 1 J = 1 Pa m^3 has been used.

(b) Similarly,

$$\left(\frac{\partial\mu(\mathrm{g})}{\partial p}\right)_T - \left(\frac{\partial\mu(\mathrm{l})}{\partial p}\right)_T = V_\mathrm{m}(\mathrm{g}) - V_\mathrm{m}(\mathrm{s}) = \Delta_\mathrm{vap}V$$

$$= \frac{M}{\rho(\mathrm{g})} - \frac{M}{\rho(\mathrm{l})}$$

$$= \frac{18.0158\,\mathrm{g\,mol^{-1}}}{0.598\times10^{3}\,\mathrm{g\,m^{-3}}} - \frac{18.0158\,\mathrm{g\,mol^{-1}}}{0.958\times10^{6}\,\mathrm{g\,m^{-3}}}$$

$$= 3.01...\times10^{-2}\,\mathrm{m^3\,mol^{-1}} = \boxed{0.0301\,\mathrm{J\,Pa^{-1}\,mol^{-1}}}$$

(c) From part (b)

$$\left(\frac{\partial\mu(\mathrm{g})}{\partial p}\right)_T - \left(\frac{\partial\mu(\mathrm{l})}{\partial p}\right)_T = \Delta_\mathrm{vap}V \quad \text{hence} \quad \left(\frac{\partial[\mu(\mathrm{g})-\mu(\mathrm{l})]}{\partial p}\right)_p = \Delta_\mathrm{vap}V$$

Rewriting this for a finite change gives $\Delta[\mu(\mathrm{g})-\mu(\mathrm{l})] = \Delta_\mathrm{vap}V\times\Delta p$. So if the pressure is increased by $\Delta p = 0.2\,\mathrm{atm}$ from 1.0 atm to 1.2 atm, the change in $\mu(\mathrm{g})-\mu(\mathrm{l})$ is

$$\Delta[\mu(\mathrm{g})-\mu(\mathrm{l})] = (0.0301...\,\mathrm{J\,Pa^{-1}\,mol^{-1}})\times(0.2\,\mathrm{atm})\times\frac{1.01325\times10^{5}\,\mathrm{Pa}}{1\,\mathrm{atm}}$$

$$= 610\,\mathrm{J\,mol^{-1}}$$

Therefore, since liquid water and vapour are in equilibrium at 100 °C and 1.0 atm, if the pressure is raised to 1.2 atm the chemical potential of water vapour will exceed that of liquid water by $\boxed{610\,\mathrm{J\,mol^{-1}}}$. The fact that $\mu(\mathrm{g}) > \mu(\mathrm{l})$ indicates that the water vapour will have a tendency to condense under these conditions.

P4B.8 Using the perfect gas equation ([1A.4–8]) the amount in moles of water vapour, n_g, in the 50 $\mathrm{dm^3}$ of air after it has bubbled through the water is

$$n_\mathrm{g} = \frac{p_{\mathrm{H_2O}}V}{RT}$$

where $p_{\mathrm{H_2O}}$ is the vapour pressure of the water. The heat required to vaporize this amount of water is $n_g\Delta_\mathrm{vap}H$:

$$q = -\frac{p_{\mathrm{H_2O}}V}{RT}\times\Delta_\mathrm{vap}H$$

where q is the heat which enters the liquid water; the minus sign is needed because the heat has left the water. This heat is equal to $q = n_\mathrm{l}C_\mathrm{m}\Delta T$ (Section 2A.4(b) on page 43) where C_m is the molar heat capacity and n_l is the amount in moles of water. n_l is given by m/M where m is the mass of water and M is the molar mass. It follows that $\Delta T = q/n_1 C_m$

$$\Delta T = \frac{q}{n_1 C_m} = \frac{q}{(m/M)C_m} = -\overbrace{\frac{p_{H_2O}V}{RT} \times \Delta_{vap}H}^{q} \times \frac{M}{mC_m}$$

$$= -\frac{(3.17\times10^3\ \text{Pa})\times(50\times10^{-3}\ \text{m}^3)}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times([25+273.15]\ \text{K})}\times(44.0\times10^3\ \text{J mol}^{-1})$$

$$\times\frac{18.0158\ \text{g mol}^{-1}}{(250\ \text{g})\times(75.5\ \text{J K}^{-1}\ \text{mol}^{-1})} = -2.68...\ \text{K}$$

So the final temperature will be $(25-2.68...)\ °\text{C} = \boxed{22.3\ °\text{C}}$

P4B.10 (a) The normal boiling point is the temperature at which the vapour pressure is equal to 1 atm, or 760 Torr. From the data, this is at $\boxed{227.5\ °\text{C}}$.

(b) The integrated form of the Clausius–Clapeyron equation, given by [4B.10–*133*], $\ln(p/p^*) = -(\Delta_{vap}H/R)(1/T - 1/T^*)$, is rewritten as

$$\ln\frac{p}{p^*} = -\frac{\Delta_{vap}H}{R}\frac{1}{T} + \frac{\Delta_{vap}H}{RT^*}$$

This implies that a plot of $\ln(p/p^*)$ against $1/T$ should be a straight line of slope $-\Delta_{vap}H/R$ and intercept $\Delta_{vap}H/RT^*$; p^* may be taken to be 760 Torr (1 atm). The plot is shown in Fig. 4.2.

$\theta/°\text{C}$	p/Torr	T^{-1}/K^{-1}	$\ln(p/p^*)$
57.4	1	0.003 025	−6.633
100.4	10	0.002 677	−4.331
133.0	40	0.002 462	−2.944
157.3	100	0.002 323	−2.028
203.5	400	0.002 098	−0.642
227.5	760	0.001 997	0.000

The data fall on a good straight line, the equation of which is

$$\ln(p/p^*) = (-6.446\times10^3)\times(T^{-1}/\text{K}^{-1}) + 12.91$$

The slope is equal to $-\Delta_{vap}H/R$, so:

$$\Delta_{vap}H = -\text{slope}\times R = -(-6.446\times10^3\ \text{K})\times(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})$$
$$= \boxed{53.6\ \text{kJ mol}^{-1}}$$

P4B.12 (a) The expression $dH = C_p dT + V dp$ implies that for a phase change

$$d\Delta_{trs}H = \Delta_{trs}C_p dT + \Delta_{trs}V dp$$

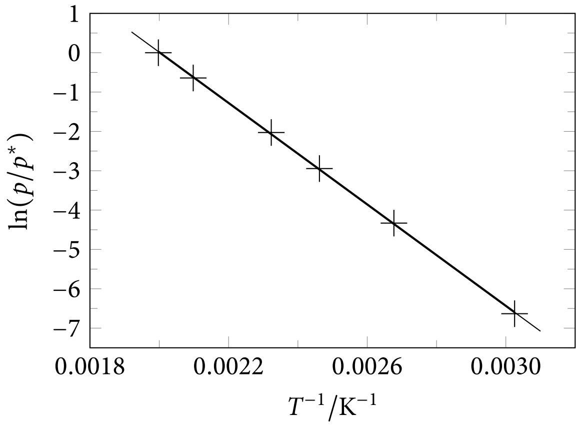


Figure 4.2

The Clayperon equation [4B.4a–*131*], $\mathrm{d}p/\mathrm{d}T = \Delta_{\mathrm{trs}}S/\Delta_{\mathrm{trs}}V$, is rearranged to give $\Delta_{\mathrm{trs}}V\mathrm{d}p = \Delta_{\mathrm{trs}}S\mathrm{d}T$ and this is used to replace $\Delta_{\mathrm{trs}}V\mathrm{d}p$ in the previous equation: $\mathrm{d}\Delta_{\mathrm{trs}}H = \Delta_{\mathrm{trs}}C_p\mathrm{d}T + \Delta_{\mathrm{trs}}S\mathrm{d}T$. Replacing $\Delta_{\mathrm{trs}}S$ by $\Delta_{\mathrm{trs}}H/T$ gives the required expression:

$$\mathrm{d}\Delta_{\mathrm{trs}}H = \Delta_{\mathrm{trs}}C_p\mathrm{d}T + \frac{\Delta_{\mathrm{trs}}H}{T}\mathrm{d}T$$

(b) Starting with the second expression, application of the quotient rule $\mathrm{d}(u/v) = (v\mathrm{d}u - u\mathrm{d}v)/v^2$ to the left hand side and $\mathrm{d}\ln x = \mathrm{d}x/x$ to the right hand side gives

$$\mathrm{d}\left(\frac{\Delta_{\mathrm{trs}}H}{T}\right) = \Delta_{\mathrm{trs}}C_p\mathrm{d}\ln T \quad \text{hence} \quad \frac{T\mathrm{d}\Delta_{\mathrm{trs}}H - \Delta_{\mathrm{trs}}H\mathrm{d}T}{T^2} = \frac{\Delta_{\mathrm{trs}}C_p\mathrm{d}T}{T}$$

This expression is rearranged for $\mathrm{d}\Delta_{\mathrm{trs}}H$ to obtain the first expression:

$$\mathrm{d}\Delta_{\mathrm{trs}}H = \Delta_{\mathrm{trs}}C_p\mathrm{d}T + \frac{\Delta_{\mathrm{trs}}H}{T}\mathrm{d}T$$

P4B.14 The variation of vapour pressure with applied pressure is given by [4B.2–*130*], $p = p^*\mathrm{e}^{V_\mathrm{m}\Delta P/RT}$. In this case the change in pressure (due to the depth) is $\Delta P = \rho g d$. Since $\rho = M/V_\mathrm{m}$, equation [4B.2–*130*] becomes

$$p = p^*\mathrm{e}^{V_\mathrm{m}(M/V_\mathrm{m})gd/RT} = p^*\mathrm{e}^{Mgd/RT}$$

At a depth of 10 m the effect on the vapour pressure is

$$p/p^* = \exp\left(\frac{(18.0158\times10^{-3}\,\mathrm{kg\,mol^{-1}})\times(9.81\,\mathrm{m\,s^{-1}})\times(10\,\mathrm{m})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times([25+273.15]\,\mathrm{K})}\right) = 1.00071$$

The fractional increase in vapour pressure is therefore $\boxed{0.00071}$ or $\boxed{0.071\,\%}$.

P4B.16 The first derivative of chemical potential with respect to temperature is given by equation [4B.1a–*128*], $(\partial\mu/\partial T)_p = -S_m$. The second derivative is therefore

$$\left(\frac{\partial^2\mu}{\partial T^2}\right)_p = -\left(\frac{\partial S_m}{\partial T}\right)_p$$

Entropy is defined by $dS = dq_{rev}/T$ ([3A.1a–*80*]) and, from section Section 3B.3 on page 90, at constant pressure $dq_{rev} = dH = C_p dT$. Therefore

$$dS_m = \frac{C_{p,m}dT}{T} \quad \text{and hence} \quad \left(\frac{\partial S_m}{\partial T}\right)_p = \frac{C_{p,m}}{T}$$

Consequently the curvature of the chemical potential with temperature is

$$\boxed{(\partial^2\mu/\partial T^2)_p = -C_{p,m}/T}$$

Heat capacity is invariably positive, so this expression implies a negative curvature (since T cannot be negative).

For water, the curvatures of the liquid and gas lines at the normal boiling point (373.15 K) are:

$$\text{liquid line:} \left(\frac{\partial^2\mu(l)}{\partial T^2}\right)_p = \frac{-C_{p,m}(l)}{T} = \frac{-75.3\,J\,K^{-1}\,mol^{-1}}{373.15\,K} = \boxed{-0.202\,J\,K^{-2}\,mol^{-1}}$$

$$\text{gas line:} \left(\frac{\partial^2\mu(g)}{\partial T^2}\right)_p = \frac{-C_{p,m}(g)}{T} = \frac{-33.6\,J\,K^{-1}\,mol^{-1}}{373.15\,K} = \boxed{-0.0900\,J\,K^{-2}\,mol^{-1}}$$

The magnitude of the curvature is therefore greater for the liquid.

Solutions to integrated activities

I4.2 (a) The expressions are plotted on the graph shown in Fig. 4.3. Note that the liquid-vapour line is only plotted for $T_3 \le T \le T_c$ because the liquid phase does not exist below the triple point and there is no distinction between liquid and vapour above the critical point. The solid-liquid line is plotted for $T \ge T_3$.

(b) The standard melting point is the temperature corresponding to a pressure of 1 bar on the solid-liquid boundary. Setting $p = 1$ bar in the equation for the solid-liquid boundary and substituting in the value of p_3 gives:

$$1 = 0.4362 \times 10^{-6} + 1000(5.60 + 11.727x)x$$

This equation is rearranged to the standard quadratic form

$$11727x^2 + 5600x - 0.9999995638 = 0$$

which on solving for x gives $x = 1.78... \times 10^{-4}$ or $x = -0.477...$. Then, since $x = T/T_3 - 1$ where $T_3 = 178.15$ K, it follows that

$$T = 178.15(1.78... \times 10^{-4} + 1) = 178.18\,K$$
$$\text{or} \quad T = 178.15(-0.477... + 1) = 93.11\,K$$

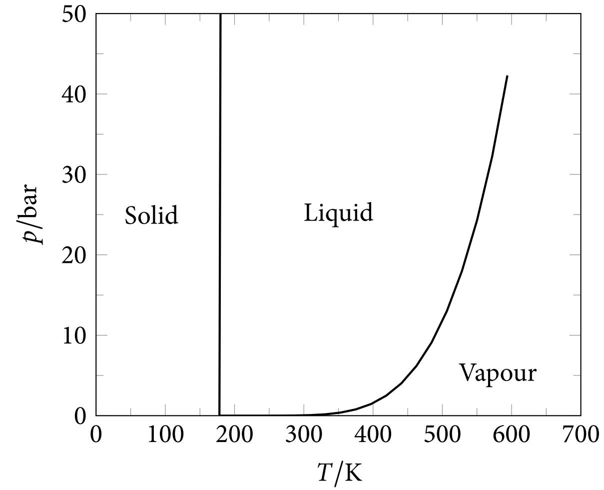


Figure 4.3

The 93.11 K solution is rejected since it lies below T_3 where the liquid, and therefore the solid-liquid boundary, does not exist. The standard melting point is therefore estimated to be $\boxed{178.18\,\text{K}}$.

(c) The standard boiling point is the temperature at the point on the liquid-vapour phase boundary corresponding to $p = 1\,\text{bar}$. Substituting this value of p into the equation for the liquid-vapour boundary and noting that $\ln 1 = 0$ gives

$$0 = -10.418/y + 21.157 - 15.996y + 14.015y^2 - 5.0120y^3 + 4.7334(1-y)^{1.70}$$

Solving numerically gives

$$y = 0.645\ldots \quad \text{and so} \quad T = y \times T_c = 0.645\ldots \times 593.95 = \boxed{383.54\,\text{K}}$$

(d) Use the Clapeyron equation for the liquid-vapour boundary [4B.8–*133*]:

$$\frac{dp}{dT} = \frac{\Delta_{\text{vap}}H}{T\Delta_{\text{vap}}V} \quad \text{which rearranges to} \quad \Delta_{\text{vap}}H = T\Delta_{\text{vap}}V \times \frac{dp}{dT}$$

To find dp/dT, use $d\ln x = dx/x$ so that $dp/dT = p \times d\ln p/dT$. The expression for $\ln p$ is inserted and differentiated, and then evaluated at the standard boiling point found above. For the evaluation of $d\ln p/dT$ it does not matter that the expression has p in bar not Pa because the slope of $\ln p$ is independent of the units of p due to the logarithm.

$$\begin{aligned}\frac{\mathrm{d}p}{\mathrm{d}T} &= p\frac{\mathrm{d}\ln p}{\mathrm{d}T} = p \times \frac{\mathrm{d}\ln p}{\mathrm{d}y} \times \frac{\mathrm{d}y}{\mathrm{d}T}\\ &= p \times \frac{\mathrm{d}}{\mathrm{d}y}\left(-\frac{10.418}{y} + 21.157 - 15.996y + 14.015y^2 - 5.0120y^3\right.\\ &\quad \left.+ 4.7334(1-y)^{1.70}\right) \times \frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{T}{T_\mathrm{c}}\right)\\ &= \frac{p}{T_\mathrm{c}} \times \left(\frac{10.418}{y^2} - 15.996 + 28.030y - 15.0360y^2\right.\\ &\quad \left.- 8.04678(1-y)^{0.70}\right)\\ &= \frac{10^5\ \mathrm{Pa}}{593.95\ \mathrm{K}}\left(\frac{10.418}{(0.645...)^2}\right.\\ &\quad - 15.996 + 28.030(0.645...) - 15.0360(0.645...)^2\\ &\quad \left.- 8.04678(1-0.645...)^{0.70}\right) = 2.84... \times 10^3\ \mathrm{Pa\,K^{-1}}\end{aligned}$$

Then

$$\begin{aligned}\Delta_\mathrm{vap}H &= T\Delta_\mathrm{vap}V \times \frac{\mathrm{d}p}{\mathrm{d}T}\\ &= (383.54\ \mathrm{K}) \times ([30.3 - 0.12] \times 10^{-3}\ \mathrm{m^3\,mol^{-1}}) \times (2.84... \times 10^3\ \mathrm{Pa\,K^{-1}})\\ &= \boxed{33.0\ \mathrm{kJ\,mol^{-1}}}\end{aligned}$$

I4.4 (a) The data are plotted in Fig. 4.4.

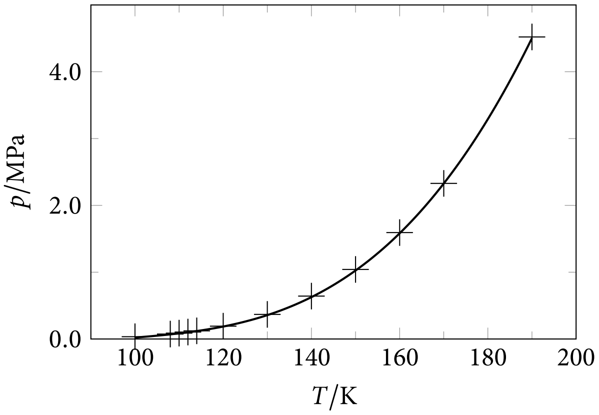


Figure 4.4

These data fit well to the cubic

$$p/\mathrm{MPa} = (4.989{\times}10^{-6}\ \mathrm{K^{-3}})T^3 - (1.452{\times}10^{-3}\ \mathrm{K^{-2}})T^2 + (0.1461\ \mathrm{K^{-1}})T - 5.058$$

This equation is used to plot the line on the graph.

(b) The standard boiling point corresponds to the temperature at which p = 1 bar or 0.1 MPa. This value is substituted into the fitted function to give

$$0.1 = (4.989{\times}10^{-6}\,\mathrm{K}^{-3})T^3 - (1.452{\times}10^{-3}\,\mathrm{K}^{-2})T^2 + (0.1461\,\mathrm{K}^{-1})T - 5.058$$

which, on solving numerically using mathematical software, yields

$$T = 1.11... \times 10^{-2}\,\mathrm{K} = \boxed{112\,\mathrm{K}}$$

(c) The Clapeyron equation for the liquid-vapour boundary is [4B.8–*133*]:

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}}H}{T\Delta_{\mathrm{vap}}V} \quad \text{hence} \quad \Delta_{\mathrm{vap}}H = T\Delta_{\mathrm{vap}}V \times \frac{\mathrm{d}p}{\mathrm{d}T}$$

The value of $\mathrm{d}p/\mathrm{d}T$ is obtained by differentiating the fitted function and substituting in the value of T found above.

$$\begin{aligned}\frac{\mathrm{d}(p/\mathrm{MPa})}{\mathrm{d}T} &= (14.967 \times 10^{-3}\,\mathrm{K}^{-3})T^2 - (2.904 \times 10^{-3}\,\mathrm{K}^{-2})T + (0.1461\,\mathrm{K}^{-1})\\ &= (14.967 \times 10^{-3}\,\mathrm{K}^{-3}) \times (1.11... \times 10^{2}\,\mathrm{K})^2\\ &\quad - (2.904 \times 10^{-3}\,\mathrm{K}^{-2}) \times (1.11... \times 10^{2}\,\mathrm{K}) + (0.1461\,\mathrm{K}^{-1})\\ &= 8.57... \times 10^{-3}\,\mathrm{K}^{-1}\end{aligned}$$

so that

$$\frac{\mathrm{d}p}{\mathrm{d}T} = 8.57... \times 10^{-3}\,\mathrm{MPa\,K}^{-1} = 8.57... \times 10^{3}\,\mathrm{Pa\,K}^{-1}$$

Therefore

$$\begin{aligned}\Delta_{\mathrm{vap}}H &= T\Delta_{\mathrm{vap}}V \times \frac{\mathrm{d}p}{\mathrm{d}T}\\ &= (1.11... \times 10^{2}\,\mathrm{K}) \times ([8.89 - 3.80 \times 10^{-2}]\,\mathrm{dm}^3\,\mathrm{mol}^{-1}) \times \frac{10^{-3}\,\mathrm{m}^3}{1\,\mathrm{dm}^3}\\ &\quad \times (8.57 \times 10^{3}\,\mathrm{Pa\,K}^{-1}) = \boxed{8.49\,\mathrm{kJ\,mol}^{-1}}\end{aligned}$$

5

Simple mixtures

5A The thermodynamic description of mixtures

Answers to discussion questions

D5A.2 The change in Gibbs energy at constant temperature is equal to the maximum additional (non-expansion) work that the system can do $\mathrm{d}G = \mathrm{d}w_{\mathrm{add,max}}$, [3D.8–*100*]. Changing the composition of a mixture gives rise to a change in Gibbs energy, given by [5A.7–*145*], $\mathrm{d}G = \mu_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}} + \mu_{\mathrm{B}}\mathrm{d}n_{\mathrm{B}} \dots$. It therefore follows that

$$\mathrm{d}w_{\mathrm{add,max}} = \mu_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}} + \mu_{\mathrm{B}}\mathrm{d}n_{\mathrm{B}} \dots$$

and so non-expansion work can arise from the changing composition of a system.

D5A.4 This is discussed in Section 5A.3 on page 150. The chemical potential of a perfect gas depends on its partial pressure p_{A} via $\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^{\ominus} + RT\ln p_{\mathrm{A}}$. Consider first the pure liquid, which has chemical potential $\mu_{\mathrm{A}}^{*}(\mathrm{l})$ and vapour pressure p_{A}^{*}. When the liquid and gas are in equilibrium, their chemical potentials are equal

$$\mu_{\mathrm{A}}^{*}(\mathrm{l}) = \mu_{\mathrm{A}}^{\ominus}(\mathrm{g}) + RT\ln p_{\mathrm{A}}^{*}$$

If A is now one component of a mixture, the chemical potentials of A in the liquid and in the gas are still equal

$$\mu_{\mathrm{A}}(\mathrm{l}) = \mu_{\mathrm{A}}^{\ominus}(\mathrm{g}) + RT\ln p_{\mathrm{A}}$$

Note that the * is not present as A is not pure. The first equation is taken away from the second to give an expression for the chemical potential of A in the liquid in terms of its partial pressure in the vapour

$$\mu_{\mathrm{A}}(\mathrm{l}) = \mu_{\mathrm{A}}^{*}(\mathrm{l}) + RT\ln\frac{p_{\mathrm{A}}}{p_{\mathrm{A}}^{*}} \qquad (5.1)$$

Raoult's law gives the partial pressure of A is terms of the mole fraction in the liquid: $p_{\mathrm{A}} = x_{\mathrm{A}}p_{\mathrm{A}}^{*}$, so it follows that $p_{\mathrm{A}}/p_{\mathrm{A}}^{*} = x_{\mathrm{A}}$ and hence

$$\mu_{\mathrm{A}}(\mathrm{l}) = \mu_{\mathrm{A}}^{*}(\mathrm{l}) + RT\ln x_{\mathrm{A}}$$

This equation relates the chemical potential of a component in a mixture to its mole fraction.

If Henry's law applies, $p_A = K_A x_A$, eqn 5.1 becomes

$$\mu_A(l) = \mu_A^*(l) + RT\ln\frac{K_A x_A}{p_A^*} = \underbrace{\mu_A^*(l) + RT\ln\frac{K_A}{p_A^*}} + RT\ln x_A$$

The term indicated by the brace is defined as a new standard chemcial potential $\mu_A^\ominus$ to give

$$\mu_A(l) = \mu_A^\ominus + RT\ln x_A$$

This expression also relates the chemical potential of a component in a mixture to its mole fraction.

Solutions to exercises

E5A.1(b) The partial molar volume of B is defined from [5A.1–*143*] as

$$V_B = \left(\frac{\partial V}{\partial n_B}\right)_{p,T,n'}$$

The polynomial given relates v to x, and so from this it is possible to compute the derivative dv/dx. This required derivative is dV/dn_B (where the partials are dropped for simplicity), which is related to dv/dx in the following way

$$\left(\frac{dV}{dn_B}\right) = \left(\frac{dV}{dv}\right)\left(\frac{dv}{dx}\right)\left(\frac{dx}{dn_B}\right)$$

Because $x = n_B/\text{mol}$, $dx/dn_B = \text{mol}^{-1}$, and because $v = V/\text{cm}^3$, $dv/dV = \text{cm}^{-3}$ and so $dV/dv = \text{cm}^3$. Hence

$$\left(\frac{dV}{dn_B}\right) = \left(\frac{dV}{dv}\right)\left(\frac{dv}{dx}\right)\left(\frac{dx}{dn_B}\right) = \left(\frac{dv}{dx}\right)\ \text{cm}^3\,\text{mol}^{-1}$$

The required derivative is

$$\left(\frac{dv}{dx}\right) = -22.5749 + 1.13784x + 0.03069\,x^2 + 0.00936\,x^3$$

hence

$$\boxed{V_B = \left(-22.5749 + 1.13784\,x + 0.03069\,x^2 + 0.00936\,x^3\right)\ \text{cm}^3\,\text{mol}^{-1}}$$

E5A.2(b) The partial molar volume of solute B (here $MgSO_4$) is defined from [5A.1–*143*] as

$$V_B = \left(\frac{\partial V}{\partial n_B}\right)_{p,T,n'}$$

The total volume is given as a function of the molality, but this volume is described as that arising from adding the solute to 1 kg of solvent. The molality of a solute is defined as (amount in moles of solute)/(mass of solvent in kg), therefore because in this case the mass of solvent is 1 kg, the molality is numerically equal to the amount in moles, n_B.

The polynomial given relates v to x, and so from this it is possible to compute the derivative dv/dx. This required derivative is dV/dn_B (where the partials are dropped for simplicity), which is related to dv/dx in the following way

$$\left(\frac{dV}{dn_B}\right) = \left(\frac{dV}{dv}\right)\left(\frac{dv}{dx}\right)\left(\frac{dx}{dn_B}\right)$$

The quantity x is defined as $b/b^\ominus$, but it has already been argued that the molality can be expressed as $n_B/(1\text{ kg})$, hence $x = n_B/(\text{mol})$ and therefore $dx/dn_B = \text{mol}^{-1}$. Because $v = V/\text{cm}^3$, $dv/dV = \text{cm}^{-3}$ and so $dV/dv = \text{cm}^3$. Hence

$$\left(\frac{dV}{dn_B}\right) = \left(\frac{dV}{dv}\right)\left(\frac{dv}{dx}\right)\left(\frac{dx}{dn_B}\right) = \left(\frac{dv}{dx}\right)\text{ cm}^3\text{ mol}^{-1}$$

The required derivative is

$$\left(\frac{dv}{dx}\right) = 69.38(x - 0.070)$$

Hence the expression for the partial molar volume of B (NaCl) is

$$V_B = [69.38(x - 0.070)]\text{ cm}^3\text{ mol}^{-1}$$

The partial molar volume when $b/b^\ominus = 0.050$ is given by

$$\begin{aligned}V_B &= 69.38(x - 0.070)\text{ cm}^3\text{ mol}^{-1} = 69.38(0.050 - 0.070)\text{ cm}^3\text{ mol}^{-1}\\ &= -1.38...\text{ cm}^3\text{ mol}^{-1} = \boxed{-1.39\text{ cm}^3\text{ mol}^{-1}}\end{aligned}$$

The total volume is calculated from the partial molar volumes of the two components, [5A.3–*144*], $V = n_A V_A + n_B V_B$. In this case V and V_B are known, so V_A, the partial molar volume of the solvent water can be found from $V_A = (V - n_B V_B)/n_A$.

The total volume when $b/b^\ominus = 0.050$ is given by

$$V = 1001.21 + 34.69 \times (0.050 - 0.070)^2 = 1001.2...\text{ cm}^3$$

The amount in moles of 1 kg of water is $(1000\text{ g})/[(16.00+2\times1.0079)\text{ g mol}^{-1}] = 55.5...\text{ mol}$, hence

$$\begin{aligned}V_A &= \frac{V - n_B V_B}{n_A} = \frac{(1001.2...\text{ cm}^3) - (0.05\text{ mol}) \times (-1.38...\text{ cm}^3\text{ mol}^{-1})}{55.5...\text{ mol}}\\ &= \boxed{18.0\text{ cm}^3\text{ mol}^{-1}}\end{aligned}$$

where, as before, for this solution a molality of 0.05 mol kg^{-1} corresponds to $n_B = 0.05$ mol.

E5A.3(b) For a binary mixture the Gibbs–Duhem equation, [5A.12b–*146*], relates changes in the chemical potentials of A and B

$$n_A d\mu_A + n_B d\mu_B = 0$$

If it is assumed that the differential can be replaced by the small change

$$(0.22\, n_B) \times (-15\ \text{J mol}^{-1}) + n_B \delta\mu_B = 0$$

$$\text{hence} \quad \delta\mu_B = -\frac{(0.22\, n_B)}{n_B}(-15\ \text{J mol}^{-1}) = \boxed{+3.3\ \text{J mol}^{-1}}$$

E5A.4(b) Because the gases are assumed to be perfect and are at the same temperature and pressure when they are separated, the pressure and temperature will not change upon mixing. Therefore [5A.18–*149*], $\Delta_{\text{mix}}S = -nR(x_A \ln x_A + x_B \ln x_B)$, applies. The amount in moles is computed from the total volume, pressure and temperature using the perfect gas equation: $n = pV/RT$. Because the separate volumes are equal, and at the same pressure and temperature, each compartment contains the same amount of gas, so the mole fractions of each gas in the mixture are equal at 0.5.

$$\begin{aligned}\Delta_{\text{mix}}S &= -nR(x_A \ln x_A + x_B \ln x_B) = -(pV/T)(x_A \ln x_A + x_B \ln x_B)\\ &= -\frac{(100\times10^3\ \text{Pa})\times(250\times10^{-6}\ \text{m}^3)}{273.15\ \text{K}}(0.5\ln 0.5 + 0.5\ln 0.5)\\ &= \boxed{+0.0634\ \text{J K}^{-1}}\end{aligned}$$

Note that the pressure in expressed in Pa and the volume in m^3; the units of the result are therefore $(\text{N m}^{-2}) \times (\text{m}^3) \times (\text{K}^{-1}) = \text{N m K}^{-1} = \text{J K}^{-1}$.

Under these conditions the Gibbs energy of mixing is given by [5A.17–*148*], $\Delta_{\text{mix}}G = nRT(x_A \ln x_A + x_B \ln x_B)$; as before $n = pV/RT$.

$$\begin{aligned}\Delta_{\text{mix}}G &= nRT(x_A \ln x_A + x_B \ln x_B) = (pV)(x_A \ln x_A + x_B \ln x_B)\\ &= [(100\times10^3\ \text{Pa})\times(250\times10^{-6}\ \text{m}^3)](0.5\ln 0.5 + 0.5\ln 0.5)\\ &= \boxed{-17.3\ \text{J}}\end{aligned}$$

The units of the result are $(\text{N m}^{-2})\times(\text{m}^3) = \text{N m} = \text{J}$. As expected, the entropy of mixing is positive and the Gibbs energy of mixing is negative.

E5A.5(b) The partial pressure of gas A, p_A above a liquid mixture is given by Raoult's Law, [5A.22–*151*], $p_A = x_A p_A^*$, where x_A is the mole fraction of A in the liquid and p_A^* is the vapour pressure over pure A. The total pressure over a mixture of A and B is $p_A + p_B$.

In this case the mixture is equimolar, so $x_A = x_B = \frac{1}{2}$. If A is 1,2-dimethylbenzene and B is 1,3-dimethylbenzene the total pressure is

$$p = x_A p_A^* + x_B p_B^* = \tfrac{1}{2}(20\ \text{kPa}) + \tfrac{1}{2}(18\ \text{kPa}) = \boxed{19\ \text{kPa}}$$

The composition of the vapour – that is the mole fractions of A and B in the vapour – is calculated from their partial pressures according to [1A.6–*9*], $p_A = y_A p$, where y_A is the mole fraction of A *in the vapour* and p is the total pressure. The partial pressure of A is also given by $p_A = x_A p_A^*$. These two expressions for p_A is equated to give

$$y_A p = x_A p_A^* \quad \text{hence} \quad y_A = \frac{x_A p_A^*}{p}$$

The composition of the vapour is therefore

$$y_A = \frac{x_A p_A^*}{p} = \frac{\frac{1}{2} \times (20\,\text{kPa})}{19\,\text{kPa}} = \boxed{0.53}$$

$$y_B = \frac{x_B p_B^*}{p} = \frac{\frac{1}{2} \times (18\,\text{kPa})}{19\,\text{kPa}} = \boxed{0.47}$$

E5A.6(b) The total volume is calculated from the partial molar volumes of the two components using [5A.3–*144*], $V = n_A V_A + n_B V_B$. The task is therefore to find the amount in moles, n_A and n_B, of A and B in a given mass m of solution. If the molar masses of A and B are M_A and M_B then it follows that

$$m = n_A M_A + n_B M_B$$

The mole fraction of A is defined as $x_A = n_A/(n_A + n_B)$, hence $n_A = x_A(n_A + n_B)$ and likewise for B. With these substitutions for n_A and n_B the previous equation becomes

$$m = x_A M_A (n_A + n_B) + x_B M_B (n_A + n_B) \quad \text{hence} \quad (n_A + n_B) = \frac{m}{x_A M_A + x_B M_B}$$

This latter expression for the total amount in moles, $(n_A + n_B)$, is used with $n_A = x_A(n_A + n_B)$ to give

$$n_A = x_A(n_A + n_B) = \frac{m x_A}{x_A M_A + x_B M_B}$$

and likewise

$$n_B = \frac{m x_B}{x_A M_A + x_B M_B}$$

With these expressions for n_A and n_B the total volume is computed from the partial molar volumes

$$\begin{aligned} V = n_A V_A + n_B V_B &= \frac{m x_A V_A}{x_A M_A + x_B M_B} + \frac{m x_B V_B}{x_A M_A + x_B M_B} \\ &= \frac{m}{x_A M_A + x_B M_B}\left[x_A V_A + x_B V_B\right] \\ &= \frac{m}{x_A M_A + (1 - x_A) M_B}\left[x_A V_A + (1 - x_A) V_B\right] \end{aligned}$$

where on the last line $x_B = (1 - x_A)$ is used.

This expression for the volume of 1.000 kg evaluates as

$$\begin{aligned} V &= \frac{1000\ \mathrm{g}}{0.3713 \times (241.1\ \mathrm{g\,mol^{-1}}) + (1 - 0.3713) \times (198.2\ \mathrm{g\,mol^{-1}})} \\ &\quad \times \left[0.3713 \times (188.2\ \mathrm{cm^3\,mol^{-1}}) + (1 - 0.3713) \times (176.14\ \mathrm{cm^3\,mol^{-1}})\right] \\ &= \boxed{843.5\ \mathrm{cm^3}} \end{aligned}$$

E5A.7(b) Consider a solution of A and B in which the fraction (by mass) of A is α. The total volume of a solution of A and B is calculated from the partial molar volumes of the two components using [5A.3–*144*], $V = n_A V_A + n_B V_B$. In this exercise V and V_A are known, so the task is therefore to find the amount in moles, n_A and n_B, of A and B in the solution of known mass density ρ.

The mass of a volume V of the solution is ρV, so the mass of A is $\alpha\rho V$. If the molar mass of A is M_A, then the amount in moles of A is $n_A = \alpha\rho V/M_A$. Similarly, $n_B = (1-\alpha)\rho V/M_B$. The volume is expressed using these quantities as

$$V = n_A V_A + n_B V_B = \frac{\alpha\rho V V_A}{M_A} + \frac{(1-\alpha)\rho V V_B}{M_B}$$

The term V cancels between the first and third terms to give

$$1 = \frac{\alpha\rho V_A}{M_A} + \frac{(1-\alpha)\rho V_B}{M_B}$$

This equation is rearranged to give an expression for V_A

$$V_A = \frac{M_A}{\alpha\rho}\left(1 - \frac{(1-\alpha)V_B\rho}{M_B}\right)$$

In this exercise let A be H_2O and B be ethanol, and as the mixture is 20% ethanol and 80% H_2O by mass, $\alpha = 0.8$. The molar mass of A (H_2O) is $M_A = 16.00 + 2 \times 1.0079 = 18.0158\ \mathrm{g\,mol^{-1}}$ and the molar mass of B (ethanol) is $M_B = 2 \times 12.01 + 16.00 + 6 \times 1.0079 = 46.0674\ \mathrm{g\,mol^{-1}}$. The above expression for V_A evaluates as

$$\begin{aligned} V_A &= \frac{M_A}{\alpha\rho}\left(1 - \frac{(1-\alpha)V_B\rho}{M_B}\right) = \frac{(18.0158\ \mathrm{g\,mol^{-1}})}{0.8 \times (0.9687\ \mathrm{g\,cm^{-3}})} \\ &\quad \times \left(1 - \frac{(1-0.8) \times (52.2\ \mathrm{cm^3\,mol^{-1}}) \times (0.9687\ \mathrm{g\,cm^{-3}})}{46.0674\ \mathrm{g\,mol^{-1}}}\right) \\ &= \boxed{18.1\ \mathrm{cm^3\,mol^{-1}}} \end{aligned}$$

In evaluating this expression the density has been converted to units of $\mathrm{g\,cm^{-3}}$: $968.7\ \mathrm{kg\,m^{-3}} = 968.7 \times 10^3 \times 10^{-6}\ \mathrm{g\,cm^{-3}} = 0.9687\ \mathrm{g\,cm^{-3}}$.

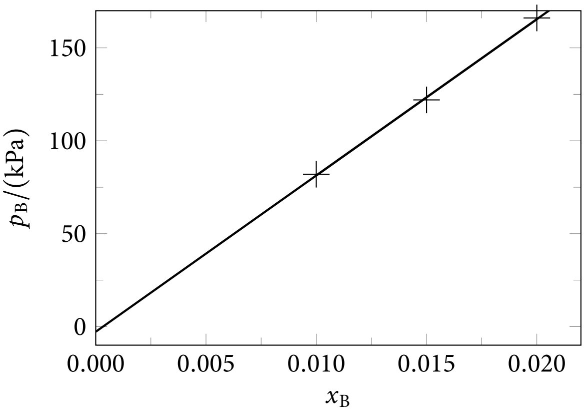


Figure 5.1

E5A.8(b) Henry's law gives the partial vapour pressure of a solute B as $p_B = K_B x_B$, [5A.24–*152*]. A test of this law is to make a plot of p_B against x_B which is expected to be a straight line with slope K_B; such a plot is shown in Fig. 5.1

The data fall on quite a good straight line, the equation of which is

$$p_{HCl}/(\text{kPa}) = 8.41 \times 10^3 \times (x_B) - 2.784$$

If Henry's law is obeyed the pressure should go to zero as x_B goes to zero, and the graph shows that this is not quite achieved. Overall the conclusion is that these data obey Henry's law reasonably well. The Henry's law constant K_B is computed from the slope as $\boxed{8.4 \times 10^3 \text{ kPa}}$.

E5A.9(b) In Section 5A.3(b) on page 152 it is explained that for practical applications Henry's law is often expressed as $p_B = K_B b_B$, where b_B is the molality of the solute, usually expressed in mol kg^{-1}. The molality is therefore calculated from the partial pressure as $b_B = p_B/K_B$.

Molality is the amount of solute per kg of solvent. The mass m of a volume V of solvent is given by $m = \rho V$, where ρ is the mass density of the solvent. If the amount of solute in volume V is n_B, the molar concentration c_B is related to the molality by

$$c_B = \frac{n_B}{V} = \frac{n_B}{m/\rho} = \rho \overbrace{\frac{n_B}{m}}^{b_B} = \rho b_B$$

Using Henry's law the concentration is therefore given by

$$c_B = \rho b_B = \rho \overbrace{\frac{p_B}{K_B}}^{b_B} = \frac{\rho x_B p}{K_B}$$

where the partial pressure p_B is expressed in terms of the mole fraction and the total pressure p, $p_B = x_B p$.

The Henry's law constant for CH_4 in benzene is 44.4×10^3 kPa kg mol^{-1} and the density of benzene is 0.879 g cm^{-3}.

$$c_{N_2}=\frac{\rho p_{N_2}}{K_{N_2}}=\frac{(0.879\times10^3\ \mathrm{kg\,m^{-3}})\times(100\ \mathrm{kPa})}{44.4\times10^3\ \mathrm{kPa\,kg\,mol^{-1}}}=1.97...\ \mathrm{mol\,m^{-3}}$$

The molar concentration is therefore $\boxed{2.0\times10^{-3}\ \mathrm{mol\,dm^{-3}}}$.

E5A.10(b) In Section 5A.3(b) on page 152 it is explained that for practical applications Henry's law is often expressed as $p_B = K_B b_B$, where b_B is the molality of the solute, usually expressed in mol kg^{-1}. The molality is therefore calculated from the partial pressure as $b_B = p_B/K_B$, and the partial pressure is expressed as $p_B = x_B p$, where p is the total pressure The Henry's law constant for N_2 in water is 1.56×10^5 kPa kg mol^{-1}, and for O_2 the constant is 7.92×10^4 kPa kg mol^{-1}

The total pressure is assumed to be 1 atm (101.325 kPa)

$$b_{N_2}=\frac{x_{N_2}p}{K_{N_2}}=\frac{0.78\times(101.325\ \mathrm{kPa})}{1.56\times10^5\ \mathrm{kPa\,kg\,mol^{-1}}}=\boxed{5.1\times10^{-4}\ \mathrm{mol\,kg^{-1}}}$$

$$b_{O_2}=\frac{x_{O_2}p}{K_{O_2}}=\frac{0.21\times(101.325\ \mathrm{kPa})}{7.92\times10^4\ \mathrm{kPa\,kg\,mol^{-1}}}=\boxed{2.7\times10^{-4}\ \mathrm{mol\,kg^{-1}}}$$

E5A.11(b) As explained in Exercise E5A.9(b) the concentration of a solute is estimated as $c_B = \rho p_B/K_B$ where ρ is the mass density of the solvent. The Henry's law constant for CO_2 in water is 3.01×10^3 kPa kg mol^{-1} and the density of water is 0.997 g cm^{-3} or 997 kg m^{-3}.

$$c_{CO_2}=\frac{\rho p_{CO_2}}{K_{CO_2}}=\frac{(997\ \mathrm{kg\,m^{-3}})\times(2.0\ \mathrm{atm})\times(101.325\ \mathrm{kPa}/1\ \mathrm{atm})}{3.01\times10^3\ \mathrm{kPa\,kg\,mol^{-1}}}$$
$$=67.1...\ \mathrm{mol\,m^{-3}}$$

The molar concentration is therefore $\boxed{0.067\ \mathrm{mol\,dm^{-3}}}$.

Solutions to problems

P5A.2 The Gibbs–Duhem equation [5A.12b–*146*], expressed in terms of partial molar volumes is $n_A dV_A + n_B dV_B = 0$. This rearranges to

$$dV_B=-\frac{n_A}{n_B}dV_A$$

Division of both the top of bottom of the fraction on the right by $(n_A + n_B)$ allows this equation to be rewritten in terms of the mole fractions

$$dV_B=-\frac{n_A/(n_A+n_B)}{n_B/(n_A+n_B)}dV_A=-\frac{x_A}{x_B}dV_A=-\frac{x_A}{(1-x_A)}dV_A$$

The partial molar volumes are functions of the composition of the mixture which is specified by x_A and x_B. Both sides are integrated between the limits $(x_A = 0, x_B = 1)$, that is pure B, and an arbitrary composition (x_A, x_B) to give

$$\int_{(x_A=0,x_B=1)}^{(x_A,x_B)} \mathrm{d}V_B = -\int_{(x_A=0,x_B=1)}^{(x_A,x_B)} \frac{x_A}{(1-x_A)}\mathrm{d}V_A$$

The left-hand side evaluates to $V_B - V_B^*$, where V_B^* is the molar volume of pure B, and V_B is the partial molar volume at the specified composition. It follows that

$$V_B = V_B^* - \int_{(x_A=0,x_B=1)}^{(x_A,x_B)} \frac{x_A}{(1-x_A)}\mathrm{d}V_A \qquad (5.2)$$

If the variation of V_A with x_A is known, then the integral on the right can be evaluated and hence a value found for V_B.

Let component A be trichloromethane and component B be propanone. The task is first to use the given data of V_m as a function of x_A to find V_A as a function of x_A. The definition of V_A is

$$V_A = \left(\frac{\partial V}{\partial n_A}\right)_{n_B}$$

which is interpreted as the slope of a plot of V against n_A, at constant n_B. The data provided is of the molar volume, defined as $V_m = V/(n_A + n_B)$, as a function of x_A, so the next step is to use these data to find V as a function of n_A at fixed n_B. Arbitrarily, set $n_B = 1$ mol so that

$$V = [n_A + (1\ \text{mol})]\,V_m$$

The mole fraction x_A is given by $x_A = n_A/[n_A + (1\ \text{mol})]$ which rearranges to

$$n_A = \frac{(1\ \text{mol}) \times x_A}{1 - x_A} \qquad (5.3)$$

It follows that

$$V = [n_A + (1\ \text{mol})]\,V_m = \left[\frac{(1\ \text{mol}) \times x_A}{1 - x_A} + (1\ \text{mol})\right] V_m = \frac{(1\ \text{mol})}{1 - x_A} V_m$$

These expressions are used to draw up the following table and plot the graph in Fig. 5.2.

x_A	$V_m/(\text{cm}^3\ \text{mol}^{-1})$	$V/(\text{cm}^3)$	$n_A/(\text{mol})$
0	73.99	73.99	0
0.194	75.29	93.41	0.241
0.385	76.50	124.39	0.626
0.559	77.55	175.85	1.268
0.788	79.08	373.02	3.717
0.889	79.82	719.10	8.009

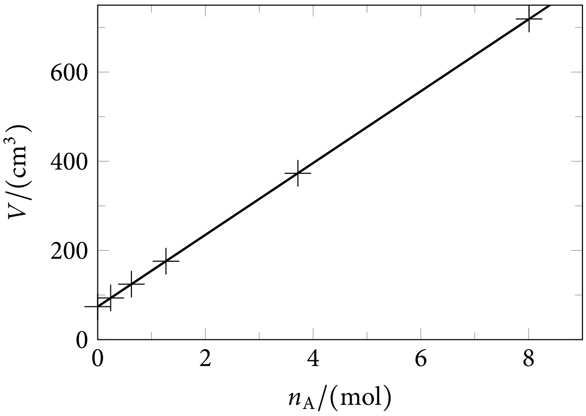


Figure 5.2

The data fall on a good straight line which implies that the partial molar volume (the slope) is nearly constant with composition. However, for there to be anything to do in the rest of the problem it is necessary to have some variation in V_A, so the data are fitted to a quadratic to give

$$V/(\mathrm{cm}^3) = 0.02524\,(n_\mathrm{A}/\mathrm{mol})^2 + 80.34\,(n_\mathrm{A}/\mathrm{mol}) + 74.03$$

From this an expression for V_A is found by differentiation (recall that n_B has been held constant)

$$V_\mathrm{A}/(\mathrm{cm}^3\,\mathrm{mol}^{-1}) = \left(\frac{\partial V}{\partial n_\mathrm{A}}\right)_{n_\mathrm{B}} = 0.05048\,(n_\mathrm{A}/\mathrm{mol}) + 80.34$$

Now that an expression for V_A is available the integral in eqn 5.2 can be evaluated. The upper limit of the integral is $(x_\mathrm{A} = 0.5, x_\mathrm{B} = 0.5)$ because the partial molar volume at $x_\mathrm{A} = 0.5$ is required. The integral will be the area under a plot of $x_\mathrm{A}/(1 - x_\mathrm{A})$ against V_A over this range from $x_\mathrm{A} = 0$ to $x_\mathrm{A} = 0.5$.

Equation 5.3 gives n_A as a function of x_A, so the partial molar volume can be expressed as

$$V_\mathrm{A}/(\mathrm{cm}^3\,\mathrm{mol}^{-1}) = 0.05048\left(\frac{x_\mathrm{A}}{1 - x_\mathrm{A}}\right) + 80.34$$

This expression is used to draw up a table of values of V_A in the required range and then to make the plot of $x_\mathrm{A}/(1 - x_\mathrm{A})$ against V_A, shown in Fig. 5.3.

$V_\mathrm{A}/(\mathrm{cm}^3\,\mathrm{mol}^{-1})$	x_A	$x_\mathrm{A}/(1 - x_\mathrm{A})$
80.3406	0.000	0.000
80.3462	0.100	0.111
80.3533	0.200	0.250
80.3623	0.300	0.429
80.3743	0.400	0.667
80.3911	0.500	1.000

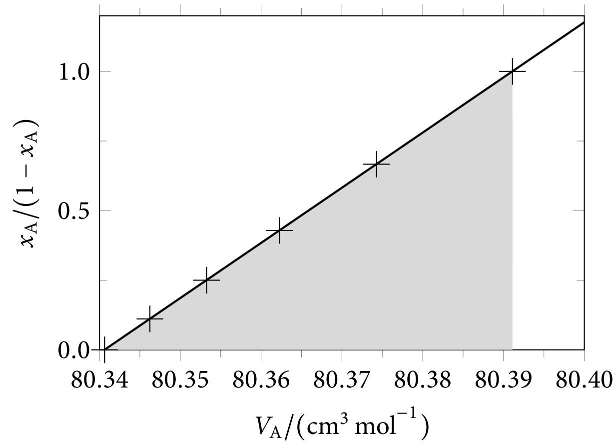


Figure 5.3

The data fall on a good straight line and therefore the required integral is simply the area of the triangle (shown shaded) bounded by $x_A/(1-x_A) = 0$ and $x_A/(1-x_A) = 1$; the corresponding values of $V_A/(\text{cm}^3\,\text{mol}^{-1})$ are 80.3406 and 80.3911. The area is $\frac{1}{2}$ × base × height

$$\text{area} = \tfrac{1}{2}(80.3911 - 80.3406) \times (1 - 0) = 0.02525\ \text{cm}^3\,\text{mol}^{-1}$$

The partial molar volume of B is therefore

$$V_B = V_B^* - \text{area} = 73.99 - 0.02525 = \boxed{73.96\ \text{cm}^3\,\text{mol}^{-1}}$$

P5A.4 The partial pressure of component A in the vapour is given by $p_A = y_A p$, where p is the total pressure and y_A the mole fraction in the vapour. The mole fractions of the two components are related by $x_B = 1 - x_A$. Using these relationships the following table is drawn up, and the data are plotted in Fig. 5.4.

x_A	y_A	$p/(\text{kPa})$	$p_A/(\text{kPa})$	x_B	y_B	$p_B/(\text{kPa})$
0	0	36.066	0	1	1	36.066
0.0898	0.0410	34.121	1.399	0.9102	0.9590	32.722
0.2476	0.1154	30.900	3.566	0.7524	0.8846	27.334
0.3577	0.1762	28.626	5.044	0.6423	0.8238	23.582
0.5194	0.2772	25.239	6.996	0.4806	0.7228	18.243
0.6036	0.3393	23.402	7.940	0.3964	0.6607	15.462
0.7188	0.4450	20.698	9.211	0.2812	0.5550	11.488
0.8019	0.5435	18.592	10.105	0.1981	0.4565	8.487
0.9105	0.7284	15.496	11.287	0.0895	0.2716	4.209
1	1	12.295	12.295	0	0	0

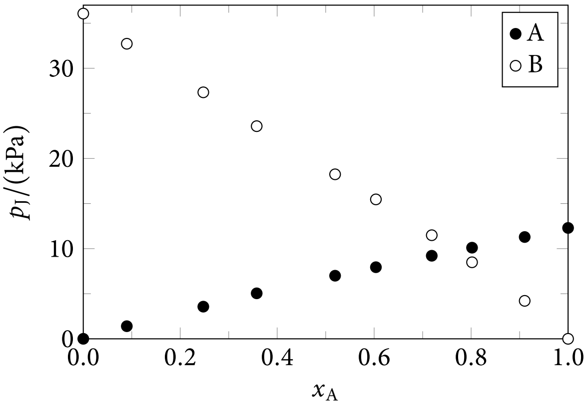


Figure 5.4

Henry's law [5A.24–*152*], applies to the solute at low concentrations $p_J = K_J x_J$. The constant is estimated from the partial pressure at the smallest mole fraction; these data are selected from the table.

$$K_A = \frac{p_A}{x_A} = \frac{1.399\ \text{kPa}}{0.0898} = \boxed{15.6\ \text{kPa}} \qquad K_B = \frac{p_B}{x_B} = \frac{4.209\ \text{kPa}}{0.0895} = \boxed{47.0\ \text{kPa}}$$

P5A.6 The mass of haemoglobin in 100 cm^3 of blood is $[(100\ \text{cm}^3)/(1000\ \text{cm}^3)] \times (150\ \text{g cm}^{-3}) = 15\ \text{g}$. In the lungs the haemoglobin is 97% saturated and so this mass binds a volume $0.97 \times (15\ \text{g}) \times (1.34\ \text{cm}^3\ \text{g}^{-1})$ of O_2. In the capillaries the saturation drops to 75%, so the volume of O_2 released is

$$(0.97 - 0.75) \times (15\ \text{g}) \times (1.34\ \text{cm}^3\ \text{g}^{-1}) = \boxed{4.4\ \text{cm}^3}$$

5B The properties of solutions

Answers to discussion question

D5B.2 The excess volume is defined as $V^E = \Delta_{\text{mix}}V - \Delta_{\text{mix}}V^{\text{ideal}}$. The volume of mixing of an ideal solution is zero, which can be understood at a molecular level as a result of the A and B molecules fitting together in just the same way that A or B molecules fit with one another. A thermodynamic explanation is that for an ideal system the partial molar volume is not a function of composition. It follows that the excess volume is equal to the volume of mixing $V^E = \Delta_{\text{mix}}V$; it is also useful to recall that $\Delta_{\text{mix}}V = V_{\text{mixed}} - V_{\text{separated}}$.

Melons are large relative to oranges. When melons pack together it is conceivable that oranges could fit into the interstices between the melons. If this were the case there would initially be no increase in volume as oranges are added to melons – meaning that the volume of the mixed oranges and melons is smaller than when the two are separate. As a result, $\Delta_{\text{mix}}V$ will be negative and so will the excess volume.

As the number of oranges is increased, the interstices would eventually all be filled, presumably when the ratio of oranges to melons is around 1:1. After this point, adding oranges will result in an increase in the volume and it is conceivable that poor packing of objects of different sizes could result in the volume of the mixture being greater than that of the separated species. In this case the excess volume will be positive.

When a melons are added to oranges the volume will always increase because there are no spaces for the melons to occupy. If just a few melons are added then these will not disrupt the packing of most of the oranges, so the excess volume will be zero. However, as more are added the inefficiency of packing will result in a positive excess volume.

D5B.4 The boiling-point constant is given by [5B.9b–*160*], $K = RT^{*2}/\Delta_{\text{vap}}H$, where T^* is the boiling point of the pure liquid and $\Delta_{\text{vap}}H$ is its enthalpy of vaporisation. However, by Trouton's rule (Section 3B.2 on page 89), $\Delta_{\text{vap}}H/T^*$ is approximately constant, so the boiling-point constant is simply $\propto T^*$. Differences in boiling-point constants are therefore identified as being due to differences in the boiling points of the pure liquids. Water and benzene have different boiling points and so have different boiling-point constants.

D5B.6 The typical experimental arrangement for observing osmosis involves a pure solvent being separated from a solution by a semipermeable membrane through which only the solvent can pass. The chemical potential of the solvent in the solution is lower than that of the pure solvent, therefore there is a tendency for the solvent to pass through the membrane from the side on which it is pure into the solution because this results in a reduction in Gibbs energy.

At a molecular level the process involves an increase in 'randomness' as increasing the amount of solvent in the solution increases the number of possible arrangements of solvent and solute molecules.

Solutions to exercises

E5B.1(b) In *Exercise* E5A.8(b) it is found that the vapour pressure obeys

$$p_B/(\text{kPa}) = 8.41 \times 10^3 \times (x_B) - 2.784 \qquad (5.4)$$

The task is to work out the mole fraction that corresponds to the given molality. The molality of B is defined as $b_B = n_B/m_A$, where n_B is the amount in moles of B and m_A is the mass of solvent A. The mole fraction of B is $n_B/(n_A + n_B)$, where n_A is the amount in moles of A. This amount is $n_A = m_A/M_A$, where M_A is the molar mass of A. These relationships allow the mole fraction to be rewritten as follows

$$x_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{m_A/M_A + n_B}$$

The amount in moles of B is written is $n_B = b_B m_A$; using this the above expression for the mole fraction becomes

$$x_B = \frac{n_B}{m_A/M_A + n_B} = \frac{b_B m_A}{m_A/M_A + b_B m_A} = \frac{b_B}{1/M_A + b_B}$$

The molar mass of A is 74.1 g mol^{-1}, therefore the mole fraction corresponding to $b_B = 0.25$ mol kg^{-1} is

$$x_A = \frac{b_B}{1/M_A + b_B} = \frac{(0.25\ \text{mol kg}^{-1})}{1/(74.1 \times 10^{-3}\ \text{kg mol}^{-1}) + (0.25\ \text{mol kg}^{-1})} = 0.0181...$$

The pressure is found by inserting this value into eqn 5.4

$$p_A/(\text{kPa}) = 8.41 \times 10^3 \times (0.0181...) - 2.784 = 1.50... \times 10^2$$

The vapour pressure of B is therefore $\boxed{1.5 \times 10^2\ \text{kPa}}$.

E5B.2(b) Raoult's law, [5A.22–*151*], $p_A = x_A p_A^*$ relates the vapour pressure to the mole fraction of A, therefore from the given data is it possible to compute x_A. The task is to relate the mole fraction of A to the masses of A (the solvent) and B (the solute), and to do this the molar masses M_A and M_B are introduced. With these $n_A = m_A/M_A$, where m_A is the mass of A, and similarly for n_B. It follows that

$$x_A = \frac{n_A}{n_A + n_B} = \frac{m_A/M_A}{m_A/M_A + m_B/M_B} = \frac{M_B m_A}{M_B m_A + M_A m_B}$$

The final form of this expression for x_A is rearranged to given an expression for M_B, which is the desired quantity; then x_A is replaced by p_A/p_A^*

$$M_B = \frac{x_A M_A m_B}{m_A(1 - x_A)} = \frac{(p_A/p_A^*) M_A m_B}{m_A[1 - (p_A/p_A^*)]}$$

The molar mass of the solvent 2-propanol C_3H_8O, A, is 60.0932 g mol^{-1}, hence

$$\begin{aligned} M_B &= \frac{(p_A/p_A^*) M_A m_B}{m_A[1 - (p_A/p_A^*)]} \\ &= \frac{[(49.62\ \text{kPa})/(50.00\ \text{kPa})] \times (60.0932\ \text{g mol}^{-1}) \times (8.69\ \text{g})}{(250\ \text{g}) \times [1 - (49.62\ \text{kPa})/(50.00\ \text{kPa})]} \\ &= \boxed{273\ \text{g mol}^{-1}} \end{aligned}$$

E5B.3(b) The freezing point depression ΔT_f is related to the molality of the solute B, b_B, by [5B.12–*161*], $\Delta T_f = K_f b_B$, where K_f is the freezing-point constant. From the data and the known value of K_f it is possible to calculate b_B. The task is then to relate this to the given masses and the desired molar mass of the solute, M_B.

The molality of B is defined as $b_B = n_B/m_A$, where m_A is the mass of the solvent A in kg. It follows that

$$b_B = \frac{n_B}{m_A} = \frac{m_B/M_B}{m_A}$$

where m_B is the mass of solute B. From the freezing point data $b_B = \Delta T_f/K_f$, therefore

$$\frac{\Delta T_f}{K_f} = \frac{m_B/M_B}{m_A} \quad \text{hence} \quad M_B = \frac{m_B K_f}{m_A \Delta T_f}$$

With the data given and the value of the freezing-point constant from the *Resource section*

$$M_B = \frac{(5.00\ \text{g}) \times (6.94\ \text{K kg mol}^{-1})}{(0.250\ \text{kg}) \times (0.780\ \text{K})} = \boxed{178\ \text{g mol}^{-1}}$$

Note that because molality is defined as (amount in moles)/(mass of solvent in kg), the mass of solvent m_A is used as 0.250 kg.

E5B.4(b) The freezing point depression ΔT_f is related to the molality of the solute B, b_B, by [5B.12–*161*], $\Delta T_f = K_f b_B$, where K_f is the freezing-point constant. The molality of the solute B is defined as $b_B = n_B/m_A$, where n_B is the amount in moles of B and m_A is the mass in kg of solvent A. The amount is related to the mass of B, m_B, using the molar mass M_B: $n_B = m_B/M_B$. It therefore follows that

$$\Delta T_f = K_f b_B = \frac{K_f m_B}{M_B m_A}$$

The molar mass of NaCl is 58.44 g mol^{-1}. A volume 200 cm^3 of water has mass 200 g to a good approximation. Using these values with the data given and the value of the freezing-point constant from the *Resource section* gives the freezing point depression as

$$\Delta T_f = \frac{K_f m_B}{M_B m_A} = \frac{(1.86\ \text{K kg mol}^{-1}) \times (2.5\ \text{g})}{(58.44\ \text{g mol}^{-1}) \times (0.200\ \text{kg})} = 0.397...\ \text{K}$$

Note that because molality is defined as (amount in moles)/(mass of solvent in kg), the mass of solvent m_A is used as 0.200 kg. The new freezing point is therefore 273.15 K − 0.397... K = $\boxed{272.75\ \text{K}}$

E5B.5(b) The osmotic pressure Π is related to the molar concentration of solute B, [B], by [5B.16–*163*], $\Pi = [\text{B}]RT$. The freezing point depression ΔT_f is related to the molality of B, b_B, by [5B.12–*161*], $\Delta T_f = K_f b_B$, where K_f is the freezing-point constant. The task is to relate [B] to b_B so that these two relationships can be used together.

The molar concentration [B] is given by $[\text{B}] = n_B/V$, where n_B is the amount in moles of B and V is the volume of the solvent A. This volume is related to the mass of A, m_A, using the mass density ρ: $V = m_A/\rho$. It therefore follows that

$$[\text{B}] = \frac{n_B}{V} = \frac{n_B}{m_A/\rho} = \overbrace{\frac{n_B}{m_A}}^{b_B} \rho = b_B \rho$$

With this the osmotic pressure is related to the molality

$$[\text{B}] = \frac{\Pi}{RT} \quad \text{hence} \quad b_B \rho = \frac{\Pi}{RT} \quad \text{and so} \quad b_B = \frac{\Pi}{\rho RT}$$

The freezing point depression for a solution exerting this osmotic pressure is therefore

$$\Delta T_\mathrm{f} = K_\mathrm{f} b_\mathrm{B} = \frac{K_\mathrm{f}\Pi}{\rho RT}$$

Note that because molality is defined as (amount in moles)/(mass of solvent in kg), the mass of solvent m_A must be in kg and therefore the mass density must be used in kg volume^{-1}.

With the data given, the value of the freezing-point constant from the *Resource section*, and taking the mass density of water as 1 g cm^{-3} = 1000 kg m^{-3} gives the freezing point depression as

$$\Delta T_\mathrm{f} = \frac{K_\mathrm{f}\Pi}{\rho RT} = \frac{(1.86\ \mathrm{K\,kg\,mol^{-1}}) \times (99.0 \times 10^3\ \mathrm{Pa})}{(1000\ \mathrm{kg\,m^{-3}}) \times (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (288\ \mathrm{K})}$$
$$= 0.0768...\ \mathrm{K}$$

In this expression all of the quantities are in SI units therefore the temperature is expected to be in K, which is verified as follows

$$\frac{(\mathrm{K\,kg\,mol^{-1}}) \times (\mathrm{Pa})}{(\mathrm{kg\,m^{-3}}) \times (\mathrm{J\,K^{-1}\,mol^{-1}}) \times (\mathrm{K})} = \frac{\mathrm{Pa}}{\mathrm{J} \times \mathrm{m^{-3}} \times \mathrm{K^{-1}}}$$
$$= \frac{\mathrm{kg\,m^{-1}\,s^{-2}}}{(\mathrm{kg\,m^2\,s^{-2}}) \times \mathrm{m^{-3}} \times \mathrm{K^{-1}}} = \mathrm{K}$$

The freezing point is therefore 273.15 K − 0.0768... K = $\boxed{273.07\ \mathrm{K}}$

E5B.6(b) The Gibbs energy of mixing is given by [5B.3–*155*], $\Delta_\mathrm{mix}G = nRT(x_\mathrm{A}\ln x_\mathrm{A} + x_\mathrm{B}\ln x_\mathrm{B})$, the entropy of mixing by [5B.4–*155*], $\Delta_\mathrm{mix}S = -nR(x_\mathrm{A}\ln x_\mathrm{A} + x_\mathrm{B}\ln x_\mathrm{B})$. $\Delta_\mathrm{mix}H$ for an ideal solution is $\boxed{\text{zero}}$.

The total amount in moles is 1.00 mol + 1.00 mol = 2.00 mol. As equal amounts in moles of the two components are mixed, the mole fractions of each are $\frac{1}{2}$.

$$\Delta_\mathrm{mix}G = nRT(x_\mathrm{A}\ln x_\mathrm{A} + x_\mathrm{B}\ln x_\mathrm{B})$$
$$= (2.00\ \mathrm{mol}) \times (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\ \mathrm{K}) \times 2 \times \left(\tfrac{1}{2}\ln\tfrac{1}{2}\right) = \boxed{-3.44 \times 10^3\ \mathrm{J}}$$
$$\Delta_\mathrm{mix}S = -nR(x_\mathrm{A}\ln x_\mathrm{A} + x_\mathrm{B}\ln x_\mathrm{B})$$
$$= -(2.50\ \mathrm{mol}) \times (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times 2 \times \left(\tfrac{1}{2}\ln\tfrac{1}{2}\right) = \boxed{+11.5\ \mathrm{J\,K^{-1}}}$$

E5B.7(b) The entropy of mixing is given by [5B.3–*155*], $\Delta_\mathrm{mix}S = -nR(x_\mathrm{A}\ln x_\mathrm{A} + x_\mathrm{B}\ln x_\mathrm{B})$, and is a maximum when $x_\mathrm{A} = x_\mathrm{B} = \frac{1}{2}$. This is evident from Fig. 5B.2 on page 156.

The task is to relate the mole fraction of A (ethylbenzene) to the masses of A and B (benzene), and to do this the molar masses M_J are introduced. With these $n_\mathrm{J} = m_\mathrm{J}/M_\mathrm{J}$, where m_J is the mass of J. It follows that

$$x_\mathrm{A} = \frac{n_\mathrm{A}}{n_\mathrm{A} + n_\mathrm{B}} = \frac{m_\mathrm{A}/M_\mathrm{A}}{m_\mathrm{A}/M_\mathrm{A} + m_\mathrm{B}/M_\mathrm{B}} = \frac{M_\mathrm{B}m_\mathrm{A}}{M_\mathrm{B}m_\mathrm{A} + M_\mathrm{A}m_\mathrm{B}}$$

This is rearranged to give an expression for m_B/m_A

$$x_A = \frac{M_B m_A}{M_B m_A + M_A m_B} = \frac{M_B}{M_B + M_A(m_B/m_A)} \quad \text{hence} \quad \frac{m_B}{m_A} = \frac{M_B}{M_A}\left(\frac{1}{x_A} - 1\right)$$

The molar mass of A (ethylbenzene, C_8H_{10}) is 106.159 g mol^{-1}, and that of B (benzene) is 78.1074 g mol^{-1}. With these values and $x_A = \frac{1}{2}$

$$\frac{m_B}{m_A} = \frac{M_B}{M_A}\left(\frac{1}{x_A} - 1\right) = \frac{78.1074\ \text{g mol}^{-1}}{106.159\ \text{g mol}^{-1}}\left(\frac{1}{1/2} - 1\right) = \boxed{0.7358}$$

More simply, if equal amounts in moles of A and B are required, the ratio of the corresponding masses of A and B must be equal to the ratio of their molar masses: $m_B/m_A = M_B/M_A$.

E5B.8(b) The ideal solubility of solute B at temperature T is given by [5B.14–*162*], $\ln x_B = (\Delta_{\text{fus}}H/R)(1/T_f - 1/T)$, where $\Delta_{\text{fus}}H$ is the enthalpy of fusion of the solute, and T_f is the freezing point of the pure solute.

$$\begin{aligned}\ln x_B &= \frac{\Delta_{\text{fus}}H}{R}\left(\frac{1}{T_f} - \frac{1}{T}\right)\\ &= \frac{5.2\times 10^3\ \text{J mol}^{-1}}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}\left(\frac{1}{(327+273.15)\ \text{K}} - \frac{1}{(280+273.15)\ \text{K}}\right) = -0.0885...\end{aligned}$$

hence $x_B = 0.915....$

The mole fraction is expressed in terms of the molality, $b_B = n_B/m_A$, where m_A is the mass of the solvent in kg, in the following way

$$x_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{m_A/M_A + n_B} = \frac{n_B/m_A}{1/M_A + n_B/m_A} = \frac{b_B}{1/M_A + b_B}$$

$$\text{hence} \quad b_B = \frac{x_B}{(1 - x_B)M_A}$$

where M_A is the molar mass of A, expressed in kg mol^{-1}. The molar mass of solvent bismuth is 208.98 g mol^{-1} or 208.98×10^{-3} kg mol^{-1}, therefore

$$b_B = \frac{x_B}{(1-x_B)M_A} = \frac{0.915...}{(1-0.915...)\times(208.98\times 10^{-3}\ \text{kg mol}^{-1})} = 51.6...\ \text{mol kg}^{-1}$$

The molality of the solution is therefore $\boxed{52\ \text{mol kg}^{-1}}$. The molar mass of solute Pb is 207.2 g mol^{-1}, so the mass of Pb which is dissolved per kg is $(51.6...\ \text{mol kg}^{-1}) \times (1\ \text{kg}) \times (207.2\ \text{g mol}^{-1}) = \boxed{11\ \text{kg}}$. With so much more solute Pb than solvent Bi, the solution cannot really be described as Pb dissolved in Bi.

E5B.9(b) The vapour pressure of the solute in an ideal dilute solution obeys Henry's law, [5A.24–*152*], $p_B = K_B x_B$, and the vapour pressure of the solvent obeys Raoult's law, [5A.22–*151*], $p_A = p_A^* x_A$.

$$\begin{aligned}p_B &= K_B x_B = (73\ \text{kPa}) \times 0.066 = 4.81...\ \text{kPa}\\ p_A &= p_A^* x_A = (23\ \text{kPa}) \times (1 - 0.066) = 21.4...\ \text{kPa}\\ p_{\text{tot}} &= p_A + p_A = (4.81...\ \text{kPa}) + (21.4...\ \text{kPa}) = 26.3...\ \text{kPa}\end{aligned}$$

Therefore the pressure are $\boxed{p_B = 4.8\ \text{kPa}}$, $\boxed{p_A = 21\ \text{kPa}}$, and $\boxed{p_{\text{tot}} = 26\ \text{kPa}}$.

The partial pressure of the gas is given by $p_A = y_A p_{\text{tot}}$, where y_A is the mole fraction in the vapour

$$y_A = \frac{p_A}{p_{\text{tot}}} = \frac{21.4...\ \text{kPa}}{26.3...\ \text{kPa}} = \boxed{0.82}$$
$$y_B = \frac{p_B}{p_{\text{tot}}} = \frac{4.81...\ \text{kPa}}{26.3...\ \text{kPa}} = \boxed{0.18}$$

E5B.10(b) Let 1,2-dimethylbenzene be A and 1,3-dimethylbenzene be B. If the solution is ideal the vapour pressure obeys Raoult's law, [5A.22–*151*], $p_J = p_J^* x_J$. The mixture will boil when the sum of the partial vapour pressures of A and B equal the external pressure, here 19 kPa.

$$p_{\text{ext}} = p_A + p_B = x_A p_A^* + x_B p_B^* = x_A p_A^* + (1 - x_A) p_B^*$$
$$\text{hence } x_A = \frac{p_{\text{ext}} - p_B^*}{p_A^* - p_B^*} \quad \text{and by analogy } x_B = \frac{p_{\text{ext}} - p_A^*}{p_B^* - p_A^*}$$

$$x_A = \frac{(19\ \text{kPa}) - (18\ \text{kPa})}{(20\ \text{kPa}) - (18\ \text{kPa})} = \boxed{0.5} \quad x_B = \frac{(19\ \text{kPa}) - (20\ \text{kPa})}{(18\ \text{kPa}) - (20\ \text{kPa})} = \boxed{0.5}$$

The partial pressure of the gas is given by $p_J = y_J p_{\text{ext}}$, where y_J is the mole fraction in the gas, and p_J is given by $p_J = p_J^* x_J$, hence $y_J = x_J p_J^* / p_{\text{ext}}$

$$y_A = \frac{x_A p_A^*}{p_{\text{ext}}} = \frac{(0.50) \times (20\ \text{kPa})}{(19\ \text{kPa})} = \boxed{0.53}$$
$$y_B = \frac{x_B p_B^*}{p_{\text{ext}}} = \frac{(0.50...) \times (18\ \text{kPa})}{(19\ \text{kPa})} = \boxed{0.47}$$

E5B.11(b) The vapour pressure of component J in the solution obeys Raoult's law, [5A.22–*151*], $p_J = p_J^* x_J$, where x_J is the mole fraction in the solution. Is the gas the partial pressure is $p_J = y_J p_{\text{tot}}$, where y_J is the mole fraction in the vapour.

These relationships give rise to four equations

$$p_A = p_A^* x_A \quad p_B = p_B^*(1 - x_A) \quad p_A = p_{\text{tot}} y_A \quad p_B = p_{\text{tot}}(1 - y_A)$$

where $x_A + x_B = 1$ is used and likewise for the gas. In these equations x_A and p_{tot} are the unknowns to be found. The expressions for p_A are set equal, as are those for p_B, to give

$$p_A^* x_A = p_{\text{tot}} y_A \quad \text{hence} \quad p_{\text{tot}} = \frac{p_A^* x_A}{y_A}$$
$$p_B^*(1 - x_A) = p_{\text{tot}}(1 - y_A) \quad \text{hence} \quad p_{\text{tot}} = \frac{p_B^*(1 - x_A)}{1 - y_A}$$

These two expressions for p_{tot} are set equal and the resulting equation rearranged to find x_A

$$\frac{p_A^* x_A}{y_A} = \frac{p_B^*(1 - x_A)}{1 - y_A} \quad \text{hence} \quad x_A = \frac{p_B^* y_A}{p_A^*(1 - y_A) + p_B^* y_A}$$

With the data given

$$x_A = \frac{p_B^* y_A}{p_A^*(1 - y_A) + p_B^* y_A} = \frac{(82.1\ \text{kPa}) \times (0.612)}{(68.8\ \text{kPa})*(1 - 0.612) + (82.1\ \text{kPa}) \times (0.612)}$$
$$= 0.653... \qquad \text{and} \qquad x_B = 1 - 0.653... = 0.346...$$

The composition of the liquid is therefore $\boxed{x_A = 0.653}$ and $\boxed{x_B = 0.347}$.

The total pressure is computed from $p_A = p_{\text{tot}} y_A$ and $p_A = p_A^* x_A$ to give $p_{\text{tot}} = x_A p_A^* / y_A$

$$p_{\text{tot}} = \frac{x_A p_A^*}{y_A} = \frac{(0.653...) \times (68.8\ \text{kPa})}{0.612} = \boxed{73.4\ \text{kPa}}$$

E5B.12(b) If the solution is ideal, the vapour pressure of component J in the solution obeys Raoult's law, [5A.22–*151*], $p_J = p_J^* x_J$, where x_J is the mole fraction in the solution. In the gas the partial pressure is $p_J = y_J p_{\text{tot}}$, where y_J is the mole fraction in the vapour.

Assuming ideality, the total pressure is computed as

$$p_{\text{tot}} = p_A + p_B = p_A^* x_A + p_B^*(1 - x_A)$$
$$= (110.1\ \text{kPa}) \times (0.4217) + (76.5\ \text{kPa}) \times (1 - 0.4217) = 90.7\ \text{kPa}$$

The normal boiling point is when the total pressure is 1 atm, but the pressure predicted by Raoult's law is significantly different from this. Raoult's law therefore does not apply and the solution is $\boxed{\text{not ideal}}$.

It is not possible to find y_A, the composition of the vapour, from $p_A = p_{\text{tot}} y_A$ because p_A cannot be computed from the data given.

Solutions to problems

P5B.2 The freezing point depression ΔT_f is related to the molality of the solute B, b_B, by [5B.12–*161*], $\Delta T_f = K_f b_B$, where K_f is the freezing-point constant. The molality corresponding to the given freezing-point depression is therefore

$$b_{B,\text{app}} = \frac{\Delta T_f}{K_f} = \frac{0.0703\ \text{K}}{1.86\ \text{K kg mol}^{-1}} = 0.0377...\ \text{mol kg}^{-1}$$

The stated molality of the solution is 0.0096 mol kg^{-1}, so it is evident that there are more species in the solution than the number of molecules of $Th(NO_3)_4$ added. The ratio of $b_{B,\text{app}}$ to b_B gives an indication of the number of species present per molecule dissolved

$$\frac{b_{B,\text{app}}}{b_B} = \frac{0.0377...\ \text{mol kg}^{-1}}{0.0096\ \text{mol kg}^{-1}} = 3.93...$$

Therefore, each molecule of $Th(NO_3)_4$ appears to dissociate into about $\boxed{4}$ species in solution.

P5B.4 The ideal solubility of solute B at temperature T is given by [5B.14–*162*], $\ln x_B = (\Delta_{fus}H/R)(1/T_f - 1/T)$, where $\Delta_{fus}H$ is the enthalpy of fusion of the solute, and T_f is the freezing point of the pure solute.

The first task is to relate the quoted solubility to the mole fraction of the solute. The data gives the solubility in g of solute per 100 g of solvent: let this quantity be S and, for convenience, let the mass of solvent be m_A. The amount in moles of solute is $n_B = S/M_B$, where M_B is the molar mass of the solute in g mol^{-1}. Likewise, the amount in moles of solvent is $n_A = m_A/M_A$, where M_A is the molar mass of the solvent in g mol^{-1}. For the data given it is invariably the case that $n_A \gg n_B$, so the mole fraction of B is well-approximated as $x_B = n_B/n_A = SM_A/m_A M_B$.

With this the relationship for the ideal solubility is developed as

$$\ln\left(\frac{SM_A}{m_A M_B}\right) = \left(\frac{\Delta_{fus}H}{R}\right)\left(\frac{1}{T_f} - \frac{1}{T}\right)$$

$$\ln S = -\ln\left(\frac{M_A}{m_A M_B}\right) + \frac{\Delta_{fus}H}{RT_f} - \frac{\Delta_{fus}H}{R}\frac{1}{T}$$

The proposed relationship for the solubility, $S = S_0 e^{\tau/T}$, becomes, on taking logarithms, $\ln S = \ln S_0 + \tau/T$. This is compared with the last line to identify the terms as

$$\ln S_0 = -\ln\left(\frac{M_A}{m_A M_B}\right) + \frac{\Delta_{fus}H}{RT_f} \qquad \tau = -\frac{\Delta_{fus}H}{R}$$

To test how the data fit to the proposed relationship a plot of $\ln S$ against $1/T$ is made; such a plots is shown in Fig. 5.5.

$\theta/°C$	$S/(g\,(100\text{ g solv})^{-1})$	T/K	$(10^3/T)/(K^{-1})$	$\ln S$
0	36.4	273	3.66	3.59
20	34.9	293	3.41	3.55
40	33.7	313	3.19	3.52
60	32.7	333	3.00	3.49
80	31.7	353	2.83	3.46

The data fit to quite a good straight line, the equation of which is

$$\ln S/(g\,(100\text{ g solv})^{-1}) = 0.165 \times (10^3/T)/(K^{-1}) + 2.99$$

The immediate problem is that the parameter τ is expected to be negative (because $\tau = -\Delta_{fus}H/R$, and $\Delta_{fus}H$ is positive), but the graph has a positive slope. The data do not, even at the simplest level, conform to the predictions of the ideal solubility equation.

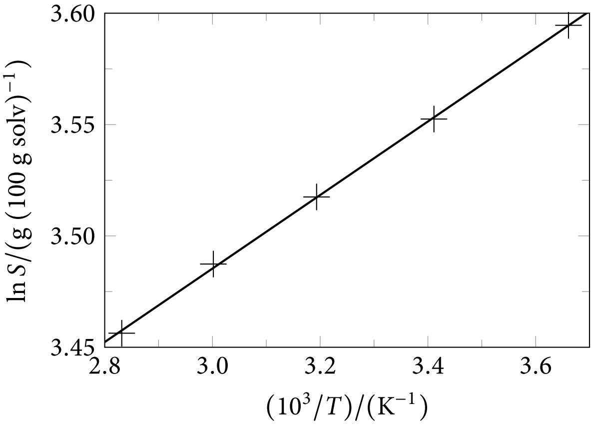


Figure 5.5

P5B.6 The definition of the chemical potential of component A, μ_A, is

$$\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{n_B,p,T}$$

To use this definition an expression for G as a function of the n_J is required.

The excess Gibbs energy G^E is defined in [5B.5–*156*], $G^E = \Delta_{\text{mix}}G - \Delta_{\text{mix}}G^{\text{ideal}}$, therefore $\Delta_{\text{mix}}G = G^E + \Delta_{\text{mix}}G^{\text{ideal}}$. The Gibbs energy of mixing is also expressed as $\Delta_{\text{mix}}G = G - G_{\text{unmixed}}$, where G is the Gibbs energy of the mixture and G_{unmixed} is the Gibbs energy of the unmixed components. It follows that $G = \Delta_{\text{mix}}G + G_{\text{unmixed}}$, and because $\Delta_{\text{mix}}G = G^E + \Delta_{\text{mix}}G^{\text{ideal}}$

$$G = \overbrace{G^E + \Delta_{\text{mix}}G^{\text{ideal}}}^{\Delta_{\text{mix}}G} + G_{\text{unmixed}}$$

These quantities are all molar, so the Gibbs energy of a mixture of n_A moles of A and n_B moles of B is

$$G = (n_A + n_B)G^E + (n_A + n_B)\Delta_{\text{mix}}G^{\text{ideal}} + n_A G^*_{\text{m,A}} + n_B G^*_{\text{m,B}}$$

where $G^*_{\text{m,A}}$ is the molar Gibbs energy of pure A.

The ideal Gibbs energy of mixing (per mole) is given by [5B.3–*155*], $\Delta_{\text{mix}}G^{\text{ideal}} = RT(x_A \ln x_A + x_B \ln x_B)$, and the expression for G^E is given in the problem; this latter is rewritten $gRTx_Ax_B$ using $x_B = (1 - x_A)$. The final expression for G is

$$G = (n_A+n_B)gRTx_Ax_B+(n_A+n_B)RT(x_A \ln x_A+x_B \ln x_B)+n_A G^*_{\text{m,A}}+n_B G^*_{\text{m,B}}$$

The mole fractions are rewritten in terms of n_A and n_B to give

$$\begin{aligned}G &= (n_A+n_B)gRT\left(\frac{n_A}{n_A+n_B}\right)\left(\frac{n_B}{n_A+n_B}\right)\\ &\quad +(n_A+n_B)RT\left[\left(\frac{n_A}{n_A+n_B}\right)\ln\left(\frac{n_A}{n_A+n_B}\right)+\left(\frac{n_B}{n_A+n_B}\right)\ln\left(\frac{n_B}{n_A+n_B}\right)\right]\\ &\quad + n_A G^*_{m,A}+n_B G^*_{m,B}\\ &= \frac{gRTn_An_B}{n_A+n_B}+RT\left[n_A\ln\left(\frac{n_A}{n_A+n_B}\right)+n_B\ln\left(\frac{n_B}{n_A+n_B}\right)\right]+n_AG^*_{m,A}+n_BG^*_{m,B}\\ &= \frac{gRTn_An_B}{n_A+n_B}+RT\left[n_A\ln n_A-n_A\ln(n_A+n_B)+n_B\ln n_B-n_B\ln(n_A+n_B)\right]\\ &\quad + n_AG^*_{m,A}+n_BG^*_{m,B}\end{aligned}$$

The algebra used in going to the last line is used to make it easier to compute the derivative. In finding the derivative recall that terms such as $n_A\ln n_A$ require the application of the product rule.

$$\begin{aligned}\left(\frac{\partial G}{\partial n_A}\right)_{n_B} &= \frac{gRTn_B}{n_A+n_B}-\frac{gRTn_An_B}{(n_A+n_B)^2}\\ &\quad + RT\left[\ln n_A+1-\ln(n_A+n_B)-\frac{n_A}{(n_A+n_B)}-\frac{n_B}{(n_A+n_B)}\right]+G^*_{m,A}\\ &= gRT(x_B-x_Ax_B)+RT(1+\ln x_A-x_A-x_B)+G^*_{m,A}\\ &= gRTx_B(1-x_A)+RT\ln x_A+G^*_{m,A}\\ &= gRTx_B^2+RT\ln x_A+G^*_{m,A}\end{aligned}$$

On the second line the mole fractions are re-introduced, and in the subsequent manipulations the relationship $x_A + x_B = 1$ is used. $G^*_{m,A}$ is identified as the chemical potential of pure A, μ^*_A, giving the result

$$\boxed{\mu_A = \mu^*_A + gRTx_B^2 + RT\ln x_A}$$

This function is plotted in Fig. 5.6.

As g increases the deviation from ideal behaviour (the solid line) increases, with the effect being larger at small x_A, corresponding to larger x_B.

P5B.8 (a) The van 't Hoff equation is [5B.16–*163*], $\Pi = [B]RT$. If the 'pressure' P is expressed as (mass/area), then to transform it to (force/area) requires multiplication by the acceleration of free fall, g, because force = mass × acceleration: $\Pi = gP$.

If the 'concentration' c is expressed as (mass/volume), then to transform it to (moles/volume) requires the use of the molar mass, M: $[B] = c/M$. With these substitutions the van 't Hoff equation becomes

$$gP = \frac{cRT}{M} \quad \text{hence} \quad P = \left(\frac{c}{M}\right)\left(\frac{R}{g}\right)T \quad \text{hence} \quad P = \left(\frac{c}{M}\right)R'T$$

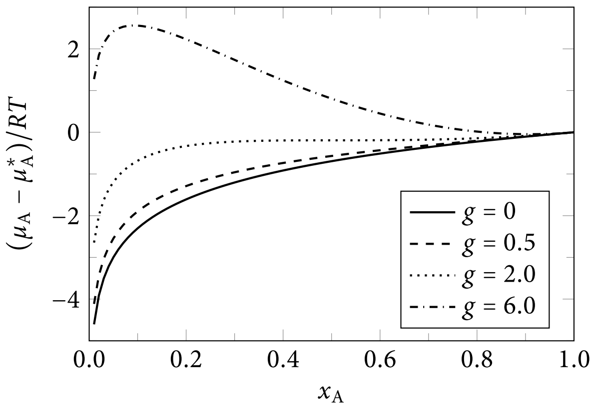


Figure 5.6

where $R' = R/g$. The final equation is of the form of the van 't Hoff equation, but with a modified measure of concentration, c/M, and a modified gas constant, R'.

This equation is rearranged to give an expression for R', and the units of this quantity are then found by inserting the units of the quantities involved

$$R' = \frac{PM}{cT} = \frac{(\text{g cm}^{-2}) \times (\text{g mol}^{-1})}{(\text{g cm}^{-3}) \times (\text{K})} = \text{g cm K}^{-1}\ \text{mol}^{-1}$$

The numerical value of R' is found from its definition

$$R' = \frac{R}{g} = \frac{8.3145\,\text{J K}^{-1}\ \text{mol}^{-1}}{9.8067\ \text{m s}^{-2}} = 0.84784\ \text{kg m K}^{-1}\ \text{mol}^{-1}$$

The units of R' are found by using $1\ \text{J} = 1\ \text{kg m}^2\,\text{s}^{-2}$. The final step is to convert the numerical value of R' from $(\text{kg m K}^{-1}\ \text{mol}^{-1})$ to the required $(\text{g cm K}^{-1}\ \text{mol}^{-1})$

$$(0.84784\ \text{kg m K}^{-1}\ \text{mol}^{-1}) \times \frac{1000\ \text{g}}{1\ \text{kg}} \times \frac{100\ \text{cm}}{1\ \text{m}} = \boxed{84784\ \text{g cm K}^{-1}\ \text{mol}^{-1}}$$

(b) From now on the van 't Hoff equation is written $\Pi = (c/M)RT$ where the units of Π and c are as described in (a), and R is $84784\ \text{g cm K}^{-1}\ \text{mol}^{-1}$. As described in Section 5B.2(e) on page 162, if it is assumed that the osmotic pressure is given by a virial-type equation [5B.18–*163*] where just the first two terms are retained, a plot of Π/c against c should give a straight line with intercept RT/M. The data are plotted in Fig. 5.7.

$(10^{-2}\Pi/c)$ $/(\mathrm{g\,cm^{-2}/g\,cm^{-3}})$	$c/(\mathrm{g\,cm^{-3}})$	$(10^{-2}\Pi/c)$ $/(\mathrm{g\,cm^{-2}/g\,cm^{-3}})$	$c/(\mathrm{g\,cm^{-3}})$
2.6	0.005 0	19.0	0.145
2.9	0.010	31.0	0.195
3.6	0.020	38.0	0.245
4.3	0.033	52	0.27
6.0	0.057	63	0.29
12.0	0.100		

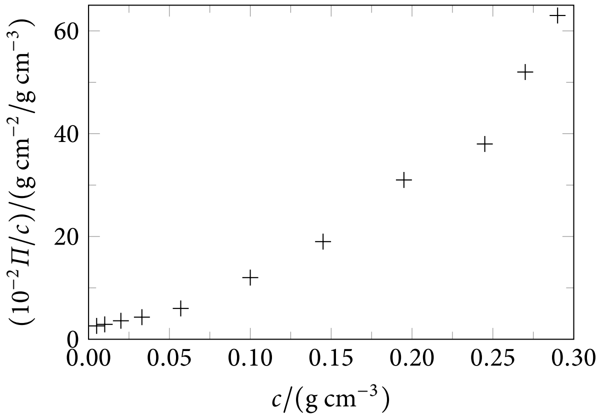


Figure 5.7

It is evident from the graph that the data do not conform to this expectation. One approach is to select only the data at the lowest concentrations because in this limit the expectation is that the two-term virial equation will be sufficient to describe the data. Such a plot is shown in Fig. 5.8.

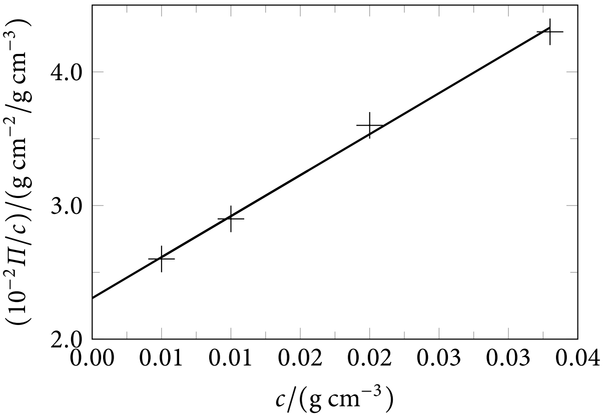


Figure 5.8

The data fit reasonably well to a straight line with intercept 2.307. From this the molar mass is calculated

$$\text{intercept} = RT/M \quad \text{hence} \quad M = \frac{(84784\ \text{g cm K}^{-1}\ \text{mol}^{-1}) \times (298.15\ \text{K})}{10^2 \times 2.307\ \text{g cm}^{-2}/\text{g cm}^{-3}}$$

which gives $\boxed{M = 1.1 \times 10^5\ \text{g mol}^{-1}}$.

(c) Over the full range of concentrations the plot of Π/c against c is non-linear, so the solvent is characterised a 'good'. This may be attributed to both solvent and polymer being non-polar.

(d) The virial-style equation with three coefficients is

$$\Pi = \frac{c}{M}RT\left[1 + B\frac{c}{M} + C\left(\frac{c}{M}\right)^2\right] \quad \text{hence} \quad \frac{\Pi}{c} = \frac{RT}{M}\left[1 + B\frac{c}{M} + C\left(\frac{c}{M}\right)^2\right]$$

It is convenient to take the factor of M into the virial coefficients to give

$$\frac{\Pi}{c} = \frac{RT}{M}\left(1 + B'c + C'c^2\right)$$

where $B' = B/M$ and likewise for C'. Using this, the data Π/c are fitted to a quadratic in c.

If the fitted function is required to have the same intercept at $c = 0$ as in part (a), the fitted function to the first 8 data points (chosen as these gave the best fit) is

$$(\Pi/c)/(\text{g cm}^{-2}/\text{g cm}^{-3}) = 55563(c/(\text{g cm}^{-3}))^2 + 3784.2(c/(\text{g cm}^{-3})) + 230.7$$

It follows that

$$\frac{RT}{M}B' = 3784.2\ \text{g}^{-1}\ \text{cm}^4$$

From part (a) $RT/M = 230.7\ \text{g cm}^{-2}/\text{g cm}^{-3}$, therefore

$$B' = (3784.2\ \text{g}^{-1}\ \text{cm}^4)/(230.7\ \text{g cm}^{-2}/\text{g cm}^{-3}) = \boxed{16.4\ \text{g}^{-1}\ \text{cm}^3}$$

By a similar line of argument, $\boxed{C' = 241\ \text{g}^{-2}\ \text{cm}^6}$.

(e) The proposed virial equation with $g = \frac{1}{4}$ is developed into a straight-line plot as follows

$$\begin{aligned}\frac{\Pi}{c} &= \frac{RT}{M}\left(1 + B'c + \tfrac{1}{4}B'^2c^2\right)\\ &= \frac{RT}{M}\left(1 + \tfrac{1}{2}B'c\right)^2\\ \text{hence} \quad \left(\frac{\Pi}{c}\right)^{1/2} &= \left(\frac{RT}{M}\right)^{1/2}\left(1 + \tfrac{1}{2}B'c\right) \qquad (5.5)\end{aligned}$$

A plot of $(\Pi/c)^{1/2}$ against c should be a straight line; such a plot is shown in Fig. 5.9.

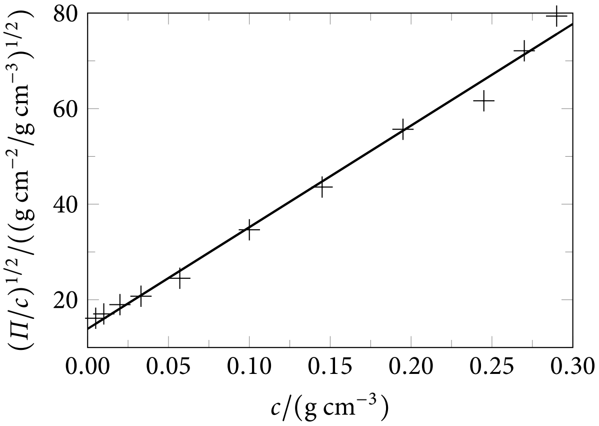


Figure 5.9

The data fit to a modest straight line with equation

$$(\Pi/c)^{1/2}/((\mathrm{g\,cm^{-2}/g\,cm^{-3}})^{1/2}) = 212.75(c/(\mathrm{g\,cm^{-3}})) + 13.902$$

From eqn 5.5 it follows that (slope)/(intercept)=$\frac{1}{2}B'$

$$B' = 2 \times \frac{212.75}{13.902} = \boxed{30.6\ \mathrm{g^{-1}\ cm^{3}}}$$

The third virial coefficient is $\frac{1}{4}B'^2$ which gives $\boxed{C' = 234\ \mathrm{g^{-2}\ cm^{6}}}$. The agreement with the results from part (d) is modest.

P5B.10 The ideal Gibbs energy of mixing (per mole) is given by [5B.3–*155*], $\Delta_{\text{mix}}G^{\text{ideal}} = RT(x_A \ln x_A + x_B \ln x_B)$. The relationship is plotted for several temperatures in Fig. 5.10.

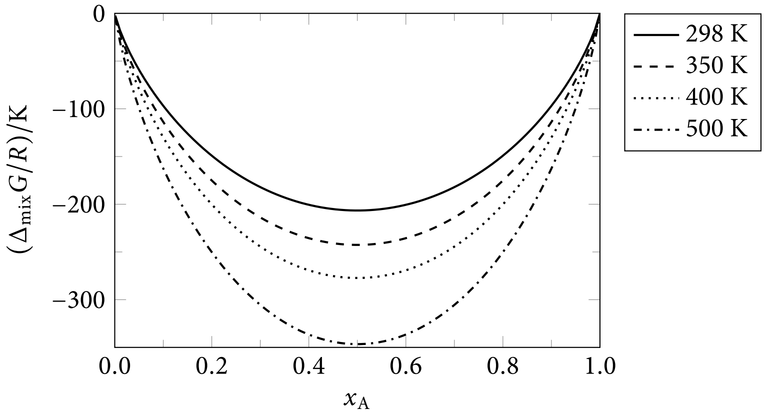


Figure 5.10

The dependence of $\Delta_{\text{mix}}G$ on temperature is evidently greatest at $x_A = \frac{1}{2}$. This is rationalised by noting that $(\partial\Delta_{\text{mix}}G/\partial T)_p = -\Delta_{\text{mix}}S$ and that $\Delta_{\text{mix}}S$ is a maximum at $x_A = \frac{1}{2}$. The composition with the greatest temperature dependence thus coincides with composition at which the entropy change is greatest, which is $x_A = \frac{1}{2}$.

P5B.12 The ideal solubility is given by [5B.14–*162*]

$$\ln x_B = \frac{\Delta_{\text{fus}}H}{R}\left(\frac{1}{T_f} - \frac{1}{T}\right) \quad \text{hence} \quad x_B = \exp\left(\frac{\Delta_{\text{fus}}H}{RT_f}\right)\exp\left(\frac{-\Delta_{\text{fus}}H}{RT}\right)$$

The first exponential is independent of T and the derivative of the second term is computed using the chain rule.

$$\frac{dx_B}{dT} = \exp\left(\frac{\Delta_{\text{fus}}H}{RT_f}\right)\frac{\Delta_{\text{fus}}H}{RT^2}\exp\left(\frac{-\Delta_{\text{fus}}H}{RT}\right)$$

Changing T_f simple scales the derivative but does not otherwise affect the temperature dependence. For the plots shown in Fig. 5.11 a typical fusion temperature of 300 K is used, and typical $\Delta_{\text{fus}}H$ values of +10 kJ mol^{-1}, +20 kJ mol^{-1}, and +30 kJ mol^{-1} are considered.

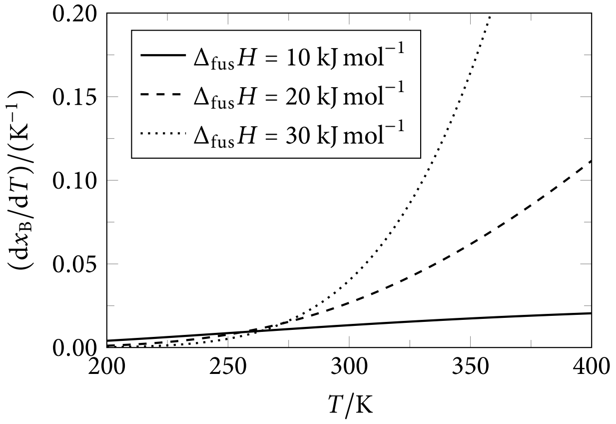


Figure 5.11

The temperature dependence of the solubility is stronger the greater ΔH_{fus}, and for these sets of parameters the solubility increases with T. The plot shows a maximum at much higher (and rather unrealistic) temperatures.

5C Phase diagrams of binary systems: liquids

Answers to discussion questions

D5C.2 A low-boiling azeotrope has a boiling temperature lower than that of either component, so it is easier for the molecules to move into the vapour 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 for the molecules to move into the vapour 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.

Solutions to exercises

E5C.1(b) The temperature–composition phase diagram is a plot of the boiling point against (1) composition of the liquid, x_A and (2) composition of the vapour, y_A. The horizontal axis is labelled z_A, which is interpreted as x_A or y_A according to which set of data are being plotted. In addition to the data in the table, the boiling points of the pure liquids are added. The plot is shown in Fig.5.12; the lines are best-fit polynomials of order 3.

$\theta/°C$	x_A	y_A	$\theta/°C$	x_A	y_A
124	1	1	140	0.30	0.61
125	0.91	0.99	145	0.18	0.45
130	0.65	0.91	150	0.098	0.25
135	0.45	0.77	155	0	0

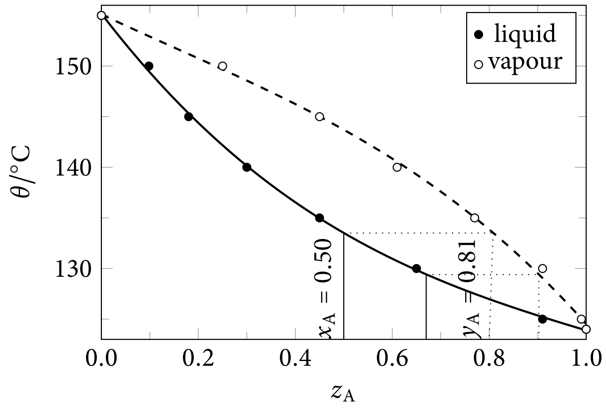


Figure 5.12

(i) The vapour composition corresponding to a liquid composition of x_A = 0.50 is found by taking the vertical line at this composition up to the intersection with the liquid curve, and then moving across horizontally to the intersection with the vapour curve; this occurs at $\boxed{y_A = 0.81}$, which gives the composition of the vapour. The exact points of intersection can be found either from the graph or by using the fitted functions.

(ii) A composition $x_B = 0.33$ corresponds to $x_A = 0.67$; from the graph this corresponds to a vapour composition $\boxed{y_A = 0.90}$.

E5C.2(b) At the lowest temperature shown in the diagram the mixture is in the two-phase region, and the two phases have composition of approximately $x_B = 0.88$ and $x_B = 0.05$. The level rule shows that there is about 2.3 times more of the B-poor than of the B-rich phase. As the temperature is raised the B-rich phase becomes slightly less rich in B, and the other phase becomes richer in B. The lever rule implies that the proportion of the B-poor phase increases as the temperature rises.

At temperature T_2 the vertical line intersects the phase boundary. At this point the B-rich phase disappears and only one phase, with $x_B = 0.3$, is present.

E5C.3(b) The molar masses of aniline and hexane are $93.1253\text{ g mol}^{-1}$ and $86.1706\text{ g mol}^{-1}$, respectively. The mole fraction of aniline (A) is

$$x_A = \frac{(42.8\text{ g})/(93.1253\text{ g mol}^{-1})}{(42.8\text{ g})/(93.1253\text{ g mol}^{-1}) + (75.2\text{ g})/(86.1706\text{ g mol}^{-1})} = 0.344...$$

Hence $x_A = \boxed{0.345}$. Let the two phases be α ($x_A = 0.308$) and β ($x_A = 0.618$). The proportions of these two phases, n_β/n_α is given by the level rule, [5C.6–*170*]

$$\frac{n_\beta}{n_\alpha} = \frac{l_\alpha}{l_\beta} = \frac{0.344... - 0.308}{0.618 - 0.344...} = \boxed{0.135}$$

The aniline-poor phase is more abundant by a factor of about 7.

E5C.4(b) An approximate phase diagram is shown in Fig. 5.13; the given data points are shown with dots and these are simply joined with straight lines as a guide to the eye. The shape conforms to the expected phase diagram for such a system.

(i) At 48 °C the possibility of phase separation exists; as the amount of B added to A increases, the mole fraction of A decreases and the phase diagram is traversed along the dashed line from right to left. When the mole fraction of A is high a single phase forms, but as the mole fraction goes below about 0.5 phase separation occurs. Initially, according to the lever rule, the proportion of the B-rich phase is very small, but as more and more B is added the proportion of this phase increases. When the x_A is just over 0.35, there is very little of the A-rich phase present and as the mole fraction decreases further a one-phase zone is reached in which there is complete miscibility.

(ii) A temperature of 52.4 °C is equal to the upper critical temperature, and therefore the expectation is that A and B will mix in all proportions to give a single phase.

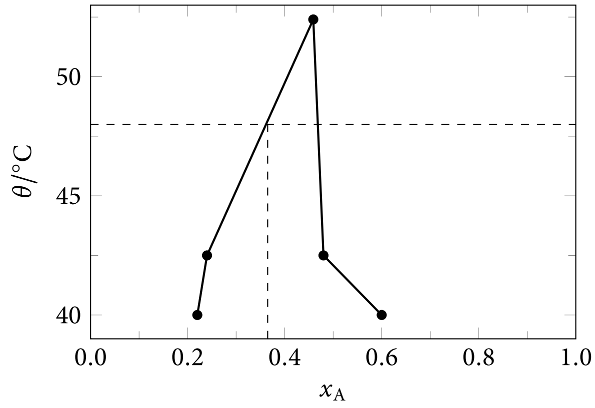


Figure 5.13

Solutions to problems

P5C.2 If it is assumed that Raoult's law applies, [5A.22–*151*], the partial vapour pressures of DE and DP are

$$p_{DE} = x_{DE}p^*_{DE} \qquad p_{DP} = x_{DP}p^*_{DP}$$

where x_J are the mole fractions and p^*_J are the vapour pressures over the pure liquids. The total pressure is taken to be $p_{tot} = p_{DE} + p_{DP}$.

(a) The total pressure is given by

$$\begin{aligned} p_{tot} &= p_{DE} + p_{DP} = x_{DE}p^*_{DE} + x_{DP}p^*_{DP} \\ &= 0.60 \times (22.9\text{ kPa}) + 0.40 \times (17.1\text{ kPa}) = \boxed{20.6\text{ kPa}} \end{aligned}$$

(b) The mole fraction in the vapour, y_J, is related to the total pressure by $p_J = y_J p_{tot}$, so it follows that

$$y_J = \frac{p_J}{p_{tot}} = \frac{x_J p^*_J}{p_{tot}}$$

Therefore

$$\begin{aligned} y_{DE} &= \frac{x_{DE}p^*_{DE}}{p_{tot}} = \frac{0.60 \times (22.9\text{ kPa})}{0.60 \times (22.9\text{ kPa}) + 0.40 \times (17.1\text{ kPa})} = \boxed{0.67} \\ y_{DP} &= \frac{x_{DP}p^*_{DP}}{p_{tot}} = \frac{0.40 \times (17.1\text{ kPa})}{0.60 \times (22.9\text{ kPa}) + 0.40 \times (17.1\text{ kPa})} = \boxed{0.33} \end{aligned}$$

P5C.4 (a) The temperature–composition phase diagram is a plot of the boiling point against (1) composition of the liquid, x_B, the mole fraction of butan-1-ol and (2) composition of the vapour, y_B. The horizontal axis is labelled z_B, which is interpreted as x_B or y_B according to which set of data are being plotted. In addition to the data in the table, the boiling point of pure chlorobenzene is added. The resulting phase diagram is shown in Fig. 5.14; the data points are just connected by best-fit polynomials.

T/K	x_B	y_B	T/K	x_B	y_B
404.86	0	0	390.15	0.3687	0.5138
396.57	0.1065	0.2859	389.03	0.5017	0.5840
393.94	0.1700	0.3691	388.66	0.6091	0.6409
391.60	0.2646	0.4505	388.57	0.7171	0.7070

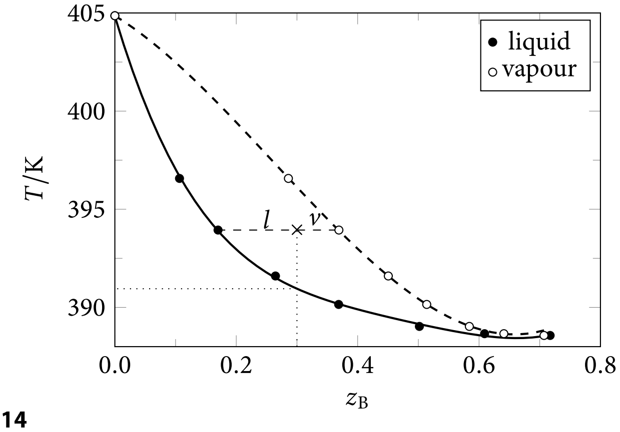


Figure 5.14

(b) At a composition $x_B = 0.3$, indicated by the dotted line, the boiling point is when this line intersects the liquid line, which is at a temperature of $\boxed{391\ \mathrm{K}}$.

(c) At 393.94 K the compositions are given by the points at which the horizontal dashed line cuts the liquid and vapour curves (which in this case also coincide with the given data points). The compositions are therefore $\boxed{x_B = 0.17}$ and $\boxed{y_B = 0.37}$.

The relative proportions of the two phases are given by the lever rule, the mid point of the lever being $x = 0.3$; the distances l and v are marked on the diagram

$$\frac{n_l}{n_v} = \frac{v}{l} = \frac{0.37 - 0.30}{0.30 - 0.17} = \boxed{0.54}$$

Therefore the vapour is about twice as abundant as the liquid phase.

P5C.6 Let phase α have $x_A = 0.2$ and phase β have $x_A = 0.6$. By the lever rule, [5C.6–*170*], the ratio of abundances of the two phases is

$$\frac{n_\alpha}{n_\beta} = \frac{l_\beta}{l_\alpha}$$

where l_α is the 'distance' between the overall composition (here 0.4) and the composition of phase α (here 0.2),and likewise for β

$$\frac{n_\alpha}{n_\beta} = \frac{l_\beta}{l_\alpha} = \frac{0.4 - 0.2}{0.6 - 0.4} = 1$$

The abundance of the two phases is therefore equal.

P5C.8 The relationship between the total pressure p and y_A is given in [5C.5–*167*]

$$p = \frac{p_A^* p_B^*}{p_A^* + (p_B^* - p_A^*)y_A}$$

Division by p_A^*, and then division of the numerator and denominator of the fraction on the right by p_B^* gives the required form

$$\frac{p}{p_A^*} = \frac{p_B^*}{p_A^* + (p_B^* - p_A^*)y_A} = \frac{1}{(p_A^*/p_B^*) + (1 - p_A^*/p_B^*)y_A}$$

The plot is shown in Fig. 5.15.

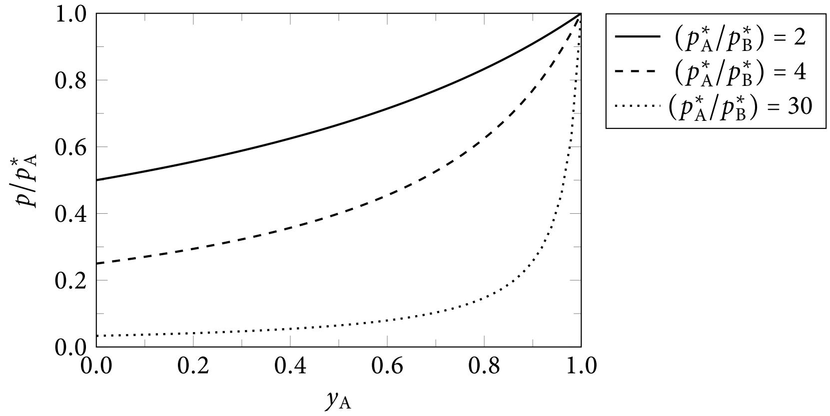


Figure 5.15

P5C.10 The values of x_A at which $\Delta_{mix}G$ is a minimum are found by solving [5C.7–*174*]

$$\ln\frac{x_A}{1 - x_A} + \xi(1 - 2x_A) = 0 \qquad (5.6)$$

This equation is rearranged to give an expression for ξ, which is plotted in Fig. 5.16

$$\xi = \frac{\ln(x_A/[1 - x_A])}{2x_A - 1}$$

The way to interpret this graph is to choose a value for ξ and then read across to locate the minima. If $\xi < 2$ there are no values of x_A which solve the equation, and hence no minima. For $\xi > 2$ there are two values of x_A at which the plotted function intersects a horizontal line at a given value of ξ. The larger ξ becomes the close one intersection (position of a minimum) moves towards $x_A = 0$ and the other towards $x_A = 1$.

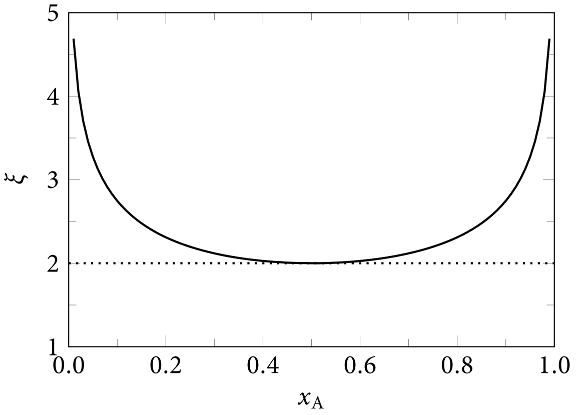


Figure 5.16

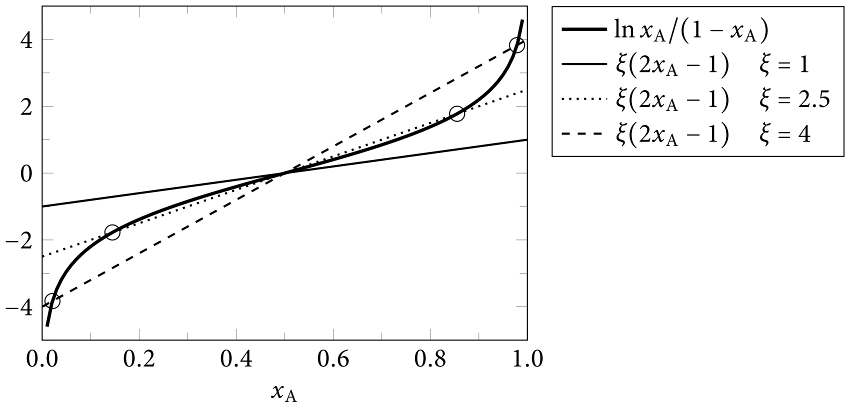


Figure 5.17

An alternative way to explore the solutions to eqn 5.6 is to plot $\ln x_A/(1-x_A)$ against x_A, and on the same graph to plot $\xi(2x_A-1)$ also against x_A. The values of x_A at which the two curves intersect gives the position of the minima. Such a plot is shown in Fig. 5.17

The plot illustrates that there are no intersections when $\xi < 2$, and that, as before, the intersections that occur when $\xi > 2$ (highlighted as ○) move to the edges of the plot as ξ increases. There is always an intersection at $x_A = 0$, and as is seen from Fig. 5B.5 this corresponds to a minimum for $\xi < 2$, and a maximum for $\xi > 2$.

Mathematical software can also be used to solve eqn 5.6 numerically for given values of ξ. For example, for $\xi = 2.5$ the solutions are $x_A = 0.855$ and $x_A = 0.145$.

5D Phase diagrams of binary systems: solids

Answers to discussion questions

D5D.2 The schematic phase diagram is shown in Fig. 5.18. Incongruent melting means that the compound AB_2 does not occur in the liquid phase.

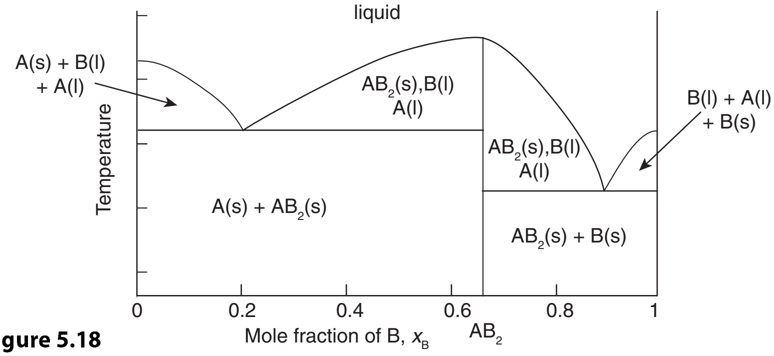


Figure 5.18

Solutions to exercises

E5D.1(b) The schematic phase diagram is shown in Fig 5.19. The solid points are the data given in the *Exercise*, and lines are simply plausible connections between these points. The small area to the left of $x_{N_2H_4} = 0.07$, enclosed by the phase boundary and the line at −80 °C, corresponds to N_2H_4(l)+NH_3(l)+NH_3(s).

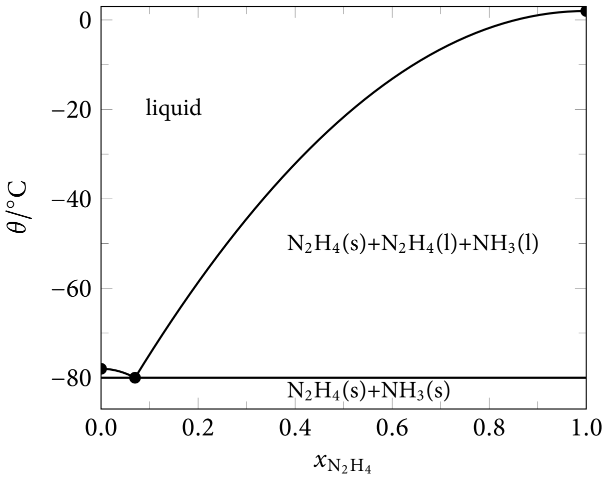


Figure 5.19

E5D.2(b) The schematic phase diagram is shown in Fig 5.20. The solid points are the data given in the *Exercise*, and lines are simply plausible connections between these points. (The dash-dotted lines are referred in to *Exercise* E5D.3(b).)

The stated mixture has $x_{B_2H_6} = 4/(1+4) = 0.8$ and is indicated by the vertical dashed line. The mixture cools until about 116 K at which point solid first forms. The solid which forms is the 1:1 compound and as this happens the liquid becomes richer in B_2H_6. Cooling continues with more and more of the 1:1 compound being formed until 104 K, the second eutectic, at which point the system completely solidifies to a two-phase material consisting of the 1:1 compound and solid B_2H_6.

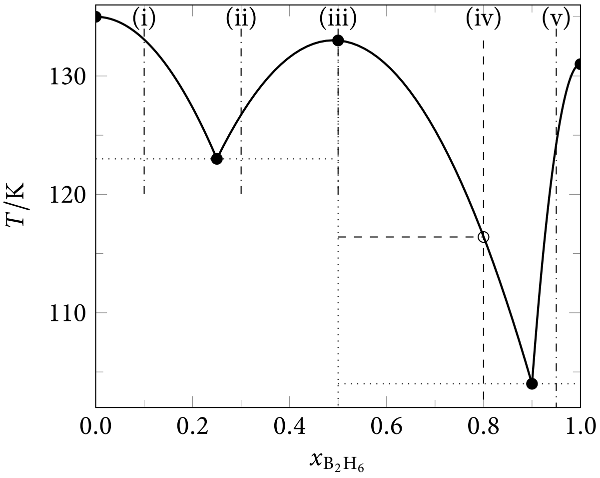


Figure 5.20

E5D.3(b) The compositions at which the cooling curves are plotted are indicated by the vertical dash-dotted lines on the phase diagram for *Exercise* E5D.2(b), Fig. 5.20. The cooling curves are shown in Fig 5.21. The break points, where solid phases start to form are shown by the short horizontal lines, and the dotted lines indicate the temperatures of the two eutectics (123 K and 104 K). The horizontal segments correspond to solidification of a eutectic. Cooling curve (c) corresponds to direct solidification of the 1:1 complex.

E5D.4(b) The feature that indicates incongruent melting is the intersection of the two liquid curves at around $x_B \approx 0.37$. The incongruent melting point is marked T_1. The composition of the eutectic is $\boxed{x_B \approx 0.58}$ and its melting point is labelled T_2.

E5D.5(b) The cooling curves are shown in Fig 5.22; the break points are shown by the short horizontal lines, and the temperatures T_1 and T_2 are indicated. For isopleth *a* the first break point is where the isopleth crosses the liquid curve between temperatures T_1 and T_2; this is followed by a eutectic halt at T_2. For isopleth *b* the first break point is somewhat above T_1 where the isopleth crosses the liquid curve, there is a second break point where the isopleth crosses the boundary at T_1, and then a eutectic halt at T_2.

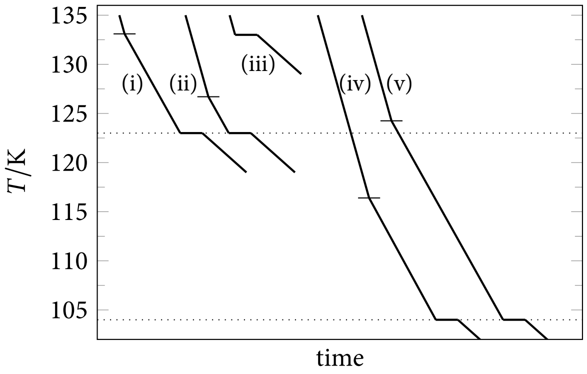


Figure 5.21

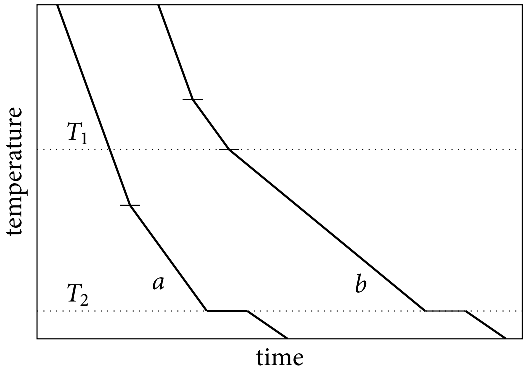


Figure 5.22

E5D.6(b) Figure 5.23 shows the phase diagram to which dotted horizontal lines have added at the relevant temperatures.

(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 labelled x_1 in the figure. That composition is $x_B = x_1 = \boxed{0.63}$.

(iii) At 300 °C the solubility of AB_2 in B is indicated by the point x_2. At this point two phases coexist: solid AB_2 and a liquid mixture of A and B with mole fraction $x_B = x_2 = 0.41$. Although the liquid does not contain any AB_2 units, the liquid can be thought of as a mixture of dissociated AB_2 in A. Let the amount in moles of the compound be n_c and that of free A be n_a. Thus, the amount of A (regardless of whether free or in the compound) is $n_A = n_a + n_c$ and the amount of B is $n_B = 2n_c$. The mole fraction of B is

$$x_B = x_2 = \frac{n_B}{n_A + n_B} = \frac{2n_c}{(n_a + n_c) + 2n_c} = \frac{2n_c}{n_a + 3n_c}$$

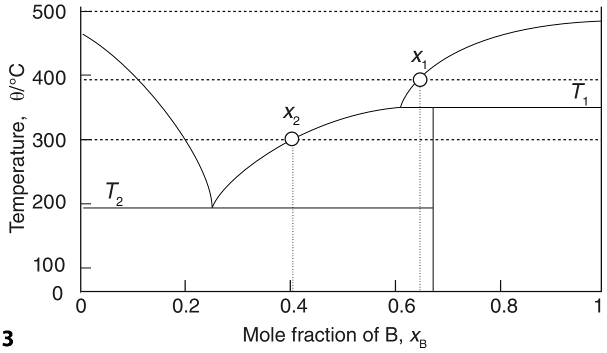


Figure 5.23

This relationship is rearranged and terms in n_c are collected on one side and those in n_a on the other to give $n_a x_2 = n_c(2 - 3x_2)$. The mole ratio of compound to free A is given by

$$\frac{n_c}{n_a} = \frac{x_2}{2 - 3x_2} = \frac{0.41}{2 - 3 \times 0.41} = \boxed{0.53}$$

Solutions to problems

P5D.2 The mole fraction of sulfur, x_S, corresponding to compound P_nS_m is computed from the molar masses of sulfur and phosphorus, M_S and M_P, as

$$x_S = \frac{mM_S}{mM_S + nM_P} = \frac{m \times (32.06\,\mathrm{g\,mol^{-1}})}{m \times (32.06\,\mathrm{g\,mol^{-1}}) + n \times (30.97\,\mathrm{g\,mol^{-1}})}$$

Using this expression, mole fractions corresponding to the three compounds are: (1) P_4S_3, 0.44; (2) P_4S_7, 0.64; (3) P_4S_{10}, 0.72.

The phase diagram is a variation of that shown in Fig. 5D.4 on page 178 except that instead of one compound being formed there are three. The diagram therefore separates into four sections, as shown schematically in Fig. 5.24. Note that no information is given on the temperature or composition of the eutectics, so these have simply been selected arbitrarily.

The diagram has four eutectics labelled e_1, e_2, e_3, and e_4; eight two-phase liquid-solid regions, t_1 through t_8; and four two-phase solid regions, S_1, S_2, S_3, and S_4. The composition and physical state of the regions are as follows:

l: liquid S and P

S_1: solid P and solid P_4S_3

S_2: solid P_4S_3 and solid P_4S_7

S_3: solid P_4S_7 and solid P_4S_{10}

S_4: solid P_4S_{10} and solid S

t_1: liquid P and S and solid P

t_2: liquid P and S and solid P_4S_3

t_3: liquid P and S and solid P_4S_3

t_4: liquid P and S and solid P_4S_7

t_5: liquid P and S and solid P_4S_7

t_6: liquid P and S and solid P_4S_{10}

t_7: liquid P and S and solid P_4S_{10}

t_8: liquid P and S and solid S

The cooling curve is shown to the right of the phase diagram in Fig. 5.24. A break in the curve occurs at point $b_1 \approx 125\,^\circ\text{C}$ as a result of solid P_4S_3 forming; a eutectic halt occurs at point $e_1 \approx 20\,^\circ\text{C}$.

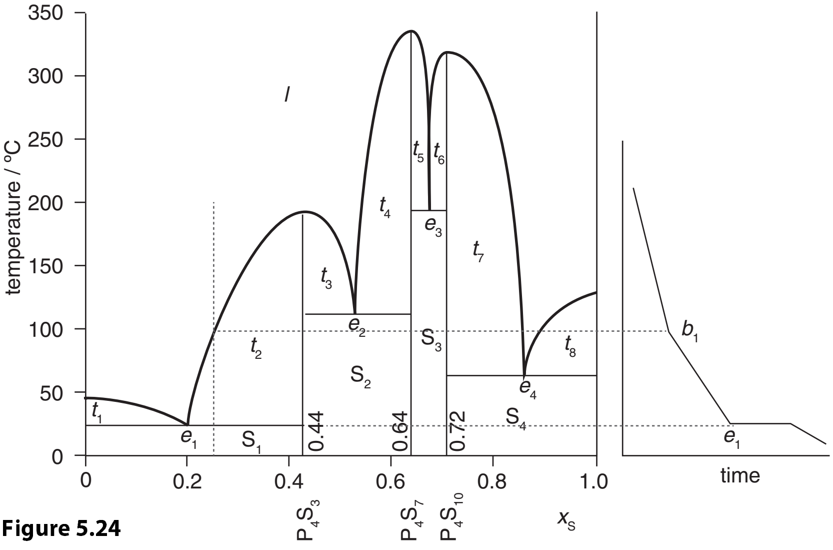


Figure 5.24

P5D.4 The information is used to construct the phase diagram shown in Fig 5.25; the solid dots correspond to the data and the lines are simply plausible connections between these points.

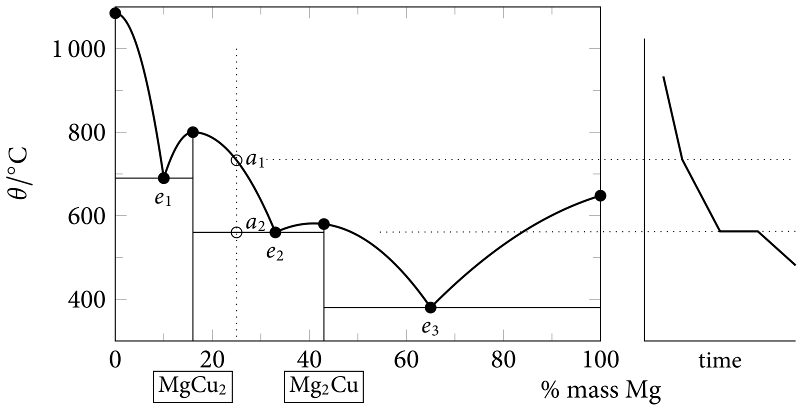


Figure 5.25

In Mg_nCu_m the mass percentage of Mg is computed from the molar masses of Mg and Cu, M_{Mg} and M_{Cu}, as

$$100 \times \frac{nM_{\text{Mg}}}{nM_{\text{Mg}} + mM_{\text{Cu}}}$$

For $MgCu_2$ the percentage is

$$100 \times \frac{1 \times (24.31\,\mathrm{g\,mol^{-1}})}{1 \times (24.31\,\mathrm{g\,mol^{-1}}) + 2 \times (63.55\,\mathrm{g\,mol^{-1}})} = 16$$

For Mg_2Cu the percentage by mass of Mg is 43.

For the isopleth at 25% Mg at high temperatures the initially system corresponds to a single-phase liquid system. At a_1 (at about 730 °C) $MgCu_2$ begins to come out of solution and the liquid becomes richer in Mg, moving toward e_2. At a_2 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 is shown next to the phase diagram.

P5D.6 The schematic phase diagram is shown in Fig 5.26. The solid points are the data given in the *Exercise*, and the lines are simply plausible connections between these points; the open circle is the incongruent melting of K_2FeCl_4. An expanded section of the phase diagram is shown as this includes the part of interest.

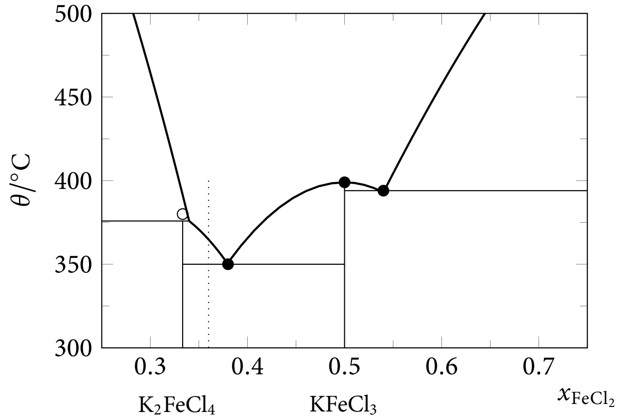


Figure 5.26

The compounds $KFeCl_3$ and K_2FeCl_4 correspond to $x_{FeCl_2} = \frac{1}{2}$ and $x_{FeCl_2} = \frac{1}{3}$, respectively; these compositions are shown on the diagram.

When a melt of composition $x_{FeCl_2} = 0.36$ is cooled (the dotted line), solid is first deposited when the temperature falls to around 360 °C. The solid consists of K_2FeCl_4, and as the temperature falls further the liquid grows progressively richer in $FeCl_2$. This process continues until the temperature falls to 350 °C, at which point the liquid has the same composition as the eutectic and the whole sample solidifies to a mixture of K_2FeCl_4 and $KFeCl_3$.

5E Phase diagrams of ternary systems

Answers to discussion questions

D5E.2 The lever rule, [5C.6–*170*], applies in a ternary system, but with an important caveat. For binary systems the tie lines to which the rule appplies are always horizontal and so can be added to the phase diagram at will. In contrast, for a ternary system the tie lines have no such simple orientation and have to be determined experimentally. Thus the lever rule applies, but in order to use it additional information is needed about the tie lines at the composition of interest.

D5E.4 The composition represented by point *c* is approximately $x_{\rm Ni} = 0.73$, $x_{\rm Fe} = 0.20$, $x_{\rm Cr} = 0.07$. This is a three-phase region, with Fe, Ni and γFeNi present.

Solutions to exercises

E5E.1(b) The ternary phase diagram is shown in Fig 5.27.

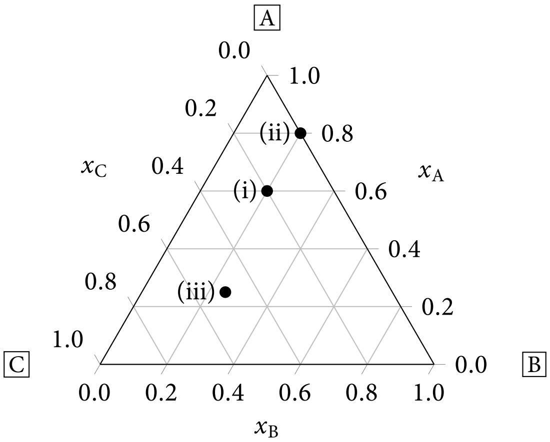


Figure 5.27

E5E.2(b) The composition by mass needs to be converted to mole fractions, which requires the molar masses: $M_{\rm NaCl} = 58.44\ {\rm g\,mol^{-1}}$, $M_{\rm H_2O} = 18.016\ {\rm g\,mol^{-1}}$, and $M_{\rm Na_2SO_4\cdot 10\,H_2O} = 322.20\ {\rm g\,mol^{-1}}$. Imagine that the solution contains 33 g NaCl, 33 g $\rm Na_2SO_4\cdot 10\,H_2O$ and hence $(100-33-33) = 34$ g $\rm H_2O$. The mole fraction of NaCl is

$$x_{\rm NaCl} = \frac{m_{\rm NaCl}/M_{\rm NaCl}}{m_{\rm NaCl}/M_{\rm NaCl} + m_{\rm Na_2SO_4\cdot 10\,H_2O}/M_{\rm Na_2SO_4\cdot 10\,H_2O} + m_{\rm H_2O}/M_{\rm H_2O}}$$

$$= \frac{(33\ {\rm g})/(58.44\ {\rm g\,mol^{-1}})}{(33\ {\rm g})/(58.44\ {\rm g\,mol^{-1}}) + (33\ {\rm g})/(322.20\ {\rm g\,mol^{-1}}) + (34\ {\rm g})/(18.016\ {\rm g\,mol^{-1}})}$$

$$= 0.22$$

Likewise, $x_{\mathrm{Na_2SO_4\cdot 10\,H_2O}} = 0.040$ and $x_{\mathrm{H_2O}} = 0.74$; this point is plotted in the ternary phase diagram shown in Fig 5.28.

The line with varying amounts of water but the same relative amounts of the two salts (in this case, equal by mass), passes through this point and the vertex corresponding to $x_{\mathrm{H_2O}} = 1$. This line intersects the NaCl axis at a mole fraction corresponding to a 50:50 mixture (by mass) of the two salts

$$x_{\mathrm{NaCl}} = \frac{(50\ \mathrm{g})/(58.44\ \mathrm{g\,mol^{-1}})}{(50\ \mathrm{g})/(58.44\ \mathrm{g\,mol^{-1}}) + (50\ \mathrm{g})/(322.20\ \mathrm{g\,mol^{-1}})} = 0.85$$

The line is shown on the diagram.

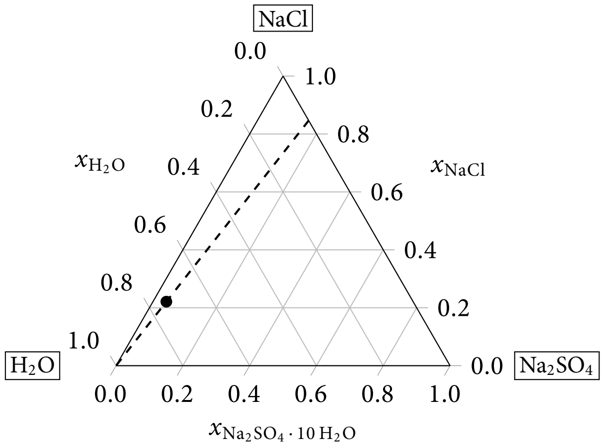


Figure 5.28

E5E.3(b) The composition by mass needs to be converted to mole fractions, which requires the molar masses: $M_{\mathrm{CHCl_3}} = 119.37\ \mathrm{g\,mol^{-1}}$, $M_{\mathrm{H_2O}} = 18.016\ \mathrm{g\,mol^{-1}}$, and $M_{\mathrm{CH_3COOH}} = 60.052\ \mathrm{g\,mol^{-1}}$. The mole fraction of $\mathrm{CHCl_3}$ is

$$\begin{aligned} x_{\mathrm{CHCl_3}} &= \frac{m_{\mathrm{CHCl_3}}/M_{\mathrm{CHCl_3}}}{m_{\mathrm{CHCl_3}}/M_{\mathrm{CHCl_3}} + m_{\mathrm{CH_3COOH}}/M_{\mathrm{CH_3COOH}} + m_{\mathrm{H_2O}}/M_{\mathrm{H_2O}}} \\ &= \frac{(8.8\ \mathrm{g})/(119.37\ \mathrm{g\,mol^{-1}})}{(8.8\ \mathrm{g})/(119.37\ \mathrm{g\,mol^{-1}}) + (3.7\ \mathrm{g})/(60.052\ \mathrm{g\,mol^{-1}}) + (55.0\ \mathrm{g})/(18.016\ \mathrm{g\,mol^{-1}})} \\ &= 0.023 \end{aligned}$$

Likewise, $x_{\mathrm{CH_3COOH}} = 0.019$ and $x_{\mathrm{H_2O}} = 0.958$. This point in marked with the open circle on the phase diagram shown in Fig. 5.29; it falls clearly in the one-phase region.

(i) When water is added to the mixture the composition moves the distance to the lower-left corner. The system remains in the one-phase region throughout.

(ii) When ethanoic acid is added to the mixture the composition moves along the dashed line to the vertex. The system remains in the one-phase region throughout.

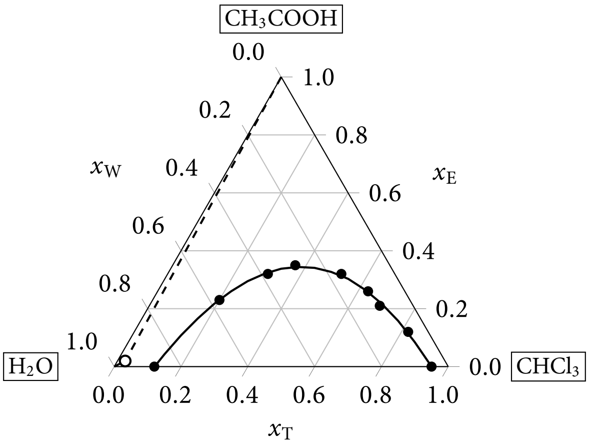


Figure 5.29

E5E.4(b) The points corresponding to the given compositions are marked with letters on the phase diagram shown in Fig. 5.30. Composition (i) is in a two-phase region, (ii) is in a three-phase region, (iii) is in a two-phase region, and (iv) appears to lie on the line separating different phases.

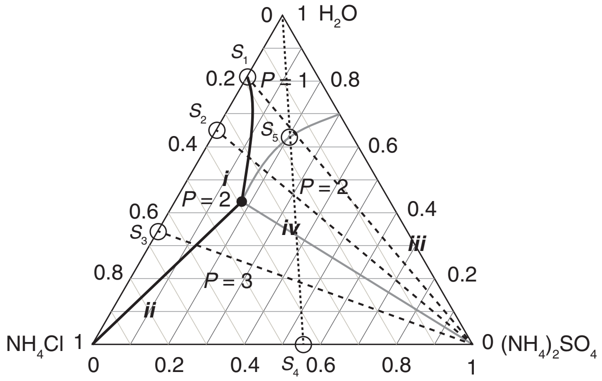


Figure 5.30

E5E.5(b) (i) Saturated solutions of NH_4Cl in H_2O in the presence of solid NH_4Cl appear as points on the left-hand edge of the phase diagram. Three representative compositions are shown in Fig. 5.30: S_1 corresponds to the point at which the solution becomes a single phase, and is therefore the highest concentration that can be achieved; S_2 has a higher mole fraction of NH_4Cl than S_1 so it corresponds to a saturated solution in the presence of solid NH_4Cl; S_3 corresponds to yet more solid being present.

Adding $(NH_4)_2SO_4$ to each of these solutions corresponds to traversing the dashed lines from S_i to the lower right-hand vertex which corresponds to pure $(NH_4)_2SO_4$. Starting from S_1 the system first traverses a one-phase region, meaning that both salts are entirely dissolved, before moving into a two phase region which implies that one of the salts will precipitate out. The tie lines are not given, but presumably as the amount of $(NH_4)_2SO_4$ increases the composition of the aqueous solution moves along the curve to the point where the four lines meet. At this point the last drop of solution vanishes.

Starting from S_2 the system first traverses a two-phase region, meaning that the $(NH_4)_2SO_4$ is going into solution. Eventually the system moves into a one-phase region, which implies that addition of $(NH_4)_2SO_4$ has caused the excess solid NH_4Cl to dissolve. As with the path starting from S_1, this path eventually crosses into a two-phase region where the behaviour is as has already been described.

Starting from S_3 the system first traverses a two-phase region but in contrast to S_1 and S_2 it never enters a one-phase region.

(ii) It is first necessary to convert the given masses to mole fractions, using $M_{NH_4Cl} = 53.49\ \mathrm{g\,mol^{-1}}$ and $M_{(NH_4)_2SO_4} = 132.14\ \mathrm{g\,mol^{-1}}$. The mole fraction of NH_4Cl is

$$x_{NH_4Cl} = \frac{(25\ \mathrm{g})/(53.49\ \mathrm{g\,mol^{-1}})}{(25\ \mathrm{g})/(53.49\ \mathrm{g\,mol^{-1}}) + (75\ \mathrm{g})/(132.14\ \mathrm{g\,mol^{-1}})} = 0.45$$

and hence $x_{(NH_4)_2SO_4} = 1 - x_{NH_4Cl} = 0.55$; this point is shown in Fig. 5.30 as S_4. Adding water to such a mixture involves traversing the dotted line from S_4 to the apex of the diagram, which corresponds to pure H_2O.

To start with the system is entirely solid, but when the line between the three-phase to two-phase region is crossed the two phases in question are some kind of solid and an aqueous solution, which appears for the first time. As the two-phase region is traversed the composition of this aqueous solution traverses the gray line until point S_5 where it meets the dotted line. After this, the system moves into a one-phase region: all the solids are dissolved.

Solutions to problems

P5E.2 (a) The given points are shown by filled dots in the phase diagram shown in Fig. 5.31. The fact that CO_2 and nitroethane have a two-phase region between $x_{\text{nitroethane}} = 0.08$ and 0.84, and that there is a plait point at $x_{CO_2} = 0.18$, $x_{\text{nitroethane}} = 0.53$ establishes some limits on the two-phase region, the outline of which is indicated by a plausible line. Similarly, the CO_2/DEC two-phase region is established by the given data.

(b) Mixtures with nitroethane and CO_2 in a fixed ratio, but with increasing amounts of DEC, fall on a straight line from some point on the right-hand edge to the lower-left apex (pure DEC). The two dashed lines shown just touch the two-phase regions, so all compositions between these lines lie in the one-phase region; this is the region where addition of DEC never causes phase separation.

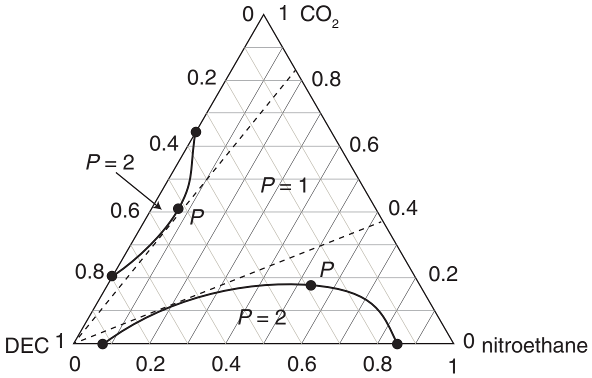


Figure 5.31

5F **Activities**

Answers to discussion questions

D5F.2 Raoult's law, $p_J = x_J p_J^*$, [5A.22–*151*], expresses the partial pressure of J in the gas phase in terms of its mole fraction in the liquid phase, x_J, and the vapour pressure over the pure liquid, p_J^*. This law only applies to ideal solutions, and indeed is taken as a defining property of such solutions.

For non-ideal solutions Raoult's law is modified to $p_J = a_J p_J^*$, where a_J is the activity. However, this relationship is best viewed as the definition of the activity in terms of two measurable quantities, the pressures: $a_J = p_J/p_J^*$. In the limit $x_J \rightarrow 1$ the activity becomes equal to the mole fraction, so the general equation involving the activity moves smoothly over to the relationship which applies to ideal solutions. It is convenient to retain such similar relationships for the ideal and non-ideal cases.

D5F.4 The coulombic (electrostatic) interactions of the ions in solution with each other are responsible for the deviation of their activity coefficients from the ideal value of 1. As a result of these interactions there is a build up of charge of opposite sign around any given ion, called the *ionic atmosphere*, in the overall electrically neutral solution. The energy, and hence the chemical potential, of any given ion is lowered as a result of the existence of this ionic atmosphere. The lowering of the chemical potential below its ideal value is identified with a negative value of $RT \ln \gamma_\pm$ and hence a value of $\gamma_\pm$ less than unity.

D5F.6 The term B in the extended Debye–Hückel law, [5F.30a–*189*], and the Davies equation, [5F.30b–*189*], can be interpreted as an indicator of the distance of closest approach of the ions. However, both B and the parameter C in the latter equation are best thought of as empirical parameters to be obtained by fitting experimental data.

Solutions to exercises

E5F.1(b) The activity in terms of the vapour pressure p is given by [5F.2–*183*], $a = p/p^*$, where p^* is the vapour pressure of the pure solvent. The vapour pressure of pure water at 100 °C, the normal boiling point, is 1 atm. Therefore $a = p/p^* = (90.00\,\text{kPa})/[(1\,\text{atm}) \times (101.325\,\text{kPa})/(1\,\text{atm})] = \boxed{0.8882}$.

E5F.2(b) On the basis of Raoult's law, the activity in terms of the vapour pressure p_A is given by [5F.2–*183*], $a_A = p_A/p_A^*$, where p_A^* is the vapour pressure of the pure solvent. With the data given $a_A = p_A/p_A^* = (0.02239\,\text{atm})/(0.02308\,\text{atm}) = 0.9701... = \boxed{0.9701}$.

The activity coefficient is defined through [5F.4–*183*], $a_A = \gamma_A x_A$. The mole fraction of solvent water (A) is computed as

$$\begin{aligned} x_A &= \frac{n_A}{n_A + n_A} \\ &= \frac{(0.920 \times 10^3\,\text{g})/(18.0158\,\text{g}\,\text{mol}^{-1})}{(0.920 \times 10^3\,\text{g})/(18.0158\,\text{g}\,\text{mol}^{-1}) + (0.122 \times 10^3\,\text{g})/(241\,\text{g}\,\text{mol}^{-1})} \\ &= 0.990... \end{aligned}$$

Hence $\gamma_A = a_A/x_A = (0.9701...)/(0.990...) = \boxed{0.980}$.

E5F.3(b) On the basis of Raoult's law, the activity in terms of the vapour pressure p_J is given by [5F.2–*183*], $a_J = p_J/p_J^*$, where p_J^* is the vapour pressure of the pure solvent. The partial vapour pressure of component J in the gas is given by $p_J = y_J p_{\text{tot}}$. In this case

$$a_A = \frac{p_A}{p_A^*} = \frac{y_A p_{\text{tot}}}{p_A^*} = \frac{0.314 \times (1.00\,\text{atm}) \times [(101.325\,\text{kPa})/(1\,\text{atm})]}{73.0\,\text{kPa}} = 0.435...$$

The activity of A is therefore $a_A = \boxed{0.436}$. The activity coefficient is defined through [5F.4–*183*], $a_J = \gamma_J x_J$, therefore $\gamma_A = a_A/x_A = 0.435.../0.220 = \boxed{1.98}$.

For the other component the mole fractions are $y_B = 1 - y_A = 0.686$ and $x_B = 1 - x_A = 0.780$. The rest of the calculation follows as before

$$a_B = \frac{p_B}{p_B^*} = \frac{y_B p_{\text{tot}}}{p_B^*} = \frac{0.686 \times (1.00\,\text{atm}) \times [(101.325\,\text{kPa})/(1\,\text{atm})]}{92.1\,\text{kPa}} = 0.754...$$

The activity of B is therefore $a_B = \boxed{0.755}$ and its activity coefficient is given by $\gamma_B = a_B/x_B = 0.754.../0.780 = \boxed{0.968}$.

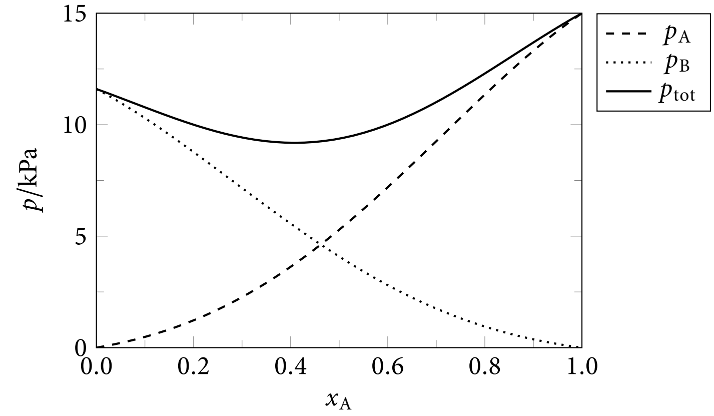


Figure 5.32

E5F.4(b) For this model of non-ideal solutions the vapour pressures are given by [5F.18–*186*], $p_A = p_A^* x_A \exp(\xi[1-x_A]^2)$ and likewise for p_B; the total pressure is given by $p_{tot} = p_A + p_B$. The vapour pressures are plotted in Fig. 5.32.

E5F.5(b) Ionic strength is defined in [5F.28–*188*]

$$I = \tfrac{1}{2}\sum_i z_i^2 (b_i/b^\ominus)$$

where the sum runs over all the ions in the solution, z_i is the charge number on ion i, and b_i is its molality. It is convenient to draw up a table of the contribution to the ionic strength from each ion, where the contribution is defined as $z_i^2(b_i/b^\ominus)$. For $K_3[Fe(CN)_6]$ note that the molality of the K^+ produced when it dissolves is three times the molality of the solute.

solute (molality/mol kg^{-1})	ion	$b_i/b^\ominus$	z_i	contribution
$K_3[Fe(CN)_6]$ (0.040)	K^+	0.120	+1	0.120
	$[Fe(CN)_6]^{3-}$	0.040	−3	0.360
KCl (0.030)	K^+	0.030	+1	0.030
	Cl^-	0.030	−1	0.030
NaBr (0.050)	Na^+	0.050	+1	0.050
	Cl^-	0.050	−1	0.050

The total of the contributions in the right-most column is 0.640, therefore the ionic strength is $I = \frac{1}{2} \times 0.640 = \boxed{0.320}$.

E5F.6(b) Ionic strength is defined in [5F.28–*188*]

$$I = \tfrac{1}{2}\sum_i z_i^2 (b_i/b^\ominus)$$

where the sum runs over all the ions in the solution, z_i is the charge number on ion i, and b_i is its molality.

(a) The aim here is to increase the ionic strength by 1.00 – 0.110 = 0.890; the task is therefore to compute the mass m of KNO_3 which, when added to a mass m_w of water, gives this increase in the ionic strength.

A solution of KNO_3 of molality b contributes K^+ at molality b and NO_3^- at molality b. The contribution to the ionic strength is therefore $\frac{1}{2}[(+1)^2 \times b + (-1)^2 \times b]/b^\ominus = b/b^\ominus$.

The molality arising from dissolving mass m of KNO_3 in a mass m_w of solvent is $(m/M)/m_w$, where M is the molar mass. It therefore follows that to achieve the desired increase in ionic strength

$$\frac{m}{Mm_w} \times \frac{1}{b^\ominus} = 0.890 \quad \text{hence} \quad m = 0.890 \times Mm_w b^\ominus$$

The molar mass of KNO_3 is 101.11 g mol^{-1}; using this, and recalling that the molality is expressed in mol kg^{-1}, gives

$$\begin{aligned} m &= 0.890 \times (101.11 \times 10^{-3}\ \text{kg mol}^{-1}) \times (0.500\ \text{kg}) \times (1\ \text{mol kg}^{-1}) \\ &= 44.9... \times 10^{-3}\ \text{kg} \end{aligned}$$

Hence the $\boxed{45.0\ \text{g}}$ of KNO_3 needs to be added to achieve the desired ionic strength.

(i) The argument is as in (a) except that the added solute $Ba(NO_3)_2$ makes a different contribution to the ionic strength. A solution of $Ba(NO_3)_2$ of molality b contributes Ba^{2+} at molality b and NO_3^- at molality $2b$. The contribution to the ionic strength is therefore $\frac{1}{2}[(+2)^2 \times b + (-1)^2 \times 2b]/b^\ominus = 3b/b^\ominus$. It therefore follows that to achieve the desired increase in ionic strength

$$3 \times \frac{m}{Mm_w} \times \frac{1}{b^\ominus} = 0.890 \quad \text{hence} \quad m = \tfrac{1}{3} \times 0.890 \times Mm_w b^\ominus$$

The molar mass of $Ba(NO_3)_2$ is 261.35 g mol^{-1}; using this, and recalling that the molality is expressed in mol kg^{-1}, gives

$$\begin{aligned} m &= \tfrac{1}{3} \times 0.890 \times (261.35 \times 10^{-3}\ \text{kg mol}^{-1}) \times (0.500\ \text{kg}) \times (1\ \text{mol kg}^{-1}) \\ &= 38.7... \times 10^{-3}\ \text{kg} \end{aligned}$$

Hence the $\boxed{38.8\ \text{g}}$ of $Ba(NO_3)_2$ needs to be added to achieve the desired ionic strength.

E5F.7(b) The Debye–Hückel limiting law, [5F.27–*188*], is used to estimate the mean activity coefficient, $\gamma_\pm$, at 25 °C in water

$$\log \gamma_\pm = -0.509\,|z_+z_-|\,I^{1/2} \qquad I = \tfrac{1}{2}\sum_i z_i^2 (b_i/b^\ominus)$$

where $z_\pm$ are the charge numbers on the ions from the salt of interest and I is the ionic strength, defined in [5F.28–*188*]. In the definition of I the sum runs over all the ions in the solution, z_i is the charge number on ion i, and b_i is its molality.

A solution of $Ca(NO_3)_2$ of molality b contributes Ca^{2+} at molality b and NO_3^- at molality $2b$. The contribution to the ionic strength is therefore $\frac{1}{2}[(+2)^2 \times b + (-1)^2 \times 2b]/b^\ominus = 3b/b^\ominus$. A solution of NaCl of molality b' contributes Na^+ at molality b' and Cl^- at molality b'. The contribution to the ionic strength is therefore $\frac{1}{2}[(+1)^2 \times b' + (-1)^2 \times b']/b^\ominus = b'/b^\ominus$. The ionic strength of the solution is therefore

$$(3b+b')/b^\ominus = [3\times(0.035\,\mathrm{mol\,kg^{-1}})+1\times(0.020\,\mathrm{mol\,kg^{-1}})]/(1\,\mathrm{mol\,kg^{-1}}) = 0.125$$

For solute $Ca(NO_3)_2$ $z_+ = +2$ and $z_- = -1$ so the limiting law evaluates as

$$\log\gamma_\pm = -0.509\,|z_+z_-|\,I^{1/2} = -0.509\,|(+2)\times(-1)|\,(0.125)^{1/2} = -0.359...$$

The mean activity coefficient is therefore $\gamma_\pm = 10^{-0.359...} = 0.436... = \boxed{0.44}$.

E5F.8(b) The Davies equation is given in [5F.30b–*189*]

$$\log\gamma_\pm = \frac{-A\,|z_+z_-|\,I^{1/2}}{1+BI^{1/2}} + CI$$

Because the electrolyte is 1:1 with univalent ions, the ionic strength is simply $I = b_{KCl}/b^\ominus$. There is no obvious straight-line plot using which the data can be tested against the Davies equation, therefore a non-linear fit is made using mathematical software and assuming that $A = 0.509$; recall that the molalities must be expressed in $\mathrm{mol\,kg^{-1}}$. The best-fit values are $\boxed{B = 1.53}$ and $C = -0.0686$. With these values the predicted activity coefficients are 0.927, 0.902 and 0.816, which is very good agreement.

Solutions to problems

P5F.2 The Margules equations predict a vapour pressure given by [5F.18–*186*], $p_A = p_A^* x_A \exp(\xi[1-x_A]^2)$; for small x_A the vapour pressure is given by [5F.19–*186*], $p_A = p_A^* x_A \exp(\xi)$. Plots showing how the vapour pressures varies with x_A for the two cases are shown in Fig. 5.33; an expansion for small x_A is also shown. A deviation of 10% between the two expressions occurs by about $x_A = 0.02$.

P5F.4 The Debye–Hückel limiting law, [5F.27–*188*], and the Davies equation, [5F.30b–*189*], are, respectively,

$$\log\gamma_\pm = -0.509\,|z_+z_-|\,I^{1/2} \qquad \log\gamma_\pm = \frac{-0.509\,|z_+z_-|\,I^{1/2}}{1+BI^{1/2}} + CI$$

Figure 5.34 shows a graphical comparison of the predictions of these two equations for the case of a 1:1 univalent electrolyte in aqueous solution at 25 °C, with $B = 1.50$ and $C = 0$; for such an electrolyte $I = b/b^\ominus$. The two predictions for $\gamma_\pm$ differ by about 10% when $I = 0.18$ ($I^{1/2} = 0.42$).

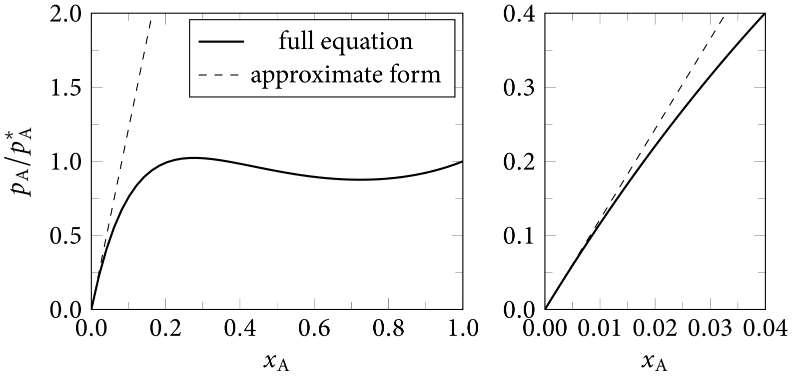


Figure 5.33

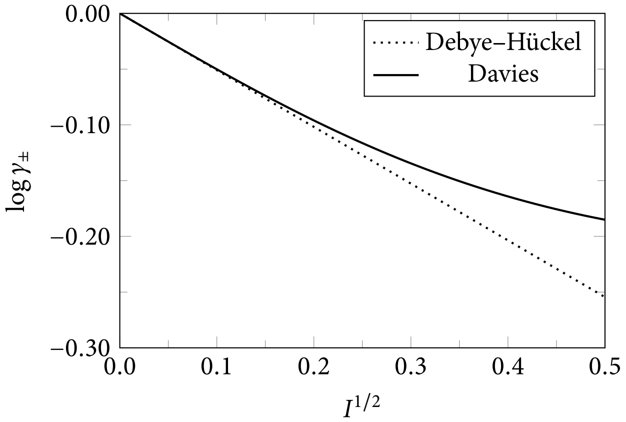


Figure 5.34

Answers to integrated activities

I5.2 On the basis of Raoult's law, the activity in terms of the vapour pressure p_J is given by [5F.2–*183*], $a_J = p_J/p_J^*$, where p_J^* is the vapour pressure of the pure solvent. The activity coefficient is defined through [5F.4–*183*], $a_J = \gamma_J x_J$, therefore $\gamma_J = p_J/p_J^* x_J$.

The data as given do not include values for the vapour pressure over the pure liquids, so the first task is to plot p_J against x_J and extrapolate to $x_J = 1$ to find p_J^*. The vapour pressures are plotted in this way Fig. 5.35, and the linear extrapolations to find the vapour pressures of the pure substances are also shown. These give the values $p_E^* = 7.45$ kPa and $p_B^* = 35.41$ kPa; using these values the activity coefficients are computed as shown in the table.

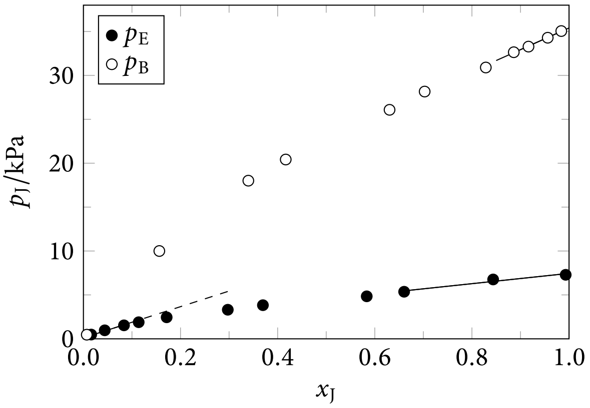


Figure 5.35

x_E	p_E/kPa	x_B	p_B/kPa	γ_E	γ_B	γ_E(Henry)	G^E/kJ mol^{-1}
0.0160	0.484	0.9840	35.05	4.06	1.01	1.70	0.08
0.0439	0.967	0.9561	34.29	2.96	1.01	1.24	0.16
0.0835	1.535	0.9165	33.28	2.47	1.03	1.03	0.26
0.1138	1.89	0.8862	32.64	2.23	1.04	0.93	0.34
0.1714	2.45	0.8286	30.90	1.92	1.05	0.80	0.42
0.2973	3.31	0.7027	28.16	1.49	1.13	0.63	0.55
0.3696	3.83	0.6304	26.08	1.39	1.17	0.58	0.59
0.5834	4.84	0.4166	20.42	1.11	1.38	0.47	0.53
0.6604	5.36	0.3396	18.01	1.09	1.50	0.46	0.52
0.8437	6.76	0.1563	10.00	1.07	1.81	0.45	0.41
0.9931	7.29	0.0069	0.47	0.98	1.92	0.41	−0.03

On the basis of Henry's law, the activity in terms of the vapour pressure p_J is given by [5F.10–*184*], $a_J = p_J/K_J$, where K_J is the Henry's law constant for J as a solute. The activity coefficient is defined as before, $a_J = \gamma_J x_J$, and therefore $\gamma_J = p_J/K_J x_J$.

To find the Henry's law constant for E, the limiting slope of a plot of p_E against x_E is taken. The three data points given at the lowest values of x_E do not extrapolate back to the origin, which is not in accord with Henry's law. Arguably there are several equally valid ways of proceeding here, but one is to force the best-fit line to pass through the origin and then use the first three data points; this leads to the slope is shown by the dashed line in Fig. 5.35. The limiting slope, taken in this way is 17.77 and so $K_E = 17.77$ kPa. This value is used to compute the activity coefficients for E based on Henry's law, and the results are shown in column headed γ_E(Henry) in the table above. The outcome is not satisfactory because the expecting limiting behaviour $\gamma_E \rightarrow 1$ as $x_E \rightarrow 0$ is not evidenced.

The excess Gibbs energy is define in [5B.5–*156*] as $G^{\mathrm{E}} = \Delta_{\mathrm{mix}}G - \Delta_{\mathrm{mix}}G^{\mathrm{ideal}}$. As explained in Section 5F.3 on page 185, the Gibbs energy of mixing is given in terms of the activities as $\Delta_{\mathrm{mix}}G = nRT\,(x_{\mathrm{A}}\ln a_{\mathrm{A}} + x_{\mathrm{B}}\ln a_{\mathrm{B}})$, whereas the ideal Gibbs energy of mixing is $\Delta_{\mathrm{mix}}G^{\mathrm{ideal}} = nRT\,(x_{\mathrm{A}}\ln x_{\mathrm{A}} + x_{\mathrm{B}}\ln x_{\mathrm{B}})$. The activities are written as $a_{\mathrm{A}} = \gamma_{\mathrm{A}}x_{\mathrm{A}}$ and hence

$$\begin{aligned}
G^{\mathrm{E}} &= \Delta_{\mathrm{mix}}G - \Delta_{\mathrm{mix}}G^{\mathrm{ideal}}\\
&= nRT\,(x_{\mathrm{A}}\ln a_{\mathrm{A}} + x_{\mathrm{B}}\ln a_{\mathrm{B}}) - nRT\,(x_{\mathrm{A}}\ln x_{\mathrm{A}} + x_{\mathrm{B}}\ln x_{\mathrm{B}})\\
&= nRT\,(x_{\mathrm{A}}\ln \gamma_{\mathrm{A}}x_{\mathrm{A}} + x_{\mathrm{B}}\ln \gamma_{\mathrm{B}}x_{\mathrm{B}}) - nRT\,(x_{\mathrm{A}}\ln x_{\mathrm{A}} + x_{\mathrm{B}}\ln x_{\mathrm{B}})\\
&= nRT\,(x_{\mathrm{A}}\ln \gamma_{\mathrm{A}} + x_{\mathrm{B}}\ln \gamma_{\mathrm{B}})
\end{aligned}$$

Using the final expression G^{E}/n is computed from the given data and using the activity coefficients (based on Raoult's law) already derived. The computed values are given in the table.

I5.4 On the basis of Raoult's law, the activity in terms of the vapour pressure p_{J} is given by [5F.2–*183*], $a_{\mathrm{J}} = p_{\mathrm{J}}/p_{\mathrm{J}}^{*}$, where p_{J}^{*} is the vapour pressure of the pure substance. The activity coefficient is defined through [5F.4–*183*], $a_{\mathrm{J}} = \gamma_{\mathrm{J}}x_{\mathrm{J}}$, therefore $\gamma_{\mathrm{J}} = p_{\mathrm{J}}/p_{\mathrm{J}}^{*}x_{\mathrm{J}}$. The partial pressure in the gas phase is determined from the mole fraction in the gas phase, y_{J}, $p_{\mathrm{J}} = y_{\mathrm{J}}p_{\mathrm{tot}}$, so the final calculation is $\gamma_{\mathrm{J}} = y_{\mathrm{J}}p_{\mathrm{tot}}/p_{\mathrm{J}}^{*}x_{\mathrm{J}}$.

The total pressure is given in kPa, whereas the vapour pressure over pure oxygen is given in Torr. The conversion is

$$(p\ \mathrm{kPa}) = (p'\ \mathrm{Torr}) \times \frac{(101.325\,\mathrm{kPa})/(1\ \mathrm{atm})}{(760\ \mathrm{Torr})/(1\ \mathrm{atm})}$$

The temperature-composition phase diagram is shown in Fig. 5.36 and the computed values of the activity coefficient are given in the table below. The fact that the activity coefficient is close to 1 indicates near-ideal behaviour.

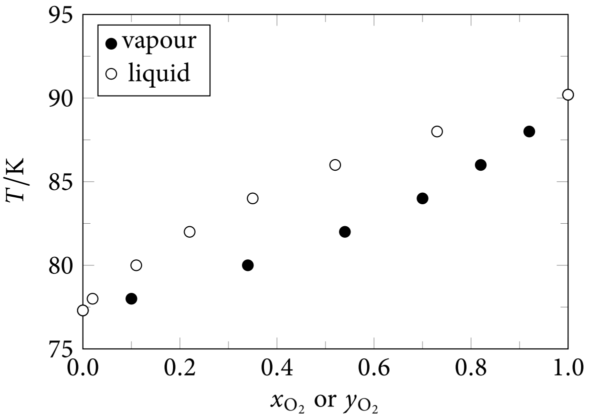


Figure 5.36

T/K	$x_{\mathrm{O_2}}$	$y_{\mathrm{O_2}}$	$p^*_{\mathrm{O_2}}/\mathrm{Torr}$	$\gamma_{\mathrm{O_2}}$
77.3	0	0	154	
78	0.10	0.02	171	0.88
80	0.34	0.11	225	1.08
82	0.54	0.22	294	1.04
84	0.70	0.35	377	0.99
86	0.82	0.52	479	0.99
88	0.92	0.73	601	0.99
90.2	1.00	1.00	760	0.99

I5.6 (a) To develop the expression for K into the form requested it is useful to rewrite [MA] and $[\mathrm{M}]_{\mathrm{free}}$ in terms of the total concentration of macromolecule, [M]. The total amount of A in the dialysis bag is $[\mathrm{A}]_{\mathrm{in}} = [\mathrm{A}]_{\mathrm{free}} + [\mathrm{A}]_{\mathrm{bound}}$, but the amount of A bound is equal to the amount of the macromolecule ligand complex, MA: $[\mathrm{A}]_{\mathrm{bound}} = [\mathrm{MA}]$, therefore

$$[\mathrm{A}]_{\mathrm{in}} = [\mathrm{A}]_{\mathrm{free}} + [\mathrm{MA}] \quad \text{hence} \quad [\mathrm{MA}] = [\mathrm{A}]_{\mathrm{in}} - [\mathrm{A}]_{\mathrm{free}}$$

Recall that $[\mathrm{A}]_{\mathrm{free}} = [\mathrm{A}]_{\mathrm{out}}$ and that, by definition $\nu = ([\mathrm{A}]_{\mathrm{in}} - [\mathrm{A}]_{\mathrm{out}})/[\mathrm{M}]$, it therefore follows that

$$[\mathrm{MA}] = [\mathrm{A}]_{\mathrm{in}} - [\mathrm{A}]_{\mathrm{out}} = \nu[\mathrm{M}]$$

Now consider the macromolecule, the total concentration of which is [M]. It follows that $[\mathrm{M}] = [\mathrm{MA}] + [\mathrm{M}]_{\mathrm{free}}$. The expression just derived for [MA], $[\mathrm{MA}] = \nu[\mathrm{M}]$ is substituted in to give $[\mathrm{M}] = \nu[\mathrm{M}] + [\mathrm{M}]_{\mathrm{free}}$, from which it follows that $[\mathrm{M}]_{\mathrm{free}} = [\mathrm{M}](1-\nu)$

With these expressions for $[\mathrm{M}]_{\mathrm{free}}$ and [MA], the expression for K is developed into the requested form

$$K = \frac{[\mathrm{MA}]c^{\ominus}}{[\mathrm{M}]_{\mathrm{free}}[\mathrm{A}]_{\mathrm{free}}} = \frac{\nu[\mathrm{M}]c^{\ominus}}{[\mathrm{M}](1-\nu)[\mathrm{A}]_{\mathrm{out}}} = \frac{\nu c^{\ominus}}{(1-\nu)[\mathrm{A}]_{\mathrm{out}}}$$

where $[\mathrm{A}]_{\mathrm{free}} = [\mathrm{A}]_{\mathrm{out}}$ is also used.

(b) The equilibrium constant K' describes the equilibrium between a macomolecule with a single binding site, S, and the bound complex, SA

$$K' = \frac{[\mathrm{SA}]c^{\ominus}}{[\mathrm{S}]_{\mathrm{free}}[\mathrm{A}]_{\mathrm{free}}}$$

In part (a) ν is defined as the average number of bound ligands per macromolecule, and is therefore given by $\nu = [\mathrm{A}]_{\mathrm{bound}}/[\mathrm{M}]$. Whereas M has N binding sites, S only has one site, so the average number of ligands bound per S is ν/N. This number is also expressed (by analogy with the earlier discussion) as $[\mathrm{A}]_{\mathrm{bound}}/[\mathrm{S}]$, so it follows that $\nu/N = [\mathrm{A}]_{\mathrm{bound}}/[\mathrm{S}]$. The final step is to realise that the concentration of bound ligand is equal to the concentration of the S–A complex, so $[\mathrm{A}]_{\mathrm{bound}} = [\mathrm{SA}]$. It therefore follows that $\nu/N = [\mathrm{SA}]/[\mathrm{S}]$. This is rearranged to $[\mathrm{SA}] = [\mathrm{S}]\nu/N$, which is one of the terms needed in the expression for K'.

The other term is $[\mathrm{S}]_{\mathrm{free}}$ which is related to [S] as follows. The total concentration of S is given by $[\mathrm{S}] = [\mathrm{S}]_{\mathrm{free}} + [\mathrm{SA}]$, hence $[\mathrm{S}]_{\mathrm{free}} = [\mathrm{S}] - [\mathrm{SA}]$. Substituting $[\mathrm{SA}] = [\mathrm{S}]\nu/N$ gives $[\mathrm{S}]_{\mathrm{free}} = [\mathrm{S}] - [\mathrm{S}]\nu/N = (1-\nu/N)[\mathrm{S}]$. The expression for the equilibrium constant is now developed as

$$K' = \frac{[\mathrm{SA}]c^{\ominus}}{[\mathrm{S}]_{\mathrm{free}}[\mathrm{A}]_{\mathrm{free}}} = \frac{([\mathrm{S}]\nu/N)c^{\ominus}}{(1-\nu/N)[\mathrm{S}][\mathrm{A}]_{\mathrm{free}}} = \frac{\nu c^{\ominus}}{[\mathrm{A}]_{\mathrm{free}}(N-\nu)}$$

where to go to the final expression the numerator and demoninator are multiplied by N and [S] is cancelled. The *Scatchard equation* follows by taking the factor $(N-\nu)$ to the left

$$K'N - K'\nu = \frac{\nu c^{\ominus}}{[\mathrm{A}]_{\mathrm{free}}}$$

(c) The straight line plot is $\nu/[\mathrm{A}]_{\mathrm{free}}$ against ν. The task is therefore to determine ν from the data. Note that the data given are the *total* concentrations of EB in and outside the bag. It therefore follows that

$$[\mathrm{EB}]_{\mathrm{total,in}} = [\mathrm{EB}]_{\mathrm{bound}} + [\mathrm{EB}]_{\mathrm{free}} = [\mathrm{EB}]_{\mathrm{bound}} + [\mathrm{EB}]_{\mathrm{out}}$$

It follows that $[\mathrm{EB}]_{\mathrm{bound}} = [\mathrm{EB}]_{\mathrm{total,in}} - [\mathrm{EB}]_{\mathrm{out}}$. Recall that ν is defined as $\nu = [\mathrm{EB}]_{\mathrm{bound}}/[\mathrm{M}]$, therefore

$$\nu = \frac{[\mathrm{EB}]_{\mathrm{total,in}} - [\mathrm{EB}]_{\mathrm{out}}}{[\mathrm{M}]}$$

The given data and the derived values of ν are shown in the following table ($1\ \mu\mathrm{M} = 1\ \mu\mathrm{mol\,dm^{-3}}$), and plotted in Fig. 5.37.

$[\mathrm{EB}]_{\mathrm{out}}/\mu\mathrm{M}$	$[\mathrm{EB}]_{\mathrm{in}}/\mu\mathrm{M}$	ν	$(\nu/[\mathrm{EB}]_{\mathrm{out}})/(\mu\mathrm{M}^{-1})$
0.042	0.292	0.250	5.95
0.092	0.590	0.50	5.41
0.204	1.204	1.00	4.90
0.526	2.531	2.01	3.81
1.150	4.150	3.00	2.61

The data fit to quite a good straight line, the equation of which is

$$(\nu/[\mathrm{EB}]_{\mathrm{out}})/(\mu\mathrm{M}^{-1}) = -1.17 \times \nu + 6.12$$

The slope is $-K'/c^{\ominus}$ where $c^{\ominus}$ is the standard concentration, $1\ \mathrm{mol\,dm^{-3}}$, but because $[\mathrm{EB}]_{\mathrm{out}}$ is used in μM, $c^{\ominus} = 10^6\ \mu\mathrm{M}$. It follows that the (dimensionless) equilibrium constant is $\boxed{K' = 1.17 \times 10^6}$. The intercept gives $K'N/c^{\ominus}$, hence $\boxed{N = 5.23}$: this is the average number of binding sites per DNA molecule. The graph is a good straight line, indicating that the data fit the model quite well.

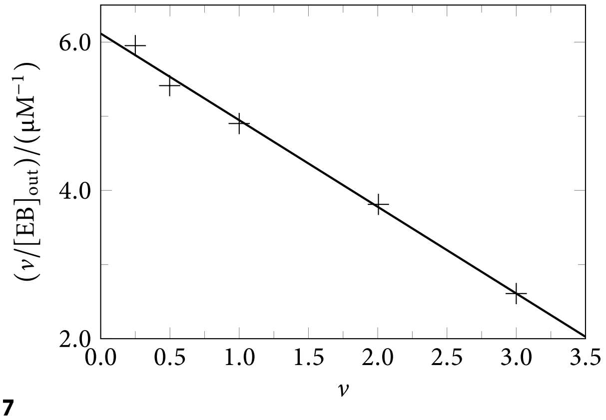


Figure 5.37

I5.8 The dissolution of the protein according to the given equilibrium is described by a solubility constant K_s

$$\mathrm{PX}_{\nu}(\mathrm{s}) \rightleftharpoons \mathrm{P}^{\nu+}(\mathrm{aq}) + \nu\,\mathrm{X}^{-}(\mathrm{aq}) \qquad K_s = a_{\mathrm{P}} a_{\mathrm{X}}^{\nu}$$

where the solubility constant is written in terms of the activities. Introducing the activity coefficients and molalities, b, gives

$$K_s = \gamma_{\pm}^{\nu+1} b_{\mathrm{P}} b_{\mathrm{X}}^{\nu}$$

At low to moderate ionic strengths the Debye–Hückel limiting law, [5F.27–*188*], $\log\gamma_{\pm} = -A|z_{-}z_{+}|I^{1/2}$, is a reasonable approximation for the activity coefficients.

Addition of a salt, such as $(\mathrm{NH_4})_2\mathrm{SO_4}$, causes I to increase, $\log\gamma_{\pm}$ to become more negative, and hence $\gamma_{\pm}$ to decrease. However, K_s is an equilibrium constant and remains unchanged. Therefore, the molality of $\mathrm{P}^{\nu+}$ increases and the protein solubility increases proportionately.

This effect is also explicable in terms of Le Chatelier's principle. As the ionic strength increases by the addition of an inert electrolyte such as $(\mathrm{NH_4})_2\mathrm{SO_4}$, the ions of the protein that are in solution attract one another less strongly, so that the equilibrium is shifted in the direction of increased solubility.

The explanation of the salting out effect is somewhat more complicated and can be related to the failure the Debye–Hückel limiting law at higher ionic strengths. At high ionic strengths the Davies equation, [5F.30b–*189*], is a better approximation

$$\log\gamma_{\pm} = \frac{-A\,|z_{+}z_{-}|\,I^{1/2}}{1 + BI^{1/2}} + CI$$

At low concentrations of inert salt, $I^{1/2} > I$, the first term dominates, $\gamma_{\pm}$ decreases with increasing I, and salting in occurs; however, at high concentrations, $I > I^{1/2}$, the second term dominates, $\gamma_{\pm}$ increases with increasing I, and salting out occurs. The Le Chatelier's principle explanation is that the water molecules are tied up by ion-dipole interactions and become unavailable for solvating the protein, thereby leading to decreased solubility.

I5.10 In Section 5B.2(e) on page 162 the derivation of the expression for the osmostic pressure starts by equating the chemical potential of A as a pure liquid subject to pressure p with that of A in a solution of mole fraction x_A containing solute B and subject to pressure $p+\Pi$: $\mu_A^*(p) = \mu_A(x_A, p+\Pi)$. The chemical potential of A in the solution is then expressed as $\mu_A(x_A, p+\Pi) = \mu_A^*(p+\Pi) + RT\ln x_A$, which assumes ideality. If the solution is not ideal, then the mole fraction is replaced by the activity a_A to give

$$\mu_A^*(p) = \mu_A^*(p+\Pi) + RT\ln a_A$$

The derivation then proceeds as before yielding the intermediate result $-RT\ln a_A = V_m\Pi$ for the non-ideal solution.

The osmotic coefficient ϕ is defined as $\phi = -(x_A/x_B)\ln a_A$, hence $\ln a_A = -\phi x_B/x_A$. This expression for $\ln a_A$ is substituted into $-RT\ln a_A = V_m\Pi$ to give $RT\phi x_B/x_A = V_m\Pi$. The final steps assume that the solution is dilute so that $x_A \approx 1$ and $x_B = n_B/(n_A+n_B) \approx n_B/n_A$

$$\begin{aligned} RT\phi\frac{x_B}{x_A} &= V_m\Pi \\ \text{hence}\quad RT\phi\frac{n_B}{n_A} &= V_m\Pi \\ RT\phi\frac{n_B}{n_A V_m} &= \Pi \\ RT\phi[B] &= \Pi \end{aligned}$$

To go to the last line $V = n_A V_m$ and $[B] = n_B/V$ are used.

6

Chemical equilibrium

6A The equilibrium constant

Answers to discussion questions

D6A.2 The terms appearing in the equilibrium constant are the activities of the species involved in the equilibrium, and these terms arise because the chemical potential of each species depends on its activity. If a pure liquid or pure solid is part of the equilibrium, its chemical potential contributes to the value of $\Delta_r G^\ominus$. However, as the substance is in its pure form there is no composition dependence of its chemical potential and hence no term in the equilibrium constant. Put another way, such species have unit activity.

Solutions to exercises

E6A.1(b) In general if the extent of a reaction changes by an amount $\Delta\xi$ then the amount of a component J changes by $\nu_J\Delta\xi$ where ν_J is the stoichiometric number for species J (positive for products, negative for reactants). In this case $\nu_A = -2$ and $\nu_B = +1$.

$$n_A = n_{A,0} + \Delta n_A = n_{A,0} + \nu_A\Delta\xi = (1.75\text{ mol}) + (-2)\times(0.30\text{ mol}) = \boxed{1.15\text{ mol}}$$

$$n_B = n_{B,0} + \Delta n_B = n_{B,0} + \nu_B\Delta\xi = (0.12\text{ mol}) + 1\times(0.30\text{ mol}) = \boxed{0.42\text{ mol}}$$

E6A.2(b) The reaction Gibbs energy $\Delta_r G$ is defined by [6A.1–*204*], $\Delta_r G = (\partial G/\partial\xi)_{p,T}$. Approximating the derivative by finite changes gives

$$\Delta_r G = \left(\frac{\partial G}{\partial\xi}\right)_{p,T} \approx \frac{\Delta G}{\Delta\xi} = \frac{-2.41\text{ kJ}}{+0.051\text{ mol}} = \boxed{-47\text{ kJ mol}^{-1}}$$

E6A.3(b) A reaction is exergonic if $\Delta_r G < 0$ and endergonic if $\Delta_r G > 0$. From the *Resource section* the standard Gibbs energy change for the formation of liquid benzene from its elements in their reference states at 298 K is $\Delta_f G^\ominus = +124.3\text{ kJ mol}^{-1}$. This is positive so the reaction is $\boxed{\text{endergonic}}$.

E6A.4(b) The reaction quotient is defined by [6A.10–*207*], $Q = \prod_J a_J^{\nu_J}$. For the reaction $2A + B \rightarrow 2C + D$, $\nu_A = -2$, $\nu_B = -1$, $\nu_C = +2$, and $\nu_D = +1$. The reaction quotient is then

$$Q = a_A^{-2}a_B^{-1}a_C^{2}a_D = \frac{a_C^2 a_D}{a_A^2 a_B}$$

E6A.5(b) The equilibrium constant is defined by [6A.14–*207*], $K = \left(\prod_J a_J^{\nu_J}\right)_{\text{equilibrium}}$. The 'equilibrium' subscript indicates that the activities are those at equilibrium rather than at an arbitrary stage in the reaction; however this subscript is not usually written explicitly. In this case

$$K = a_{CH_4(g)}^{-1} a_{Cl_2(g)}^{-3} a_{CHCl_3(l)} a_{HCl(g)}^{3} = \frac{a_{CHCl_3(l)} a_{HCl(g)}^{3}}{a_{CH_4(g)} a_{Cl_2(g)}^{3}}$$

The activity of $CHCl_3(l)$ is 1 because it is a pure liquid. Furthermore if the gases are treated as perfect then their activities are replaced by $a_J = p_J/p^\ominus$. The equilibrium constant becomes

$$K = \frac{(p_{HCl}/p^\ominus)^3}{(p_{CH_4}/p^\ominus)(p_{Cl_2}/p^\ominus)^3} = \frac{p_{HCl}^3 p^\ominus}{p_{CH_4} p_{Cl_2}^3}$$

E6A.6(b) The standard reaction Gibbs energy is given by [6A.13a–*207*]

$$\Delta_r G^\ominus = \sum_{\text{Products}} \nu \Delta_f G^\ominus - \sum_{\text{Reactants}} \nu \Delta_f G^\ominus$$

The relationship between $\Delta_r G^\ominus$ and K, [6A.15–*208*], $\Delta_r G^\ominus = -RT \ln K$, is then used to calculate the equilibrium constant.

(i) For the reaction of mercury with chlorine

$$\begin{aligned}\Delta_r G^\ominus &= \Delta_f G^\ominus(HgCl_2, s) - \{\Delta_f G^\ominus(Hg, l) + \Delta_f G^\ominus(Cl_2, g)\}\\ &= \Delta_f G^\ominus(HgCl_2, s) = -178.6\ \text{kJ mol}^{-1}\end{aligned}$$

Then

$$K = e^{-\Delta_r G^\ominus/RT} = \exp\left(-\frac{-178.6 \times 10^3\ \text{J mol}^{-1}}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K})}\right) = \boxed{2.02 \times 10^{31}}$$

(ii) For the reduction of copper ions by zinc

$$\begin{aligned}\Delta_r G^\ominus &= \Delta_f G^\ominus(Zn^{2+}, aq) + \Delta_f G^\ominus(Cu, s)\\ &\quad - \{\Delta_f G^\ominus(Zn, s) + \Delta_f G^\ominus(Cu^{2+}, aq)\}\\ &= \Delta_f G^\ominus(Zn^{2+}, aq) - \Delta_f G^\ominus(Cu^{2+}, aq)\\ &= (-147.06\ \text{kJ mol}^{-1}) - (+65.49\ \text{kJ mol}^{-1}) = -2.12... \times 10^5\ \text{J mol}^{-1}\end{aligned}$$

Then

$$K = e^{-\Delta_r G^\ominus/RT} = \exp\left(-\frac{-2.12... \times 10^5\ \text{J mol}^{-1}}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K})}\right) = \boxed{1.80 \times 10^{37}}$$

Neither reaction has $K < 1$ at 298 K.

E6A.7(b) The relationship between $\Delta_r G^\ominus$ and the equilibrium constant is given by [6A.15–*208*], $\Delta_r G^\ominus = -RT \ln K$. The ratio of the equilibrium constants for the two reactions is

$$\frac{K_1}{K_2} = \frac{e^{-\Delta_r G_1^\ominus/RT}}{e^{-\Delta_r G_2^\ominus/RT}} = \exp\left(-\frac{\Delta_r G_1^\ominus - \Delta_r G_2^\ominus}{RT}\right)$$

$$= \exp\left(-\frac{(-200 \times 10^3\ \mathrm{J\,mol^{-1}}) - (+30 \times 10^3\ \mathrm{J\,mol^{-1}})}{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (300\ \mathrm{K})}\right) = \boxed{1.1 \times 10^{40}}$$

E6A.8(b) The reaction Gibbs energy at an arbitrary stage is given by [6A.11–*207*], $\Delta_r G = \Delta_r G^\ominus + RT \ln Q$. In this case $\Delta_r G^\ominus = -4.73\ \mathrm{kJ\,mol^{-1}}$. The values of $\Delta_r G$ for each value of Q are:

(i) At $Q = 0.10$

$$\Delta_r G = (-4.73 \times 10^3\ \mathrm{J\,mol^{-1}}) + (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\ \mathrm{K}) \times \ln(0.10)$$

$$= -1.04... \times 10^4\ \mathrm{J\,mol^{-1}} = \boxed{-10\ \mathrm{kJ\,mol^{-1}}}$$

(ii) At $Q = 1.0$

$$\Delta_r G = (-4.73 \times 10^3\ \mathrm{J\,mol^{-1}}) + (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\ \mathrm{K}) \times \ln(1.0)$$

$$= -4.73... \times 10^3\ \mathrm{J\,mol^{-1}} = \boxed{-4.7\ \mathrm{kJ\,mol^{-1}}} \quad (= \Delta_r G^\ominus)$$

(iii) At $Q = 10$

$$\Delta_r G = (-4.73 \times 10^3\ \mathrm{J\,mol^{-1}}) + (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\ \mathrm{K}) \times \ln(10)$$

$$= +9.75... \times 10^2\ \mathrm{J\,mol^{-1}} = \boxed{+0.98\ \mathrm{kJ\,mol^{-1}}}$$

(iv) At $Q = 100$

$$\Delta_r G = (-4.73 \times 10^3\ \mathrm{J\,mol^{-1}}) + (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\ \mathrm{K}) \times \ln(100)$$

$$= +6.68... \times 10^3\ \mathrm{J\,mol^{-1}} = \boxed{+6.7\ \mathrm{kJ\,mol^{-1}}}$$

The equilibrium constant K is the value of Q for which $\Delta_r G = 0$. From the above values, K will therefore be somewhere between 1.0 and 10. To find exactly where by linear interpolation, note that according to $\Delta_r G = \Delta_r G^\ominus + RT \ln Q$, a plot of $\Delta_r G$ against $\ln Q$ should be a straight line. Consider the two points on either side of zero, that is, (ii) and (iii). The point $\Delta_r G = 0$ occurs a fraction $(4.73...)/(0.975... + 4.73...) = 0.829...$ of the way between points (ii) and (iii), so is at

$$\ln K = \ln 1 + (0.822...) \times (\ln 10 - \ln 1) = 1.90...$$

Hence $K = e^{1.90...} = \boxed{6.75}$

The value is calculated directly by setting $\Delta_r G = 0$ and $Q = K$ in $\Delta_r G = \Delta_r G^\ominus + RT \ln Q$ and rearranging for K

$$K = e^{-\Delta_r G^\ominus/RT} = \exp\left(-\frac{-4.73 \times 10^3\ \mathrm{J\,mol^{-1}}}{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\ \mathrm{K})}\right) = \boxed{6.75}$$

which is the same result as obtained from the linear interpolation.

E6A.9(b) For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ the following table is drawn up by supposing that there are n moles of N_2O_4 initially and that at equilibrium a fraction α has dissociated.

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial amount	n		0
Change to reach equilibrium	$-\alpha n$		$+2\alpha n$
Amount at equilibrium	$(1-\alpha)n$		$2\alpha n$
Mole fraction, x_J	$\dfrac{1-\alpha}{1+\alpha}$		$\dfrac{2\alpha}{1+\alpha}$
Partial pressure, p_J	$\dfrac{(1-\alpha)p}{1+\alpha}$		$\dfrac{2\alpha p}{1+\alpha}$

The total amount in moles is $n_{\text{tot}} = (1-\alpha)n + 2\alpha n = (1+\alpha)n$. This value is used to find the mole fractions. In the last line, $p_J = x_J p$ has been used. Treating all species as perfect gases so that $a_J = (p_J/p^\ominus)$, the equilibrium constant is

$$K = \frac{a_{NO_2}^2}{a_{N_2O_4}} = \frac{(p_{NO_2}/p^\ominus)^2}{(p_{N_2O_4}/p^\ominus)} = \frac{p_{NO_2}^2}{p_{N_2O_4}p^\ominus} = \frac{\left(\frac{2\alpha p}{1+\alpha}\right)^2}{\left(\frac{(1-\alpha)p}{1+\alpha}\right)p^\ominus} = \frac{4\alpha^2}{(1-\alpha)(1+\alpha)}\frac{p}{p^\ominus}$$

In this case $\alpha = 0.201$ and $p = 1.00$ bar; recall that $p^\ominus = 1$ bar.

$$K = \frac{4 \times 0.201^2}{(1-0.201)\times(1+0.201)} \times \frac{1.00\text{ bar}}{1\text{ bar}} = \boxed{0.168}$$

E6A.10(b) The relationship between K and K_c is [6A.18b–*209*], $K = K_c \times (c^\ominus RT/p^\ominus)^{\Delta\nu}$. For the reaction $3N_2(g) + H_2(g) \rightleftharpoons 2HN_3(g)$

$$\Delta\nu = \nu_{HN_3} - \nu_{N_2} - \nu_{H_2} = 2 - 3 - 1 = -2 \quad \text{hence} \quad \boxed{K = K_c \times (c^\ominus RT/p^\ominus)^{-2}}$$

$p^\ominus/c^\ominus R$ evaluates to 12.03 K so the relationship can alternatively be written as $K = K_c \times [(12.03)/(T/\text{K})]^2$.

E6A.11(b) The following table is drawn up:

	A	+	B	$\rightleftharpoons$	C	+	2D
Initial amount, $n_{J,0}$/mol	2.00		1.00		0		3.00
Change, Δn_J/mol	−0.79		−0.79		+0.79		+1.58
Equilibrium amount, n_J/mol	1.21		0.21		0.79		4.58
Mole fraction, x_J	0.178...		0.0309...		0.116...		0.674...
Partial pressure, p_J	$(0.178...)p$		$(0.0309...)p$		$(0.116...)p$		$(0.674...)p$

To go to the second line, the fact that 0.79 mol of C has been produced is used to deduce the changes in the other species given the stoichiometry of the reaction. For example, 1 mol of A is consumed for every 1 mol of C formed, so $\Delta\nu_A = -\Delta\nu_C = -0.79$ mol. The total amount in moles is $n_{\text{tot}} = (1.21\text{ mol}) + (0.21\text{ mol}) + (0.79\text{ mol}) + (4.58\text{ mol}) = 6.79\text{ mol}$. This value is used to find the mole fractions. In the last line, $p_J = x_J p$ has been used.

(i) The mole fractions are given in the above table.

(ii) Treating all species as perfect gases so that $a_J = p_J/p^\ominus$ the equilibrium constant is

$$K = \frac{a_C a_D^2}{a_A a_B} = \frac{(p_C/p^\ominus)(p_D/p^\ominus)^2}{(p_A/p^\ominus)(p_B/p^\ominus)} = \frac{p_C p_D^2}{p_A p_B p^\ominus} = \frac{x_C x_D^2}{x_A x_B}\frac{p}{p^\ominus}$$
$$= \frac{\left(\frac{79}{679}\right)\left(\frac{458}{679}\right)^2}{\left(\frac{121}{679}\right)\left(\frac{3}{97}\right)} \times \frac{1.00\text{ bar}}{1\text{ bar}} = 9.60... = \boxed{9.6}$$

(iii) The relationship between $\Delta_r G^\ominus$ and K [6A.15–*208*], $\Delta_r G^\ominus = -RT\ln K$, is used to calculate $\Delta_r G^\ominus$:

$$\Delta_r G^\ominus = -(8.3145\text{ J K}^{-1}\text{ mol}^{-1}) \times ([25+273.15]\text{ K}) \times \ln 9.60...$$
$$= \boxed{-5.6\text{ kJ mol}^{-1}}$$

E6A.12(b) The reaction for which $\Delta_r G^\ominus$ corresponds to the standard Gibbs energy of formation of $UH_3(s)$ is

$$U(s) + \tfrac{3}{2}H_2(g) \rightleftharpoons UH_3(s)$$

that is, the formation of one mole of UH_3 from the elements in their reference states. The equilibrium partial pressure of hydrogen is used to calculate the equilibrium constant K, which is then used with $\Delta_r G^\ominus = -RT\ln K$ [6A.15–*208*] to find $\Delta_r G^\ominus$.

Treating hydrogen as a perfect gas, so that $a_{H_2} = p_{H_2}/p^\ominus$, and recalling that $a_J = 1$ for a pure solid gives

$$K = \frac{a_{UH_3(s)}}{a_{U(s)} \times a_{H_2(g)}^{3/2}} = \frac{1}{1 \times (p_{H_2}/p^\ominus)^{3/2}} = \left(\frac{p^\ominus}{p_{H_2}}\right)^{3/2} = \left(\frac{10^5\text{ Pa}}{139\text{ Pa}}\right)^{3/2}$$
$$= 1.92... \times 10^4$$

Hence

$$\Delta_r G^\ominus = -RT\ln K$$
$$= -(8.3145\text{ J K}^{-1}\text{ mol}^{-1}) \times (500\text{ K}) \times \ln(1.92... \times 10^4) = \boxed{-41.0\text{ kJ mol}^{-1}}$$

E6A.13(b) The reaction corresponding to the standard Gibbs energy change of formation of PH_3 is

$$\tfrac{1}{4}P_4(s) + \tfrac{3}{2}H_2(g) \rightleftharpoons PH_3(g)$$

This is the reaction in question. The reaction Gibbs energy for an arbitrary reaction quotient is given by [6A.11–*207*], $\Delta_r G = \Delta_r G^\ominus + RT\ln Q$. White phosphorus ($P_4$, the reference state of phosphorus) is a solid and so has $a = 1$; the other species are treated as perfect gases so that $a_J = p_J/p^\ominus$. Therefore the reaction quotient Q is

$$Q = \frac{a_{PH_3}}{a_{P_4}^{1/4}a_{H_2}^{3/2}} = \frac{(p_{PH_3}/p^\ominus)}{(p_{H_2}/p^\ominus)^{3/2}} = \frac{p_{PH_3} \times p^{\ominus 1/2}}{p_{H_2}^{3/2}} = \frac{(0.6\text{ bar}) \times (1\text{ bar})^{1/2}}{(1.0\text{ bar})^{3/2}} = 0.60$$

Hence

$$\begin{aligned}\Delta_r G &= \Delta_r G^\ominus + RT\ln Q\\ &= (+13.4 \times 10^3\text{ J mol}^{-1}) + (8.3145\text{ J K}^{-1}\text{ mol}^{-1}) \times (298\text{ K}) \times \ln(0.60)\\ &= \boxed{+12\text{ kJ mol}^{-1}}\end{aligned}$$

Because $\Delta_r G > 0$ the spontaneous direction of the reaction under these conditions is from right to left.

E6A.14(b) The standard Gibbs energy change for the reaction is given in terms of the standard Gibbs energies of formation by [6A.13a–*207*]:

$$\Delta_r G^\ominus = \Delta_f G^\ominus(PbI_2, aq) - \Delta_f G^\ominus(PbI_2, s)$$

This is rearranged for $\Delta_f G^\ominus(PbI_2, aq)$ and $\Delta_r G^\ominus$ is replaced by $-RT\ln K$ [6A.15–*208*] to give

$$\begin{aligned}\Delta_f G^\ominus(PbI_2, aq) &= \Delta_r G^\ominus + \Delta_f G^\ominus(PbI_2, s) = -RT\ln K + \Delta_f G^\ominus(PbI_2, s)\\ &= -(8.3145\text{ J K}^{-1}\text{ mol}^{-1}) \times (298.15\text{ K}) \times \ln(1.4 \times 10^{-8})\\ &\quad + (-173.64 \times 10^3\text{ J mol}^{-1}) = \boxed{-1.3 \times 10^2\text{ kJ mol}^{-1}}\end{aligned}$$

Solutions to problems

P6A.2 The required reaction can be generated from the following sum:

$$\begin{array}{ll} CO(g) + H_2(g) \rightleftharpoons H_2CO(l) & \Delta_r G^\ominus(1) = +28.95\text{ kJ mol}^{-1}\\ H_2CO(l) \rightleftharpoons H_2CO(g) & \Delta_r G^\ominus(2)\\ \hline CO(g) + H_2(g) \rightleftharpoons H_2CO(g) & \Delta_r G^\ominus(3) = \Delta_r G^\ominus(1) + \Delta_r G^\ominus(2)\end{array}$$

If $H_2CO(g)$ is treated as a perfect gas, so that $a_{H_2CO(g)} = p_{H_2CO}/p^\ominus$, then noting that $a_J = 1$ for a pure liquid, the equilibrium constant for the second reaction is

$$K_2 = \frac{a_{H_2CO(g)}}{a_{H_2CO(l)}} = \frac{(p_{H_2CO}/p^\ominus)}{1} = \frac{p_{H_2CO}}{p^\ominus} = \frac{1500\text{ Torr}}{1\text{ bar}} \times \frac{1\text{ atm}}{760\text{ Torr}} \times \frac{1.01325\text{ bar}}{1\text{ atm}}$$

$$= 1.99...$$

Using [6A.15–*208*], $\Delta_r G^\ominus = -RT\ln K$, the equilibrium constant for the required reaction is

$$
\begin{aligned}
K_3 &= e^{-\Delta_r G^\ominus(3)/RT}\\
&= \exp\left(-\frac{\Delta_r G^\ominus(1)+\Delta_r G^\ominus(2)}{RT}\right) = \exp\left(-\frac{\Delta_r G^\ominus(1)-RT\ln K_2}{RT}\right)\\
&= K_2\exp\left(-\frac{\Delta_r G^\ominus(1)}{RT}\right) = (1.99...)\times\exp\left(-\frac{28.95\times10^3\ \mathrm{J\,mol^{-1}}}{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(298\ \mathrm{K})}\right)\\
&= \boxed{1.69\times10^{-5}}
\end{aligned}
$$

P6A.4 The reaction Gibbs energy for an arbitrary reaction quotient is given by [6A.11–*207*], $\Delta_r G = \Delta_r G^\ominus + RT\ln Q$. Q is given by [6A.10–*207*], $Q = \prod_J a_J^{\nu_J}$. In each case $a_J = 1$ for pure solids and $a_J = p_J/p^\ominus$ for gases, assuming perfect behaviour.

Reaction (i): $H_2O(g) \rightleftharpoons H_2O(s)$

$$
\begin{aligned}
Q &= \frac{a_{H_2O(s)}}{a_{H_2O(g)}} = \frac{1}{(p_{H_2O}/p^\ominus)} = \frac{p^\ominus}{p_{H_2O}}\\
\Delta_r G &= \Delta_r G^\ominus + RT\ln\left(\frac{p^\ominus}{p_{H_2O}}\right)\\
&= (-23.6\times10^3\ \mathrm{J\,mol^{-1}}) + (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(190\ \mathrm{K})\\
&\quad\times\ln\left(\frac{1\ \mathrm{bar}}{0.13\times10^{-6}\ \mathrm{bar}}\right) = \boxed{+1.5\ \mathrm{kJ\,mol^{-1}}}
\end{aligned}
$$

Reaction (ii): $H_2O(g) + HNO_3(g) \rightleftharpoons HNO_3.H_2O(s)$

$$
\begin{aligned}
Q &= \frac{a_{HNO_3.H_2O(s)}}{a_{H_2O(g)}a_{HNO_3(g)}} = \frac{1}{(p_{H_2O}/p^\ominus)(p_{HNO_3}/p^\ominus)} = \frac{p^{\ominus 2}}{p_{H_2O}p_{HNO_3}}\\
\Delta_r G &= \Delta_r G^\ominus + RT\ln\left(\frac{p^{\ominus 2}}{p_{H_2O}p_{HNO_3}}\right)\\
&= (-57.2\times10^3\ \mathrm{J\,mol^{-1}}) + (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(190\ \mathrm{K})\\
&\quad\times\ln\left(\frac{(1\ \mathrm{bar})^2}{(0.13\times10^{-6}\ \mathrm{bar})\times(0.41\times10^{-9}\ \mathrm{bar})}\right) = \boxed{+2.0\ \mathrm{kJ\,mol^{-1}}}
\end{aligned}
$$

Reaction (iii): $2H_2O(g) + HNO_3(g) \rightleftharpoons HNO_3.2H_2O(s)$

$$
\begin{aligned}
Q &= \frac{a_{HNO_3.2H_2O(s)}}{a^2_{H_2O(g)}a_{HNO_3(g)}} = \frac{1}{(p_{H_2O}/p^\ominus)^2(p_{HNO_3}/p^\ominus)} = \frac{p^{\ominus 3}}{p^2_{H_2O}p_{HNO_3}}\\
\Delta_r G &= \Delta_r G^\ominus + RT\ln\left(\frac{p^{\ominus 3}}{p^2_{H_2O}p_{HNO_3}}\right)\\
&= (-85.6\times10^3\ \mathrm{J\,mol^{-1}}) + (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(190\ \mathrm{K})\\
&\quad\times\ln\left(\frac{(1\ \mathrm{bar})^3}{(0.13\times10^{-6}\ \mathrm{bar})^2\times(0.41\times10^{-9}\ \mathrm{bar})}\right) = \boxed{-1.4\ \mathrm{kJ\,mol^{-1}}}
\end{aligned}
$$

Reaction (iv): $3H_2O(g) + HNO_3(g) \rightleftharpoons HNO_3.3H_2O(s)$

$$Q = \frac{a_{HNO_3.3H_2O(s)}}{a^3_{H_2O(g)}a_{HNO_3(g)}} = \frac{1}{(p_{H_2O}/p^\ominus)^3(p_{HNO_3}/p^\ominus)} = \frac{p^{\ominus 4}}{p^3_{H_2O}p_{HNO_3}}$$

$$\begin{aligned}\Delta_r G &= \Delta_r G^\ominus + RT\ln\left(\frac{p^{\ominus 4}}{p^3_{H_2O}p_{HNO_3}}\right)\\ &= (-112.8\times 10^3\ \mathrm{J\,mol^{-1}}) + (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(190\ \mathrm{K})\\ &\qquad\times\ln\left(\frac{(1\ \mathrm{bar})^4}{(0.13\times 10^{-6}\ \mathrm{bar})^3\times(0.41\times 10^{-9}\ \mathrm{bar})}\right) = \boxed{-3.5\ \mathrm{kJ\,mol^{-1}}}\end{aligned}$$

The results show that $\Delta_r G < 0$ for reactions (iii) and (iv), so $HNO_3.2H_2O$ and $HNO_3.3H_2O$ can form spontaneously under the prevailing conditions. To identify which of these solids is most stable, consider the conversion of $HNO_3.2H_2O$ into $HNO_3.3H_2O$. The required reaction is constructed by adding reaction (iv) to the reverse of reaction (iii):

	$\Delta_r G/(\mathrm{kJ\,mol^{-1}})$
$HNO_3.2H_2O(s) \rightleftharpoons 2H_2O(g) + HNO_3(g)$	$+1.35...$
$3H_2O(g) + HNO_3(g) \rightleftharpoons HNO_3.3H_2O(s)$	$-3.50...$
$HNO_3.2H_2O(s) + H_2O(g) \rightleftharpoons HNO_3.3H_2O(s)$	$\boxed{-2.2}$

Since $\Delta_r G < 0$ for this conversion, it follows that $\boxed{HNO_3.3H_2O}$ is the thermodynamically most stable solid (at least out of the four considered) under the prevailing conditions.

P6A.6 The standard reaction enthalpy and entropy are calculated using standard enthalpies of formation and standard molar entropies respectively ([2C.5a–*55*] and [3C.3a–*94*])

$$\begin{aligned}\Delta_r H^\ominus &= 2\Delta_f H^\ominus(NO_2, g) - \Delta_f H^\ominus(N_2O_4, g)\\ &= 2\times(+33.18\ \mathrm{kJ\,mol^{-1}}) - (+9.16\ \mathrm{kJ\,mol^{-1}}) = +57.20\ \mathrm{kJ\,mol^{-1}}\\ \Delta_r S^\ominus &= 2S^\ominus_m(NO_2, g) - S^\ominus_m(N_2O_4, g)\\ &= 2\times(+240.06\ \mathrm{J\,K^{-1}\,mol^{-1}}) - (+304.29\ \mathrm{J\,K^{-1}\,mol^{-1}}) = +175.83\ \mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

The relationship between the equilibrium constant and $\Delta_r G^\ominus$ is [6A.15–*208*], $\Delta_r G^\ominus = -RT\ln K$, and $\Delta_r G^\ominus$ is related to $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ according to [3D.9–*100*], $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$. Therefore

$$\begin{aligned}K &= e^{-\Delta_r G^\ominus/RT} = e^{-(\Delta_r H^\ominus - T\Delta_r S^\ominus)/RT} = e^{-\Delta_r H^\ominus/RT}e^{\Delta_r S^\ominus/R}\\ &= \underbrace{\exp\left(-\frac{+57.20\times 10^3\ \mathrm{J\,mol^{-1}}}{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(298\ \mathrm{K})}\right)}_{\text{enthalpy contribution to } K}\times\underbrace{\exp\left(\frac{+175.83\ \mathrm{J\,K^{-1}\,mol^{-1}}}{8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}}\right)}_{\text{entropy contribution to } K}\\ &= e^{-23.0...}\times e^{21.1...} = (9.41...\times 10^{-11})\times(1.52...\times 10^{9}) = 0.144\end{aligned}$$

The calculation shows that $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ make contributions to K in opposite directions: $\Delta_r H^\ominus$ acts to make K very small while $\Delta_r S^\ominus$ acts to make K very large and the overall result is that K is close to 1. The negative value of $\Delta_r H^\ominus$ can be interpreted in terms of the forward reaction involving the breaking of the N–N bond in N_2O_4, while the positive value of $\Delta_r S^\ominus$ can be attributed to the reaction forming two moles of gas from one mole. At 298 K the calculation shows that the $\Delta_r H^\ominus$ contribution is slightly larger than the $\Delta_r S^\ominus$ contribution which is reflected in K being less than 1.

6B The response of equilibria to the conditions

Answer to discussion question

D6B.2 This is discussed in Section 6B.1 on page 212 and in Section 6B.2 on page 213.

Solutions to exercises

E6B.1(b) For the reaction $Br_2(g) \rightleftharpoons 2Br(g)$ the following table is drawn up by supposing that there are n moles of Br_2 initially and that at equilibrium a fraction α has dissociated.

	Br_2	$\rightleftharpoons$	$2Br$
Initial amount	n		0
Change to reach equilibrium	$-\alpha n$		$+2\alpha n$
Amount at equilibrium	$(1-\alpha)n$		$2\alpha n$
Mole fraction, x_J	$\dfrac{1-\alpha}{1+\alpha}$		$\dfrac{2\alpha}{1+\alpha}$
Partial pressure, p_J	$\dfrac{(1-\alpha)p}{1+\alpha}$		$\dfrac{2\alpha p}{1+\alpha}$

The total amount in moles is $(1-\alpha)n+2\alpha n = (1+\alpha)n$. This value is used to find the mole fractions. In the last line, $p_J = x_J p$ [1A.6–9] has been used. Treating all species as perfect gases, so that $a_J = (p_J/p^\ominus)$, the equilibrium constant is

$$K = \frac{a_{Br}^2}{a_{Br_2}} = \frac{(p_{Br}/p^\ominus)^2}{(p_{Br_2}/p^\ominus)} = \frac{p_{Br}^2}{p_{Br_2}p^\ominus} = \frac{\left(\frac{2\alpha p}{1+\alpha}\right)^2}{\left(\frac{(1-\alpha)p}{1+\alpha}\right)p^\ominus} = \frac{4\alpha^2}{(1-\alpha)(1+\alpha)}\frac{p}{p^\ominus}$$

In this case $\alpha = 0.24$ and $p = 1.00$ bar; recall that $p^\ominus = 1$ bar.

$$K = \frac{4\times 0.24^2}{(1-0.24)\times(1+0.24)} \times \frac{1.00\text{ bar}}{1\text{ bar}} = 0.244... = \boxed{0.24}$$

The temperature dependence of K is given by [6B.4–*215*],

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

assuming that $\Delta_r H^\ominus$ is constant over the temperature range of interest.

$$\ln K_2 = \ln(0.244...) - \frac{112 \times 10^3\ \mathrm{J\,mol^{-1}}}{8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}}\left(\frac{1}{2000\ \mathrm{K}} - \frac{1}{1600\ K}\right) = 0.275...$$

That is, $K_2 = \boxed{1.3}$, a larger value than at 1600 K, as expected for this endothermic reaction.

E6B.2(b) The data in the *Resource section* is used to calculate $\Delta_r G^\ominus$ and $\Delta_r H^\ominus$ at 298 K

$$\begin{aligned}\Delta_r G^\ominus &= \Delta_f G^\ominus(\mathrm{CHCl_3, l}) + 3\Delta_f G^\ominus(\mathrm{HCl, g}) - \Delta_f G^\ominus(\mathrm{CH_4, g})\\ &= (-73.7\ \mathrm{kJ\,mol^{-1}}) + 3 \times (-95.30\ \mathrm{kJ\,mol^{-1}}) - (-50.72\ \mathrm{kJ\,mol^{-1}})\\ &= -3.08... \times 10^2\ \mathrm{kJ\,mol^{-1}}\\ \Delta_r H^\ominus &= \Delta_f H^\ominus(\mathrm{CHCl_3, l}) + 3\Delta_f H^\ominus(\mathrm{HCl, g}) - \Delta_f H^\ominus(\mathrm{CH_4, g})\\ &= (-134.1\ \mathrm{kJ\,mol^{-1}}) + 3(-92.31\ \mathrm{kJ\,mol^{-1}}) - (-74.81\ \mathrm{kJ\,mol^{-1}})\\ &= -3.36... \times 10^2\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

The equilibrium constant at 25 °C (= 298.15 K) is calculated from $\Delta_r G^\ominus$ using [6A.15–*208*], $\Delta_r G^\ominus = -RT \ln K$

$$\ln K = -\frac{\Delta_r G^\ominus}{RT} = -\frac{-3.08... \times 10^5\ \mathrm{J\,mol^{-1}}}{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (298.15\ \mathrm{K})} = 1.24... \times 10^2$$

$$\text{hence} \quad K = 1.29... \times 10^{54} = \boxed{1.3 \times 10^{54}}$$

Assuming that $\Delta_r H^\ominus$ is constant over the temperature range of interest, the temperature dependence of K is given by [6B.4–*215*],

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

This is used to calculate the equilibrium constant at 50 °C (= 323.15 K)

$$\begin{aligned}\ln K_2 &= \ln(1.29... \times 10^{54}) - \frac{-3.36... \times 10^5\ \mathrm{J\,mol^{-1}}}{8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}}\left(\frac{1}{323.15\ \mathrm{K}} - \frac{1}{298.15\ \mathrm{K}}\right)\\ &= 1.14... \times 10^2\end{aligned}$$

That is, $K_2 = \boxed{3.6 \times 10^{49}}$, a smaller value than at 25 °C, as expected for this exothermic reaction.

E6B.3(b) Assuming that $\Delta_r H^\ominus$ is constant over the temperature range of interest, the temperature dependence of K is given by [6B.4–*215*],

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Using $\Delta_r G^\ominus = -RT\ln K$ to substitute for K_1 and setting $\ln K_2 = \ln 1 = 0$ (the crossover point) gives

$$\frac{\Delta_r G^\ominus(T_1)}{RT_1} = -\frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

Rearranging for T_2 gives

$$T_2 = \frac{T_1\Delta_r H^\ominus}{\Delta_r H^\ominus - \Delta_r G^\ominus(T_1)} = \frac{(1120\text{ K})\times(+125\text{ kJ mol}^{-1})}{(+125\text{ kJ mol}^{-1})-(+22\text{ kJ mol}^{-1})} = \boxed{1.4\times 10^3\text{ K}}$$

E6B.4(b) The van 't Hoff equation [6B.2–*214*], $\mathrm{d}\ln K/\mathrm{d}T = \Delta_r H^\ominus/RT^2$, is rearranged to obtain an expression for $\Delta_r H^\ominus$

$$\begin{aligned}\Delta_r H^\ominus &= RT^2\frac{\mathrm{d}\ln K}{\mathrm{d}T}\\ &= RT^2\frac{\mathrm{d}}{\mathrm{d}T}\left(A+\frac{B}{T}+\frac{C}{T^3}\right) = RT^2\left(-\frac{B}{T^2}-\frac{3C}{T^4}\right) = -R\left(B+\frac{3C}{T^2}\right)\\ &= -(8.3145\text{ J K}^{-1}\text{ mol}^{-1})\times\left((-1176\text{ K})+\frac{3\times(2.1\times10^7\text{ K}^3)}{(450\text{ K})^2}\right)\\ &= 7.19...\times10^3\text{ J mol}^{-1} = \boxed{7.2\text{ kJ mol}^{-1}}\end{aligned}$$

The standard reaction entropy is obtained by first finding an expression for $\Delta_r G^\ominus$ using [6A.15–*208*]

$$\Delta_r G^\ominus = -RT\ln K = -RT\left(A+\frac{B}{T}+\frac{C}{T^3}\right) = -R\left(AT+B+\frac{C}{T^2}\right)$$

The equation $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$ [3D.9–*100*] is then rearranged to find $\Delta_r S^\ominus$

$$\begin{aligned}\Delta_r S^\ominus &= \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T} = \frac{1}{T}\left(\underbrace{-R\left(B+\frac{3C}{T^2}\right)}_{\Delta_r H^\ominus}+\underbrace{R\left(AT+B+\frac{C}{T^2}\right)}_{-\Delta_r G^\ominus}\right)\\ &= R\left(A-\frac{2C}{T^3}\right) = (8.3145\text{ J K}^{-1}\text{ mol}^{-1})\times\left(-2.04-\frac{2\times(2.1\times10^7\text{ K}^2)}{(450\text{ K})^3}\right)\\ &= \boxed{-21\text{ J K}^{-1}\text{ mol}^{-1}}\end{aligned}$$

An alternative approach to finding $\Delta_r S^\ominus$ is to use the variation of G with T which is given by [3E.8–*107*], $(\partial G/\partial T)_p = -S$. This implies that $\mathrm{d}\Delta_r G^\ominus/\mathrm{d}T = -\Delta_r S^\ominus$ where the derivative is complete (not partial) because $\Delta_r G^\ominus$ is independent of pressure. Using the expression for $\Delta_r G^\ominus$ from above it follows that

$$\Delta_r S^\ominus = -\frac{\mathrm{d}\Delta_r G^\ominus}{\mathrm{d}T} = -\frac{\mathrm{d}}{\mathrm{d}T}\left(\underbrace{-R\left(AT+B+\frac{C}{T^2}\right)}_{\Delta_r G^\ominus}\right) = R\left(A-\frac{2C}{T^3}\right)$$

which is the same expression obtained above.

E6B.5(b) Treating all species as perfect gases so that $a_J = p_J/p^{\ominus}$, the equilibrium constant for the reaction $CH_3OH(g) + NOCl(g) \rightleftharpoons HCl(g) + CH_3NO_2(g)$ is

$$\begin{aligned}K &= \frac{a_{CH_3NO_2}a_{HCl}}{a_{CH_3OH}a_{NOCl}} = \frac{(p_{CH_3NO_2}/p^{\ominus})(p_{HCl}/p^{\ominus})}{(p_{CH_3OH}/p^{\ominus})(p_{NOCl}/p^{\ominus})} = \frac{p_{CH_3NO_2}p_{HCl}}{p_{CH_3OH}p_{NOCl}}\\ &= \frac{(x_{CH_3NO_2}p)(x_{HCl}p)}{(x_{CH_3OH}p)(x_{NOCl}p)} = \frac{x_{CH_3NO_2}x_{HCl}}{x_{CH_3OH}x_{NOCl}} = K_x\end{aligned}$$

where K_x is the part of the equilibrium constant expression that contains the equilibrium mole fractions of reactants and products. Because K is independent of pressure, and $K = K_x$ in this case, it follows that K_x does not change when the pressure is changed. Hence the percentage change in K_x is $\boxed{\text{zero}}$.

E6B.6(b) The following table is drawn up for the $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ reaction, supposing that in order to reach equilibrium the reaction proceeds to the right by an amount z moles.

	N_2	+	O_2	$\rightleftharpoons$	$2NO$
Initial amount	$n_{N_2,0}$		$n_{O_2,0}$		0
Change to reach equilibrium	$-z$		$-z$		$+2z$
Amount at equilibrium	$n_{N_2,0} - z$		$n_{O_2,0} - z$		$2z$
Mole fraction, x_J	$\frac{n_{N_2,0} - z}{n_{tot}}$		$\frac{n_{O_2,0} - z}{n_{tot}}$		$\frac{2z}{n_{tot}}$
Partial pressure, p_J	$\frac{(n_{N_2,0} - z)p}{n_{tot}}$		$\frac{(n_{O_2,0} - z)p}{n_{tot}}$		$\frac{2zp}{n_{tot}}$

The total amount in moles is $n_{tot} = n_{N_2,0} + n_{O_2,0}$ at all times. Treating all species as perfect gases so that $a_J = p_J/p^{\ominus}$ the equilibrium constant is

$$\begin{aligned}K &= \frac{a_{NO}^2}{a_{N_2}a_{O_2}} = \frac{(p_{NO}/p^{\ominus})^2}{(p_{N_2}/p^{\ominus})(p_{O_2}/p^{\ominus})} = \frac{p_{NO}^2}{p_{N_2}p_{O_2}}\\ &= \frac{(2zp/n)^2}{[(n_{N_2,0} - z)p/n_{tot}]\,[(n_{O_2,0} - z)p/n_{tot}]} = \frac{4z^2}{(n_{N_2,0} - z)(n_{O_2,0} - z)}\end{aligned}$$

Rearranging gives

$$K(n_{N_2,0} - z)(n_{O_2,0} - z) = 4z^2$$

$$\text{Hence}\quad (4 - K)z^2 + K(n_{N_2,0} + n_{O_2,0})z - n_{N_2,0}n_{O_2,0}K = 0$$

The initial amounts are calculated as

$$n_{N_2,0} = \frac{5.0\text{ g}}{28.02\text{ g mol}^{-1}} = 0.178...\text{ mol} \qquad n_{O_2,0} = \frac{2.0\text{ g}}{32.00\text{ g mol}^{-1}} = 0.0625...\text{ mol}$$

Substituting the values for n_J and K into the above equation, dividing through by mol^2 and writing $x = z/\text{mol}$ yields the quadratic

$$(3.99...)x^2 + (4.07... \times 10^{-4})x - 1.88... \times 10^{-5} = 0$$

which has solutions $x = 2.12... \times 10^{-3}$ and $x = -2.22... \times 10^{-3}$ implying $z = (2.12... \times 10^{-3}\ \text{mol})$ or $z = (-2.22... \times 10^{-3}\ \text{mol})$. The negative value of z is rejected because that would imply a negative amount of NO. The mole fraction of NO present at equilibrium is therefore

$$x_{\text{NO}} = \frac{2z}{n_{\text{N}_2,0} + n_{\text{O}_2,0}} = \frac{2 \times (2.12... \times 10^{-3}\ \text{mol})}{(0.178...\ \text{mol}) + (0.0625...\ \text{mol})} = \boxed{0.018}$$

E6B.7(b) The temperature dependence of K is given by [6B.4–*215*]

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{hence} \quad \Delta_r H^\ominus = -\frac{R\ln(K_2/K_1)}{(1/T_2) - (1/T_1)}$$

(i) If the equilibrium constant is doubled then $K_2/K_1 = 2$

$$\Delta_r H^\ominus = -\frac{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times \ln 2}{[1/(325\ \text{K})] - (1/[310\ \text{K}])} = \boxed{+38.7\ \text{kJ mol}^{-1}}$$

(ii) If the equilibrium constant is halved then $K_2/K_1 = 1/2$

$$\Delta_r H^\ominus = -\frac{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times \ln(1/2)}{[1/(325\ \text{K})] - (1/[310\ \text{K}])} = \boxed{-38.7\ \text{kJ mol}^{-1}}$$

E6B.8(b) The relationship between $\Delta_r G^\ominus$ and K is given by [6A.15–*208*], $\Delta_r G^\ominus = -RT\ln K$. Hence if $K = 1$, $\Delta_r G^\ominus = -RT\ln 1 = 0$. Furthermore $\Delta_r G^\ominus$ is related to $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ by [3D.9–*100*], $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$, so if $K = 1$

$$\Delta_r H^\ominus - T\Delta_r S^\ominus = 0 \quad \text{hence} \quad T = \frac{\Delta_r H^\ominus}{\Delta_r S^\ominus}$$

Values of $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ at 298 K are calculated using data from the *Resource section*.

$$\begin{aligned}
\Delta_r H^\ominus &= \Delta_f H^\ominus(\text{CuSO}_4,\text{s}) + 5\Delta_f H^\ominus(\text{H}_2\text{O},\text{g}) - \Delta_f H^\ominus(\text{CuSO}_4.5\text{H}_2\text{O},\text{s}) \\
&= (-771.36\ \text{kJ mol}^{-1}) + 5 \times (-241.82\ \text{kJ mol}^{-1}) - (-2279.7\ \text{kJ mol}^{-1}) \\
&= +299.24\ \text{kJ mol}^{-1} \\
\Delta_r S^\ominus &= S_m^\ominus(\text{CuSO}_4,\text{s}) + 5S_m^\ominus(\text{H}_2\text{O},\text{g}) - S_m^\ominus(\text{CuSO}_4.5\text{H}_2\text{O},\text{s}) \\
&= (109\ \text{J K}^{-1}\ \text{mol}^{-1}) + 5 \times (188.83\ \text{J K}^{-1}\ \text{mol}^{-1}) - (300.4\ \text{J K}^{-1}\ \text{mol}^{-1}) \\
&= 752.75\ \text{J K}^{-1}\ \text{mol}^{-1}
\end{aligned}$$

Substituting these values into the equation found above, assuming that $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ do not vary significantly with temperature over the range of interest, gives:

$$T = \frac{\Delta_r H^\ominus}{\Delta_r S^\ominus} = \frac{299.24 \times 10^3\ \text{J mol}^{-1}}{752.75\ \text{J K}^{-1}\ \text{mol}^{-1}} = \boxed{398\ \text{K}}$$

E6B.9(b) (i) Treating the vapour as a perfect gas so that $a_J = p_J/p^\ominus$, and noting that pure solids have $a_J = 1$, the equilibrium constant for the dissociation $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$ is

$$K = \frac{a_{NH_3,g}a_{HCl,g}}{a_{NH_4Cl,s}} = \frac{(p_{NH_3}/p^\ominus)(p_{HCl}/p^\ominus)}{1} = \frac{p_{NH_3}p_{HCl}}{p^{\ominus 2}}$$

Furthermore, because NH_3 and HCl are formed in a 1 : 1 ratio, they each have a mole fraction of 1/2 and the partial pressure of each is half the total pressure: $p_{A_2} = p_B = \frac{1}{2}p$. The equilibrium constant at 427 °C is therefore

$$K = \frac{(\frac{1}{2}p)(\frac{1}{2}p)}{p^{\ominus 2}} = \frac{p^2}{4p^{\ominus 2}} = \frac{(608\ \text{kPa})^2}{4 \times (100\ \text{kPa})^2} = 9.24... = \boxed{9.24}$$

(ii) The standard reaction Gibbs energy at 427 °C is obtained using $\Delta_r G^\ominus = -RT\ln K$ [6A.15–*208*]

$$\begin{aligned}\Delta_r G^\ominus &= -(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times ([427 + 273.15]\ \text{K}) \times \ln(9.24...)\\ &= -1.29... \times 10^4\ \text{J mol}^{-1} = \boxed{-12.9\ \text{kJ mol}^{-1}}\end{aligned}$$

(iii) The variation of K with temperature, assuming that $\Delta_r H^\ominus$ does not vary with T over the temperature range of interest, is given by [6B.4–*215*]

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{hence} \quad \Delta_r H^\ominus = -\frac{R\ln(K_2/K_1)}{(1/T_2) - (1/T_1)}$$

Noting that the above equilibrium constant expression $K = p^2/4p^{\ominus 2}$ implies that $\ln(K_2/K_1) = \ln(p_2^2/p_1^2)$, $\Delta_r H^\ominus$ is calculated as

$$\begin{aligned}\Delta_r H^\ominus &= -\frac{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times \ln\left((1115\ \text{kPa})^2/(608\ \text{kPa})^2\right)}{[1/(459 + 273.15)\ \text{K}] - [1/(427 + 273.15)\ \text{K}]}\\ &= +1.61... \times 10^5\ \text{J mol}^{-1} = \boxed{+162\ \text{kJ mol}^{-1}}\end{aligned}$$

(iv) The standard reaction entropy is obtained from $\Delta_r G^\ominus$ and $\Delta_r H^\ominus$ by rearranging $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$ [3D.9–*100*]:

$$\begin{aligned}\Delta_r S^\ominus &= \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T} = \frac{(1.61... \times 10^5\ \text{J mol}^{-1}) - (-1.29... \times 10^4\ \text{J mol}^{-1})}{700.15\ \text{K}}\\ &= \boxed{+249\ \text{J K}^{-1}\ \text{mol}^{-1}}\end{aligned}$$

Solutions to problems

P6B.2 (a) The reaction $CH_4(g) \rightleftharpoons C(s, \text{graphite}) + 2H_2$ is the reverse of the formation reaction of methane, so

$$\begin{aligned}\Delta_r H^\ominus &= -\Delta_f H^\ominus(CH_4, g) = -(-74.85\ \text{kJ mol}^{-1}) = +74.85\ \text{kJ mol}^{-1}\\ \Delta_r S^\ominus &= -\Delta_f S^\ominus(CH_4, g) = -(-80.67\ \text{J K}^{-1}\ \text{mol}^{-1}) = +80.67\ \text{J K}^{-1}\ \text{mol}^{-1}\end{aligned}$$

The equilibrium constant K is calculated using $\Delta_r G^\ominus = -RT\ln K$ [6A.15–*208*], with $\Delta_r G^\ominus$ being obtained from $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$ [3D.9–*100*]

$$\begin{aligned}K &= e^{-\Delta_r G^\ominus/RT} = \exp\left(-\frac{\Delta_r H^\ominus - T\Delta_r S^\ominus}{RT}\right)\\ &= \exp\left(-\frac{(74.85\times 10^3\,\mathrm{J\,mol^{-1}}) - (298\,\mathrm{K})\times(80.67\,\mathrm{J\,K^{-1}\,mol^{-1}})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})}\right)\\ &= \boxed{1.24\times 10^{-9}}\end{aligned}$$

(b) The temperature dependence of K is given by [6B.4–*215*]

$$\ln K_2 = \ln K_1 - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

assuming that $\Delta_r H^\ominus$ is constant over the temperature range of interest. The value of K at 50 °C is therefore

$$\begin{aligned}\ln K_2 &= \ln(1.24...\times 10^{-9})\\ &\quad - \frac{74.85\times 10^3\,\mathrm{J\,mol^{-1}}}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\left(\frac{1}{(50+273.15)\,\mathrm{K}} - \frac{1}{298\,\mathrm{K}}\right)\\ &= -18.1... \quad \text{hence} \quad K_2 = \boxed{1.30\times 10^{-8}}\end{aligned}$$

(c) The following table is drawn up, assuming that the initial amount of methane is n and that at equilibrium a fraction α has dissociated. Graphite is a solid so is not included in the calculations.

	$CH_4(g)$	$\rightleftharpoons$ $2H_2(g)$	+ $C(s)$
Initial amount	n	0	—
Change to reach equilibrium	$-\alpha n$	$+2\alpha n$	—
Amount at equilibrium	$(1-\alpha)n$	$2\alpha n$	—
Mole fraction, x_J	$\frac{1-\alpha}{1+\alpha}$	$\frac{2\alpha}{1+\alpha}$	—
Partial pressure, p_J	$\frac{(1-\alpha)p}{1+\alpha}$	$\frac{2\alpha p}{1+\alpha}$	—

The total amount in moles is $n_{tot} = (1-\alpha)n + 2\alpha n = (1+\alpha)n$. This value is used to find the mole fractions. Treating CH_4 and H_2 as perfect gases, so that $a_J = p_J/p^\ominus$, and recalling that pure solids have $a_J = 1$, the equilibrium constant is

$$\begin{aligned}K &= \frac{a_{H_2}^2 a_C}{a_{CH_4}} = \frac{(p_{H_2}/p^\ominus)^2\times 1}{(p_{CH_4}/p^\ominus)} = \frac{p_{H_2}^2}{p_{CH_4}p^\ominus} = \frac{\left(\frac{2\alpha p}{1+\alpha}\right)^2}{\left(\frac{(1-\alpha)p}{1+\alpha}\right)p^\ominus}\\ &= \frac{4\alpha^2}{(1-\alpha)(1+\alpha)}\frac{p}{p^\ominus} = \frac{4\alpha^2}{1-\alpha^2}\frac{p}{p^\ominus}\end{aligned}$$

Rearranging for α gives

$$\alpha = \left(\frac{K}{4(p/p^{\ominus}) + K}\right)^{\frac{1}{2}} = \left(\frac{1.24... \times 10^{-9}}{4 \times (0.010\,\text{bar})/(1\,\text{bar}) + 1.24... \times 10^{-9}}\right)^{\frac{1}{2}}$$

$$= \boxed{1.76 \times 10^{-4}}$$

(d) If the pressure is increased, K will not change, because the equilibrium constant is independent of pressure. However, the above expression for the degree of dissociation, $\alpha = [K/(4p/p^{\ominus} + K)]^{1/2}$, indicates that α will decrease as p increases due to the denominator becoming larger. This is in accord with Le Chatelier's principle, which predicts that an increase in pressure will cause the reaction to adjust so as to minimise the pressure increase. This it can do by reducing the number of particles in the gas phase, which implies a shift $\mathrm{CH_4(g)} \leftarrow \mathrm{2H_2(g) + C(s)}$, corresponding to a lower degree of dissociation.

If the temperature is increased, then the van 't Hoff equation [6B.2–*214*], $\mathrm{d}\ln K/\mathrm{d}T = \Delta_r H^{\ominus}/RT^2$ predicts that K will increase because $\Delta_r H^{\ominus}$ is positive for this reaction, so that $\mathrm{d}\ln K/\mathrm{d}T$ and therefore also $\mathrm{d}K/\mathrm{d}T$ is positive. The expression for the degree of dissociation, $\alpha = [K/(4p/p^{\ominus} + K)]^{1/2}$, shows that this increase in K will result in an increase in α. This is most clearly seen by noting that because $\alpha \ll (p/p^{\ominus})$ the expression for α may be approximated as $[K/(4p/p^{\ominus})]^{1/2}$ which will increase as K increases. The result that α increases with T is again in accord with Le Chatelier's principle, which predicts that for this endothermic reaction the equilibrium will shift towards the products if the temperature rises.

P6B.4 The van 't Hoff equation [6B.2–*214*] is

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta_r H^{\ominus}}{RT^2} \quad \text{which can also be written} \quad -\frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)} = \frac{\Delta_r H^{\ominus}}{R}$$

The second form implies that a graph of $-\ln K$ against $1/T$ should be a straight line of slope $\Delta_r H^{\ominus}/R$; such a plot is shown in Fig. 6.1.

T/K	K	$1/(T/K)$	$-\ln K$
300	4.0×10^{31}	0.003 33	−72.8
500	4.0×10^{18}	0.002 00	−42.8
1 000	5.1×10^{8}	0.001 00	−20.0

The data fall on a good straight line, the equation of which is

$$\ln K = (-2.259 \times 10^4) \times 1/(T/\text{K}) + 2.463$$

$\Delta_r H^{\ominus}/R$ is determined from the slope

$$\Delta_r H^{\ominus} = R \times (\textit{slope} \times \text{K}) = (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (-2.259 \times 10^4\,\text{K})$$

$$= \boxed{-1.9 \times 10^2\,\text{kJ mol}^{-1}}$$

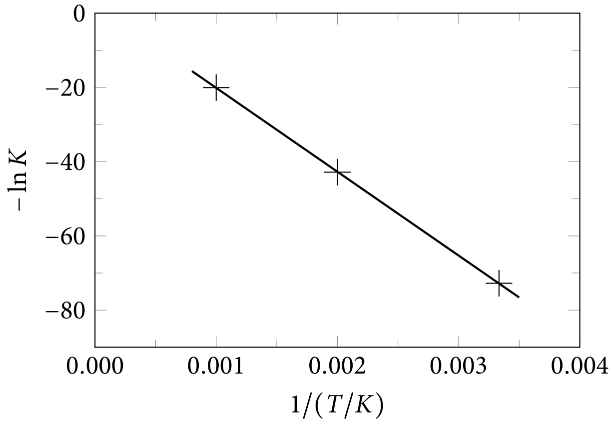


Figure 6.1

P6B.6 Treating NH_3 as an ideal gas (so that $a_J = p_J/p^\ominus$) and noting that pure solids have $a_J = 1$, the equilibrium constant for the decomposition $CaCl_2.NH_3(s) \rightleftharpoons CaCl_2(s) + NH_3(g)$ is

$$K = \frac{a_{CaCl_2,s}a_{NH_3,g}}{a_{CaCl_2.NH_3,s}} = \frac{1 \times (p_{NH_3}/p^\ominus)}{1} = \frac{p_{NH_3}}{p^\ominus}$$

At 400 K, the value of K is therefore $(1.71\text{ kPa})/(100\text{ kPa}) = 0.0171$.

The starting point for finding the temperature dependence of $\Delta_r G^\ominus$ is the temperature dependence of K, which is given by [6B.4–*215*]

$$\ln K_2 = \ln K_1 - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Using $\Delta_r G^\ominus = -RT\ln K$ [6A.15–*208*] to replace $\ln K_2$ by $-\Delta_r G^\ominus/RT_2$, and setting $T_2 = T$ where T is any temperature between 350 K and 470 K, gives

$$-\frac{\Delta_r G^\ominus}{RT} = \ln K_1 - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)$$

This expression is rearranged for $\Delta_r G^\ominus$

$$\Delta_r G^\ominus = -RT\ln K_1 + T\Delta_r H^\ominus\left(\frac{1}{T} - \frac{1}{T_1}\right) = \Delta_r H^\ominus - \left(R\ln K_1 + \frac{\Delta_r H^\ominus}{T_1}\right)T$$

Setting $T_1 = 400$ K and $K_1 = 0.0171$ as calculated above gives

$$\begin{aligned}\Delta_r G^\ominus &= +78\times10^3\text{ J mol}^{-1} - \Bigg((8.3145\text{ J K}^{-1}\text{ mol}^{-1})\times\ln(0.0171)\\ &\quad + \frac{78\times10^3\text{ J mol}^{-1}}{400\text{ K}}\Bigg)T\\ &= (+78\times10^3\text{ J mol}^{-1}) - (1.6\times10^2\text{ J K}^{-1}\text{ mol}^{-1})T\end{aligned}$$

or, dividing through by kJ mol^{-1}: $\boxed{\Delta_r G^\ominus/\text{kJ mol}^{-1} = 78 - 0.16(T/\text{K})}$

P6B.8 The following table is drawn up for the $I_2(g) \rightleftharpoons 2I(g)$ equilibrium:

	I_2	$\rightleftharpoons$	$2I$
Initial amount	n_{I_2}		0
Change to reach equilibrium	$-\alpha n_{I_2}$		$+2\alpha n_{I_2}$
Amount at equilibrium	$(1-\alpha)n_{I_2}$		$2\alpha n_{I_2}$
Mole fraction, x_J	$\dfrac{1-\alpha}{1+\alpha}$		$\dfrac{2\alpha}{1+\alpha}$
Partial pressure, p_J	$\dfrac{(1-\alpha)p}{1+\alpha}$		$\dfrac{2\alpha p}{1+\alpha}$

The total amount in moles is $n_{\text{tot}} = (1-\alpha)n_{I_2} + 2\alpha n_{I_2} = (1+\alpha)n_{I_2}$. This value is used to find the mole fractions. Treating all species as perfect gases, so that $a_J = p_J/p^\ominus$, the equilibrium constant is:

$$K = \frac{a_I^2}{a_{I_2}} = \frac{(p_I/p^\ominus)^2}{(p_{I_2}/p^\ominus)} = \frac{p_I^2}{p_{I_2}p^\ominus} = \frac{\left(\frac{2\alpha p}{1+\alpha}\right)^2}{\left(\frac{(1-\alpha)p}{1+\alpha}\right)p^\ominus} = \frac{4\alpha^2}{(1-\alpha)(1+\alpha)}\frac{p}{p^\ominus}$$

The total amount in moles is found from the pressure using the perfect gas law [1A.4–*8*], $pV = n_{\text{tot}}RT$. With this, α can then be determined.

$$pV = n_{\text{tot}}RT = (1+\alpha)n_{I_2}RT \quad \text{hence} \quad \alpha = \frac{pV}{n_{I_2}RT} - 1$$

These expressions are used to calculate α and hence K from the given data; the results are shown in the table below. The standard enthalpy of dissociation is then found using the van 't Hoff equation [6B.2–*214*]:

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta_r H^\ominus}{RT^2} \quad \text{which can also be written} \quad -\frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)} = \frac{\Delta_r H^\ominus}{R}$$

The second form implies that a graph of $-\ln K$ against $1/T$ should be a straight line of slope $\Delta_r H^\ominus/R$; the plot is shown in Fig. 6.2.

T/K	$100p$/atm	$10^4 n_{I_2}$/mol	α	K	$10^4/(T/K)$	$-\ln K$
973	6.244	2.4709	0.0846	1.824×10^{-3}	10.277	6.307
1 073	7.500	2.4555	0.1888	1.123×10^{-2}	9.320	4.489
1 173	9.181	2.4366	0.3415	4.911×10^{-2}	8.525	3.014

The data fall on a good straight line, the equation of which is

$$\ln K = 1.880 \times 10^4/(T/K) - 13.02$$

$\Delta_r H^\ominus/R$ is determined from the slope

$$\begin{aligned}\Delta_r H^\ominus &= R \times (\textit{slope} \times \mathrm{K}) = (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (1.880 \times 10^4\ \mathrm{K}) \\ &= \boxed{+156\ \mathrm{kJ\,mol^{-1}}}\end{aligned}$$

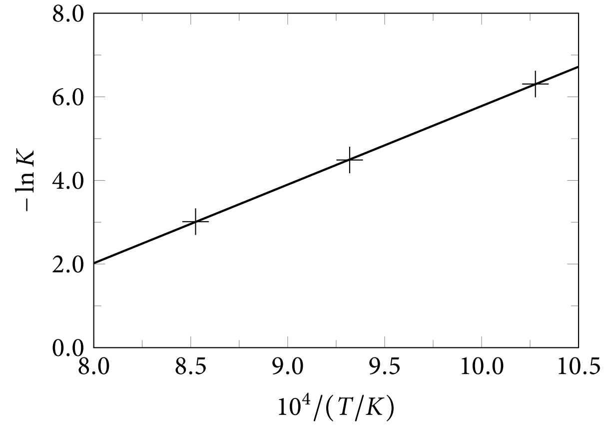


Figure 6.2

P6B.10 The equilibrium for which $\Delta_r H^\ominus$ is the enthalpy change of solution is $A(g) \rightleftharpoons A(solv)$ where A is H_2 or CO. Replacing activities of solutes by molar concentrations and activities of gases by partial pressures, the equilibrium constant for this reaction is:

$$K = \frac{a_{A,solv}}{a_{A,g}} = \frac{([A]/c^\ominus)}{p_A/p^\ominus} = \frac{s_A}{c^\ominus/p^\ominus} = \frac{s_A}{(1\ \mathrm{mol\,dm^{-3}})/(1\ \mathrm{bar})} = s_A/\mathrm{mol\,dm^{-3}\,bar^{-1}}$$

where $s_A = [A]/p_A$ is the solubility. The standard enthalpy of solution is obtained using the van 't Hoff equation [6B.2–*214*], $\mathrm{d}\ln K/\mathrm{d}T = \Delta_r H^\ominus/RT^2$. Replacing $\Delta_r H^\ominus$ by $\Delta_{sol}H^\ominus$ and noting from inside the front cover that $\ln x = \ln 10 \times \log x$ gives

$$\begin{aligned}\Delta_{sol}H^\ominus &= RT^2\frac{\mathrm{d}\ln K}{\mathrm{d}T} = RT^2 \ln 10 \times \frac{\mathrm{d}\log K}{\mathrm{d}T}\\ &= RT^2 \ln 10 \times \frac{\mathrm{d}}{\mathrm{d}T}\log(s/\mathrm{mol\,cm^{-3}\,bar^{-1}})\end{aligned}$$

where the expression for K from above has been used. It does not matter whether s is in $\mathrm{mol\,dm^{-3}\,bar^{-1}}$ or $\mathrm{mol\,cm^{-3}\,bar^{-1}}$ because the only difference is a constant factor which vanishes on differentiating the logarithm. The enthalpies of solvation for H_2 and CO are therefore

$$\begin{aligned}H_2:\quad \Delta_{sol}H^\ominus &= RT^2 \ln 10 \times \frac{\mathrm{d}}{\mathrm{d}T}\left(-5.39 - \frac{768}{T/K}\right) = RT^2 \ln 10 \times \frac{768\ \mathrm{K}}{T^2}\\ &= R\ln 10 \times (768\ \mathrm{K}) = (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln 10 \times (768\ \mathrm{K})\\ &= \boxed{+14.7\ \mathrm{kJ\,mol^{-1}}}\end{aligned}$$

$$\begin{aligned}\text{CO:}\quad \Delta_{\text{sol}}H^{\ominus} &= RT^2 \ln 10 \times \frac{\mathrm{d}}{\mathrm{d}T}\left(-5.98 - \frac{980}{T/K}\right) = RT^2 \ln 10 \times \frac{980\ \mathrm{K}}{T^2} \\ &= R\ln 10 \times (980\ \mathrm{K}) = (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln 10 \times (980\ \mathrm{K}) \\ &= \boxed{+18.8\ \mathrm{kJ\,mol^{-1}}}\end{aligned}$$

P6B.12 The relationship between K and K_c is given by [6A.18b–*209*]

$$K = K_c \times \left(\frac{c^{\ominus}RT}{p^{\ominus}}\right)^{\Delta\nu} \qquad \text{where} \quad \Delta\nu = \nu(\text{products}) - \nu(\text{reactants})$$

This expression for K is substituted into the van 't Hoff equation [6B.2–*214*], $\mathrm{d}\ln K/\mathrm{d}T = \Delta_r H^{\ominus}/RT^2$

$$\frac{\mathrm{d}}{\mathrm{d}T}\ln\left[K_c \times \left(\frac{c^{\ominus}RT}{p^{\ominus}}\right)^{\Delta\nu}\right] = \frac{\Delta_r H^{\ominus}}{RT^2}$$

The left hand side of this expression is evaluated to give

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}T}\ln\left[K_c \times \left(\frac{c^{\ominus}RT}{p^{\ominus}}\right)^{\Delta\nu}\right] &= \frac{\mathrm{d}}{\mathrm{d}T}\left[\ln K_c + \Delta\nu \ln\left(\frac{c^{\ominus}R}{p^{\ominus}}\right) + \Delta\nu \ln T\right] \\ &= \frac{\mathrm{d}\ln K_c}{\mathrm{d}T} + \frac{\Delta\nu}{T}\end{aligned}$$

so that

$$\frac{\mathrm{d}\ln K_c}{\mathrm{d}T} + \frac{\Delta\nu}{T} = \frac{\Delta_r H^{\ominus}}{RT^2} \qquad \text{hence} \qquad \boxed{\frac{\mathrm{d}\ln K_c}{\mathrm{d}T} = \frac{\Delta_r H^{\ominus}}{RT^2} - \frac{\Delta\nu}{T}}$$

If $\Delta_r H^{\ominus}$ is assumed not to vary with temperature between T_1 and T_2, this expression may be integrated between T_1 and T_2:

$$\int_{T_1}^{T_2} \mathrm{d}\ln K_c = \int_{T_1}^{T_2}\left(\frac{\Delta_r H^{\ominus}}{RT^2} - \frac{\Delta\nu}{T}\right)\mathrm{d}T$$

to give

$$\boxed{\ln K_c(T_2) - \ln K_c(T_1) = -\frac{\Delta_r H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) - \Delta\nu \ln\left(\frac{T_2}{T_1}\right)}$$

6C Electrochemical cells

Answers to discussion questions

D6C.2 A galvanic cell is an electrochemical cell that produces electricity as a result of the spontaneous reaction occuring inside it. An electrolytic cell is an electrochemical cell in which a non-spontaneous reaction is driven by an external source of current.

D6C.4 The relationship between the cell potential and the Gibbs energy change of the cell reaction, $\Delta_r G = -\nu F E_{\text{cell}}$ only applies under reversible conditions. This is achieved by balancing the cell with an equal and opposite externally applied potential. Under these circumstances, no current flows.

Solutions to exercises

E6C.1(b) (i) The reduction half-reactions, together with their standard electrode potentials from the *Resource section*, are

$$\begin{array}{lll} \text{R:} & \text{Ag}_2\text{CrO}_4(\text{s}) + 2\text{e}^- \rightarrow 2\text{Ag}(\text{s}) + \text{CrO}_4^{2-}(\text{aq}) & E^\ominus(\text{R}) = +0.45\ \text{V} \\ \text{L:} & \text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq}) & E^\ominus(\text{L}) = +1.36\ \text{V} \end{array}$$

The cell reaction is obtained by subtracting the left-hand reduction half-reaction from the right-hand reduction half reaction

$$\text{Ag}_2\text{CrO}_4(\text{s}) + 2\text{Cl}^-(\text{aq}) \rightarrow 2\text{Ag}(\text{s}) + \text{Cl}_2(\text{g}) + \text{CrO}_4^{2-}(\text{aq})$$

The standard cell potential is calculated as the difference of the two standard electrode potentials [6D.3–*224*], $E^\ominus_{\text{cell}} = E^\ominus(\text{R}) - E^\ominus(\text{L})$

$$E^\ominus_{\text{cell}} = (+0.45\ \text{V}) - (+1.36\ \text{V}) = \boxed{-0.91\ \text{V}}$$

(ii) The reduction half-reactions and their standard electrode potentials are

$$\begin{array}{lll} \text{R:} & \text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq}) & E^\ominus(\text{R}) = +0.15\ \text{V} \\ \text{L:} & \text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq}) & E^\ominus(\text{L}) = +0.77\ \text{V} \end{array}$$

The cell reaction is obtained by subtracting the left-hand reduction half-reaction from the right-hand reduction half-reaction, after first multiplying the left- hand half-reaction by two so that the numbers of electrons in both half-reactions are the same.

$$\text{Sn}^{4+}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Sn}^{2+}(\text{aq}) + 2\text{Fe}^{3+}(\text{aq})$$

The standard cell potential is

$$E^\ominus_{\text{cell}} = (+0.15\ \text{V}) - (+0.77\ \text{V}) = \boxed{-0.26\ \text{V}}$$

(iii) The reduction half-reactions and their standard electrode potentials are

$$\begin{array}{ll} \text{R:} & \text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \\ \text{L:} & \text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s}) \end{array}$$

with $E^\ominus(\text{R}) = +1.23$ V and $E^\ominus(\text{L}) = +0.34$ V. The cell reaction (R – L) is therefore

$$\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + \text{Cu}(\text{s}) \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + \text{Cu}^{2+}(\text{aq})$$

and the standard cell potential is

$$E^\ominus_{\text{cell}} = (+1.23\ \text{V}) - (+0.34\ \text{V}) = \boxed{+0.89\ \text{V}}$$

E6C.2(b) (i) The required reduction half-reactions are

$$\begin{array}{lll} \text{R:} & 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) & E^\ominus(R) = -0.83\ V \\ \text{L:} & 2Na^+(aq) + 2e^- \rightarrow 2Na(s) & E^\ominus(L) = -2.71\ V \end{array}$$

The cell reaction (R – L) generated from these reduction half-reactions is $2H_2O(l) + 2Na(s) \rightarrow H_2(g) + 2OH^-(aq) + 2Na^+(aq)$ which is equivalent to the required reaction. The cell required is

$$Na(s)|NaOH(aq)|H_2(g)|Pt(s)$$

The platinum electrode is an 'inert metal' that acts as a source or sink of electrons. Note that there is no interface between the half cells because they have a common electrolyte (NaOH(aq)). The standard cell potential is

$$E^\ominus_{cell} = E^\ominus(R) - E^\ominus(L) = (-0.83\ V) - (-2.71\ V) = \boxed{+1.88\ V}$$

(ii) The required reduction half-reactions are

$$\begin{array}{lll} \text{R:} & I_2(g) + 2e^- \rightarrow 2I^-(aq) & E^\ominus(R) = +0.54\ V \\ \text{L:} & 2H^+(aq) + 2e^- \rightarrow H_2(g) & E^\ominus(L) = 0\ \text{(by definition)} \end{array}$$

The cell reaction (R – L) generated from these reduction half-reactions is $I_2(g) + H_2(g) \rightarrow 2I^-(aq) + 2H^+(aq)$ which is equivalent to the required reaction. The cell required is

$$Pt(s)|H_2(g)|HI(aq)|I_2(g)|Pt(s)$$

and the standard cell potential is

$$E^\ominus_{cell} = E^\ominus(R) - E^\ominus(L) = \boxed{+0.54\ V}$$

(iii) One possible pair of reduction half-equations is

$$\begin{array}{lll} \text{R:} & 2H^+(aq) + 2e^- \rightarrow H_2(g) & E^\ominus(R) = 0\ \text{(by definition)} \\ \text{L:} & 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) & E^\ominus(L) = -0.83\ V \end{array}$$

The cell reaction (R – L) generated from these reduction half-reactions is $2H^+(aq) + 2OH^-(aq) \rightarrow 2H_2O(l)$ which is equivalent to (twice) the required reaction. The required cell is

$$Pt(s)|H_2(g)|NaOH(aq)||HCl(aq)|H_2(g)|Pt(s)$$

and the standard cell potential is

$$E^\ominus_{cell} = E^\ominus(R) - E^\ominus(L) = -(-0.83\ V) = \boxed{+0.83\ V}$$

An alternative pair of reduction half-equations is

$$\begin{array}{lll} \text{R:} & O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) & E^\ominus(R) = +1.23\ V \\ \text{L:} & O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq) & E^\ominus(L) = +0.40\ V \end{array}$$

for which the required cell is

$$\mathrm{Pt(s)|O_2(g)|NaOH(aq)||HCl(aq)|O_2(g)|Pt(s)}$$

The cell reaction is the same as before and the standard cell potential is therefore also the same: $E^{\ominus}_{\text{cell}} = (+1.23\ \text{V}) - (+0.40\ \text{V}) = +0.83\ \text{V}$.

E6C.3(b) (i) The reduction half-reactions for the cell in question are:

$$\begin{array}{ll} \text{R:} & \mathrm{2AgCl(s) + 2e^- \rightarrow 2Ag(s) + 2Cl^-(aq)} \\ \text{L:} & \mathrm{2H^+(aq) + 2e^- \rightarrow H_2(g)} \end{array}$$

which reveal that $\nu = 2$ for the given cell reaction. The Nernst equation [6C.4–*221*] is $E_{\text{cell}} = E^{\ominus}_{\text{cell}} - (RT/\nu F)\ln Q$. Noting that $a_{\text{J}} = 1$ for pure solids the Nernst equation in this case is

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{2F}\ln\left(\frac{a^2_{\mathrm{H^+}}a^2_{\mathrm{Cl^-}}}{a_{\mathrm{H_2}}}\right)$$

Note that HCl(aq) must be treated as separate $\mathrm{H^+}$ and $\mathrm{Cl^-}$ ions since it is a strong acid and therefore fully dissociated in water. If the $\mathrm{H_2}$ is treated as a perfect gas then $a_{\mathrm{H_2}} = p_{\mathrm{H_2}}/p^{\ominus}$, which gives $a_{\mathrm{H_2}} = 1$ in this case because the hydrogen is at the standard pressure. This gives

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{F}\ln\left(a_{\mathrm{H^+}}a_{\mathrm{Cl^-}}\right)$$

As discussed in Section 5F.4 on page 187 the activities of the $\mathrm{H^+}$ and $\mathrm{Cl^-}$ are given by $a = \gamma_{\pm}(b/b^{\ominus})$ where $\gamma_{\pm}$ is the mean activity coefficient of the electrolyte which in this case is common to both electrodes. Making this substitution and denoting the molality of the common HCl solution by b gives

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{F}\ln\left(\frac{\gamma^2_{\pm}b^2}{b^{\ominus 2}}\right)$$

(ii) The relationship between the cell potential and $\Delta_{\text{r}}G$ is given by [6C.2–*217*], $\Delta_{\text{r}}G = -\nu FE_{\text{cell}}$:

$$\Delta_{\text{r}}G = -2 \times (96485\ \text{C mol}^{-1}) \times (0.4658\ \text{V}) = \boxed{-89.9\ \text{kJ mol}^{-1}}$$

where 1 C V = 1 J has been used.

(iii) The Debye–Hückel limiting law [5F.27–*188*] is $\log\gamma_{\pm} = -A|z_+z_-|I^{1/2}$. In this equation $A = 0.509$ for an aqueous solution at 25 °C, z_+ and z_- are the charges on the ions, and I is the ionic strength which for a solution containing two types of ion is given by [5F.29–*188*], $I = \frac{1}{2}(b_+z_+^2 + b_-z_-^2)/b^{\ominus}$. For an HCl solution of molality b, $z_+ = 1$ (for $\mathrm{H^+}$), $z_- = -1$ (for $\mathrm{Cl^-}$) and $b_+ = b_- = b$. Therefore

$$\begin{aligned}\log\gamma_{\pm} &= -A\left|z_+z_-\right|\left(\tfrac{1}{2}(b_+z_+^2 + b_-z_-^2)/b^{\ominus}\right)^{1/2} \\ &= -A \times \left|(+1)\times(-1)\right| \times \left(\tfrac{1}{2}(b\times 1^2 + b\times(-1)^2)/b^{\ominus}\right)^{1/2} = -A\left(\frac{b}{b^{\ominus}}\right)^{1/2}\end{aligned}$$

The Nernst equation from part (i) is rearranged for $E^\ominus_\text{cell}$ and the expression for $\gamma_\pm$ is substituted in, noting from inside the front cover that $\ln x = \ln 10 \times \log x$.

$$\begin{aligned}E^\ominus_\text{cell} &= E_\text{cell} + \frac{RT}{F}\ln\left(\frac{\gamma_\pm^2 b^2}{b^{\ominus 2}}\right) = E_\text{cell} + \frac{2RT}{F}\left[\ln\left(\frac{b}{b^\ominus}\right) + \ln 10 \times \log\gamma_\pm\right]\\ &= E_\text{cell} + \frac{2RT}{F}\left[\ln\left(\frac{b}{b^\ominus}\right) - \ln 10 \times A\left(\frac{b}{b^\ominus}\right)^{1/2}\right]\\ &= (+0.4658\ \text{V}) + \frac{2\times(8.3145\ \text{J K}^{-1}\,\text{mol}^{-1})\times(298.15\ \text{K})}{96485\ \text{C mol}^{-1}}\\ &\quad\times\left[\ln\left(\frac{0.01\ \text{mol kg}^{-1}}{1\ \text{mol kg}^{-1}}\right) - \ln 10\times(0.509)\times\left(\frac{0.01\ \text{mol kg}^{-1}}{1\ \text{mol kg}^{-1}}\right)^{1/2}\right]\\ &= \boxed{+0.223\ \text{V}}\end{aligned}$$

Finally, note that $E^\ominus_\text{cell} = E^\ominus(\text{R}) - E^\ominus(\text{L}) = E^\ominus(\text{AgCl/Ag, Cl}^-) - E^\ominus(\text{H}^+/\text{H}_2)$. Because $E^\ominus(\text{H}^+/\text{H}_2) = 0$ (by definition), it follows that $E^\ominus(\text{AgCl/Ag, Cl}) = E^\ominus_\text{cell} = \boxed{+0.223\ \text{V}}$

E6C.4(b) The reduction half-reactions for the cell in question are

$$\begin{aligned}&\text{R:}\quad 2\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{NO}_2(\text{g}) + 2\text{H}_2\text{O(l)}\\ &\text{L:}\quad \text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn(s)}\end{aligned}$$

which reveal that $\nu = 2$ for the given cell reaction. As explained in Section 6C.3(a) on page 219 the maximum non-expansion (electrical) work that a reaction when it advances by an infinitesimal amount $\mathrm{d}\xi$ at some composition is given by $\mathrm{d}w_\text{e} = \Delta_\text{r}G\,\mathrm{d}\xi$. The reaction Gibbs energy $\Delta_\text{r}G$ therefore represents the work done per mole of reaction, that is, when the reaction advances by $\Delta\xi = 1$ mol at constant composition. The reaction Gibbs energy is related to the cell potential according to [6C.2–*217*], $\Delta_\text{r}G = -\nu F E_\text{cell}$, so assuming that the cell is operating under standard conditions the electrical work that can be done (per mole of reaction) is

$$\begin{aligned}\mathrm{d}w_\text{e}/\mathrm{d}\xi &= \Delta_\text{r}G^\ominus = -2FE^\ominus_\text{cell} = -2\times(96485\ \text{C mol}^{-1})\times(-0.040\ \text{V})\\ &= \boxed{+7.7\ \text{kJ mol}^{-1}}\end{aligned}$$

The positive value indicates that work has been done on the system by the surroundings.

E6C.5(b) The Nernst equation [6C.4–*221*] is $E_\text{cell} = E^\ominus_\text{cell} - (RT/\nu F)\ln Q$. If Q changes from Q_1 to Q_2 then the change in cell potential is given by

$$E_\text{cell,1} - E_\text{cell,2} = \left[E^\ominus_\text{cell} - \frac{RT}{\nu F}\ln Q_2\right] - \left[E^\ominus_\text{cell} - \frac{RT}{\nu F}\ln Q_1\right] = -\frac{RT}{\nu F}\ln\left(\frac{Q_2}{Q_1}\right)$$

For $\nu = 3$ and $Q_2/Q_1 = 5$ the change in cell potential is

$$E_{\text{cell},1} - E_{\text{cell},2} = -\frac{(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})}{3 \times (96485\,\text{C}\,\text{mol}^{-1})} \times \ln 5 = \boxed{-0.014\,\text{V}}$$

where $1\,\text{J}\,\text{C}^{-1} = 1\,\text{V}$ is used.

Solutions to problems

P6C.2 The reduction half-reactions for the specified cell are

$$\begin{array}{ll} \text{R:} & \tfrac{1}{2}\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2\text{O}(\text{l}) \\ \text{L:} & 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) \end{array}$$

for which $\nu = 2$. The cell reaction (R − L) is $\tfrac{1}{2}\text{O}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$, which corresponds to the formation reaction for $\text{H}_2\text{O}(\text{l})$ from its elements. The standard Gibbs energy of formation of $\text{H}_2\text{O}(\text{l})$ is therefore equal to $\Delta_\text{r}G^\ominus$ for this reaction; in turn this is given by [6C.2–*217*], $\Delta_\text{r}G^\ominus = -\nu F E^\ominus_\text{cell}$.

$$\Delta_\text{f}G^\ominus(\text{H}_2\text{O},\text{l}) = -\nu F E^\ominus_\text{cell} = -2\times(96485\,\text{C}\,\text{mol}^{-1})\times(+1.23\,\text{V}) = \boxed{-237\,\text{kJ}\,\text{mol}^{-1}}$$

P6C.4 (a) The reduction half-reactions for the cell are:

$$\begin{array}{ll} \text{R:} & \text{Ag}^+(\text{aq},m_\text{R}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) \\ \text{L:} & \text{Ag}^+(\text{aq},m_\text{L}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) \end{array}$$

for which $\nu = 1$. The overall cell reaction is

$$\text{Ag}^+(\text{aq},m_\text{R}) \rightarrow \text{Ag}^+(\text{aq},m_\text{L})$$

If m_L is increased, then there is an increased tendency for the cell reaction to shift in the direction $\text{Ag}^+(\text{aq},m_\text{R}) \leftarrow \text{Ag}^+(\text{aq},m_\text{L})$. Therefore $\Delta_\text{r}G$ for the cell reaction will increase, and so E_cell will $\boxed{\text{decrease}}$ because $\Delta_\text{r}G = -\nu F E_\text{cell}$. This is confirmed by the Nerst equation for this cell

$$E_\text{cell} = E^\ominus_\text{cell} - \frac{RT}{F}\ln\left(\frac{a_{\text{Ag}^+(\text{aq},m_\text{L})}}{a_{\text{Ag}^+(\text{aq},m_\text{R})}}\right)$$

If m_L is increased then $a_{\text{Ag}^+(\text{aq},m_\text{L})}$ will increase and consequently E_cell will decrease.

(b) The reduction half-reactions for the cell are

$$\begin{array}{ll} \text{R:} & 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g},p_\text{R}) \\ \text{L:} & 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g},p_\text{L}) \end{array}$$

for which $\nu = 2$. The overall cell reaction is

$$\text{H}_2(\text{g},p_\text{L}) \rightarrow \text{H}_2(\text{g},p_\text{R})$$

If p_L is increased then there is an increased tendency for the cell reaction as written to move in the forwards direction. Therefore $\Delta_\text{r}G$ for the cell will decrease and so E_{cell} will $\boxed{\text{increase}}$. This is confirmed by the Nernst equation. Treating the hydrogen as a perfect gas so that $a_{\text{H}_2} = p_{\text{H}_2}/p^{\ominus}$, the Nernst equation for this cell is

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{2F}\ln\left(\frac{p_{\text{R}}}{p_{\text{L}}}\right)$$

If p_{L} is increased then E_{cell} will increase.

(c) The reduction half-reactions for the cell are

$$\begin{aligned}&\text{R:}\quad \text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})\\ &\text{L:}\quad [\text{Fe(CN)}_6]^{3-}(\text{aq}) + \text{e}^- \rightarrow [\text{Fe(CN)}_6]^{4-}(\text{aq})\end{aligned}$$

The overall cell reaction, after multiplying the left-hand reduction half-reaction by 2 so that both half-reactions have $\nu = 2$, is

$$\begin{aligned}&\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2[\text{Fe(CN)}_6]^{4-}(\text{aq})\\ &\quad\rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + 2[\text{Fe(CN)}_6]^{3-}(\text{aq})\end{aligned}$$

If the pH in the right-hand compartment is decreased, corresponding to an increase in the H^+ concentration, then there will be an increased tendency for the cell reaction as written to move in the forward direction. Therefore $\Delta_{\text{r}}G$ for the cell will decrease and so E_{cell} will $\boxed{\text{increase}}$. This is confirmed by the Nernst equation. Noting that pure solids and liquids have $a_{\text{J}} = 1$, the Nernst equation for this cell is

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{2F}\ln\left(\frac{a_{\text{Mn}^{2+}}\,a^2_{[\text{Fe(CN)}_6]^{3-}}}{a^4_{\text{H}^+}\,a^2_{[\text{Fe(CN)}_6]^{4-}}}\right)$$

If the pH is decreased then a_{H^+} will increase and therefore E_{cell} will increase.

(d) The reduction half-reactions for the cell are

$$\begin{aligned}&\text{R:}\quad \text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-\\ &\text{L:}\quad \text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-\end{aligned}$$

The overall cell reaction is

$$\text{Br}_2(\text{l}) + 2\text{Cl}^-(\text{aq}) \rightarrow 2\text{Br}^-(\text{aq}) + \text{Cl}_2(\text{g})$$

If the concentration of HCl in the left-hand compartment is increased, then there will be an increased tendency for the overall cell reaction as written to shift in the forward direction. Therefore $\Delta_{\text{r}}G$ for the cell will decrease and so E_{cell} will $\boxed{\text{increase}}$. This is confirmed by the Nernst equation. Noting that pure liquids have $a_{\text{J}} = 1$ the Nernst equation for this cell is

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{2F}\ln\left(\frac{a^2_{\text{Br}^-}\,a_{\text{Cl}_2}}{a^2_{\text{Cl}^-}}\right)$$

If HCl is added then a_{Cl^-} will increase so E_{cell} will increase.

(e) TO DO/CHECK

(f) The reduction half-reactions for the cell are

$$\begin{array}{ll} \text{R:} & \text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \\ \text{L:} & \text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s}) \end{array}$$

The overall cell reaction is

$$\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq, L}) + \text{Fe}(\text{s}) \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + \text{Fe}^{2+}(\text{aq})$$

where $\text{H}^+(\text{aq, L})$ has been written to emphasise that it is H^+ in the left-hand compartment that is involved in the reaction. If acid is added to both compartments then the acid added to the right-hand compartment will have no effect, because $\text{H}^+(\text{aq, R})$ does not appear in the overall cell reaction. However, the acid added to the left-hand compartment will increase the tendency of the cell reaction as written to move in the forward direction. Therefore $\Delta_r G$ for the cell will decrease and so E_{cell} will $\boxed{\text{increase}}$.

This is confirmed by the Nernst equation. Noting that pure solids and liquids have $a_J = 1$, the Nernst equation for this cell is

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{2F} \ln\left(\frac{a_{\text{Mn}^{2+}} a_{\text{Fe}^{2+}}}{a^4_{\text{H}^+(\text{aq,L})}}\right)$$

The addition of acid to the left-hand compartment will increase $a_{\text{H}^+(\text{aq,L})}$ which will result in E_{cell} increasing. The fact that acid has also been added to the right-hand compartment has no effect on E_{cell} because $a_{\text{H}^+(\text{aq,R})}$ does not appear in the Nernst equation.

6D Electrode potentials

Answer to discussion questions

D6D.2 This is discussed in *Impact* 10.

Solutions to exercises

E6D.1(b) (i) The following electrodes are combined

$$\begin{array}{lll} \text{R:} & \text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s}) & E^{\ominus}(\text{R}) = +0.34\ \text{V} \\ \text{L:} & \text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}(\text{s}) & E^{\ominus}(\text{L}) = -0.14\ \text{V} \end{array}$$

The cell reaction (R – L) is $\text{Cu}^{2+}(\text{aq}) + \text{Sn}(\text{s}) \rightarrow 2\text{Cu}(\text{s}) + \text{Sn}^{2+}(\text{aq})$, which is equivalent to the required reaction, and has $\nu = 2$. The standard cell potential is given by [6D.3–*224*], $E^{\ominus}_{\text{cell}} = E^{\ominus}(\text{R}) - E^{\ominus}(\text{L})$

$$E^{\ominus}_{\text{cell}} = (+0.34\ \text{V}) - (-0.14\ \text{V}) = +0.48\text{V}$$

The relationship between the equilibrium constant and the standard cell potential is given by [6C.5–*221*], $E^{\ominus}_{\text{cell}} = (RT/\nu F)\ln K$. Rearranging gives

$$\ln K = \frac{\nu F}{RT}E^{\ominus}_{\text{cell}} = \frac{2 \times (96485\ \text{C mol}^{-1})}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K})} \times (+0.48\ \text{V}) = 37.3...$$

where $1\ \text{V} = 1\ \text{J C}^{-1}$ is used. Hence $K = \boxed{1.7 \times 10^{16}}$.

(ii) The following electrodes are combined

$$\begin{array}{lll} \text{R:} & \text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)} & E^{\ominus}(\text{R}) = +0.34\ \text{V} \\ \text{L:} & 2\text{Cu}^{+}(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Cu(s)} & E^{\ominus}(\text{L}) = +0.52\ \text{V} \end{array}$$

The cell reaction is $\text{Cu}^{2+}(\text{aq}) + \text{Cu(s)} \rightarrow 2\text{Cu}^{+}(\text{aq})$ which is the required reaction, and has $\nu = 2$. Therefore, using the same equations as in part (i)

$$E^{\ominus}_{\text{cell}} = E^{\ominus}(\text{R}) - E^{\ominus}(\text{L}) = (+0.34\ \text{V}) - (+0.52\ \text{V}) = -0.18\ \text{V}$$

$$\ln K = \frac{\nu F}{RT} E^{\ominus}_{\text{cell}} = \frac{2 \times (96485\ \text{C mol}^{-1})}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K})} \times (-0.18\ \text{V}) = -14.0...$$

Hence $K = \boxed{8.2 \times 10^{-7}}$

E6D.2(b) The reduction half-reactions for the given cell are

$$\begin{array}{ll} \text{R:} & 2\text{Bi}^{3+}(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Bi(s)} \\ \text{L:} & \text{Bi}_2\text{S}_3(\text{s}) + 6\text{e}^- \rightarrow 2\text{Bi(s)} + 3\text{S}^{2-}(\text{aq}) \end{array}$$

The cell reaction (R – L) is $2\text{Bi}^{3+}(\text{aq}) + 3\text{S}^{2-}(\text{aq}) \rightarrow \text{Bi}_2\text{S}_3(\text{s})$. The equilibrium constant for this reaction is calculated using [6C.5–*221*], $E^{\ominus}_{\text{cell}} = (RT/\nu F) \ln K$. Rearranging for $\ln K$ and noting that $\nu = 6$ gives

$$\ln K = \frac{\nu F}{RT} E^{\ominus}_{\text{cell}} = \frac{6 \times (96485\ \text{C mol}^{-1})}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298.15\ \text{K})} \times (+0.96\ \text{V}) = 2.24... \times 10^{2}$$

where $1\ \text{V} = 1\ \text{J C}^{-1}$ is used. Hence $K = 2.30... \times 10^{97}$.

The dissolution reaction, $\text{Bi}_2\text{S}_3(\text{s}) \rightarrow 2\text{Bi}^{3+}(\text{aq}) + 3\text{S}^{2-}(\text{aq})$, corresponds to the reverse of the cell reaction as written above. The required equilibrium constant is therefore the reciprocal of the one just calculated

$$K_{\text{diss}} = \frac{1}{2.30... \times 10^{97}} = \boxed{4.3 \times 10^{-98}}$$

E6D.3(b) (i) The reduction half-reactions for the specified cell, and their electrode potentials, are

$$\begin{array}{lll} \text{R:} & \text{O}_2(\text{g}) + 4\text{H}^{+}(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O(l)} & E^{\ominus}(\text{R}) = +1.23\ \text{V} \\ \text{L:} & 2\text{RSSR(aq)} + 4\text{H}^{+}(\text{aq}) + 4\text{e}^- \rightarrow 4\text{RSH(aq)} & E^{\ominus}(\text{L}) = -0.34\ \text{V} \end{array}$$

where RSH represents cysteine, $\text{HSCH}_2\text{CH(NH}_2\text{)CO}_2\text{H}$, and RSSR represents cystine, the oxidised dimer $[\text{SCH}_2\text{CH(NH}_2\text{)CO}_2\text{H}]_2$.

The overall cell reaction is

$$\text{O}_2(\text{g}) + 4\text{RSH(aq)} \rightarrow 2\text{H}_2\text{O(l)} + 2\text{RSSR(aq)} \qquad \nu = 4$$

and the standard cell potential is

$$E^{\ominus}_{\text{cell}} = E^{\ominus}(\text{R}) - E^{\ominus}(\text{L}) = (+1.23\ \text{V}) - (-0.34\ \text{V}) = +1.57\ \text{V}$$

The standard reaction Gibbs energy is related to the standard cell potential according to [6C.3–*221*], $\Delta_r G^\ominus = -\nu F E^\ominus_{\text{cell}}$. Therefore

$$\begin{aligned}\Delta_r G^\ominus &= -\nu F E^\ominus_{\text{cell}} = -4 \times (96485\,\text{C mol}^{-1}) \times (+1.57\text{ V}) \\ &= \boxed{-6.1 \times 10^2\text{ kJ mol}^{-1}}\end{aligned}$$

E6D.4(b) Under basic conditions, the required reduction half-equations and their standard electrode potentials are

$$\begin{array}{lll}\text{R:} & 2\text{Cl}_2(\text{g}) + 4\text{e}^- \rightarrow 4\text{Cl}^-(\text{aq}) & E^\ominus(\text{R}) = +1.36\text{ V} \\ \text{L:} & \text{O}_2(\text{g}) + 2\text{H}_2\text{O(l)} + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq}) & E^\ominus(\text{L}) = +0.40\text{ V}\end{array}$$

The cell reaction (R–L) is $2\text{Cl}_2(\text{g}) + 4\text{OH}^-(\text{aq}) \rightarrow 4\text{Cl}^-(\text{aq}) + \text{O}_2(\text{g}) + 2\text{H}_2\text{O(l)}$. The standard cell potential is

$$E^\ominus_{\text{cell}} = E^\ominus(\text{R}) - E^\ominus(\text{L}) = (+1.36\text{ V}) - (+0.40\text{ V}) = +0.96\text{ V}$$

The positive value of $E^\ominus_{\text{cell}}$ indicates that $\boxed{\text{yes}}$, chlorine has a thermodynamic tendency to oxidize water to oxygen gas under standard conditions in basic solution.

Solutions to problems

P6D.2 (a) The reduction half-reactions for the reduction of CO_2 and CO to methane are

$$\begin{array}{ll}\text{R:} & \text{CO(g)} + 6\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow \text{CH}_4(\text{g}) + \text{H}_2\text{O(l)} \\ \text{L:} & \text{CO}_2(\text{g}) + 8\text{H}^+(\text{aq}) + 8\text{e}^- \rightarrow \text{CH}_4(\text{g}) + 2\text{H}_2\text{O(l)}\end{array}$$

The right-hand reduction half-reaction is multiplied by four and the left-half reduction half-reaction by three so that both involve the same number of electrons, $\nu = 24$. Subtraction of the left-hand half-reaction from the right-hand half-reaction gives the overall cell reaction as

$$4\text{CO(g)} + 2\text{H}_2\text{O(l)} \rightarrow \text{CH}_4(\text{g}) + 3\text{CO}_2(\text{g}) \quad \nu = 24$$

The standard reaction Gibbs energy of this reaction is calculated using standard formation Gibbs energies from the *Resource section*.

$$\begin{aligned}\Delta_r G^\ominus &= 3\Delta_f G^\ominus(\text{CO}_2,\text{g}) + \Delta_f G^\ominus(\text{CH}_4,\text{g}) \\ &\quad - 4\Delta_f G^\ominus(\text{CO},\text{g}) - 2\Delta_f G^\ominus(\text{H}_2\text{O},\text{l}) \\ &= 3 \times (-394.36\text{ kJ mol}^{-1}) + (-50.72\text{ kJ mol}^{-1}) \\ &\quad - 4 \times (-137.17\text{ kJ mol}^{-1}) - 2 \times (-237.13\text{ kJ mol}^{-1}) \\ &= -210.86\text{ kJ mol}^{-1}\end{aligned}$$

The negative value of $\Delta_r G^\ominus$ indicates that the cell reaction as written is spontaneous under standard conditions. This means that, in the spontaneous cell reaction, reduction is taking place at the right-hand electrode. Therefore the $\boxed{\text{right-hand electrode}}$ is the cathode.

(b) The cell potential under standard conditions, corresponding to all gases being at 1 bar pressure assuming perfect gas behaviour, is calculated from $\Delta_r G^\ominus$ using [6C.3–*221*]. Note from above that $\nu = 24$.

$$E^\ominus_{\text{cell}} = -\frac{\Delta_r G^\ominus}{\nu F} = -\frac{-210.86 \times 10^3\ \text{J mol}^{-1}}{24 \times (96485\ \text{C mol}^{-1})} = \boxed{+0.09106\ \text{V}}$$

P6D.4 The reduction half-equations for the cell are

$$\begin{aligned} &\text{R:} \quad \text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{Hg}(\text{l}) + 2\text{Cl}^-(\text{aq}) \\ &\text{L:} \quad 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) \end{aligned}$$

The overall cell reaction is

$$\text{Hg}_2\text{Cl}_2(\text{s}) + \text{H}_2(\text{g}) \rightarrow 2\text{Hg}(\text{l}) + 2\text{H}^+(\text{aq}) + 2\text{Cl}^-(\text{aq}) \qquad \nu = 2$$

Noting that pure solids and liquids have $a_J = 1$, the Nernst equation is

$$E_{\text{cell}} = E^\ominus_{\text{cell}} - \frac{RT}{2F}\ln\left(\frac{a^2_{\text{H}^+}a^2_{\text{Cl}^-}}{a_{\text{H}_2}}\right)$$

Because the hydrogen gas is at standard pressure, $a_{\text{H}_2} = 1$. Hence

$$E_{\text{cell}} = E^\ominus_{\text{cell}} - \frac{RT}{2F}\ln\left(a^2_{\text{H}^+}a^2_{\text{Cl}^-}\right) = E^\ominus_{\text{cell}} - \frac{RT}{F}\ln\left(a_{\text{H}^+}a_{\text{Cl}^-}\right)$$

The activities in this expression are written in terms of the molality of HCl(aq), b, through $a_{\text{H}^+} = \gamma_\pm b/b^\ominus$ and $a_{\text{Cl}^-} = \gamma_\pm b/b^\ominus$ as explained in Section 6D.1(a) on page 225. This gives

$$E_{\text{cell}} = E^\ominus_{\text{cell}} - \frac{RT}{F}\ln\left(\frac{\gamma^2_\pm b^2}{b^{\ominus 2}}\right) = E^\ominus_{\text{cell}} - \frac{2RT}{F}\ln\left(\frac{b}{b^\ominus}\right) - \frac{2RT}{F}\ln\gamma_\pm$$

From the Debye–Hückel law the mean activity coefficient is given by [5F.27–*188*], $\log\gamma_\pm = -A|z_+z_-|I^{1/2}$ where A is a dimensionless constant, z_+ and z_- are the charges on the H^+ and Cl^- ions and I is the ionic strength. For an electrolyte containing only two ions, the ionic strength is given by [5F.29–*188*], $I = \frac{1}{2}(b_+z_+^2 + b_-z_-^2)/b^\ominus$. In the case of HCl, $z_+ = +1$, $z_- = -1$, and $b_+ = b_- = b$. Therefore

$$I = \tfrac{1}{2}[b \times (+1)^2 + b \times (-1)^2]/b^\ominus = b/b^\ominus$$

and hence

$$\log\gamma_\pm = -A|z_+z_-|I^{1/2} = -A \times \left|(1) \times (-1)\right| \times (b/b^\ominus)^{1/2} = -A(b/b^\ominus)^{1/2}$$

Noting from inside the front cover that $\ln x = \ln 10 \times \log x$, the expression for E_{cell} then becomes

$$E_{\text{cell}} = E^\ominus_{\text{cell}} - \frac{2RT}{F}\ln\left(\frac{b}{b^\ominus}\right) - \frac{2RT}{F} \times \ln 10 \times -A\left(\frac{b}{b^\ominus}\right)^{1/2}$$

Rearranging gives

$$\overbrace{E_{\text{cell}} + \frac{2RT}{F}\ln\left(\frac{b}{b^{\ominus}}\right)}^{y} = \overbrace{E^{\ominus}_{\text{cell}}}^{\text{intercept}} + \overbrace{\frac{2ART\ln 10}{F}}^{\text{slope}} \times \overbrace{\left(\frac{b}{b^{\ominus}}\right)^{1/2}}^{x}$$

This expression implies that a plot of y against $(b/b^{\ominus})^{1/2}$, where y is given by the expression $E_{\text{cell}} + (2RT/F)\ln(b/b^{\ominus})$, should be a straight line of intercept $E^{\ominus}_{\text{cell}}$ and slope $2ART\ln 10/F$. Recall that $b^{\ominus} = 1\ \text{mol kg}^{-1}$, so in calculating $b/b^{\ominus}$, b must be converted to mol kg^{-1}. The plot is shown in Fig. 6.3.

b/mmol kg^{-1}	E/V	$(b/b^{\ominus})^{1/2}$	y/V
1.6077	0.60080	0.04010	0.27024
3.0769	0.56825	0.05547	0.27104
5.0403	0.54366	0.07100	0.27182
7.6938	0.52267	0.08771	0.27256
10.947	0.50532	0.10463	0.27333

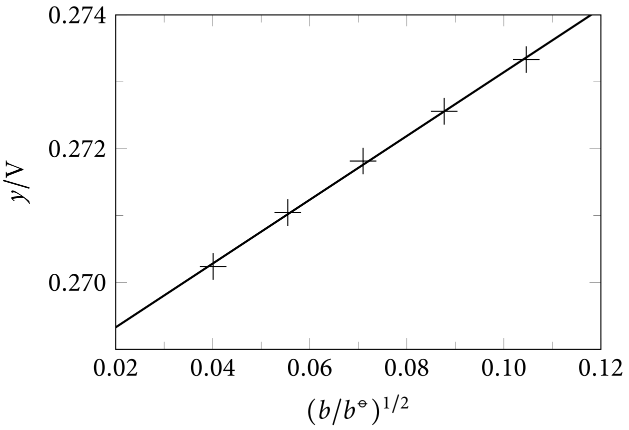


Figure 6.3

The data fall on a reasonable straight line, the equation of which is

$$y/\text{V} = 0.047678 \times (b/b^{\ominus})^{1/2} + 0.26838$$

$E^{\ominus}_{\text{cell}}$ is determined from the intercept as $\boxed{0.26838\ \text{V}}$

The mean activity coefficients are calculated using the equation

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{2RT}{F}\ln\left(\frac{b}{b^{\ominus}}\right) - \frac{2RT}{F}\ln\gamma_{\pm}$$

which was found above. Rearranging for $\ln\gamma_{\pm}$ gives

$$\ln\gamma_{\pm} = \frac{F}{2RT}\left(E^{\ominus}_{\text{cell}} - E_{\text{cell}}\right) - \ln\left(\frac{b}{b^{\ominus}}\right)$$

Using the value of $E^{\ominus}_{\text{cell}}$ obtained above with the values of E_{cell} and b from the data in the question yields the following values for $\ln \gamma_{\pm}$ and $\gamma_{\pm}$:

$b/\text{mmol kg}^{-1}$	E/V	$\ln \gamma_{\pm}$	$\gamma_{\pm}$
1.6077	0.60080	−0.036294	0.9644
3.0769	0.56825	−0.051965	0.9494
5.0403	0.54366	−0.066969	0.9352
7.6938	0.52267	−0.081438	0.9218
10.947	0.50532	−0.096482	0.9080

P6D.6 The standard potential of the AgCl/Ag,Cl$^-$ couple corresponds to the standard potential of a cell in which the right-hand electrode is the AgCl/Ag,Cl$^-$ electrode and the left-hand electrode is the standard hydrogen electrode. The reduction half-reactions for this cell are

$$\begin{array}{ll} \text{R:} & \text{AgCl(s)} + \text{e}^- \rightarrow \text{Ag(s)} + \text{Cl}^-\text{(aq)} \\ \text{L:} & \text{H}^+\text{(aq)} + \text{e}^- \rightarrow \tfrac{1}{2}\text{H}_2\text{(g)} \end{array}$$

The overall cell reaction is

$$\text{AgCl(s)} + \tfrac{1}{2}\text{H}_2\text{(g)} \rightarrow \text{Ag(s)} + \text{Cl}^-\text{(aq)} + \text{H}^+\text{(aq)} \qquad \nu = 1$$

Because $E^{\ominus}(\text{L}) = 0$ by definition, $E^{\ominus}_{\text{cell}} = E^{\ominus}(\text{R}) = E^{\ominus}(\text{AgCl/Ag, Cl}^-)$ for this cell. The given expression for the electrode potential is therefore equal to $E^{\ominus}_{\text{cell}}$.

The first step in the calculation is to obtain values of $\Delta_r G^{\ominus}$, $\Delta_r S^{\ominus}$, and $\Delta_r H^{\ominus}$ for the cell using the given expression for $E^{\ominus}_{\text{cell}}$. These are then used together with values taken from the *Resource section* of $\Delta_f G^{\ominus}$, $\Delta_f H^{\ominus}$, and $S^{\ominus}_{\text{m}}$ for the other species in the cell reaction to obtain the corresponding values for Cl$^-$.

The standard reaction Gibbs energy is related to the standard cell potential according to [6C.3–*221*], $\Delta_r G^{\ominus} = -\nu F E^{\ominus}_{\text{cell}}$. The given expression is for the dimensionless quantity $E^{\ominus}_{\text{cell}}/\text{V}$, so to obtain $E^{\ominus}_{\text{cell}}$ from this it is necessary to multiply the expression by V

$$\begin{aligned} \Delta_r G^{\ominus} &= -\nu F \times [E^{\ominus}_{\text{cell}}/\text{V}] \times \text{V} \\ &= -\nu F \times \Big[0.23659 - 4.8564 \times 10^{-4}(\theta/^{\circ}\text{C}) - 3.4205 \times 10^{-6}(\theta/^{\circ}\text{C})^2 \\ &\qquad + 5.869 \times 10^{-9}(\theta/^{\circ}\text{C})^3\Big] \times \text{V} \end{aligned}$$

The values are required at 298 K, which corresponds to $\theta = (298 - 273.15) = 24.85\ ^{\circ}\text{C}$. The value of $\Delta_r G^{\ominus}$ is therefore:

$$\begin{aligned} \Delta_r G^{\ominus} &= -1 \times (96485\ \text{C mol}^{-1}) \times \Big[0.23659 - 4.8564 \times 10^{-4} \times (24.85) \\ &\qquad - 3.4205 \times 10^{-6} \times (24.85)^2 + 5.869 \times 10^{-9} \times (24.85)^3\Big] \times \text{V} \\ &= -21.4...\ \text{kJ mol}^{-1} \end{aligned}$$

The relationship between $\Delta_r S^\ominus$ and $E^\ominus_{\text{cell}}$ is given by [6C.6–*222*], $\text{d}E^\ominus_{\text{cell}}/\text{d}T = \Delta_r S^\ominus/\nu F$. The expression for $E^\ominus_{\text{cell}}/\text{V}$ is differentiated to give

$$\frac{\text{d}(E^\ominus_{\text{cell}}/\text{V})}{\text{d}(\theta/^\circ\text{C})} = -4.8564\times10^{-4} - 6.841\times10^{-6}(\theta/^\circ\text{C}) + 1.7607\times10^{-8}(\theta/^\circ\text{C})^2$$

To relate this to $\text{d}E^\ominus_{\text{cell}}/\text{d}T$, note that because $\theta/^\circ\text{C} = T/\text{K} - 273.15$, $\text{d}(\theta/^\circ\text{C}) = \text{d}(T/\text{K})$. Noting further that $\text{d}(T/\text{K}) = \text{d}T/\text{K}$ and that $\text{d}(E^\ominus_{\text{cell}}/\text{V}) = \text{d}E^\ominus_{\text{cell}}/\text{V}$ gives

$$\frac{\text{d}(E^\ominus_{\text{cell}}/\text{V})}{\text{d}(\theta/^\circ\text{C})} = \frac{\text{d}E^\ominus_{\text{cell}}/\text{V}}{\text{d}T/\text{K}} = \frac{\text{K}}{\text{V}}\frac{\text{d}E^\ominus_{\text{cell}}}{\text{d}T} \quad \text{hence} \quad \frac{\text{d}E^\ominus_{\text{cell}}}{\text{d}T} = \frac{\text{d}(E^\ominus_{\text{cell}}/\text{V})}{\text{d}(\theta/^\circ\text{C})}\times\frac{\text{V}}{\text{K}}$$

Substituting this into [6C.6–*222*], $\text{d}E^\ominus_{\text{cell}}/\text{d}T = \Delta_r S^\ominus/\nu F$, and rearranging for $\Delta_r S^\ominus$ gives

$$\begin{aligned}\Delta_r S^\ominus &= \nu F\times\frac{\text{d}(E^\ominus_{\text{cell}}/\text{V})}{\text{d}(\theta/^\circ\text{C})}\times\frac{\text{V}}{\text{K}}\\ &= \nu F\times\left[-4.8564\times10^{-4} - 6.841\times10^{-6}(\theta/^\circ\text{C}) + 1.7607\times10^{-8}(\theta/^\circ\text{C})^2\right]\times\frac{\text{V}}{\text{K}}\\ &= 1\times(96485\,\text{C mol}^{-1})\times\Big[-4.8564\times10^{-4} - 6.841\times10^{-6}\times(24.85)\\ &\qquad + 1.7607\times10^{-8}\times(24.85)^2\Big]\times(\text{V/K}) = -62.2...\,\text{J K}^{-1}\,\text{mol}^{-1}\end{aligned}$$

Finally $\Delta_r H^\ominus$ is calculated from [3D.9–*100*], $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$

$$\begin{aligned}\Delta_r H^\ominus &= \Delta_r G^\ominus + T\Delta_r S^\ominus\\ &= (-21.4...\times10^3\,\text{J mol}^{-1}) + (298\,\text{K})\times(-62.2...\,\text{J K}^{-1}\,\text{mol}^{-1})\\ &= -40.0...\,\text{kJ mol}^{-1}\end{aligned}$$

The overall cell reaction is

$$\text{AgCl(s)} + \tfrac{1}{2}\text{H}_2\text{(g)} \rightarrow \text{Ag(s)} + \text{Cl}^-\text{(aq)} + \text{H}^+\text{(aq)}$$

These values of $\Delta_r G^\ominus$, $\Delta_r S^\ominus$, and $\Delta_r H^\ominus$ are used with data from the *Resource section* to calculate $\Delta_f G^\ominus(\text{Cl}^-)$, $\Delta_f H^\ominus(\text{Cl}^-)$, and $S^\ominus_m(\text{Cl}^-)$

Noting from Section 3D.2(a) on page 101 that $\Delta_f G^\ominus(\text{H}^+,\text{aq}) = 0$, and also that elements in their reference states have $\Delta_f G^\ominus = 0$, the standard reaction Gibbs energy for the reaction is given by

$$\Delta_r G^\ominus = \Delta_f G^\ominus(\text{Cl}^-,\text{aq}) - \Delta_f G^\ominus(\text{AgCl},\text{s})$$

$$\begin{aligned}\text{Hence}\quad \Delta_f G^\ominus(\text{Cl}^-,\text{aq}) &= \Delta_r G^\ominus + \Delta_f G^\ominus(\text{AgCl},\text{s})\\ &= (-21.4...\,\text{kJ mol}^{-1}) + (-109.79\,\text{kJ mol}^{-1}) = \boxed{-131.3\,\text{kJ mol}^{-1}}\end{aligned}$$

Similarly, noting from Section 2C.2 on page 51 that $\Delta_f H^\ominus(\text{H}^+,\text{aq}) = 0$, and that elements in their reference states have $\Delta_f H^\ominus = 0$, the standard reaction enthalpy is

$$\Delta_r H^\ominus = \Delta_f H^\ominus(\text{Cl}^-,\text{aq}) - \Delta_f H^\ominus(\text{AgCl},\text{s})$$

$$\text{Hence}\quad \Delta_f H^\ominus(\mathrm{Cl^-,aq}) = \Delta_r H^\ominus + \Delta_f H^\ominus(\mathrm{AgCl,s})$$
$$= (-40.0...\ \mathrm{kJ\,mol^{-1}}) + (-127.07\ \mathrm{kJ\,mol^{-1}}) = \boxed{-167.1\ \mathrm{kJ\,mol^{-1}}}$$

Finally, noting from Section 3C.2(b) on page 94 that $S_m^\ominus(\mathrm{H^+,aq}) = 0$, the standard reaction entropy is

$$\Delta_r S^\ominus = S_m^\ominus(\mathrm{Ag,s}) + S_m^\ominus(\mathrm{Cl^-,aq}) - S_m^\ominus(\mathrm{AgCl,s}) - \tfrac{1}{2}S_m^\ominus(\mathrm{H_2,g})$$

Hence

$$\begin{aligned} S_m^\ominus(\mathrm{Cl^-,aq}) &= \Delta_r S^\ominus + S_m^\ominus(\mathrm{AgCl,s}) + \tfrac{1}{2}S_m^\ominus(\mathrm{H_2,g}) - S_m^\ominus(\mathrm{Ag,s}) \\ &= (-62.2...\ \mathrm{J\,K^{-1}\,mol^{-1}}) + (96.2\ \mathrm{J\,K^{-1}\,mol^{-1}}) \\ &\quad + \tfrac{1}{2} \times (130.684\ \mathrm{J\,K^{-1}\,mol^{-1}}) - (42.55\ \mathrm{J\,K^{-1}\,mol^{-1}}) \\ &= \boxed{56.8\ \mathrm{J\,K^{-1}\,mol^{-1}}} \end{aligned}$$

Solutions to integrated activities

I6.2 (a) The ionic strength is given by [5F.29–*188*], $I = \frac{1}{2}\left(b_+z_+^2 + b_-z_-^2\right)/b^\ominus$, where z_+ and z_- are the charges on the ions. For the $\mathrm{CuSO_4}$ compartment, $z_+ = 2$, $z_- = -2$, and $b_+ = b_- = b_{\mathrm{CuSO_4}}$:

$$I = \tfrac{1}{2}\left(b_+z_+^2 + b_-z_-^2\right)/b^\ominus = \tfrac{1}{2}\left[b_{\mathrm{CuSO_4}} \times (+2)^2 + b_{\mathrm{CuSO_4}} \times (-2)^2\right]/b^\ominus$$
$$= 4(b_{\mathrm{CuSO_4}}/b^\ominus) = 4 \times \frac{1.00 \times 10^{-3}\ \mathrm{mol\,kg^{-1}}}{1\ \mathrm{mol\,kg^{-1}}} = \boxed{4.00 \times 10^{-3}}$$

Because the charges are the same for $\mathrm{ZnSO_4}$ it follows that $I = 4(b_{\mathrm{ZnSO_4}}/b^\ominus) = \boxed{1.20 \times 10^{-2}}$.

(b) According to the Debye–Hückel limiting law (Section 5F.4(b) on page 187), the mean activity coefficient is given by [5F.27–*188*], $\log \gamma_\pm = -A|z_+z_-|I^{1/2}$, where $A = 0.509$ for aqueous solutions at 25 °C. For the $\mathrm{CuSO_4}$ solution

$$\log \gamma_{\pm,\mathrm{CuSO_4}} = -(0.509) \times |(2) \times (-2)| \times (4.00 \times 10^{-3})^{1/2} = -0.128...$$

Hence $\gamma_{\pm,\mathrm{CuSO_4}} = 10^{-0.128...} = 0.743... = \boxed{0.743}$. For the $\mathrm{ZnSO_4}$ solution

$$\log \gamma_{\pm,\mathrm{ZnSO_4}} = -(0.509) \times |(2) \times (-2)| \times (1.20 \times 10^{-2})^{1/2} = -0.223...$$

Hence $\gamma_{\pm,\mathrm{ZnSO_4}} = 10^{-0.223...} = 0.598... = \boxed{0.598}$.

(c) Noting that pure solids have $a_J = 1$ and writing the activities of ions in solution as $a = \gamma_\pm(b/b^\ominus)$, the reaction quotient for the reaction

$$\mathrm{Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)}$$

is given by

$$Q = \frac{a_{\mathrm{Zn^{2+}}}}{a_{\mathrm{Cu^{2+}}}} = \frac{\gamma_{\pm,\mathrm{ZnSO_4}}(b_{\mathrm{Zn^{2+}}}/b^\ominus)}{\gamma_{\pm,\mathrm{CuSO_4}}(b_{\mathrm{Cu^{2+}}}/b^\ominus)} = \frac{\gamma_{\pm,\mathrm{ZnSO_4}}}{\gamma_{\pm,\mathrm{CuSO_4}}} \times \frac{b_{\mathrm{Zn^{2+}}}}{b_{\mathrm{Cu^{2+}}}}$$
$$= \frac{0.598...}{0.743...} \times \frac{3.00 \times 10^{-3}\ \mathrm{mol\,kg^{-1}}}{1.00 \times 10^{-3}\ \mathrm{mol\,kg^{-1}}} = 2.41... = \boxed{2.41}$$

(d) The reaction is thought of as being composed of the reduction half-reactions

$$\begin{aligned} &\text{R:} \quad Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \\ &\text{L:} \quad Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \end{aligned}$$

which show that $\nu = 2$ for this reaction. The standard cell potential is calculated from $\Delta_r G^\ominus$ using [6C.3–*221*], $E^\ominus_{\text{cell}} = -\Delta_r G^\ominus/\nu F$:

$$E^\ominus_{\text{cell}} = -\frac{\Delta_r G^\ominus}{\nu F} = -\frac{-212.7 \times 10^3 \text{ J mol}^{-1}}{2 \times (96485 \text{ C mol}^{-1})} = \boxed{+1.102 \text{ V}}$$

Note that $1 \text{ J C}^{-1} = 1 \text{ V}$.

(e) The cell potential is given by the Nernst equation [6C.4–*221*]:

$$\begin{aligned} E_{\text{cell}} &= E^\ominus_{\text{cell}} - \frac{RT}{\nu F} \ln Q \\ &= (+1.102 \text{ V}) - \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times ([25 + 273.15] \text{ K})}{2 \times (96485 \text{ C mol}^{-1})} \times \ln(2.41...) \\ &= \boxed{+1.09 \text{ V}} \end{aligned}$$

I6.4 The reaction for the autoprotolysis of liquid water is

$$H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$$

This reaction is split into the reduction half-reactions

$$\begin{aligned} &\text{R:} \quad H_2O(l) + e^- \rightarrow \tfrac{1}{2}H_2(g) + OH^-(aq) \\ &\text{L:} \quad H^+(aq) + e^- \rightarrow \tfrac{1}{2}H_2(g) \end{aligned}$$

Because the standard electrode potential for the left-hand half-reaction is zero by definition, the standard cell potential for this cell is equal to the standard electrode potential of the $H_2O/H_2,OH^-$ electrode. The equilibrium constant K_w for the cell reaction is then given by [6C.5–*221*], $E^\ominus_{\text{cell}} = (RT/\nu F)\ln K$. Rearranging for $\ln K$ and using $\nu = 1$, $K = K_w$, and $E^\ominus_{\text{cell}} = E^\ominus(H_2O/H_2, OH^-)$ gives

$$\ln K_w = \frac{F}{RT} \times E^\ominus(H_2O/H_2, OH^-)$$

Noting from inside the front cover that $\ln x = \ln 10 \times \log x$, and also that $\mathrm{p}K_w = -\log K_w$ allows the above equation to be rewritten as

$$\mathrm{p}K_w = -\log K_w = -\frac{\ln K_w}{\ln 10} = -\frac{F}{RT \ln 10} \times E^\ominus(H_2O/H_2, OH^-)$$

The task is therefore to find $E^\ominus(H_2O/H_2, OH^-)$ from the given data. To do this, the specified cell is written in terms of its reduction half-reactions

$$\begin{aligned} &\text{R:} \quad AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq) \\ &\text{L:} \quad H_2O(l) + e^- \rightarrow \tfrac{1}{2}H_2(g) + OH^-(aq) \end{aligned}$$

The cell reaction, which has $\nu = 1$, is

$$\mathrm{AgCl(s)} + \tfrac{1}{2}\mathrm{H_2(g)} + \mathrm{OH^-(aq)} \rightarrow \mathrm{Ag(s)} + \mathrm{Cl^-(aq)}$$

Noting that $a_J = 1$ for pure solids, and that in this cell $a_{H_2} = 1$ because the hydrogen is at standard pressure, the Nernst equation for the cell is

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{\nu F}\ln Q = E^{\ominus}_{\text{cell}} - \frac{RT}{F}\ln\left(\frac{a_{\text{Cl}^-}}{a_{\text{OH}^-}}\right)$$

Writing the activities as $a = \gamma_{\pm}(b/b^{\ominus})$, the Nernst equation becomes

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{F}\ln\left(\frac{\gamma_{\pm}(b_{\text{Cl}^-}/b^{\ominus})}{\gamma_{\pm}(b_{\text{OH}^-}/b^{\ominus})}\right) = E^{\ominus}_{\text{cell}} - \frac{RT}{F}\ln\left(\frac{b_{\text{Cl}^-}}{b_{\text{OH}^-}}\right)$$

The standard cell potential is split into contributions from the two electrodes using [6D.3–*224*], $E^{\ominus}_{\text{cell}} = E^{\ominus}(\text{R}) - E^{\ominus}(\text{L})$

$$E_{\text{cell}} = E^{\ominus}(\text{AgCl/Ag, Cl}^-) - E^{\ominus}(\text{H}_2\text{O/H}_2, \text{OH}^-) - \frac{RT}{F}\ln\left(\frac{b_{\text{Cl}^-}}{b_{\text{OH}^-}}\right)$$

Hence

$$E^{\ominus}(\text{H}_2\text{O/H}_2, \text{OH}^-) = E^{\ominus}(\text{AgCl/Ag, Cl}^-) - E_{\text{cell}} - \frac{RT}{F}\ln\left(\frac{b_{\text{Cl}^-}}{b_{\text{OH}^-}}\right)$$

This equation is used with $b_{\text{Cl}^-} = 0.01125\ \text{mol kg}^{-1}$, $b_{\text{OH}^-} = 0.0100\ \text{mol kg}^{-1}$, and the values of E_{cell} and $E^{\ominus}(\text{AgCl/Ag, Cl}^-)$ to calculate $E^{\ominus}(\text{H}_2\text{O/H}_2, \text{OH}^-)$ at each temperature. The relation derived earlier

$$\text{p}K_{\text{w}} = -(F/RT\ln 10)E^{\ominus}(\text{H}_2\text{O/H}_2, \text{OH}^-)$$

is then used to calculate $\text{p}K_{\text{w}}$. The results are given in the following table.

$\theta/°\text{C}$	T/K	E_{cell}/V	$E^{\ominus}(\text{AgCl/Ag, Cl}^-)/\text{V}$	$E^{\ominus}(\text{H}_2\text{O/H}_2, \text{OH}^-)/\text{V}$	$\text{p}K_{\text{w}}$
20.0	293.15	1.047 74	0.225 02	−0.825 70	14.20
25.0	298.15	1.048 64	0.222 30	−0.829 37	14.02
30.0	303.15	1.049 42	0.219 59	−0.832 91	13.85

To find $\Delta_{\text{r}}S^{\ominus}$ for the autoprotolysis, the relationship between $E^{\ominus}_{\text{cell}}$ and temperature [6C.6–*222*], $\text{d}E^{\ominus}_{\text{cell}}/\text{d}T = \Delta_{\text{r}}S^{\ominus}/\nu F$ is used. If $\Delta_{\text{r}}S^{\ominus}$ is constant over the temperature range this equation implies that a plot of $E^{\ominus}_{\text{cell}}$ against T should be a straight line of slope $\Delta_{\text{r}}S^{\ominus}/\nu F$. In this case $E^{\ominus}_{\text{cell}}$ for the autoprotolysis reaction is equal to $E^{\ominus}(\text{H}_2\text{O/H}_2, \text{OH}^-)$ as explained earlier. The plot is shown in Fig. 6.4.

The data fall on a good straight line, the equation of which is

$$E^{\ominus}(\text{H}_2\text{O/H}_2, \text{OH}^-)/\text{V} = -7.229\times 10^{-4}\times(T/\text{K}) - 0.6137$$

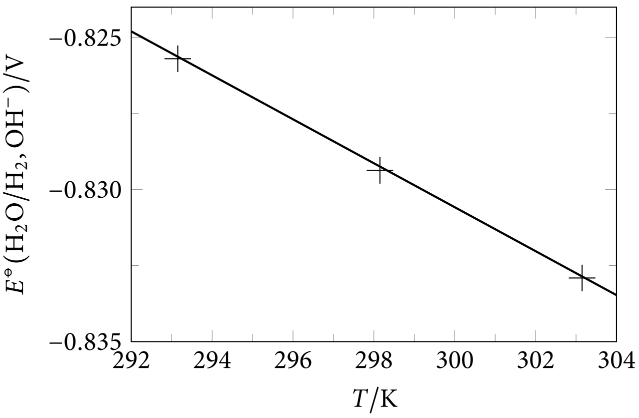


Figure 6.4

$\Delta_r S^\ominus/\nu F$ is determined from the slope

$$\begin{aligned}\Delta_r S^\ominus &= \nu F \times slope \times \mathrm{V\,K^{-1}}\\ &= 1 \times (96485\,\mathrm{C\,mol^{-1}}) \times (-7.229\times10^{-4}\,\mathrm{V\,K^{-1}})\\ &= -68.5...\,\mathrm{J\,K^{-1}\,mol^{-1}} = \boxed{-68.6\,\mathrm{J\,K^{-1}\,mol^{-1}}}\end{aligned}$$

The standard enthalpy change for the autoprotolysis is calculated from [3D.9–*100*], $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$, with $\Delta_r G^\ominus$ being given by [6C.2–*217*], $\Delta_r G^\ominus = -\nu F E^\ominus_{\text{cell}}$. In this case $E^\ominus_{\text{cell}} = E^\ominus(H_2O/H_2, OH^-)$ and $\nu = 1$. Using the value for 25.0 °C gives

$$\begin{aligned}\Delta_r H^\ominus &= \Delta_r G^\ominus + T\Delta_r S^\ominus = -\nu F E^\ominus(H_2O/H_2, OH^-) + T\Delta_r S^\ominus\\ &= -1 \times (96485\,\mathrm{C\,mol^{-1}}) \times (-0.829...\mathrm{V}) + (298.15\,\mathrm{K}) \times (-68.5...\,\mathrm{J\,K^{-1}\,mol^{-1}})\\ &= \boxed{+59.6\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

I6.6 The reduction half-reactions, and the overall cell reaction, for the specified cell (R – L) are:

$$\begin{array}{rl} \text{R:} & AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)\\ \text{L:} & H^+(aq) + e^- \rightarrow \tfrac{1}{2}H_2(g)\\ \hline \text{R – L:} & AgCl(s) + \tfrac{1}{2}H_2(g) \rightarrow Ag(s) + Cl^-(aq) + H^+(aq) \quad \nu = 1\end{array}$$

Noting that $a_J = 1$ for pure solids and that in this cell $a_{H_2} = 1$ because the hydrogen is at standard pressure, the Nernst equation is

$$E_{\text{cell}} = E^\ominus_{\text{cell}} - \frac{RT}{F}\ln(a_{Cl^-}a_{H^+})$$

In addition, the base B and its conjugate acid are in equilibrium:

$$BH^+(aq) \rightleftharpoons B(aq) + H^+(aq) \qquad K_a = \frac{a_B a_{H^+}}{a_{BH^+}}$$

The expression for K_a is rearranged to give $a_{\text{H}^+} = K_\text{a}a_{\text{BH}^+}/a_\text{B}$ and this is substituted into the Nernst equation to give

$$E_\text{cell} = E^{\ominus}_\text{cell} - \frac{RT}{F}\ln\left(a_{\text{Cl}^-}a_{\text{H}^+}\right) = E^{\ominus}_\text{cell} - \frac{RT}{F}\ln\left(\frac{a_{\text{Cl}^-}a_{\text{BH}^+}K_\text{a}}{a_\text{B}}\right)$$

Replacing activities by $a_\text{J} = \gamma_\text{J}(b_\text{J}/b^{\ominus})$ [5F.14–*185*] gives

$$E_\text{cell} = E^{\ominus}_\text{cell} - \frac{RT}{F}\ln\left(\frac{(\gamma_{\text{Cl}^-}b_{\text{Cl}^-}/b^{\ominus})(\gamma_{\text{BH}^+}b_{\text{BH}^+}/b^{\ominus})K_\text{a}}{(\gamma_\text{B}b_\text{B}/b^{\ominus})}\right)$$

In this case $b_{\text{Cl}^-} = b_{\text{BH}^+} = b_\text{B}$ so the Nernst equation simplifies to

$$E_\text{cell} = E^{\ominus}_\text{cell} - \frac{RT}{F}\ln\left(\frac{\gamma_{\text{Cl}^-}\gamma_{\text{BH}^+}}{\gamma_\text{B}}\times\frac{bK_\text{a}}{b^{\ominus}}\right) = E^{\ominus}_\text{cell} - \frac{RT}{F}\ln\left(\frac{\gamma_\pm^2 bK_\text{a}}{b^{\ominus}}\right)$$

where the mean activity coefficient of the BH^+ and Cl^- ions is given by [5F.22–*187*], $\gamma_\pm = (\gamma_{\text{Cl}^-}\gamma_{\text{BH}^+})^{1/2}$ and the neutral base B is assumed to be an ideal solute so that $\gamma_\text{B} = 1$. Noting from inside the front cover that $\ln x = \ln 10 \log x$, the Nernst equation becomes

$$\begin{aligned} E_\text{cell} &= E^{\ominus}_\text{cell} - \frac{RT\ln 10}{F}\log\left(\frac{\gamma_\pm^2 bK_\text{a}}{b^{\ominus}}\right) \\ &= E^{\ominus}_\text{cell} - \frac{RT\ln 10}{F}\left(2\log\gamma_\pm + \log\left(\frac{b}{b^{\ominus}}\right) - \text{p}K_\text{a}\right) \end{aligned}$$

where $\text{p}K_\text{a} = -\log K_\text{a}$ has been used. Next the Davies equation [5F.30b–*189*], $\log\gamma_\pm = -A|z_+z_-|I^{1/2}/(1+BI^{1/2})+CI$, is used to substitute for $\log\gamma_\pm$. The ionic strength I is given by [5F.28–*188*], $I = \frac{1}{2}\sum_i z_i^2(b_i/b^{\ominus})$, where z_i is the charge on ion species i and the sum extends over all the ions present in the solution. In this case, $b_{\text{BH}^+} = b_{\text{Cl}^-} = b$, and b_{H^+} is neglected because it will be much smaller on account of the equilibrium involving the base B. Therefore the ionic strength is

$$I = \tfrac{1}{2}\left(z_{\text{BH}^+}^2 b + z_{\text{Cl}^-}^2 b\right)/b^{\ominus} = \tfrac{1}{2}\left(1^2\times b + (-1)^2\times b\right)/b^{\ominus} = b/b^{\ominus}$$

and therefore

$$\log\gamma_\pm = -\frac{A|z_{\text{BH}^+}\times z_{\text{Cl}^-}|I^{1/2}}{1+BI^{1/2}} + CI = -\frac{A(b/b^{\ominus})^{1/2}}{1+B(b/b^{\ominus})^{1/2}} + C\left(\frac{b}{b^{\ominus}}\right)$$

Substitution of this expression into the Nernst equation derived above gives

$$E_\text{cell} = E^{\ominus}_\text{cell} - \frac{RT\ln 10}{F}\left(2\left[-\frac{A(b/b^{\ominus})^{1/2}}{1+B(b/b^{\ominus})^{1/2}} + C\left(\frac{b}{b^{\ominus}}\right)\right] + \log\left(\frac{b}{b^{\ominus}}\right) - \text{p}K_\text{a}\right)$$

which rearranges to

$$\underbrace{\frac{F(E_\text{cell}-E^{\ominus}_\text{cell})}{RT\ln 10}}_{y} = \frac{2A(b/b^{\ominus})^{1/2}}{1+B(b/b^{\ominus})^{1/2}} - 2C\left(\frac{b}{b^{\ominus}}\right) - \log\left(\frac{b}{b^{\ominus}}\right) + \text{p}K_\text{a}$$

Defining $(b/b^{\ominus})^{1/2}$ as x and the left-hand side as y, and introducing $A = 0.5091$ gives

$$y = \frac{1.0182x}{1+Bx} - 2Cx^2 - 2\log x + \mathrm{p}K_a$$

which is fitted to the data using mathematical software to give the following values for the parameters: $\boxed{B = 2.54}$, $\boxed{C = -0.204}$, and $\boxed{\mathrm{p}K_a = 6.74}$. These values have been used to draw the line on the graph shown in Fig. 6.5.

$b/\mathrm{mmol\,kg^{-1}}$	$E_{\mathrm{cell}}/\mathrm{V}$	$(b/b^{\ominus})^{1/2}$	y
0.01	0.744 52	0.100	8.823 73
0.02	0.728 53	0.141	8.553 44
0.03	0.719 28	0.173	8.397 08
0.04	0.713 14	0.200	8.293 30
0.05	0.708 09	0.224	8.207 94
0.06	0.703 80	0.245	8.135 42
0.07	0.700 59	0.265	8.081 16
0.08	0.697 90	0.283	8.035 69
0.09	0.695 71	0.300	7.998 67
0.10	0.693 38	0.316	7.959 29

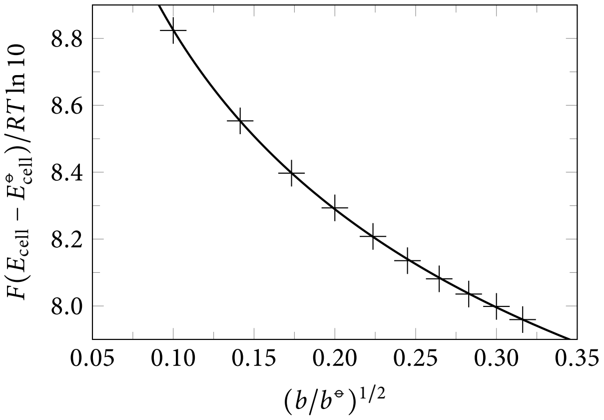


Figure 6.5

I6.8 From *Impact* 9 the reaction for the hydrolysis of ATP to ADP and inorganic phosphate $\mathrm{P_i^-}$ is

$$\mathrm{ATP(aq) + H_2O(l) \rightarrow ADP(aq) + P_i^-(aq) + H_3O^+(aq)}$$

Under biological standard conditions, that is, pH = 7, the standard reaction Gibbs energy at 37 °C is given in *Impact* 9 as $\Delta_r G^{\oplus} = -31\ \mathrm{kJ\,mol^{-1}}$.

In an environment in which pH = 7.0 and the ATP, ADP and P_i^- concentrations are all 1.0 mmol dm^{-3}, the reaction Gibbs energy is given by [6A.11–*207*],

$$\Delta_r G = \Delta_r G^{\oplus} + RT \ln Q^{\oplus}$$

where $Q^{\oplus}$ is the reaction quotient calculated relative to the biological standard state. Because pH is defined by pH $= -\log a_{H_3O^+}$, pH 7 corresponds to $a_{H_3O^+} = 10^{-7}$ so that when computing $Q^{\oplus}$ the activity of H_3O^+ is measured relative to an activity of 10^{-7} rather than an activity of 1 as is usually the case. In practice this means that $a_{H_3O^+}$ is replaced by $(a_{H_3O^+}/10^{-7})$ in the expression for $Q^{\oplus}$.

For the ATP hydrolysis reaction this gives

$$\Delta_r G = \Delta_r G^{\oplus} + RT \ln\left(\frac{a_{\mathrm{ADP}} \times a_{P_i^-} \times (a_{H_3O^+}/10^{-7})}{a_{\mathrm{ATP}} \times a_{H_2O}}\right)$$

Water is a pure liquid so $a_{H_2O} = 1$, and for the environment specified in the question, pH = 7 so $a_{H_3O^+} = 10^{-7}$. For the other species activities are approximated by concentrations according to $a_J = [J]/c^{\ominus}$ where $c^{\ominus} = 1$ mol dm^{-3}.

$$\begin{aligned}
\Delta_r G &= \Delta_r G^{\oplus} + RT \ln\left(\frac{([\mathrm{ADP}]/c^{\ominus})([P_i^-]/c^{\ominus})(10^{-7}/10^{-7})}{([\mathrm{ATP}]/c^{\ominus})}\right) \\
&= \Delta_r G^{\oplus} + RT \ln\left(\frac{[\mathrm{ADP}][P_i^-]}{[\mathrm{ATP}]c^{\ominus}}\right) \\
&= (-31 \times 10^3\ \mathrm{J\,mol^{-1}}) + (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times ([37 + 273.15]\ \mathrm{K}) \\
&\quad \times \ln\left(\frac{(1.0 \times 10^{-3}\ \mathrm{mol\,dm^{-3}}) \times (1.0 \times 10^{-3}\ \mathrm{mol\,dm^{-3}})}{(1.0 \times 10^{-3}\ \mathrm{mol\,dm^{-3}}) \times (1\ \mathrm{mol\,dm^{-3}})}\right) \\
&= \boxed{-49\ \mathrm{kJ\,mol^{-1}}}
\end{aligned}$$

This is to be compared with the value under standard biological conditions, which is −31 kJ mol^{-1}, and also with the value under the usual standard conditions. The difference between $\Delta_r G^{\ominus}$ and $\Delta_r G^{\oplus}$ is that the former has $a_{H^+} = 1$ and the latter has $a_{H^+} = 10^{-7}$. Given that

$$\Delta_r G = \Delta_r G^{\ominus} + RT \ln\left(\frac{a_{\mathrm{ADP}} a_{P_i} a_{H_3O^+}}{a_{\mathrm{ATP}} a_{H_2O}}\right)$$

setting all the activities to 1 except for that for H_3O^+ which is set to 10^{-7} gives $\Delta_r G^{\oplus}$

$$\Delta_r G^{\oplus} = \Delta_r G^{\ominus} + RT \ln 10^{-7}$$

hence

$$\begin{aligned}
\Delta_r G^{\ominus} &= \Delta_r G^{\oplus} - RT \ln 10^{-7} \\
&= (-31 \times 10^3\ \mathrm{J\,mol^{-1}}) - (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times ([37 + 273.15]\ \mathrm{K}) \times \ln 10^{-7} \\
&= +11\ \mathrm{kJ\,mol^{-1}}
\end{aligned}$$

I6.10 A bacterium could potentially oxidise ethanol to ethanal, ethanoic acid, or $CO_2(g)$, while nitrate, $NO_3^-(aq)$, could potentially be reduced to a number of possible species including $NO_2(g)$, $NO_2^-(aq)$, $NO(g)$, $N_2(g)$, or $NH_4^+(aq)$. Assuming complete oxidation of ethanol to CO_2 and complete reduction of NO_3^- to NH_4^+ the reduction half-reactions are

$$\begin{aligned}&\text{R:}\quad NO_3^-(aq) + 10H^+ + 8e^- \rightarrow NH_4^+(aq) + 3H_2O(l)\\&\text{L:}\quad 2CO_2(g) + 12H^+ + 12e^- \rightarrow CH_3CH_2OH(aq) + 3H_2O(l)\end{aligned}$$

The right-hand half reaction is multiplied by three and the left-hand half reaction by two in order that both involve the same number of electrons. The overall reaction is

$$2CH_3CH_2OH(aq) + 3NO_3^-(aq) + 6H^+(aq) \rightarrow 4CO_2(g) + 3NH_4^+(aq) + 3H_2O(l)$$

The data in the *Resource section* is used to calculate $\Delta_r G^\ominus$ for this reaction:

$$\begin{aligned}\Delta_r G^\ominus &= 4\Delta_f G^\ominus(CO_2, g) + 3\Delta_f G^\ominus(NH_4^+, aq) + 3\Delta_f G^\ominus(H_2O, l)\\&\qquad - 2\Delta_f G^\ominus(CH_3CH_2OH, aq) - 3\Delta_f G^\ominus(NO_3^-, aq) - 6\Delta_f G^\ominus(H^+, aq)\\&= 4 \times (-394.36\ \text{J mol}^{-1}) + 3 \times (-79.31\ \text{J mol}^{-1}) + 3 \times (-237.13\ \text{J mol}^{-1})\\&\qquad - 2 \times (-174.78\ \text{J mol}^{-1}) - 3 \times (-108.74\ \text{J mol}^{-1}) = \boxed{-1851\ \text{kJ mol}^{-1}}\end{aligned}$$

The negative value of $\Delta_r G^\ominus$ indicates that the reaction is exergonic, so $\boxed{\text{yes}}$, a bacterium could evolve to use this reaction to drive endergonic processes such as the formation of ATP for use in cellular processes.

The calculation is valid under standard conditions, which includes $a_{H^+} = 1$ (pH = 0). As explained in *Impact* 9 on the website of this text, pH = 0 is not normally appropriate for biological conditions so it is common to adopt the biological standard state in which pH = 7.0. The reaction Gibbs energy for the oxidation of ethanol by nitrate under standard biological conditions is calculated by using the appropriate value of a_{H^+} in [6A.11–*207*], $\Delta_r G = \Delta_r G^\ominus + RT\ln Q$, leaving all other species with $a_J = 1$. The reaction consumes six moles of H^+ so under standard biological conditions $Q = 1/a_{H^+}^6$. Noting from inside the front cover that $\ln x = \ln 10 \log x$, and also that $\text{pH} = -\log a_{H^+}$, and assuming $T = 298$ K, gives

$$\begin{aligned}\Delta_r G &= \Delta_r G^\ominus + RT\ln Q = \Delta_r G^\ominus + RT\ln\left(\frac{1}{a_{H^+}^6}\right)\\&= \Delta_r G^\ominus - 6RT\ln 10\log(a_{H^+}) = \Delta_r G^\ominus + 6RT\ln 10\times\text{pH}\\&= (-1.85... \times 10^6\ \text{J mol}^{-1}) + 6\times(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(298\ \text{K})\times\ln 10\times 7\\&= -1611\ \text{kJ mol}^{-1}\end{aligned}$$

Thus the reaction remains exergonic under standard biological conditions.

I6.12 (a) The standard reaction enthalpy is found using the van 't Hoff equation [6B.2–*214*]:

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta_r H^\ominus}{RT^2} \quad \text{which can also be written} \quad -\frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)} = \frac{\Delta_r H^\ominus}{R}$$

The second form implies that a graph of $-\ln K$ against $1/T$ should be a straight line of slope $\Delta_r H^\ominus/R$, from which $\Delta_r H^\ominus$ can be determined. The value of $\Delta_r S^\ominus$ is found by combining $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$ [3D.9–*100*] and $\Delta_r G^\ominus = -RT\ln K$ [6A.15–*208*]. Equating these expressions for $\Delta_r G^\ominus$ gives

$$-RT\ln K = \Delta_r H^\ominus - T\Delta_r S^\ominus \quad \text{hence} \quad -\ln K = \frac{\Delta_r H^\ominus}{R}\frac{1}{T} - \frac{\Delta_r S^\ominus}{R}$$

Assuming that $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ do not very significantly over the temperature range of interest this equation implies that a plot of $-\ln K$ against $1/T$ should be a straight line of intercept $-\Delta_r S^\ominus/R$, from which $\Delta_r S^\ominus$ can be determined; such a plot is shown in Fig. 6.6. The plot will have a slope of $\Delta_r H^\ominus/R$, as already deduced above.

T/K	K	$1/(T/\mathrm{K})$	$-\ln K$
233	4.13×10^{8}	0.004 29	−19.8
248	5.00×10^{7}	0.004 03	−17.7
258	1.45×10^{7}	0.003 88	−16.5
268	5.37×10^{6}	0.003 73	−15.5
273	3.20×10^{6}	0.003 66	−15.0
280	9.62×10^{5}	0.003 57	−13.8
288	4.28×10^{5}	0.003 47	−13.0
295	1.67×10^{5}	0.003 39	−12.0
303	6.02×10^{4}	0.003 30	−11.0

The data fall on a reasonable straight line, the equation of which is

$$-\ln K = -8\,787 \times 1/(T/K) + 17.62$$

$\Delta_r H^\ominus/R$ is determined from the slope

$$\begin{aligned}\Delta_r H^\ominus &= R \times (\mathit{slope} \times \mathrm{K}) = (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (-8787\ \mathrm{K})\\ &= -73.0...\ \mathrm{kJ\,mol^{-1}} = \boxed{-73.1\ \mathrm{kJ\,mol^{-1}}}\end{aligned}$$

$-\Delta_r S^\ominus/R$ is determined from the intercept

$$\begin{aligned}\Delta_r S^\ominus &= -R \times \mathit{intercept} = -(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (+17.62)\\ &= -1.46... \times 10^2\ \mathrm{J\,K^{-1}\,mol^{-1}} = \boxed{-147\ \mathrm{J\,K^{-1}\,mol^{-1}}}\end{aligned}$$

(b) The standard reaction enthalpy for the reaction $2\mathrm{ClO(g)} \rightarrow \mathrm{(ClO)_2(g)}$ is expressed in terms of standard enthalpies of formation

$$\Delta_r H^\ominus = \Delta_f H^\ominus[(\mathrm{ClO})_2, \mathrm{g}] - 2\Delta_f H^\ominus(\mathrm{ClO}, \mathrm{g})$$

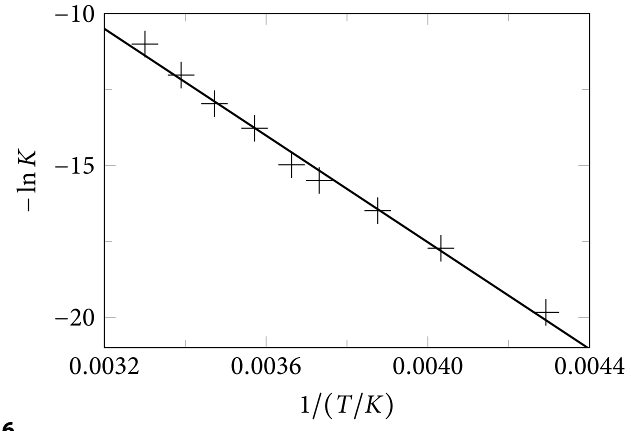


Figure 6.6

Hence

$$\begin{aligned}\Delta_f H^\ominus[(\mathrm{ClO})_2,\mathrm{g}] &= \Delta_r H^\ominus + 2\Delta_f H^\ominus(\mathrm{ClO},\mathrm{g})\\ &= (-73.0...\ \mathrm{kJ\,mol^{-1}}) + 2\times(+101.8\ \mathrm{kJ\,mol^{-1}})\\ &= \boxed{+131\ \mathrm{kJ\,mol^{-1}}}\end{aligned}$$

Similarly

$$\Delta_r S^\ominus = S_m^\ominus[(\mathrm{ClO})_2,\mathrm{g}] - 2S_m^\ominus(\mathrm{ClO},\mathrm{g})$$

Hence

$$\begin{aligned}S_m^\ominus[(\mathrm{ClO})_2,\mathrm{g}] &= \Delta_r S^\ominus + 2S_m^\ominus(\mathrm{ClO},\mathrm{g})\\ &= (-1.46...\times 10^2\ \mathrm{J\,K^{-1}\,mol^{-1}}) + 2\times(226.6\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &= \boxed{307\ \mathrm{J\,K^{-1}\,mol^{-1}}}\end{aligned}$$

7

Quantum theory

7A The origins of quantum mechanics

Answers to discussion question

D7A.2 The ultimately unsuccessful classical approach to the description of black-body radiation involved assuming that the radiation resulted from oscillating electric charges in the walls of the body, and that each oscillator has the same average energy as predicted by the equipartition principle. This view results in the ultra-violet catastrophe, in which the radiation increases without limit as the wavelength becomes shorter.

Planck assumed two things: first, that the oscillators could only have energies given by $E = nh\nu$, where ν is the frequency and n is $0,\ 1,\ 2, \ldots$; second, that the probability of an individual oscillator having a particular energy is described by the Boltzmann distribution. As the frequency of the oscillator or the value of n increases, so does its energy and the Boltzmann distribution predicts that such a state is less likely. In addition, the highest frequency oscillations may not be excited at all, that is have $n = 0$, on the grounds that the resulting state has too high an energy to be populated. Planck's theory therefore avoids the ultraviolet catastrophe by having no excitation of highest frequency oscillators.

D7A.4 By wave-particle duality it is meant 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 diffraction 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.

The development of quantum theory is much concerned with the need to embrace this wave-particle duality and, as is explained in the following Topics, this is exemplified by the introduction of the wavefunction to describe the properties of a particles and the notion of 'complementary variables' such as position and momentum.

Solutions to exercises

E7A.1(b) Wien's law [7A.1–*238*], $\lambda_{\text{max}}T = 2.9 \times 10^{-3}$ m K, is rearranged to give the wavelength at which intensity is maximised

$$\lambda_{\text{max}} = (2.9 \times 10^{-3}\ \text{m K})/T = (2.9 \times 10^{-3}\ \text{m K})/(2.7\ \text{K}) = \boxed{1.1 \times 10^{-3}\ \text{m}}$$

E7A.2(b) Assuming that the object is a black body is equivalent to assuming that Wien's law [7A.1–*238*], $\lambda_{\max}T = 2.9 \times 10^{-3}$ m K, holds. Using $\lambda\nu = c$ (where c is the speed of light in a vacuum), Wien's law is expressed in terms of the frequency of maximum intensity ($\nu_{\max}$)

$$Tc/\tilde{\nu}_{\max} = 2.9 \times 10^{-3}\ \mathrm{m\,K}$$

This is rearranged to give the temperature

$$\begin{aligned} T &= (2.9 \times 10^{-3}\ \mathrm{m\,K}) \times \nu_{\max}/c \\ &= (2.9 \times 10^{-3}\ \mathrm{m\,K}) \times \frac{(282 \times 10^{9}\ \mathrm{Hz})}{(2.9979 \times 10^{8}\ \mathrm{m\,s^{-1}})} = \boxed{2.7\ \mathrm{K}} \end{aligned}$$

E7A.3(b) Molar heat capacities of monatomic non-metallic solids obey the Einstein relation [7A.8a–*241*]

$$C_{V,\mathrm{m}}(T) = 3Rf_{\mathrm{E}}(T), \quad f_{\mathrm{E}}(T) = \left(\frac{\theta_{\mathrm{E}}}{T}\right)^2 \left(\frac{\mathrm{e}^{\theta_{\mathrm{E}}/2T}}{\mathrm{e}^{\theta_{\mathrm{E}}/T} - 1}\right)^2$$

where the solid is at temperature T and is characterized by an Einstein temperature θ_{E}. Thus, for a solid at 500 K with an Einstein temperature of 300 K

$$f_{\mathrm{E}}(500\ \mathrm{K}) = \left(\frac{300\ \mathrm{K}}{500\ \mathrm{K}}\right)^2 \left(\frac{\mathrm{e}^{(300\ \mathrm{K})/2(500\ \mathrm{K})}}{\mathrm{e}^{(300\ \mathrm{K})/(500\ \mathrm{K})} - 1}\right)^2 = 0.970...$$

Hence, $C_{V,\mathrm{m}}(500\ \mathrm{K}) = \boxed{(0.97) \times 3R}$

E7A.4(b) The energy of the quantum is given by the Bohr frequency condition [7A.9–*241*], $\Delta E = h\nu$, and the frequency is $\nu = 1/T$. The energy per mole is $\Delta E_{\mathrm{m}} = N_{\mathrm{A}}\Delta E$.

(i) For $T = 2.50$ fs

$$\begin{aligned} \Delta E &= (6.6261 \times 10^{-34}\ \mathrm{J\,s})/(2.50 \times 10^{-15}\ \mathrm{s}) = \boxed{2.65 \times 10^{-19}\ \mathrm{J}} \\ \Delta E_{\mathrm{m}} &= (2.65... \times 10^{-19}\ \mathrm{J}) \times (6.0221 \times 10^{23}\ \mathrm{mol^{-1}}) = \boxed{160\ \mathrm{kJ\,mol^{-1}}} \end{aligned}$$

(ii) For $T = 2.21$ fs

$$\begin{aligned} \Delta E &= (6.6261 \times 10^{-34}\ \mathrm{J\,s})/(2.21 \times 10^{-15}\ \mathrm{s}) = \boxed{3.00 \times 10^{-19}\ \mathrm{J}} \\ \Delta E_{\mathrm{m}} &= (3.00... \times 10^{-19}\ \mathrm{J}) \times (6.0221 \times 10^{23}\ \mathrm{mol^{-1}}) = \boxed{181\ \mathrm{kJ\,mol^{-1}}} \end{aligned}$$

(iii) For $T = 1.0$ ms

$$\begin{aligned} \Delta E &= (6.6261 \times 10^{-34}\ \mathrm{J\,s})/(1.0 \times 10^{-3}\ \mathrm{s}) = \boxed{6.6 \times 10^{-31}\ \mathrm{J}} \\ \Delta E_{\mathrm{m}} &= (6.6... \times 10^{-31}\ \mathrm{J}) \times (6.0221 \times 10^{23}\ \mathrm{mol^{-1}}) \\ &= \boxed{3.99 \times 10^{-10}\ \mathrm{kJ\,mol^{-1}}} \end{aligned}$$

E7A.5(b) The energy of a photon with wavelength λ is given by

$$\begin{aligned}E &= h\nu = hc/\lambda = (6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{8}\,\mathrm{m\,s^{-1}})/\lambda\\ &= (1.9825\times10^{-25}\,\mathrm{J})/(\lambda/\mathrm{m})\end{aligned}$$

The energy per mole is given by

$$E_\mathrm{m} = N_\mathrm{A}E = (0.11939\,\mathrm{J\,mol^{-1}})/(\lambda/\mathrm{m})$$

Hence, the following table is drawn up

	λ	E	$E_\mathrm{m}/\mathrm{kJ\,mol^{-1}}$
(a)	200 nm	991 zJ	597
(b)	150 pm	1.32 pJ	7.96×10^{5}
(c)	1.00 cm	19.8 yJ	1.19×10^{-2}

E7A.6(b) When a photon is absorbed by a free hydrogen atom, the law of conservation of energy requires the kinetic energy acquired by the atom is E_k, the energy of the absorbed photon. Assuming relativistic corrections are negligible the kinetic energy is $E_\mathrm{k} = E_\mathrm{photon} = \frac{1}{2}m_\mathrm{H}v^2$. The atom is accelerated to the speed,

$$\begin{aligned}v &= \left(\frac{2E_\mathrm{photon}}{m_\mathrm{H}}\right)^{1/2} = \left(\frac{2N_\mathrm{A}E_\mathrm{photon}}{M_\mathrm{H}}\right)^{1/2}\\ &= \left(\frac{2\times(6.0221\times10^{23}\,\mathrm{mol^{-1}})\times E_\mathrm{photon}}{(1.0079\times10^{-3}\,\mathrm{kg\,mol^{-1}})}\right)^{1/2}\\ &= (3.45...\times10^{13}\,\mathrm{m\,s^{-1}})\times\left(E_\mathrm{photon}/\mathrm{J}\right)^{1/2}\end{aligned}$$

The photon energies have been calculated in *Exercise* E7A.5(b), and thus the following table can be drawn up

	λ	E	$v/\mathrm{km\,s^{-1}}$
(a)	200 nm	991 zJ	17.3
(b)	150 pm	1.32 pJ	631
(c)	1.00 cm	19.8 yJ	0.0773

E7A.7(b) The total energy emitted from a laser at (constant) power P in a time interval Δt is $P\Delta t$. The energy of a single photon of wavelength λ is $E = hc/\lambda$. Hence, the total number of photons emitted in this time interval is the total energy emitted divided by the energy per photon (assuming the light is monochromatic)

$$N = \frac{P\Delta t}{E_\mathrm{photon}} = \frac{P\Delta t\lambda}{hc}$$

Thus, for a time interval of 1 s and a wavelength of 700 nm

(i) $P = 0.10\ \mathrm{W}$

$$N = \frac{(0.10\ \mathrm{W}) \times (1\ \mathrm{s})(700 \times 10^{-9}\ \mathrm{m})}{(6.6261 \times 10^{-34}\ \mathrm{J\,s}) \times (2.9979 \times 10^{8}\ \mathrm{m\,s^{-1}})} = \boxed{3.52 \times 10^{17}}$$

(ii) $P = 1.0\ \mathrm{W}$

$$N = \frac{(1.0\ \mathrm{W}) \times (1\ \mathrm{s})(700 \times 10^{-9}\ \mathrm{m})}{(6.6261 \times 10^{-34}\ \mathrm{J\,s}) \times (2.9979 \times 10^{8}\ \mathrm{m\,s^{-1}})} = \boxed{3.52 \times 10^{18}}$$

E7A.8(b) As described in Section 7A.2 on page 242, photoejection can only occur if the energy of the incident photon is greater than or equal to the work function of the metal ϕ. If this condition is fulfilled, the energy of the emitted photon is given by [7A.10–*243*], $E_\mathrm{k} = h\nu - \Phi = hc/\lambda - \Phi$. To convert the work function to Joules, multiply through by the elementary charge, as described in Section 7A.2 on page 242,

$$\Phi = 2.09\ \mathrm{eV} \times e = 2.09\ \mathrm{eV} \times 1.602 \times 10^{-19}\ \mathrm{J\,eV^{-1}} = 3.35... \times 10^{-19}\ \mathrm{J}$$

and since $E_\mathrm{k} = 1/2m_\mathrm{e}v^2$, $v = \sqrt{2E_\mathrm{k}/m_\mathrm{e}}$

(i) For $\lambda = 650\ \mathrm{nm}$

$$E_\mathrm{photon} = \frac{hc}{\lambda} = \frac{(6.6261 \times 10^{-34}\ \mathrm{J\,s}) \times (2.9979 \times 10^{8}\ \mathrm{m\,s^{-1}})}{650 \times 10^{-9}\ \mathrm{m}}$$
$$= 3.06... \times 10^{-19}\ \mathrm{J}$$

This is less than the threshold energy, hence $\boxed{\text{no electron ejection}}$ occurs.

(ii) For $\lambda = 195\ \mathrm{nm}$

$$E_\mathrm{photon} = \frac{(6.6261 \times 10^{-34}\ \mathrm{J\,s}) \times (2.9979 \times 10^{8}\ \mathrm{m\,s^{-1}})}{195 \times 10^{-9}\ \mathrm{m}} = 1.02... \times 10^{-18}\ \mathrm{J}$$

This is greater than the the threshold frequency, and so photoejection can occur, leading to a kinetic energy of

$$E_\mathrm{k} = hc/\lambda - \Phi = 1.02... \times 10^{-18}\ \mathrm{J} - 3.35... \times 10^{-19}\ \mathrm{J} = \boxed{6.84 \times 10^{-19}\ \mathrm{J}}$$

$$v = \sqrt{2 \times (6.84 \times 10^{-19}\ \mathrm{J})/(9.109 \times 10^{-31}\ \mathrm{kg})} = \boxed{1.23\ \mathrm{Mm\,s^{-1}}}$$

E7A.9(b) If the power, P, is constant, the total energy emitted in time Δt is $P\Delta t$. The energy of each emitted photon is $E_\mathrm{photon} = h\nu = hc/\lambda$. The total number of photons emitted in this time period is therefore the total energy emitted divided by the energy per photon

$$N = P\Delta t/E_\mathrm{photon} = P\Delta t\lambda/hc$$

The conservation of linear momentum requires that the loss of a photon must impart an equivalent momentum in the opposite direction to the spacecraft, hence the total momentum p imparted to the spacecraft in time Δt is

$$p = Np_{\text{photon}} = Nh/c = P\Delta t\lambda/hc \times h/\lambda = P\Delta t/c$$

Because $p = (mv)_{\text{spacecraft}}$, the final speed of the spacecraft is

$$\begin{aligned} v &= P\Delta t/cm_{\text{spacecraft}} \\ &= \frac{(1.5\times10^{3}\ \text{W})\times(10\ \text{y})\times(3.1536\times10^{7}\ \text{s y}^{-1})}{(2.9979\times10^{8}\ \text{m s}^{-1})\times(10\ \text{kg})} = \boxed{158\ \text{m s}^{-1}} \end{aligned}$$

Noting that the number of seconds in one year is

$$365\times24\times60\times60 = 3.1536\times10^{7}$$

E7A.10(b) The de Broglie relation is [7A.11–*244*], $\lambda = h/p = h/(mv)$. Therefore,

$$v = \frac{h}{m_\mathrm{e}\lambda} = \frac{6.6261\times10^{-34}\ \text{J s}}{(9.1094\times10^{-31}\ \text{kg})\times(100\times10^{-12}\ \text{m})} = \boxed{7.27\times10^{6}\ \text{m s}^{-1}}$$

The kinetic energy acquired by an electron accelerated through a potential $\mathcal{E}$ is $e\mathcal{E}$: $E_\mathrm{k} = \frac{1}{2}m_\mathrm{e}v^2 = e\mathcal{E}$. Solving for the potential difference gives

$$\mathcal{E} = \frac{m_\mathrm{p}v^2}{2e} = \frac{(1.6726\times10^{-27}\ \text{kg})\times(3.93\times10^{3}\ \text{m s}^{-1})^2}{2\times(1.6022\times10^{-19}\ \text{C})} = \boxed{8.19\times10^{-2}\ \text{V}}$$

E7A.11(b) The de Broglie relation is [7A.11–*244*] $\lambda = h/p = h/(mv)$. Hence,

$$v = \frac{h}{m_\mathrm{e}\lambda} = \frac{6.6261\times10^{-34}\ \text{J s}}{(1.6726\times10^{-27}\ \text{kg})\times(3\times10^{-2}\ \text{m})} = \boxed{1.3\times10^{-5}\ \text{m s}^{-1}}$$

E7A.12(b) According to the de Broglie relation, [7A.11–*244*] the momentum of a photon is

$$p = \frac{h}{\lambda} = \frac{6.6261\times10^{-34}\ \text{J s}}{350\times10^{-9}\ \text{m}} = \boxed{1.89\times10^{-27}\ \text{kg m s}^{-1}}$$

The momentum of a particle is $p = mv$, so the speed of a hydrogen molecule that has the above momentum is

$$\begin{aligned} v &= \frac{p}{m_{\mathrm{H_2}}} = \frac{p}{M_{\mathrm{H_2}}/N_\mathrm{A}} = \frac{1.89\times10^{-27}\ \text{kg m s}^{-1}}{(2.058\times10^{-3}\ \text{kg mol}^{-1})/(6.0221\times10^{23}\ \text{mol}^{-1})} \\ &= \boxed{0.566\ \text{m s}^{-1}} \end{aligned}$$

E7A.13(b) The de Broglie wavelength is [7A.11–*244*], $\lambda = h/p$. The kinetic energy of an electron accelerated through a potential $\mathcal{E}$ is $e\mathcal{E}$. Thus, since $E_\mathrm{k} = p^2/2m_\mathrm{e}$, $p = (2m_\mathrm{e}E_\mathrm{k})^{1/2} = (2m_\mathrm{e}e\mathcal{E})^{1/2}$. Hence $\lambda = h/\sqrt{(2m_\mathrm{e}e\mathcal{E}}$.

(i)

$$\lambda = \frac{6.6261\times10^{-34}\,\mathrm{J\,s}}{[2\times(9.1094\times10^{-31}\,\mathrm{kg})\times(1.6022\times10^{-19}\,\mathrm{C})\times(100\,\mathrm{V})]^{1/2}} = \boxed{123\,\mathrm{pm}}$$

(ii)

$$\lambda = \frac{6.6261\times10^{-34}\,\mathrm{J\,s}}{[2\times(9.1094\times10^{-31}\,\mathrm{kg})\times(1.6022\times10^{-19}\,\mathrm{C})\times(1.0\times10^{3}\,\mathrm{V})]^{1/2}} = \boxed{39\,\mathrm{pm}}$$

(iii)

$$\lambda = \frac{6.6261\times10^{-34}\,\mathrm{J\,s}}{[2\times(9.1094\times10^{-31}\,\mathrm{kg})\times(1.6022\times10^{-19}\,\mathrm{C})\times(100\times10^{5}\,\mathrm{V})]^{1/2}} = \boxed{3.88\,\mathrm{pm}}$$

Solutions to problems

P7A.2 Converting the wavenumbers given to wavelengths, the boundary wavelengths are

$$\lambda_1 = (1000\times10^2\,\mathrm{m^{-1}})^{-1} = 1.00\times10^{-5}\,\mathrm{m}$$
$$\lambda_2 = (1010\times10^2\,\mathrm{m^{-1}})^{-1} = 9.90...\times10^{-6}\,\mathrm{m}$$

A cavity approximates an ideal black body, hence the Planck distribution [7A.6a–*239*], applies

$$\rho(\lambda,T) = \frac{8\pi hc}{\lambda^5\left(e^{hc/\lambda kT}-1\right)}$$

Because the wavelength range is small (99 nm), the energy density is approximated by

$$\Delta E(T) = \rho(\lambda,T)\Delta\lambda$$

Taking $\lambda = 9.95...\,\mu\mathrm{m}$ gives

$$\frac{hc}{\lambda k} = \frac{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{8}\,\mathrm{m\,s^{-1}})}{(9.95...\times10^{-6}\,\mathrm{m})\times(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})} = 1.44...\times10^{3}\,\mathrm{K}$$

and

$$\frac{8\pi hc}{\lambda^5} = \frac{8\pi\times(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{8}\,\mathrm{m\,s^{-1}})}{(9.95...\times10^{-6}\,\mathrm{m})^5} = 51.1...\,\mathrm{J\,m^{-4}}$$

$$\Delta E(T) = (51.1...\,\mathrm{J\,m^{-4}})\times\frac{1}{e^{(1.44...\times10^{3}\,\mathrm{K})/T}-1}\times(99...\times10^{-9}\,\mathrm{m})$$
$$= \frac{5.06...\times10^{-6}\,\mathrm{J\,m^{-3}}}{e^{(1.44...\times10^{3}\,\mathrm{K})/T}-1}$$

(a)

$$\Delta E(298\ \mathrm{K}) = \frac{5.06...\times 10^{-6}\ \mathrm{J\,m^{-3}}}{\mathrm{e}^{(1.44...\times 10^{3}\ \mathrm{K})/(298\ \mathrm{K})}-1} = \boxed{3.96\times 10^{-8}\ \mathrm{J\,m^{-3}}}$$

(b)

$$\Delta E(4\ \mathrm{K}) = \frac{5.06...\times 10^{-6}\ \mathrm{J\,m^{-3}}}{\mathrm{e}^{(1.44...\times 10^{3}\ \mathrm{K})/(4\ \mathrm{K})}-1} = \boxed{5.12\times 10^{-163}\ \mathrm{J\,m^{-3}}}$$

P7A.4 The Planck distribution is [7A.6a–*239*],

$$\rho(\lambda,T) = \frac{8\pi hc}{\lambda^5\left(\mathrm{e}^{hc/\lambda kT}-1\right)}$$

The value of λ at which ρ is at a maximum is found by solving $\mathrm{d}\rho/\mathrm{d}\lambda = 0$.

$$\begin{aligned}\frac{\mathrm{d}\rho}{\mathrm{d}\lambda} &= 8\pi hc\frac{\mathrm{d}}{\mathrm{d}\lambda}\left(\lambda^{-5}(\mathrm{e}^{hc/\lambda kT}-1)^{-1}\right)\\ &= 8\pi hc\left[(\mathrm{e}^{hc/\lambda kT}-1)^{-1}\frac{\mathrm{d}\lambda^{-5}}{\mathrm{d}\lambda}+\lambda^{-5}\frac{\mathrm{d}(\mathrm{e}^{hc/\lambda kT}-1)^{-1}}{\mathrm{d}\lambda}\right]\\ &= 8\pi hc\left[-5\lambda^{-6}(\mathrm{e}^{hc/\lambda kT}-1)^{-1}+\lambda^{-5}(\mathrm{e}^{hc/\lambda kT}-1)^{-2}\frac{hc}{\lambda^2 kT}\mathrm{e}^{hc/\lambda kT}\right]\\ &= \frac{8\pi hc}{\lambda^7(\mathrm{e}^{hc/\lambda kT}-1)}\left[5\lambda+\frac{hc\mathrm{e}^{hc/\lambda kT}}{kT(\mathrm{e}^{hc/\lambda kT}-1)}\right]\end{aligned}$$

Thus, at $\lambda = \lambda_{\max}$,

$$x_{\max}\mathrm{e}^{x_{\max}} - 5(\mathrm{e}^{x_{\max}}-1) = 0$$

where $x_{\max} = hc/\lambda_{\max}kT$. This equation is solved numerically by $x_{\max} = 4.965$, giving

$$\lambda_{\max}T = \frac{hc}{4.965k} = \frac{(6.6261\times 10^{-34}\ \mathrm{J\,s})\times(2.9979\times 10^{8}\ \mathrm{m\,s^{-1}})}{4.965\times(1.3806\times 10^{-23}\ \mathrm{J\,K^{-1}})} = \boxed{2.9\times 10^{-3}\ \mathrm{K\,m}}$$

as in the text.

P7A.6 The total energy absorbed by the atmosphere is 70% of the total energy incident on the top of the atmosphere

$$343\ \mathrm{W\,m^2}\times 0.7 = 240.1\ \mathrm{W\,m^2}$$

At equilibrium, the total energy absorbed is equal to the total energy emitted, which is determined by the Stefan–Boltzmann law

$$E_{\mathrm{abs}} = E_{\mathrm{em}} = 5.672\times 10^{-8}(T/\mathrm{K})^4\ \mathrm{W\,m^2}$$

This is rearranged to

$$T = \left(240.1\ \mathrm{K^4\,W\,m^2}/5.672\times 10^{-8}\ \mathrm{W\,m^2}\right)^{1/4} = \boxed{255\ \mathrm{K}}$$

Wien's law [7A.1–*238*], $\lambda_{\max}T = 2.9\times 10^{-3}\ \mathrm{m\,K}$, is rearranged to give

$$\lambda_{\max} = (2.9\times 10^{-3}\ \mathrm{m\,K})/(255...\ \mathrm{K}) = \boxed{1.14\times 10^{-5}\ \mathrm{m}}$$

P7A.8 (a) As λ decreases, $hc/\lambda kT$ increases, and so $\mathrm{e}^{hc/\lambda kT}$ increases. Therefore, for very short wavelengths, $\mathrm{e}^{hc/\lambda kT}$ is very large and 1 is negligible compared to this. Hence,

$$\lim_{\lambda\to 0}\rho(\lambda,T)=\frac{8\pi hc}{\lambda^5\mathrm{e}^{hc/\lambda kT}}=\frac{8\pi hc}{\lambda^5}\mathrm{e}^{-hc/\lambda kT}$$

(b) Comparison with the empirical expression gives the constants as $\boxed{a=8\pi hc}$, and $\boxed{b=-hc/\lambda}$.

(c) The total energy density at temperature T is given by [7A.7–*240*],

$$E(T)=\int_0^\infty \rho(\lambda,T)\,\mathrm{d}\lambda=\int_0^\infty \frac{8\pi hc}{\lambda^5}\mathrm{e}^{-hc/\lambda kT}\mathrm{d}\lambda$$

Let $x=hc/\lambda kT$, or $\lambda=hc/xkT$. Then, $\mathrm{d}\lambda=-hc/x^2kT\,\mathrm{d}x$

$$\begin{aligned}E(T)&=8\pi hc\int_0^\infty \frac{1}{hc/xkT}\mathrm{e}^{-x}\frac{\mathrm{d}x}{x^2}=8\pi hc\left(\frac{kT}{hc}\right)^4\int_0^\infty x^3\mathrm{e}^{-x}\,\mathrm{d}x\\&=\frac{8\pi(KT)^4}{(hc)^3}\times 3!=\frac{48\pi k^4}{(hc)^3}T^4\end{aligned}$$

The integral is of the form of Integral E.3 with $n=3$ and $k=1$. This is consistent with the Stefan–Boltzmann law, as the energy density is proportional to T^4.

(d) The energy spectral density is maximized at $\lambda=\lambda_{\max}$, where $\mathrm{d}\rho/\mathrm{d}\lambda=0$. This gives

$$\begin{aligned}\frac{\mathrm{d}\rho}{\mathrm{d}\lambda}&=8\pi hc\frac{\mathrm{d}}{\mathrm{d}\lambda}\left(\lambda^{-5}\mathrm{e}^{-hc/\lambda kT}\right)\\&=8\pi hc\left[\frac{\mathrm{d}\lambda^{-5}}{\mathrm{d}\lambda}\mathrm{e}^{-hc/\lambda kT}+\lambda^{-5}\frac{\mathrm{d}\mathrm{e}^{-hc/\lambda kT}}{\mathrm{d}\lambda}\right]\\&=8\pi hc\left[-5\lambda^{-6}\mathrm{e}^{hc/\lambda kT}+\lambda^{-5}\times\frac{hc}{\lambda^5kT}\mathrm{e}^{hc/\lambda kT}\right]\\&=\frac{8\pi hc\mathrm{e}^{hc/\lambda kT}}{\lambda^7}\left[-5\lambda+\frac{hc}{kT}\right]\end{aligned}$$

This expression equals 0 at $\lambda=\lambda_{\max}$, and is solved when

$$\begin{aligned}-5\lambda_{\max}+\frac{hc}{kT}&=0\\ \lambda_{\max}T&=\frac{hc}{5k}\end{aligned}$$

That is $\lambda_{\max}T$ is a constant, which is consistent with Wien's law

P7A.10 The Einstein temperature is given by $\theta_\mathrm{E}=h\nu_\mathrm{E}/k$; this has units of K (temperature), as expected

$$\frac{(\mathrm{J\,s})\times(\mathrm{s}^{-1})}{\mathrm{J\,K^{-1}}}=\boxed{\mathrm{K}}$$

In terms of temperature, the Einstein equation for molar heat capacity is [7A.8a–*241*],

$$C_{V,\mathrm{m}}(T) = 3Rf_{\mathrm{E}}(T), \quad f_{\mathrm{E}}(T) = \left(\frac{\theta_{\mathrm{E}}}{T}\right)^2 \left(\frac{\mathrm{e}^{\theta_{\mathrm{E}}/2T}}{\mathrm{e}^{\theta_{\mathrm{E}}/T} - 1}\right)^2$$

At high temperatures, this tends towards the classical value,

$$\lim_{T\to\infty} C_{V,\mathrm{m}}(T) = 3R\left(\frac{\theta_{\mathrm{E}}}{T}\right)^2 \left(\frac{1}{1 + \theta_{\mathrm{E}}/T - 1}\right)^2 = 3R$$

This limit is valid when $\boxed{\theta_{\mathrm{E}}/T \ll 1}$, which is equivalent to $\boxed{h\nu_{\mathrm{E}}/kT \ll 1}$. The conversion between frequency and temperature is

$$\theta_{\mathrm{E}} = \frac{h}{k}\nu_{\mathrm{E}} = \frac{6.6261 \times 10^{-34}\,\mathrm{J\,s}}{1.3806 \times 10^{-23}\,\mathrm{J\,K^{-1}}}(\nu_{\mathrm{E}}/\mathrm{Hz}) = (4.79... \times 10^{-11}\ \mathrm{K}) \times (\nu_{\mathrm{E}}/\mathrm{Hz})$$

(a) For diamond, $\nu_{\mathrm{E}} = 46.5$ THz and hence $\theta_{\mathrm{E}} = 2.23... \times 10^3$ K

$$f_{\mathrm{E}}(298\ \mathrm{K}) = \left(\frac{2.23... \times 10^3\ \mathrm{K}}{298\ \mathrm{K}}\right)^2 \left(\frac{\mathrm{e}^{2.23...\times10^3\ \mathrm{K}/(2\times298\ \mathrm{K})}}{\mathrm{e}^{2.23...\times10^3\ \mathrm{K}/(298\ \mathrm{K})} - 1}\right)^2 = 0.0314$$

$$C_{V,\mathrm{m}}(298\ \mathrm{K}) = \boxed{3R \times (0.0314)}$$

(b) For copper, $\nu_{\mathrm{E}} = 7.15$ THz and hence $\theta_{\mathrm{E}} = 343...$ K

$$f_{\mathrm{E}}(298\ \mathrm{K}) = \left(\frac{343...\ \mathrm{K}}{298\ \mathrm{K}}\right)^2 \left(\frac{\mathrm{e}^{343...\ \mathrm{K}/(2\times298\ \mathrm{K})}}{\mathrm{e}^{343...\ \mathrm{K}/(298\ \mathrm{K})} - 1}\right)^2 = 0.896$$

$$C_{V,\mathrm{m}}(298\ \mathrm{K}) = \boxed{3R \times (0.896)}$$

7B Wavefunctions

Answers to discussion questions

D7B.2 These terms are best illustrated by referring to a one-dimensional system. The *probability density* $P(x)$ is defined so that $P(x)\,\mathrm{d}x$ is the *probability* of finding the system between x and $x + \mathrm{d}x$. The value of the wavefunction itself, $\psi(x)$, is the *probability amplitude*. The probability density is given in terms of this amplitude as $P(x) = \psi^*(x)\psi(x)$.

Solutions to exercises

E7B.1(b) The task is to find N such that $\psi = N\sin(3\pi x/L)$ satisfies the normalization condition [7B.4c–*248*], $\int \psi^*\psi\,\mathrm{d}\tau = 1$. In this case the integration is over x and the range is 0 to L; the function is real, so $\psi = \psi^*$.

$$N^2\int_0^L \sin^2(3\pi x/L)\mathrm{d}x = N^2[L/2 - (L/12\pi)\overbrace{\sin(6\pi L/L)}^{=\sin 6\pi=0}] = N^2(L/2)$$

The integral is of the form of Integral T.2 with $a = L$ and $k = 3\pi/L$. For the wavefunction to be normalized, the integral must be 1 and therefore the normalizing factor is $\boxed{N = (2/L)^{1/2}}$.

E7B.2(b) The task is to find N such that $\psi = N\exp(-ax)$ satisfies the normalization condition [7B.4c–*248*], $\int \psi^*\psi\,\mathrm{d}\tau = 1$. In this case the integration is over x and the range is 0 to ∞. The function is real, so $\psi = \psi^*$ and the integral is therefore $N^2\int_0^\infty \exp(-2ax)\mathrm{d}x$.

$$N^2\int_0^\infty \mathrm{e}^{-2ax}\mathrm{d}x = -(N^2/2a)\,\mathrm{e}^{-2ax}\Big|_0^\infty = -(N^2/2a)(\mathrm{e}^{-\infty} - \mathrm{e}^0) = (N^2/2a)$$

where $\exp(-\infty) = 0$ and $\exp(0) = 1$ are used. Setting the integral equal to 1 gives $\boxed{N = (2a)^{1/2}}$.

E7B.3(b)

(i) The function $\psi = \sin(ax)$ $\boxed{\text{cannot be normalized}}$ as the area under $\psi^*\psi = \sin^2(ax)$ is infinite when the limits of x are $\pm\infty$. However, over a finite region, the wavefunction can be normalized.

(ii) $\cos(ax)\exp(-x^2)$ $\boxed{\text{can be normalized}}$ as it goes to 0 as x goes to $\pm\infty$ so the integral of $\psi^*\psi$ over all space is finite.

A function is an acceptable wavefunction if it: (1) is not infinite over a finite region; (2) is single-valued; (3) is continuous; (4) has a continuous first derivative. Both functions satisfy all of these conditions and so are acceptable wavefunctions.

E7B.4(b) The probability of finding an electron in an infinitesimal region $\mathrm{d}x$ around x is $P(x)\mathrm{d}x = \psi^*(x)\psi(x)\mathrm{d}x$, provided that $\psi(x)$ is a normalized wavefunction. The wavefunction is real so that $\psi^* = \psi$, hence the probability is given by

$$P(x)\mathrm{d}x = \left[(2/L)^{1/2}\sin(3\pi x/L)\right]^2\mathrm{d}x = (2/L)\sin^2(3\pi x/L)\mathrm{d}x$$

Hence, at $x = L/6$, $P(L/6)\mathrm{d}x = (2/L)\sin(\pi/2)\mathrm{d}x = \boxed{(2/L)\mathrm{d}x}$.

E7B.5(b) The normalized wavefunction is $\psi(x) = (2/L)^{1/2}\sin(2\pi x/L)$. The probability of finding the electron between $x = 0$ and $x = L/3$ is, using Integral T.2

$$\begin{aligned}&\int_0^{L/3}(2/L)\sin^2(3\pi x/L)\,\mathrm{d}x = (2/L)\left[x/2 - (L/12\pi)\sin(6\pi x/L)\big|_0^{L/3}\right]\\ &= (2/L)([L/6 - (L/12\pi)\sin(2\pi)] - [0 - (L/12\pi)\sin(0)])\\ &= (2/L)[L/6 - 0] = \boxed{1/3}\end{aligned}$$

E7B.6(b) Both x and L have dimensions of length, so $2\pi x/L$ is dimensionless, as required for the argument of a sine function. The dimensions of the wavefunction come from the normalizing factor $(2/L)^{1/2}$ which has dimensions $(\text{length})^{-1/2}$. The probability is $|\psi(x)|^2\mathrm{d}x$: $|\psi(x)|^2$ has dimensions of $(\text{length})^{-1}$, and $\mathrm{d}x$ has dimensions of length. Hence, $|\psi(x)|^2\mathrm{d}x$ is dimensionless, as required.

E7B.7(b) A function is an acceptable wavefunction if it: (1) is not infinite over a finite region; (2) is single-valued; (3) is continuous; (4) has a continuous first derivative. Note that for a particle on a ring, the condition to be single valued implies the function must be periodic over 2π, meaning that the function 'joins up' with itself as it goes through 2π. Expressed mathematically this condition is $\psi(\phi) = \psi(\phi + 2\pi)$, where ϕ is the angle.

(i) $\cos\phi$ is periodic over 2π and satisfies all the other conditions so it $\boxed{\text{is}}$ an acceptable wavefunction.

(ii) $\sin\phi$ is periodic over 2π and satisfies all the other conditions so it $\boxed{\text{is}}$ an acceptable wavefunction.

(iii) $\cos(0.9\phi)$ is not periodic over 2π (in fact it is periodic over $(2\pi)/0.9$). The function does not 'join up' after the angle goes through 2π and therefore it $\boxed{\text{is not}}$ an acceptable wavefunction.

E7B.8(b) The normalized wavefunction is $\psi(x) = (2/L)^{1/2}\sin(3\pi x/L)$, and so the probability density is $P(x) = |\psi(x)|^2 = (2/L)\sin^2(3\pi x/L)$. This is maximized when $\sin^2(3\pi x/L) = 1$, and so when $\sin(3\pi x/L) = \pm 1$. These values occur when $3\pi x/L = \pi/2, 3\pi/2, 5\pi/2$ and hence $\boxed{x = L/6, L/2, 5L/6}$.

Nodes occur when the wavefunction goes through zero: $\sin(3\pi x/L) = 0$. The sine function is zero when $3\pi x/L = \pi, 2\pi$, hence $\boxed{x = L/3, 2L/3}$. The wavefunction goes to zero at $x = 0$ and $x = L$, but these do not count as nodes as the wavefunction does not pass through zero.

Solutions to problems

P7B.2 (a) The task is to find N such that $\psi = N\cos(\phi)$ satisfies the normalization condition [7B.4c–*248*], $\int \psi^*\psi\,\mathrm{d}\tau = 1$. In this case the integration is over ϕ and the range is 0 to 2π; the function is real so $\psi^* = \psi$. Using the identity $\sin^2 x + \cos^2 x = 1$ the integrand is expressed as $\cos^2\phi = 1 - \sin^2\phi$, and then the integral is evaluated using Integral T.2

$$N^2\int_0^{2\pi}(1-\sin^2\phi)\,\mathrm{d}\phi = N^2\left[\phi|_0^{2\pi} - (2\pi/2) + (1/4)\sin(4\pi)\right] = \pi N^2$$

Setting this equal to 1 gives $\boxed{N = (\pi)^{-1/2}}$.

(b) The task is to find N such that $\psi = N\sin(m_l\phi)$ satisfies the normalization condition [7B.4c–*248*], $\int \psi^*\psi\,\mathrm{d}\tau = 1$. In this case the integration is over ϕ and the range is 0 to 2π; the function is real so $\psi^* = \psi$. The integral is evaluated using Integral T.2

$$N^2\int_0^{2\pi}\sin^2(m_l\phi)\,\mathrm{d}\phi = N^2[(2\pi/2) - (1/4m_l)\overbrace{\sin(4m_l\pi)}^{=0}] = \pi N^2$$

where $\sin n\pi = 0$ for integer n is used. Setting the result equal to 1 gives $\boxed{N = (\pi)^{-1/2}}$.

P7B.4 The task is to find N such that $\psi = N\exp(-ax^2)\exp(-by^2)$ satisfies the normalization condition [7B.4c–*248*], $\int \psi^*\psi\,\mathrm{d}\tau = 1$. The integration is over x and y, with both ranging from $-\infty$ to ∞. The wavefunction is real, and so the integral to evaluate is

$$N^2\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\mathrm{e}^{-2ax^2}\mathrm{e}^{-2by^2}\,\mathrm{d}x\mathrm{d}y$$

This integral separates into a product of two integrals

$$N^2\int_{-\infty}^{\infty}\mathrm{e}^{-2ax^2}\mathrm{d}x\int_{-\infty}^{\infty}\mathrm{e}^{-2by^2}\mathrm{d}y$$

For both the integrand is even, such that it is the same at x and $-x$, or y and $-y$. Hence the integral between $-\infty$ and ∞ is simply twice that between 0 and ∞. Using this gives

$$4N^2\int_{0}^{\infty}\mathrm{e}^{-2ax^2}\mathrm{d}x\int_{0}^{\infty}\mathrm{e}^{-2by^2}\mathrm{d}y$$

The integrals are evaluated using Integral G.1 to give

$$4N^2\times\tfrac{1}{2}(\pi/2a)^{1/2}\times\tfrac{1}{2}(\pi/2b)^{1/2} = N^2(\pi^2/4ab)^{1/2}$$

Setting this equal to 1 gives $\boxed{N = (4ab/\pi^2)^{1/2}}$.

P7B.6 The task is to find N such that $\psi(x) = N\mathrm{e}^{-ax^2}$, satisfies the normalization condition [7B.4c–*248*], $\int \psi^*\psi\,\mathrm{d}\tau = 1$. The integration is over x ranging from $-\infty$ to ∞. The required integral is

$$N^2\int_{-\infty}^{\infty}\mathrm{e}^{-2ax^2}\,\mathrm{d}x$$

The integrand is even, and so the integral from $-\infty$ to ∞ is twice the integral from 0 to ∞. The integral is evaluated using Integral G.1

$$2N^2\int_{0}^{\infty}\mathrm{e}^{-2ax^2}\mathrm{d}x = 2N^2\times\tfrac{1}{2}(\pi/2a)^{1/2}$$

Setting this equal to one gives $N = (2a/\pi)^{1/4}$.

The total probability of finding the particle at a distance $x \geq x_0$ is therefore

$$(2a/\pi)^{1/2}\int_{x_0}^{\infty}\mathrm{e}^{-2ax^2}\,\mathrm{d}x$$

With $a = 0.2\ \mathrm{m}^{-2}$ and $x_0 = 1$ m this integral becomes

$$(0.4/\pi)^{1/2}\int_{1}^{\infty}\mathrm{e}^{-0.4\times x^2}\,\mathrm{d}x$$

which evaluates numerically to $\boxed{0.186}$.

P7B.8 The probability of finding the particle within the range $x = a$ to $x = b$, and $y = c$ to $y = d$ is

$$\begin{aligned}P(a \to b, c \to d) &= \int_a^b \int_c^d |\psi(x,y)|^2 \,\mathrm{d}x\mathrm{d}y \\ &= \int_a^b \int_c^d (2/L)^2 \sin^2(\pi x/L)\sin^2(\pi y/L)\,\mathrm{d}x\mathrm{d}y\end{aligned}$$

The integral separates into integrals over x and y

$$= \int_a^b (2/L)\sin^2(\pi x/L)\,\mathrm{d}x \times \int_c^d (2/L)\sin^2(\pi x/L)\,\mathrm{d}x$$

Both integrals are evaluated using Integral T.2 to give the probability as

$$\left(\frac{b-a}{L} - \frac{1}{2\pi}\left[\sin\left(\frac{2\pi b}{L}\right) - \sin\left(\frac{2\pi a}{L}\right)\right]\right)\left(\frac{d-c}{L} - \frac{1}{2\pi}\left[\sin\left(\frac{2\pi d}{L}\right) - \sin\left(\frac{2\pi c}{L}\right)\right]\right)$$

Hence

(a) $a = 0, b = L/2, c = 0, d = L/2; P = \boxed{1/4}$

(b) $a = L/4, b = 3L/4, c = L/4, d = 3L/4; P = \frac{1}{4}(1 + 2/\pi)^2 = \boxed{0.670}$

P7B.10 (a) Normalization requires finding N such that $N^2 \int_{-\infty}^{\infty} \exp(-x^2/a^2)\mathrm{d}x = 1$. Because the integrand is symmetric, the integral from $-\infty$ to $+\infty$ is twice that from 0 to $+\infty$. With this, the integral is evaluated using Integral G.1

$$2N^2 \int_0^{\infty} \mathrm{e}^{-x^2/a^2}\mathrm{d}x = 2N^2 \times \tfrac{1}{2}(\pi a^2)^{1/2}$$

Setting this equal to 1 gives $\boxed{N = (\pi a^2)^{-1/4}}$. The required probability is given by

$$\begin{aligned}\int_{-a}^{a} \left[(\pi a^2)^{-1/4}\exp(-x^2/a^2)\right]^2 \mathrm{d}x &= 2(\pi a^2)^{-1/2}\int_0^a \exp(-x^2/a^2)\mathrm{d}x \\ &= \mathrm{erf}(1) = \boxed{0.843}\end{aligned}$$

This integral has no analytical solution, but is easily evaluated using mathematical software.

7C Operators and observables

Answers to discussion questions

D7C.2 In quantum mechanics an observable quantity (such as energy, position or momentum) is represented by a particular operator $\hat{\Omega}$. If the wavefunction is ψ the average value of the quantity represented by the operator $\hat{\Omega}$ is given by $\langle\Omega\rangle = \int \psi^*\hat{\Omega}\psi\,\mathrm{d}\tau$, called the expectation value. For the special case that ψ is an eigenfunction of $\hat{\Omega}$, the expectation value is the eigenvalue corresponding to this eigenfunction.

Solutions to exercises

E7C.1(b) To construct the potential energy operator, replace the position x in the classical expression by the position operator $\hat{x}$. This operator is just multiplication by x, $\hat{x} = x\times$, therefore the potential energy operator is $\boxed{\hat{V} = D_e(1 - e^{-ax})^2}$.

E7C.2(b) A function ψ is an eigenfunction of an operator $\hat{\Omega}$ if $\hat{\Omega}\psi = \omega\psi$ where ω is a constant called the eigenvalue.

(i) $(d^2/dx^2)\cos(kx) = -k^2\cos(kx)$. Hence $\cos kx$ $\boxed{\text{is}}$ an eigenfunction of the operator d^2/dx^2, with eigenvalue $\boxed{-k^2}$.

(ii) $(d^2/dx^2)e^{ikx} = (d/dx)ike^{ikx} = -k^2e^{ikx}$. Hence e^{ikx} $\boxed{\text{is}}$ an eigenfunction of the operator d^2/dx^2, with eigenvalue $\boxed{-k^2}$.

(iii) $(d^2/dx^2)kx = (d/dx)k = 0 = 0 \times kx$. Hence kx $\boxed{\text{is}}$ an eigenfunction of the operator d^2/dx^2 with eigenvalue $\boxed{0}$.

(iv) $(d^2/dx^2)e^{-ax^2} = (d/dx)(-2axe^{-ax^2}) = 2ae^{-ax^2}(2ax^2 - 1)$. Hence this function is $\boxed{\text{not}}$ an eigenfunction of the operator d^2/dx^2.

E7C.3(b) Wavefunctions ψ_1 and ψ_2 are orthogonal if $\int \psi_1^*\psi_2\,d\tau = 0$, [7C.8–*254*]. Here $\psi_1(x) = \sin(4\pi x/L)$, $\psi_2(x) = \sin(2\pi x/L)$, and the region is $0 \le x \le L$. The integral is evaluated using Integral T.5

$$\begin{aligned}\int \psi_1^*\psi_2 d\tau &= \int_0^L \sin(4\pi x/L)\sin(2\pi x/L)\,dx\\ &= [(L/4\pi)\sin(2\pi) - (L/12\pi)\sin(6\pi)] = 0\end{aligned}$$

where $\sin(n\pi) = 0$ for integer n is used. Thus, the two wavefunctions are orthogonal.

E7C.4(b) Wavefunctions ψ_1 and ψ_2 are orthogonal if $\int \psi_1^*\psi_2\,d\tau = 0$, [7C.8–*254*]. Here $\psi_1(x) = \cos(3\pi x/L)$, $\psi_2(x) = \cos(5\pi x/L)$, and the region is $-L/2 \le x \le L/2$. The integral is evaluated using Integral T.6

$$\begin{aligned}\int \psi_1^*\psi_2\,d\tau &= \int_{-L/2}^{L/2} \cos(3\pi x/L)\cos(5\pi x/L)\,dx\\ &= (-L/4\pi)\sin(-2\pi x/L) + (L/16\pi)\sin(8\pi x/L)\big|_{-L/2}^{L/2}\\ &= [(-L/4\pi)\sin(-\pi) + (L/16\pi)\sin(4\pi)]\\ &\quad - [(-L/4\pi)\sin(\pi) + (L/16\pi)\sin(-4\pi)] = 0\end{aligned}$$

where $\sin(n\pi) = 0$ for integer n is used. Thus, the two wavefunctions are orthogonal.

E7C.5(b) Two wavefunctions ψ_i and ψ_j are orthogonal if $\int \psi_i^* \psi_j \, d\tau = 0$, [7C.8–*254*]. In this case the integration is from $\phi = 0$ to $\phi = 2\pi$. Let $\psi_i = \exp(i\phi)$, the wavefunction with $m_l = +1$, and $\psi_j = \exp(-2i\phi)$, the wavefunction with $m_l = -2$. Note that the functions are complex, so $\psi_i^* = \exp(-i\phi)$. The integrand is therefore

$$\psi_i^* \psi_j = \exp(-i\phi)\exp(-2i\phi) = \exp(-3i\phi)$$

and the integral evaluates as

$$\begin{aligned}\int_0^{2\pi} \exp(-3i\phi)\, d\phi &= (-1/3i)\exp(-3i\phi)|_0^{2\pi} \\ &= (-1/3i)[\overbrace{\exp(-6\pi i)}^{=1} - \overbrace{\exp(i0)}^{=1}] = 0\end{aligned}$$

The identity $\exp(ix) = \cos x + i\sin x$ (*The chemist's toolkit* 16 in Topic 7C on page 256) is used to evaluate $\exp(-6\pi i) = \cos(-6\pi) + i\sin(-6\pi) = 1 + 0 = 1$. The integral is zero, so the functions are indeed orthogonal.

E7C.6(b) The normalized wavefunction is $\psi(x) = (2/L)^{1/2}\sin(\pi x/L)$. The operator for position is $\hat{x} = x$, therefore the expectation value of the position of the electron is [7C.11–*256*]

$$\langle x \rangle = \int \psi^* \hat{x} \psi \, d\tau = (2/L)\int_0^L x\sin^2(\pi x/L)\, dx$$

This integral is of the form of Integral T.11 with $k = \pi/L$ and $a = L$

$$\begin{aligned}&= \frac{2}{L}\left[\frac{L^2}{4} - \frac{L}{4\times\pi/L}\overbrace{\sin\left(\frac{2\pi L}{L}\right)}^{=\sin 2\pi=0} - \frac{1}{8\times(\pi/L)^2}\left\{\overbrace{\cos\left(\frac{2\pi L}{L}\right)}^{=\cos 2\pi=1} - 1\right\}\right] \\ &= \frac{2}{L}\times\frac{L^2}{4} = \boxed{L/2}\end{aligned}$$

Because the probability density $|\psi(x)|^2$ is symmetric about $x = L/2$, the expected result is $\langle x \rangle = L/2$.

E7C.7(b) The normalized wavefunction is $\psi(x) = (2/L)^{1/2}\sin(\pi x/L)$. The expectation value of the momentum is $\int \psi^* \hat{p}_x \psi \, dx$, and the momentum operator is $\hat{p}_x = (\hbar/i)d/dx$, therefore

$$\begin{aligned}\langle p_x \rangle &= (2/L)\int_0^L \sin(\pi x/L)\hat{p}_x \sin(\pi x/L)\, dx \\ &= (2\hbar/iL)\int_0^L \sin(\pi x/L)(d/dx)\sin(\pi x/L)\, dx\end{aligned}$$

Using $(d/dx)\sin(\pi x/L) = (\pi/L)\cos(\pi x/L)$ gives

$$\langle p_x \rangle = (2\pi\hbar/iL^2)\int_0^L \sin(\pi x/L)\cos(\pi x/L)\, dx$$

The integral is of the form of Integral T.7 with $a = L$, $k = \pi/L$

$$\langle p_x \rangle = \frac{2\pi\hbar}{\mathrm{i}L^2} \times \frac{1}{2\times\pi/L} \sin^2\left(\frac{\pi L}{L}\right) = \boxed{0}$$

This result is interpreted as meaning that there are equal probabilities of having momentum in the positive and negative x directions.

E7C.8(b) For the case when $m_l = +1$ the normalized wavefunction is $\psi_{+1}(\phi) = (2\pi)^{-1/2}\mathrm{e}^{\mathrm{i}\phi}$. This is complex, and so $\psi^*_{+1} = (2\pi)^{-1/2}\mathrm{e}^{-\mathrm{i}\phi}$. The angular momentum operator is $(\hbar/\mathrm{i})(\mathrm{d}/\mathrm{d}\phi)$, therefore its expectation value is given by

$$\begin{aligned}\int_0^{2\pi} \psi^*_{+1}(\hbar/\mathrm{i})(\mathrm{d}/\mathrm{d}\phi)\psi_{+1}\,\mathrm{d}\phi &= (1/2\pi)(\hbar/\mathrm{i})\int_0^{2\pi} \mathrm{e}^{-\mathrm{i}\phi}(\mathrm{d}/\mathrm{d}\phi)\mathrm{e}^{\mathrm{i}\phi}\,\mathrm{d}\phi\\ &= (1/2\pi)(\hbar/\mathrm{i})(\mathrm{i})\int_0^{2\pi} \mathrm{e}^{-\mathrm{i}\phi}\mathrm{e}^{\mathrm{i}\phi}\,\mathrm{d}\phi\\ &= (1/2\pi)(\hbar/\mathrm{i})(\mathrm{i})\int_0^{2\pi} 1\,\mathrm{d}\phi\\ &= (1/2\pi)(\hbar/\mathrm{i})(\mathrm{i})(2\pi) = \boxed{\hbar}\end{aligned}$$

For the general case the normalized wavefunction is $\psi_{m_l}(\phi) = (2\pi)^{-1/2}\mathrm{e}^{\mathrm{i}m_l\phi}$ and $\psi^*_{m_l}(\phi) = (2\pi)^{-1/2}\mathrm{e}^{\mathrm{i}m_l\phi}$.

$$\begin{aligned}\int_0^{2\pi} \psi^*_{m_l}(\hbar/\mathrm{i})(\mathrm{d}/\mathrm{d}\phi)\psi_{m_l}\,\mathrm{d}\phi &= (1/2\pi)(\hbar/\mathrm{i})\int_0^{2\pi} \mathrm{e}^{-\mathrm{i}m_l\phi}(\mathrm{d}/\mathrm{d}\phi)\mathrm{e}^{\mathrm{i}m_l\phi}\,\mathrm{d}\phi\\ &= (1/2\pi)(\hbar/\mathrm{i})(\mathrm{i}m_l)\int_0^{2\pi} \mathrm{e}^{-m_l\mathrm{i}\phi}\mathrm{e}^{\mathrm{i}m_l\phi}\,\mathrm{d}\phi\\ &= (1/2\pi)(\hbar/\mathrm{i})(\mathrm{i}m_l)(2\pi) = \boxed{m_l\hbar}\end{aligned}$$

E7C.9(b) The uncertainty in the momentum is given by $\Delta p = m\Delta v$ where m is the mass and Δv is the uncertainty in the velocity. The minimum uncertainty in the position of the electron is given as $\boxed{100\ \text{pm}}$.

The uncertainties in position and momentum are must obey the Heisenberg uncertainty principle [7C.13a–*258*], $\Delta p\Delta q \geq (\hbar/2)$, which in this case is expressed as $m\Delta v\Delta q \geq (\hbar/2)$. This is rearranged to give the uncertainty in the velocity, $\Delta v \geq \hbar/(2m\Delta q)$, giving a minimum uncertainty of $\Delta v_{\text{min}} = \hbar/(2m\Delta q)$, which is evaluated as

$$\frac{1.0546\times10^{-34}\ \text{J s}}{2\times(9.1094\times10^{-31}\ \text{kg})\times(100\times10^{-12}\ \text{m})} = \boxed{5.79\times10^5\ \text{m s}^{-1}}$$

E7C.10(b) The desired uncertainty in the momentum is

$$\begin{aligned}\Delta p &= 0.0010\times10^{-2}p = 1.00\times10^{-5}m_\mathrm{e}v\\ &= 1.00\times10^{-5}\times(9.1094\times10^{-31}\ \text{kg})\times(995\times10^3\ \text{m s}^{-1})\\ &= 9.06...\times10^{-30}\ \text{kg m s}^{-1}\end{aligned}$$

The Heisenberg uncertainty principle, [7C.13a–*258*] is rearranged to give the uncertainty in the position as $\Delta q \geq \hbar/(2\Delta p)$, which gives a minimum uncertainty of $\Delta q_{\text{min}} = \hbar/(2\Delta p)$. This is evaluated as

$$\frac{1.0546 \times 10^{-34}\ \text{J s}}{2 \times (9.06... \times 10^{-30}\ \text{kg m s}^{-1})} = \boxed{5.82 \times 10^{-6}\ \text{m}}$$

Solutions to problems

P7C.2 (a) Consider the integral $I = \int_0^L \sin(n\pi x/L)\sin(m\pi x/L)\,dx$. Using the identity, $\sin A \sin B = \frac{1}{2}\cos(A-B) - \frac{1}{2}\cos(A+B)$ with $A = n\pi x/L$ and $B = m\pi x/L$, this can be rewritten as

$$I = \tfrac{1}{2}\int_0^L \cos[(n-m)\pi x/L]\,dx - \tfrac{1}{2}\int_0^L \cos[(n+m)\pi x/L]\,dx \quad (7.1)$$

(b) In the case of $n = 2$, $m = 1$ the two integrands are $\cos(\pi x/L)$ and $\cos(3\pi x/L)$ which are plotted in Fig. 7.1

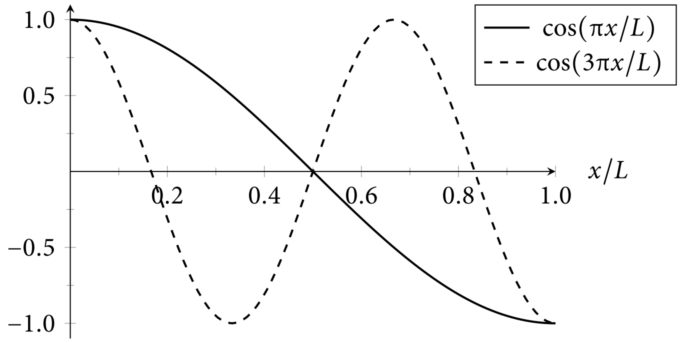


Figure 7.1

(c) It is seen that each of these functions are antisymmetric about $x = L/2$, such that the value of the function as $L/2 + \delta$ is minus that at $L/2 - \delta$. As a result, the integral of these functions over a symmetrical region about $x = L/2$ is zero.

An alternative way of coming to the same conclusion is to note that the integral of the first half of a cosine wave is zero on account of the enclosed area above and below the x-axis being the same (the solid curve). Similarly, the integral of three complete half cosine waves is also zero (the dashed curve).

(d) For the general case n and m and both integers, and so $n \pm m$ are also integers. The two integrands in eqn 7.1, when considered over the range $x = 0 \rightarrow L$, will each comprise a complete number of half cosine waves. By the same argument as in (c), these functions will integrate to zero and hence the wavefunctions are orthogonal for $n \neq m$.

P7C.4 An operator $\hat{\Omega}$ is hermitian if $\int \psi_i^* \hat{\Omega}\psi_j \,\mathrm{d}\tau = \left[\int \psi_j^* \hat{\Omega}\psi_i \,\mathrm{d}\tau\right]^*$, [7C.7–*253*]. Proceed by integrating by parts (*The chemist's toolkit* 15 in Topic 7C on page 254) to give

$$\int_0^{2\pi} \psi_i^* \left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}\phi}\right)\psi_j \,\mathrm{d}\phi = \frac{\hbar}{\mathrm{i}}\left(\underbrace{\psi_i^*\psi_j\big|_0^{2\pi}}_{\mathrm{A}} - \int_0^{2\pi} \psi_j \frac{\mathrm{d}\psi_i^*}{\mathrm{d}\phi}\,\mathrm{d}\phi\right)$$

The term A is zero because the wavefunction must be single valued, requiring $\psi_i(\phi) = \psi_i(\phi + 2\pi)$, and so $\psi_i(0) = \psi_i(2\pi)$. It follows that

$$\int_0^{2\pi} \psi_i^* \left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}\phi}\right)\psi_j \,\mathrm{d}\phi = -\frac{\hbar}{\mathrm{i}}\int_0^{2\pi} \psi_j \frac{\mathrm{d}\psi_i^*}{\mathrm{d}\phi}\,\mathrm{d}\phi$$

The term of the right is written as a complex conjugate to give

$$\int_0^{2\pi} \psi_i^* \left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}\phi}\right)\psi_j \,\mathrm{d}\phi = \left[\frac{\hbar}{\mathrm{i}}\int_0^{2\pi} \psi_j^* \frac{\mathrm{d}\psi_i}{\mathrm{d}\phi}\,\mathrm{d}\phi\right]^* = \left[\int_0^{2\pi} \psi_j^* \left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}\phi}\right)\psi_i \,\mathrm{d}\phi\right]^*$$

Note that because the complex conjugate of the whole term is taken, to compensate for this the complex conjugate of the terms inside the bracket need to be taken too $\psi = [\psi^*]^*$; $\mathrm{i}^* = -\mathrm{i}$ is also used. This final equation is consistent with [7C.7–*253*] and so demonstrates that the angular momentum operator is hermitian.

P7C.6 The expectation value is given by [7C.11–*256*], $\langle\Omega\rangle = \int \psi^* \hat{\Omega}\psi \,\mathrm{d}\tau$, where ψ is normalized. However, if ψ is an eigenfunction of $\hat{\Omega}$ each measurement gives the corresponding eigenvalue, and this is therefore also the expectation value.

(a) The function $N\exp(\mathrm{i}kx)$ is an eigenfunction of the linear momentum operator $\hat{p}_x = (\hbar/\mathrm{i})(\mathrm{d}/\mathrm{d}x)$

$$\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}N\mathrm{e}^{\mathrm{i}kx} = \frac{\hbar}{\mathrm{i}} \times N\mathrm{i}k\mathrm{e}^{\mathrm{i}kx} = \hbar k \times N\mathrm{e}^{\mathrm{i}kx}$$

and the eigenvalue is $\boxed{\hbar k}$. Hence, the expectation value is equal to this.

(b) The wavefunction $N\cos kx$ is not an eigenfunction of the linear momentum operator, so the expectation value has to be computed by evaluating the integral. First consider the effect of applying this operator to the wavefunction

$$\hat{p}_x\psi = (\hbar/\mathrm{i})(\mathrm{d}/\mathrm{d}x)N\cos(kx) = -(\hbar k/\mathrm{i})N\sin kx$$

It follows that the expectation value is given by

$$\langle p_x\rangle = -(\hbar k/\mathrm{i})N^2\int_{-\infty}^{\infty}\cos(kx)\sin(kx)\,\mathrm{d}x = \boxed{0}$$

The integrand is an odd function, meaning that its value at $-x$ is the negative of that at x, which means that its integral over a symmetric range is zero.

(c) The wavefunction Ne^{-ax^2} is not an eigenfunction of the linear momentum operator. Consider the effect of applying this operator to the wavefunction

$$\hat{p}_x\psi = (\hbar/\mathrm{i})(\mathrm{d}/\mathrm{d}x)Ne^{-ax^2} = (\hbar/\mathrm{i}) \times -2axNe^{-ax^2}$$

The expectation value of the momentum is then

$$\langle p_x \rangle = (-2aN^2\hbar/\mathrm{i}) \int_{-\infty}^{\infty} xe^{-2ax^2}\,\mathrm{d}x = \boxed{0}$$

As before, the integrand is an odd function so its integral over a symmetric range is zero.

P7C.8 (a) The wavefunction $\psi(x) = \cos(\chi)e^{\mathrm{i}kx} + \sin(\chi)e^{-\mathrm{i}kx}$ is a superposition of the functions $\psi_+ = e^{\mathrm{i}kx}$ and $\psi_- = e^{-\mathrm{i}kx}$. These are eigenfunctions of the linear momentum operator with eigenvalues $+\hbar k$ and $-\hbar k$ respectively, as

$$\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\,e^{\mathrm{i}kx}}{\mathrm{d}x} = \frac{\hbar}{\mathrm{i}} \times \mathrm{i}ke^{\mathrm{i}kx} = \hbar ke^{\mathrm{i}kx} \qquad \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\,e^{-\mathrm{i}kx}}{\mathrm{d}x} = \frac{\hbar}{\mathrm{i}} \times -\mathrm{i}ke^{-\mathrm{i}kx} = -\hbar ke^{-\mathrm{i}kx}$$

As the wavefunction is a superposition of eigenfunctions of the linear momentum operator, the probability of measuring a particular momentum eigenvalue is the square modulus of the corresponding coefficent, $|c_k|^2$ in the expression for ψ. Hence the probability of finding the electron with linear momentum $+k\hbar$ is $|c_+|^2 = |\cos\chi|^2 = \boxed{\cos^2\chi}$

(b) The probability of finding the electron with linear momentum $-k\hbar$ is $|c_-|^2 = |\sin\chi|^2 = \boxed{\sin^2\chi}$

(c) If the probability of finding the electron with momentum $+k\hbar$ is 0.9, then $|c_+|^2 = 0.9$, and assuming that c_+ is real and positive , $c_+ = \sqrt{0.9} = \boxed{0.95}$. The probabilities must sum to 1 and so the probability of finding the electron with momentum $-k\hbar$ is 0.1, then $|c_+|^2 = 0.1$ and so $c_- = \sqrt{0.1} = \boxed{0.32}$

(d) The kinetic energy operator is $\hat{E}_\mathrm{k} = \hat{p}_x^2/2m = -(\hbar^2/2m)\mathrm{d}^2/\mathrm{d}x^2$, where m is the mass of the electron. Consider applying this operator to $\psi_\pm$

$$\hat{E}_\mathrm{k}\psi_+ = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}e^{\mathrm{i}kx} = \frac{\hbar^2k^2}{2m}e^{\mathrm{i}kx}$$
$$\hat{E}_\mathrm{k}\psi_- = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}e^{-\mathrm{i}kx} = \frac{\hbar^2k^2}{2m}e^{-\mathrm{i}kx}$$

Hence, both components are eigenfunctions of the kinetic energy operator with the same eigenvalue, $(\hbar k)^2/2m$, and so the overall wavefunction is also an eigenfunction of the kinetic energy operator, eigenvalue $(\hbar k)^2/2m$. The kinetic energy of the electron is thus $\boxed{(\hbar k)^2/2m}$

P7C.10 (a) Figure 7.2 shows that as N increases the symmetrical peak around $x = 0$ narrows and sharpens.

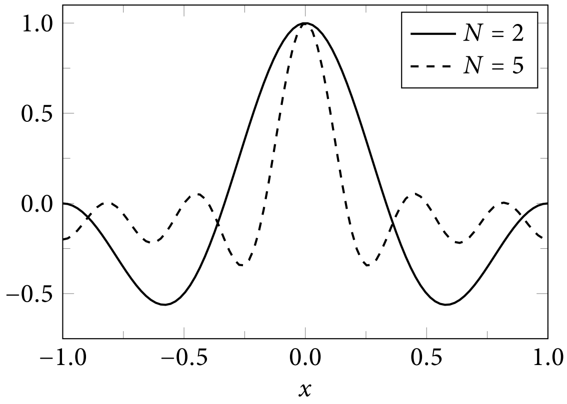


Figure 7.2

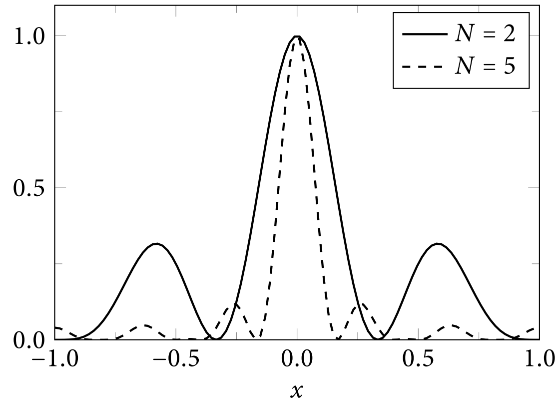


Figure 7.3

(b) Figure 7.3 shows that, as before, the probability density narrows and sharpens as the superposition is extended.

(c) In order to compute $\langle x^2 \rangle$, the expectation value of x^2, it is necessary to normalize the wavefunction. If attention is focused on the finite range $-1 \leq x \leq +1$ the normalizing factor $\mathcal{N}$ is found by evaluating

$$\mathcal{N}^2 = \left\{ \frac{1}{N^2} \int_{-1}^{+1} \left[\sum_{k=1}^{N} \cos(k\pi x) \right]^2 \mathrm{d}x \right\}^{-1}$$

Because the square of a sum involving (possibly) many terms is involved, this appears to be a formidable task. However, some experimentation with some modest values of N using mathematical software implies that the term in the braces is simply $(1/N)$, so the normalizing factor is $\mathcal{N} =$

$(N)^{1/2}$. With this, the expectation value is computed using

$$\langle x^2\rangle = (N)\times(1/N^2)\int_{-1}^{+1}\left[\sum_{k=1}^{N}\cos(k\pi x)\right]^2 x^2\,\mathrm{d}x$$

Mathematical software gives the values 0.0628 for $N = 5$, 0.0305 for $N = 10$, and 0.0254 for $N = 12$. The corresponding values of $\langle x^2\rangle^{1/2}$ are 0.251, 0.175 and 0.159. There is a decreasing trend in the value of $\langle x^2\rangle^{1/2}$ which makes sense as the superposition becomes narrower as N increases.

(d) This wavefunction is the superposition of N terms each of which has the form $N^{-1}\cos(k\pi x)$. Momentum is more easily discussed by using the identity $\cos(k\pi x) = \frac{1}{2}(\mathrm{e}^{\mathrm{i}k\pi x} + \mathrm{e}^{-\mathrm{i}k\pi x})$. The wavefunction is then a superposition of N terms of the form $(1/2N)\mathrm{e}^{\mathrm{i}k\pi x}$ and N of the form $(1/2N)\mathrm{e}^{-\mathrm{i}k\pi x}$. The first of these terms corresponds to a momentum $+k\hbar$, and the second to a momentum $-k\hbar$.

The normalizing factor is $N^{1/2}$, so the coefficient of each of the terms in the expansion (of the form $\mathrm{e}^{\pm\mathrm{i}k\pi x}$) is $N^{1/2}/2N = 1/2N^{1/2}$. The probability of observing the momentum corresponding to any one term is given by the square is this coefficient, which is $1/4N$.

P7C.12 To evaluate the commutator of the position and momentum operators consider the effect of the commutator on an arbitrary function ψ

$$[\hat{p}_x,\hat{x}]\psi = (\hat{p}_x\hat{x} - \hat{x}\hat{p}_x)\psi = \left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}(x\psi)}{\mathrm{d}x} - x\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)$$

to evaluate the first derivative the product rule is used

$$= \frac{\hbar}{\mathrm{i}}\left(x\frac{\mathrm{d}\psi}{\mathrm{d}x} + \psi\frac{\mathrm{d}x}{\mathrm{d}x} - x\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) = \frac{\hbar}{\mathrm{i}}\psi$$

Because $[\hat{p}_x,\hat{x}]\psi = (\hbar/\mathrm{i})\psi$ it follows that the commutator is the constant term $\hbar/\mathrm{i}$. Hence the expectation value is given by

$$\langle[\hat{p}_x,\hat{x}]\rangle = \frac{\int\psi^*(\hbar/\mathrm{i})\psi\,\mathrm{d}\tau}{\int\psi^*\psi\,\mathrm{d}\tau} = \boxed{\hbar/\mathrm{i}}$$

P7C.14 To evaluate the commutator consider its effect on an arbitrary wavefunction ψ

$$\begin{aligned}[\hat{a},\hat{a}^\dagger]\psi &= (\hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a})\psi\\ &= \left(\frac{1}{\sqrt{2}}(\hat{x}+\mathrm{i}\hat{p}_x)\frac{1}{\sqrt{2}}(\hat{x}-\mathrm{i}\hat{p}_x) - \frac{1}{\sqrt{2}}(\hat{x}-\mathrm{i}\hat{p}_x)\frac{1}{\sqrt{2}}(\hat{x}+\mathrm{i}\hat{p}_x)\right)\psi\\ &= \tfrac{1}{2}\left[(\hat{x}^2 - \mathrm{i}\hat{x}\hat{p}_x + \mathrm{i}\hat{p}_x\hat{x} + \hat{p}_x^2) - (\hat{x}^2 + \mathrm{i}\hat{x}\hat{p}_x - \mathrm{i}\hat{p}_x\hat{x} + \hat{p}_x^2)\right]\psi\\ &= \mathrm{i}(\hat{p}_x\hat{x} - \hat{x}\hat{p}_x)\psi\end{aligned}$$

The quantity in the parentheses is the commutator $[\hat{p}_x, \hat{x}]$. The commutator of the position and momentum operators is given by [7C.16–*259*], $[\hat{x}, \hat{p}_x] = \mathrm{i}\hbar$, therefore $[\hat{p}_x, \hat{x}] = -\mathrm{i}\hbar$

$$[\hat{a}, \hat{a}^\dagger]\psi = \mathrm{i}[\hat{p}_x, \hat{x}]\psi = \mathrm{i}(-\mathrm{i}\hbar)\psi = \hbar\psi$$

Hence $[\hat{a}, \hat{a}^\dagger] = \boxed{\hbar}$.

7D Translational motion

Answers to discussion questions

D7D.2 The hamiltonian for a particle in a two- or three-dimensional box is separable into a sum of terms each of which depends on just one of the variables x, y or z. Therefore the solutions to the Schrödinger equation are products of separate functions of each of these variables, $\Psi(x, y, z) = \psi(x)\psi(y)\psi(z)$. In the hamiltonian the terms in the three variables are all of the same form, so the wavefunctions are likewise of the same form. Similarly, the boundary conditions along each direction are the same, so the quantization which this imposes is the same. As a result the wavefunctions are simply a product of the wavefunctions that would be found by solving the Schrödinger equation along each direction separately.

The energy levels of two- and three-dimensional boxes can be degenerate, that is there are different wavefunctions which have the same energy. This is usually a consequence of the box having a certain kind of symmetry, for example in a two-dimensional box in which the two sides are the same length the levels with quantum numbers $n_1 = l$, $n_2 = m$ and $n_1 = m$, $n_2 = l$ are degenerate.

Solutions to exercises

E7D.1(b) The linear momentum of a free electron is given by

$$p = \hbar k = (1.0546 \times 10^{-34}\,\mathrm{J\,s}) \times (5 \times 10^{9}\,\mathrm{m}^{-1}) = \boxed{5 \times 10^{-25}\,\mathrm{kg\,m\,s}^{-1}}$$

where $1\,\mathrm{J} = 1\,\mathrm{kg\,m}^2\,\mathrm{s}^{-2}$ is used; note that $1\,\mathrm{nm}^{-1} = 1 \times 10^{9}\,\mathrm{m}^{-1}$. The kinetic energy is given by [7D.2–*261*]

$$E_\mathrm{k} = \frac{(\hbar k)^2}{2m} = \frac{((1.0546 \times 10^{-34}\,\mathrm{J\,s}) \times (5 \times 10^{9}\,\mathrm{m}^{-1}))^2}{2 \times (9.1094 \times 10^{-31}\,\mathrm{kg})} = \boxed{2 \times 10^{-19}\,\mathrm{J}}$$

E7D.2(b) The electron is travelling in the positive x direction hence the momentum and the velocity v are both positive. The momentum of this particle is given by

$$p = mv = (1.0 \times 10^{-3}\,\mathrm{kg}) \times (+10\,\mathrm{m\,s}^{-1}) = +0.01\,\mathrm{kg\,m\,s}^{-1}$$

The values of k is therefore

$$k = \frac{p}{\hbar} = \frac{+0.01\ \mathrm{kg\,m\,s^{-1}}}{1.0546\times10^{-34}\ \mathrm{J\,s}} = +9.5\times10^{31}\ \mathrm{m^{-1}}$$

where $1\ \mathrm{J} = 1\ \mathrm{kg\,m^2\,s^{-2}}$ is used. The wavefunction is then, with x is measured in metres,

$$\psi(x) = \mathrm{e}^{\mathrm{i}kx} = \boxed{\mathrm{e}^{+\mathrm{i}(9.5\times10^{31}\ \mathrm{m^{-1}})x}}$$

E7D.3(b) The energy levels of a particle in a box are given by [7D.6–*263*], $E_n = n^2h^2/8mL^2$, where n is the quantum number. With the mass equal to that of the electron and the length as 1.5 nm, the energies are

$$\begin{aligned}E_n &= \frac{n^2h^2}{8mL^2} = n^2\times\frac{(6.6261\times10^{-34}\ \mathrm{J\,s})^2}{8\times(9.1094\times10^{-31}\ \mathrm{kg})\times(1.5\times10^{-9}\ \mathrm{m})^2}\\ &= n^2\times(2.67...\times10^{-20}\ \mathrm{J})\end{aligned}$$

To convert to $\mathrm{kJ\,mol^{-1}}$, multiply through by Avogadro's constant and divide by 1000.

$$= n^2\times(2.67...\times10^{-20}\ \mathrm{J})\times\frac{6.0221\times10^{23}\ \mathrm{mol^{-1}}}{1000} = n^2\times(16.1...\ \mathrm{kJ\,mol^{-1}})$$

To convert to electronvolts divide through by the elementary charge

$$= n^2\times(2.67...\times10^{-20}\ \mathrm{J})\times\frac{1}{1.6022\times10^{-19}\ \mathrm{C}} = n^2\times(0.167...\ \mathrm{eV})$$

To convert to reciprocal centimetres, divide by hc, with c in $\mathrm{cm\,s^{-1}}$

$$\begin{aligned}&= n^2\times\frac{(2.67...\times10^{-20}\ \mathrm{J})}{(6.6261\times10^{-34}\ \mathrm{J\,s})\times(2.9979\times10^{10}\ \mathrm{cm\,s^{-1}})}\\ &= n^2\times(1.34...\times10^{3}\ \mathrm{cm^{-1}})\end{aligned}$$

The energy separation between two levels with quantum numbers n_1 and n_2 is

$$\Delta E(n_1,n_2) = E_{n_2} - E_{n_1} = (n_2^2 - n_1^2)\times(2.67...\times10^{-20}\ \mathrm{J})$$

The values in the other units are found by using the appropriate value of the constant, computed above.

(i) $\Delta E(2,3) = \boxed{1.3\times10^{-19}\ \mathrm{J}}$, $\boxed{81\ \mathrm{kJ\,mol^{-1}}}$, $\boxed{0.84\ \mathrm{eV}}$, or $\boxed{6.7\times10^{3}\ \mathrm{cm^{-1}}}$

(ii) $\Delta E(6,7) = \boxed{3.5\times10^{-19}\ \mathrm{J}}$, $\boxed{2.1\times10^{2}\ \mathrm{kJ\,mol^{-1}}}$, $\boxed{2.2\ \mathrm{eV}}$, or $\boxed{1.8\times10^{4}\ \mathrm{cm^{-1}}}$

E7D.4(b) The wavefunctions are $\psi_1(x) = (2/L)^{1/2}\sin(\pi x/L)$ and $\psi_3(x) = (2/L)^{1/2} \times \sin(3\pi x/L)$. They are orthogonal if $\int \psi_1^* \psi_2 \, d\tau = 0$. In this case the integral is taken from $x = 0$ to $x = L$ as outside this range the wavefunctions are zero. The required integral is of the form of Integral T.5, with $A = \pi/L, B = 3\pi/L$, and $a = L$

$$\begin{aligned}\frac{2}{L}\int_0^L \sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{3\pi x}{L}\right) dx &= \frac{2}{L}\left[\frac{\sin(-2\pi L/L)}{-4\pi/L} - \frac{\sin(4\pi L/L)}{8\pi/L}\right] \\ &= \frac{2}{L}\left[\frac{\sin(-2\pi)}{-4\pi/L} - \frac{\sin(4\pi)}{8\pi/L}\right] = 0\end{aligned}$$

where $\sin n\pi = 0$ for integer n is used. The two wavefunctions are orthogonal.

E7D.5(b) The particle in a box wavefunction with quantum number n is given by $\psi_n(x) = (2/L)^{1/2}\sin(n\pi x/L)$ The probability of finding the electron in a small region of space δx centred on position x is approximated as $\psi^2(x)\delta x$. For this *Exercise* $x = 0.66L, \delta x = 0.02L$.

For the case where $n = 1$

$$\begin{aligned}\psi_1(0.66L)^2 \times 0.02L &= \left[\sqrt{2/L}\sin\left(\pi(0.66L)/L\right)\right]^2 \times 0.02L \\ &= (2/L)\sin^2(0.66\pi) \times 0.02L = \boxed{0.031}\end{aligned}$$

For the case where $n = 2$

$$\begin{aligned}\psi_2(0.66L)^2 \times 0.02L &= \left[\sqrt{2/L}\sin\left(2 \times \pi(0.66L)L\right)\right]^2 \times 0.02L \\ &= (2/L)\sin^2(1.32\pi) \times 0.02L = \boxed{0.029}\end{aligned}$$

E7D.6(b) The wavefunction with $n = 2$ and is $\psi_2(x) = \sqrt{2/L}\sin(2\pi x/L)$, which leads to a probability density $P_2(x) = |\psi_2(x)|^2 = (2/L)\sin^2(2\pi x/L)$. Graphs of these functions are shown in Fig 7.4.

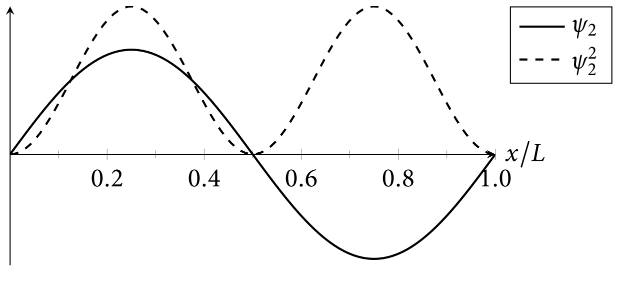


Figure 7.4

The probability density is symmetric about $x = L/2$. Therefore, there is an equal probability of observing the particle at an arbitrary position x' and at $L - x'$, so it follows that the average position of the particle must be at $L/2$.

E7D.7(b) The wavefunction with $n = 1$ is $\psi_1(x) = \sqrt{2/L}\sin(\pi x/L)$, which leads to a probability density $P_1(x) = |\psi_1(x)|^2 = (2/L)\sin^2(\pi x/L)$. Graphs of these functions are shown in Fig 7.5.

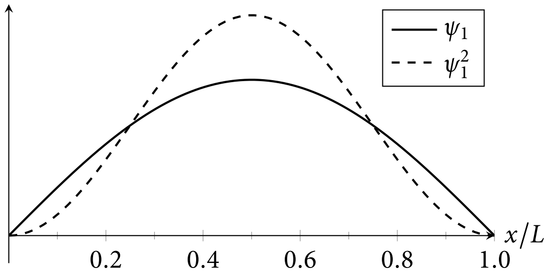


Figure 7.5

The probability density is symmetric about $x = L/2$. Therefore, there is equal probability density at positions $(L/2) + \delta$ and $(L/2) - \delta$, so it follows that the average position of the particle must be at $L/2$.

The expectation value of x^2 is found from the integral $\int_0^L P_1(x)x^2\,dx$. Although the probability density will be the same at positions $(L/2) - \delta$ and $(L/2) + \delta$, the function x^2 will increase by more between $(L/2)$ and $(L/2) + \delta$, than between $(L/2) - \delta$ and $(L/2)$, so in the integral the point at $(L/2) + \delta$ has greater weight. It is therefore expected that $\langle x^2 \rangle > (L/2)^2$.

E7D.8(b) For an electron in a cubic well, of side length L the energy of the state characterized by quantum numbers n_1, n_2 and n_3 is given by [7D.13b–*267*], $E_{n_x,n_y,n_z} = h^2(n_x^2+n_y^2+n_z^2)/8m_eL^2$ where n_x, n_y, n_z are integers ≥ 1. Hence, the minimum or zero-point energy has $n_x = n_y = n_z = 1$,

$$E_{1,1,1} = h^2(1^2 + 1^2 + 1^2)/8m_eL^2 = 3h^2/8m_eL^2$$

Setting this equal to the rest energy, m_ec^2 gives

$$3h^2/8m_eL^2 = m_ec^2$$

$$L = \sqrt{3/8} \times (h/m_ec) = \boxed{\sqrt{3/8}\,\lambda_C}$$

where $\lambda_C = h/(m_ec)$ is the Compton wavelength.

E7D.9(b) The wavefunction for a particle in a one-dimensional box with length L and in the state with $n = 5$ is $\psi(x) = \sqrt{2/L}\sin(5\pi x/L)$ giving a probability density of $P(x) = |\psi(x)|^2 = (2/L)\sin^2(5\pi x/L)$.

As this is a trigonometric function, the function is maximized when $\sin^2(5\pi x/L) = 1$, which is when $\sin(5\pi x/L) = \pm 1$; these values occur when the argument of the sine function is an odd multiple of $\pi/2$

$$5\pi x/L = \pi/2, 3\pi/2, 5\pi/2, 7\pi/2, \ldots \text{ hence } x = \boxed{L/10, 3L/10, L/2, 7L/10, 9L/10}$$

The probability density is zero when the wavefunction is zero, which is when the argument of the sine function is a multiple of π

$$5\pi x/L = 0, \pi, 2\pi, \ldots \quad \text{hence} \quad x = \boxed{0, L/5, 2L/5, 3L/5, 4L/5, L}$$

E7D.10(b) The energy levels of a particle in a cubical box with side L are given by [7D.13b–*267*], $E_n = h^2n^2/8mL^2$, with $n^2 = n_x^2 + n_y^2 + n_z^2$. When the side is decreased to $0.9 \times L$ the energies become $E_n' = h^2n^2/8m(0.9 \times L)^2 = h^2n^2/8m(0.81 \times L^2)$ giving a fractional change of

$$\frac{E_n' - E_n}{E_n} = \frac{[h^2n^2/8m(0.81 \times L^2)] - [h^2n^2/8mL^2]}{h^2n^2/8mL^2} = \frac{1}{0.81} - 1 = \boxed{0.235}$$

E7D.11(b) The energy levels of a particle in a box of length L are given by [7D.6–*263*], $E_n = h^2n^2/8mL^2$. This energy is equal to the average thermal energy when $kT/2 = h^2n^2/8mL^2$, leading to $\boxed{n = (2L/h)(mkT)^{1/2}}$.

For an argon atom, mass 39.95 m_u in a box for length 0.1 cm this evaluates as

$$\begin{aligned} n &= \frac{2(0.1 \times 10^{-2}\ \text{m})}{6.6261 \times 10^{-34}\ \text{J s}} \\ &\quad \times \left[(39.95 \times 1.6605 \times 10^{-27}\ \text{kg}) \times (1.3806 \times 10^{-23}\ \text{J K}^{-1}) \times (298\ \text{K})\right]^{1/2} \\ &= \boxed{5.0 \times 10^{7}} \end{aligned}$$

E7D.12(b) The wavefunction of a particle in a square box of side length L with quantum numbers $n_1 = 1, n_2 = 3$ is $\psi_{1,3}(x, y) = (2/L)\sin(\pi x/L)\sin(3\pi y/L)$. The corresponding probability density is $P_{1,3}(x, y) = (2/L)^2 \sin^2(\pi x/L)\sin^2(3\pi y/L)$. The probability density is maximized when $\sin^2(\pi x/L) \times \sin^2(3\pi y/L) = 1$ which occurs only when each sin term is equal to ±1. The term in x is equal to 1 when $\pi x/L = \pi/2$ and hence $x = L/2$. For the term in y

$$\begin{aligned} &\sin(3\pi y/L) = \pm 1 \\ &\qquad 3\pi y/L = \pi/2, 3\pi/2, 5\pi/2 \quad \text{hence} \quad y = L/6, L/2, 5L/6. \end{aligned}$$

Hence the maxima occur at $(x, y) = \boxed{(L/2, L/6), (L/2, L/2), (L/2, 5L/6)}$

Nodes occur when the wavefunction passes through zero, which is when either of the sin terms are zero, excluding the boundaries at $x = 0, L$ $y = 0, L$ because at these points the wavefunction does not pass through zero. There are therefore no nodes associated with the function $\sin(\pi x/L)$. In the y-direction there are nodes when

$$\begin{aligned} &\sin(3\pi y/L) = 0 \\ &\qquad 3\pi y/L = \pi, 2\pi \quad \text{hence} \quad y = L/3, 2L/3 \end{aligned}$$

There is thus a node when $y = L/3$ and for any value of x, that is a nodal line at $\boxed{y = L/3 \text{ and parallel to the } x\text{-axis}}$. Likewise the node at $y = 2L/3$ corresponds to a nodal line at $\boxed{y = 2L/3 \text{ and parallel to the } x\text{-axis}}$.

E7D.13(b) The energy levels for a 2D rectangular box, side lengths L_1, L_2 are

$$E_{n_1,n_2} = \frac{h^2}{8m}\left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2}\right)$$

where n_1 and n_2 are integers greater than or equal to 1.

For the specific case where $L_1 = L, L_2 = 2L$,

$$E_{n_1,n_2} = \frac{h^2}{8m}\left(\frac{n_1^2}{L^2} + \frac{n_2^2}{(2L)^2}\right) = \frac{h^2}{8mL^2}\left(n_1^2 + \frac{n_2^2}{4}\right)$$

The energy of the state with $n_1 = 2, n_2 = 8$ is then

$$E_{2,2} = \frac{h^2}{8mL^2}\left(2^2 + \frac{8^2}{4}\right) = \frac{h^2}{8mL^2}(20)$$

By inspection, the first term in the sum is equal to 4 and the second is equal to 16, it can be arranged for these to be swapped. This requires $n_1^2 = 16$ and so $n_1 = 4$ and $n_2^2/4 = 4$, and so $n_2 = 4$. Hence, the state $\boxed{(4,4) \text{ is degenerate with } (2,8)}$.

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 rectangular 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 (that is $n_2/2$ must be an integer) and (b) is distinct from (n_1, n_2). A box with incommensurable sides, say, L and $\sqrt{2}L$, would have $\boxed{\text{no degenerate levels}}$.

E7D.14(b) The energy levels of a cubic box are given by [7D.13b–*267*]

$$E_{n_1,n_2,n_3} = \frac{h^2}{8mL^2}(n_1^2 + n_2^2 + n_3^2)$$

where n_1, n_2, n_3 are integers greater than or equal to 1. Hence the lowest energy state is that with $n_1 = n_2 = n_3 = 1$, with energy

$$E_{(1,1,1)} = \frac{h^2}{8mL^2}(1^2 + 1^2 + 1^2) = \frac{h^2}{8mL^2}(3)$$

and so the energy of the level with energy 14/3 times that of the lowest is $14h^2/8mL^2$, which will be produced by states for which $n_1^2+n_2^2+n_3^2 = 14$. There are six states with this energy, $(n_1, n_2, n_3) = (1,2,3), (1,3,2), (2,1,3), (2,3,1), (3,1,2), (3,2,1)$, and so the degeneracy is $\boxed{6}$.

E7D.15(b) The transmission probability [7D.20a–*269*] depends on the energy of the tunnelling particle relative to the barrier height ($\varepsilon = E/V_0 = (1.5\text{ eV})/(2.0\text{ eV})$

= 0.75), the width of the barrier, (L = 100 pm), and the decay parameter of the wavefunction inside the barrier (κ)

$$\kappa = \frac{(2m(E-V_0))^{1/2}}{\hbar}$$
$$= \frac{(2\times(1.6726\times10^{-27}\,\text{kg})\times[(2.0-1.5)\,\text{eV}\times1.6022\times10^{-19}\,\text{J eV}^{-1}])^{1/2}}{1.0546\times10^{-34}\,\text{J s}}$$
$$= 1.58...\times10^{11}\ \text{m}^{-1}$$

Such that $\kappa L = (1.58...\times10^{11}\ \text{m}^{-1})\times(100\times10^{-12}\ \text{m}) = 15.8...$, and so the transmission probability is given by

$$T = \left[1+\frac{(\mathrm{e}^{\kappa L}-\mathrm{e}^{-\kappa L})^2}{16\varepsilon(1-\varepsilon)}\right]^{-1} = \left[1+\frac{(\mathrm{e}^{15.8...}-\mathrm{e}^{-15.8...})^2}{16\times0.75\times(1-0.75)}\right]^{-1} = \boxed{5.7\times10^{-14}}$$

Solutions to problems

P7D.2 (i) The energy levels of a particle in a cubic box are given by [7D.13b–*267*] $E(n_x,n_y,n_z) = h^2n^2/8mL^2$ where $n^2 = n_x^2+n_y^2+n_z^2$, and L is the side length of the box, such that its volume is $V = L^3$. For a cubic box, volume 1.00 m^3, $L = (1.00\ \text{m}^3)^{1/3} = 1.00$ m. The mass of a N_2 molecule is 28.00 m_u = 4.6494 × 10^{-26} kg. To find the value of n that makes the energy equal to the average thermal energy, set $E_n = \frac{3}{2}kT$ and solve for n

$$n = \frac{L\sqrt{12mkT}}{h}$$
$$= \frac{(1.00\ \text{m})\times\left[12\times(4.6494\times10^{-26}\ \text{kg})\times(300\ \text{K})\times(1.3806\times10^{-23}\,\text{J K}^{-1})\right]^{1/2}}{6.6261\times10^{-34}\,\text{J s}}$$
$$= \boxed{7.25\times10^{10}}$$

(ii) The separation between neighbouring levels is

$$\Delta E = E_{n+1}-E_n = \frac{h^2}{8mL^2}\left[(n+1)^2-n^2\right] = \frac{h^2(2n+1)}{8mL^2}$$

and so for this case

$$\Delta E = \frac{(6.6261\times10^{-34}\,\text{J s})^2\times(2\times7.25\times10^{10}+1)}{8\times(4.6494\times10^{-26}\ \text{kg})\times(1.00\ \text{m})^2} = \boxed{1.71\times10^{-31}\ \text{J}}$$

(iii) The de Broglie wavelength is given by [7A.11–*244*], $\lambda = h/p$, and the kinetic energy is $E_k = p^2/2m$. In this case $E_k = \frac{3}{2}kT$, hence $p^2/2m = \frac{3}{2}kT$ which is rearranged for the momentum to give $p = \sqrt{3mkT}$. Hence, the de Broglie wavelength is

$$\lambda = \frac{h}{\sqrt{3mkT}}$$
$$= \frac{6.6261\times10^{-34}\,\text{J s}}{\left[3\times(4.6494\times10^{-26}\ \text{kg})\times(1.3806\times10^{-23}\,\text{J K}^{-1})\times(300\ \text{K})\right]^{1/2}}$$
$$= \boxed{27.6\ \text{pm}}$$

P7D.4 The wavefunction with $n = 2$ is $\psi_2(x) = (2/L)^{1/2}\sin(2\pi x/L)$, and this is used in [7C.11–*256*], $\langle\Omega\rangle = \int\psi^*\hat{\Omega}\psi\,\mathrm{d}\tau$, to compute the expectation value for the cases $\hat{\Omega} = \hat{p}_x = (\hbar/\mathrm{i})\mathrm{d}/\mathrm{d}x$ and $\hat{\Omega} = \hat{p}_x^2$. The effect of $\hat{p}_x$ on the wavefunction is

$$\hat{p}_x\psi_2 = (\hbar/\mathrm{i})\mathrm{d}/\mathrm{d}x\left[(2/L)^{1/2}\sin(2\pi x/L)\right] = (\hbar/\mathrm{i})(2/L)^{1/2}(2\pi/L)\cos(2\pi x/L)$$

and the effect of $\hat{p}_x^2$ is found by applying $\hat{p}_x$ to this result

$$\begin{aligned}\hat{p}_x^2\psi_2 &= (\hbar/\mathrm{i})\mathrm{d}/\mathrm{d}x\left[(\hbar/\mathrm{i})(2/L)^{1/2}(2\pi/L)\cos(2\pi x/L)\right]\\ &= \hbar^2(2/L)^{1/2}(2\pi/L)^2\sin(2\pi x/L)\end{aligned}$$

Hence

$$\langle p_x\rangle = \int_0^L \psi_2^*\hat{p}_x\psi_2\mathrm{d}x = (\hbar/\mathrm{i})(2/L)(2\pi/L)\int_0^L \sin(2\pi x/L)\cos(2\pi x/L)\mathrm{d}\,x$$

This integral is of the form of Integral T.7 with $k = 2\pi/L$, $a = L$

$$\langle p_x\rangle = (\hbar/\mathrm{i})(2/L)(2\pi/L)\times(L/4\pi)\sin^2(2\pi L/L) = \boxed{0}$$

$$\langle p_x^2\rangle = \int_0^L \psi_2^*\hat{p}_x^2\psi_2\,\mathrm{d}x = \hbar^2(2/L)(2\pi/L)^2\int_0^L \sin^2(2\pi x/L)\,\mathrm{d}x$$

This integral is of the form of Integral T.2 with $k = 2\pi/L$, $a = L$

$$\langle p_x^2\rangle = \hbar^2(2/L)(2\pi/L)^2\times[L/2-(L/8\pi)\sin(4\pi L/L)] = \boxed{4\pi^2\hbar^2/L^2}$$

P7D.6 The wavefunction of the state with quantum number n, in the range $0 \le x \le L$, is $\psi_n(x) = (2/L)^{1/2}\sin(n\pi x/L)$.

(a) The probability density is $P_n(x) = |\psi_n(x)|^2 = (2/L)\sin^2(n\pi x/L)$ which is symmetric about $x = L/2$, meaning that $P_n(L/2+x) = P_n(L/2-x)$ for all x. Hence, the particle is equally likely to be at position x as at $L-x$, and so the average position must be in the middle of this range, i.e. $\boxed{\langle x\rangle = L/2}$.

(b) The particle has kinetic energy (only) when it is in the box, but as it is constrained to be within the box it must move back and forth at a constant speed between the two infinite walls. Therefore the probability of the particle travelling with momentum $+p$ (to the right) is equal to the probability of it travelling with momentum $-p$ (to the left), and so the average value of the momentum must be $\boxed{0}$.

(c)

$$\langle x^2\rangle = \int_0^L \psi_n^*\hat{x}^2\psi_n\,\mathrm{d}x = (2/L)\int_0^L x^2\sin^2(n\pi x/L)\,\mathrm{d}x$$

The integral is of the form of Integral T.12 with $a = L$ and $k = n\pi/L$

$$\begin{aligned}\langle x^2\rangle = (2/L)[L^3/6 &- \left\{L^3/4\pi n - L^3/8n^3\pi^3\right\}\sin(2n\pi L/L)\\ &- \left\{L^3/4n^2\pi^2\right\}\cos(2n\pi L/L)] = \boxed{L^2(1/3-1/2n^2\pi^2)}\end{aligned}$$

(d) The wavefunction is an eigenfunction of the hamiltonian which, because the potential is zero inside the box, is just the operator for kinetic energy. This operator can be written $\hat{p}_x^2/2m$, so the wavefunction is also an eigenfunction of $\hat{p}_x^2$ with eigenvalue $2m$ times the energy eigenvalue. In this case, the eigenvalue of $\hat{p}_x^2$ is $2m \times n^2h^2/8mL^2 = n^2h^2/4L^2$. Because the wavefunction is an eigenfunction of $\hat{p}_x^2$, the expectation value is equal to the eigenvalue: $\langle p_x^2\rangle = \boxed{n^2h^2/4L^2}$.

P7D.8 (a) Because the particle is moving back and forth with constant speed its probability density within the box must be uniform at P_0. The total probability must be 1, so it follows that $\int_0^L P_0\,\mathrm{d}x = 1$. Evaluating the integral give $P_0L = 1$, hence $P_0 = 1/L$, as required.

(b) The average value of any quantity is the value of that quantity in an infinitesimal interval at an arbitrary position, multiplied by the probability of being in that interval and then summed (integrated) over all possible positions. If the probability density is $P(x)$, the required average is $\langle x^n\rangle = \int_0^L x^nP(x)\mathrm{d}x$. The integral is only over the range 0 to L because outside this region the probability density is zero.

(c)

$$\begin{aligned}\langle x\rangle &= \int_0^L xP(x)\,\mathrm{d}x = (1/L)\int_0^L x\,\mathrm{d}x\\ &= (1/L)\,(x^2/2)\big|_0^L = (1/L)(L^2/2-0) = \boxed{L/2}\\ \langle x^2\rangle &= \int_0^L x^2P(x)\,\mathrm{d}x = (1/L)\int_0^L x^2\,\mathrm{d}x\\ &= (1/L)\,(x^3/3)\big|_0^L = (1/L)(L^3/3-0) = \boxed{L^2/3}\end{aligned}$$

(d) $\langle x\rangle$ is identical with the quantum result for all values of n. The quantum result for $\langle x^2\rangle$ is $L^2(1/3 - 1/2n^2\pi^2)$. For large n the second term in parentheses becomes negligible compared to the first, in which case $\langle x^2\rangle = L^2/3$, which is the classical result. The correspondence principle is satisfied.

P7D.10 (a) Outside the box, $L/2 < x < -L/2$, the potential is infinite and so the wavefunction is zero. Inside the box the potential is zero and the Schrödinger equation is $(-\hbar^2/2m)\mathrm{d}^2\psi/\mathrm{d}x^2 = E\psi$. The wavefunction must be continuous at the walls of the box so the boundary conditions are $\boxed{\psi(\pm L/2) = 0}$

(b) Substituting $\psi(x) = \cos(kx)$ into the Schrödinger equation gives

$$\begin{aligned}-(\hbar^2/2m)(\mathrm{d}^2/\mathrm{d}x^2)\cos kx &= -(\hbar^2/2m)(-k^2\cos kx)\\ &= E\cos kx\end{aligned}$$

which is true if $E = \hbar^2k^2/2m$. The boundary conditions are satisfied if $\cos(\pm kL/2) = \cos(kL/2) = 0$, which occurs if $kL/2 = (2n+1)\pi/2$ for integer n; it follows that $k = (2n+1)\pi/L$. Negative values of n do not generate distinct solutions: for example if $n = -2$, $k = -3\pi/L$ and the wavefunction is $\cos(-3\pi x/L)$. However, because $\cos(-\theta) = \cos(\theta)$ this wavefunction is $\cos(3\pi x/L)$, which is that for $n = 1$. All negative values of n therefore simply duplicate solutions given by positive values of n. In summary

$$\psi_n(x) = \cos([2n+1]\pi x/L) \qquad E_n = h^2(2n+1)^2/8mL^2 \qquad n = 0, 1 \ldots$$

It follows that the three lowest energy wavefunctions are $\psi_0 = \cos(\pi x/L)$, $\psi_1 = \cos(3\pi x/L)$, and $\psi_3 = (\cos 5\pi x/L)$; these are depicted in Fig. 7.6

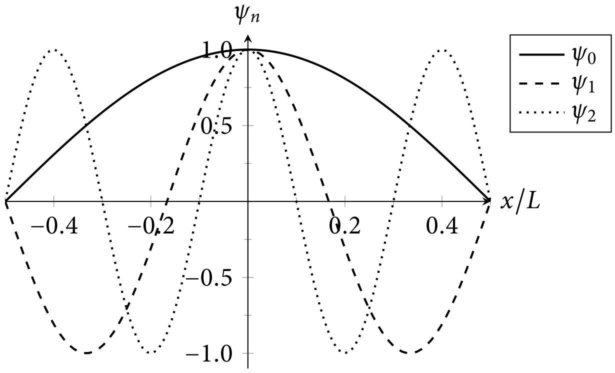


Figure 7.6

(c) Substituting $\psi(x) = \sin k'x$ into the Schrödinger equation gives

$$-(\hbar^2/2m)(\mathrm{d}^2/\mathrm{d}x^2)(\sin k'x) = -(\hbar^2/2m)(-k'^2 \sin k'x) = E \sin k'x$$

The energy is therefore $E = \hbar^2 k'^2/2m$. The boundary conditions are $\sin(\pm k'L/2) = 0$, which is satisfied by $k'L/2 = n'\pi$ for integer n'. Negative values of n' do not generate distinct wavefunctions and $n' = 0$ is not permitted as the wavefunction is zero everywhere. In summary

$$\psi'_{n'}(x) = \sin(2n'\pi x/L) \qquad E_{n'} = h^2(2n')^2/8mL^2 \qquad n' = 1, 2 \ldots$$

The wavefunctions with the three lowest energies are thus $\psi'_1 = \sin(2\pi x/L)$, $\psi'_2 = \sin(4\pi x/L)$, and $\psi'_3 = \sin(6\pi x/L)$; these are depicted in Fig. 7.7.

(d) Expressed as multiples of $h^2/8mL^2$ the cosine solutions have energies 1, 9, 25, ..., and the sine solutions have energies 4, 16, 36, ... These are the same set of energies as for the box between 0 and L, $n^2h^2/8mL^2$.

(e) The normalized cos wavefunctions are $\psi = N\cos[(2n+1)\pi x/L]$, and are normalized when $\int_{-L/2}^{L/2} \psi^*\psi\,\mathrm{d}x = 1$. The integral is evaluated by first using the identity $\cos^2 x + \sin^2 x = 1$ and then Integral T.2

$$N^2 \int_{-L/2}^{L/2} \cos^2[(2n+1)\pi x/2L]\,\mathrm{d}x = N^2 \int_{L/2}^{L/2} 1 - \sin^2[(2n+1)\pi x/2L]\,\mathrm{d}x$$

$$= N^2\, x - N^2\{x/2 - (L/2(2n+1)\pi)\sin[(2n+1)\pi x/L]\}\Big|_{L/2}^{-L/2} = N^2(L/2)$$

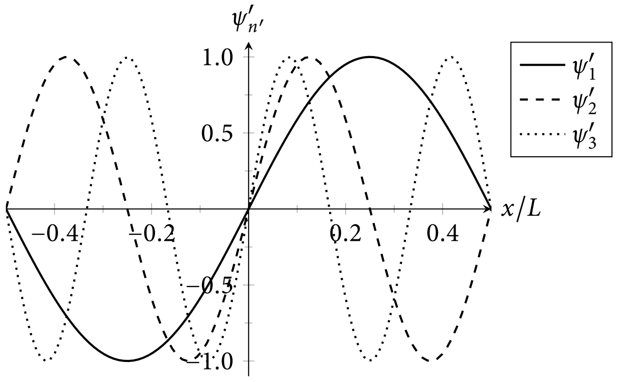


Figure 7.7

setting this equal to 1 gives $\boxed{N = (2/L)^{1/2}}$. Similarly for the sin functions, again using Integral T.2

$$N^2 \int_0^L \sin^2[2n'\pi x/L]\mathrm{d}x = N^2 \left[x/2 - (L/8n'\pi)\sin(4n'\pi x/L)\right|_{L/2}^{L/2}$$
$$= N^2(L/2)$$

setting this equal to 1 gives $\boxed{N = (2/L)^{1/2}}$.

(f) The probability density for all wavefunctions is symmetric about the center of the box, which at this case is at $x = 0$. Hence, the average value of x must be at the center, and so $\langle x\rangle = 0$.

P7D.12 The text defines the transmission probability as the ratio $|A'|^2/|A|^2$, where the coefficients A and A' are defined in [7D.15–*268*] and [7D.18–*269*] respectively. Four equations are given in [7D.19a–*269*] and [7D.19b–*269*] for the five unknown coefficients of the full wavefunction.

(a) $A + B = C + D$

(b) $Ce^{\kappa W} + De^{-\kappa W} = A'e^{ikW}$

(c) $ikA - ikB = \kappa C - \kappa D$

(d) $\kappa Ce^{\kappa W} - \kappa De^{-\kappa W} = ikA'e^{ikW}$

The coefficient A' is needed in terms of A alone, and hence B, C and D need to be eliminated. B occurs only in (a) and (c). Solving these equations and setting the results equal to each other yields

$$B = C + D - A = A - (\kappa/ik)C + (\kappa/ik)D$$

Solving this for C,

$$C = \frac{2A + D(\kappa/ik - 1)}{\kappa/ik + 1} = \frac{2Aik + D(\kappa - ik)}{\kappa + ik}$$

The desired A' appears only in (b) and (d). Solve these for A' and set them equal to each other.

$$A' = \mathrm{e}^{-\mathrm{i}kW}(C\mathrm{e}^{\kappa W} - D\mathrm{e}^{-\kappa W}) = (\kappa \mathrm{e}^{-\mathrm{i}kW}/\mathrm{i}k)(C\mathrm{e}^{\kappa W} - D\mathrm{e}^{-\kappa W})$$

Solve the resulting equation for C, and set it equal to the previously obtained expression for C

$$C = \frac{(\kappa/\mathrm{i}k + 1)D\mathrm{e}^{-2\kappa W}}{\kappa/\mathrm{i}k - 1} = \frac{(\kappa + \mathrm{i}k)D\mathrm{e}^{-2\kappa W}}{\kappa - \mathrm{i}k} = \frac{2A\mathrm{i}k + D(\kappa - \mathrm{i}k)}{\kappa + \mathrm{i}k}$$

Solve this resulting equation for D in terms of A

$$\frac{(\kappa + \mathrm{i}k)^2\mathrm{e}^{-2\kappa W} - (\kappa - \mathrm{i}k)^2}{(\kappa - \mathrm{i}k)(\kappa + \mathrm{i}k)} D = \frac{2A\mathrm{i}k}{\kappa + \mathrm{i}k}$$

and 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 the expression for C yields

$$C = \frac{2A\mathrm{i}k(\kappa + \mathrm{i}k)\mathrm{e}^{-2\kappa W}}{(\kappa + \mathrm{i}k)^2\mathrm{e}^{-2\kappa W} - (\kappa - \mathrm{i}k)^2}$$

Substituting this into expression (b) for A'

$$A' = \frac{2A\mathrm{i}k\mathrm{e}^{-\mathrm{i}kW}}{(\kappa + \mathrm{i}k)^2\mathrm{e}^{-2\kappa L} - (\kappa - \mathrm{i}k)^2}[(\kappa + \mathrm{i}k)\mathrm{e}^{-\kappa W} + (\kappa - \mathrm{i}k)\mathrm{e}^{-\kappa L}]$$

$$\frac{A'}{A} = \frac{4\mathrm{i}k\kappa\mathrm{e}^{-\mathrm{i}kW}\mathrm{e}^{-\kappa W}}{(\kappa + \mathrm{i}k)^2\mathrm{e}^{-2\kappa L} - (\kappa - \mathrm{i}k)^2} = \frac{4\mathrm{i}k\kappa\mathrm{e}^{-\mathrm{i}kW}}{(\kappa + \mathrm{i}k)^2\mathrm{e}^{-\kappa L} - (\kappa - \mathrm{i}k)^2\mathrm{e}^{\kappa W}}$$

This leads to a transition probability of

$$T = \left|\frac{A'}{A}\right|^2 = \left(\frac{4\mathrm{i}k\kappa\mathrm{e}^{-\mathrm{i}kW}}{(\kappa + \mathrm{i}k)^2\mathrm{e}^{-\kappa L} - (\kappa - \mathrm{i}k)^2\mathrm{e}^{\kappa W}}\right)\left(\frac{-4\mathrm{i}k\kappa\mathrm{e}^{\mathrm{i}kW}}{(\kappa - \mathrm{i}k)^2\mathrm{e}^{-\kappa L} - (\kappa + \mathrm{i}k)^2\mathrm{e}^{\kappa W}}\right)$$

The denominator, expanded separately is

$$\begin{aligned}
&(\kappa + \mathrm{i}k)^2(\kappa - \mathrm{i}k)^2\mathrm{e}^{-2\kappa W} - (k - \mathrm{i}k)^4 - (k + \mathrm{i}k)^4 + (\kappa - \mathrm{i}k)^2(\kappa + \mathrm{i}k)^2\mathrm{e}^{2\kappa W} \\
&= (\kappa^2 + k^2)^2(\mathrm{e}^{2\kappa W} + \mathrm{e}^{-2\kappa W}) - (\kappa^2 - 2\mathrm{i}\kappa k - k^2)^2 - (\kappa^2 + 2\mathrm{i}\kappa k - k^2)^2 \\
&= (\kappa^4 + 2\kappa^2 k^2 + k^4)(\mathrm{e}^{2\kappa W} + \mathrm{e}^{-2\kappa W}) - (2\kappa^4 - 12\kappa^2 k^2 + 2k^4)
\end{aligned}$$

The term $12\kappa^2 k^2$ can be written as $-4\kappa^2 k^2 + 16k^2\kappa^2$, which allows terms to be collected

$$(\kappa^4+2\kappa^2k^2+k^4)(\mathrm{e}^{2\kappa W}-2+\mathrm{e}^{-2\kappa W})+16\kappa^2k^2 = (\kappa^2+k^2)^2(\mathrm{e}^{\kappa W}-\mathrm{e}^{-\kappa W})^2+16\kappa^2k^2$$

Hence, the probability is

$$T = \frac{16k^2\kappa^2}{(\kappa^2 + k^2)^2(\mathrm{e}^{\kappa W} - \mathrm{e}^{-\kappa W})^2 + 16\kappa^2 k^2}$$

to proceed to eqn 7D.20a, invert this expression

$$T = \left(\frac{(\kappa^2+k^2)^2(\mathrm{e}^{\kappa W}-\mathrm{e}^{-\kappa W})^2+16\kappa^2k^2}{16k^2\kappa^2}\right)^{-1}$$
$$= \left(\frac{(\kappa^2+k^2)^2(\mathrm{e}^{\kappa W}-\mathrm{e}^{-\kappa W})^2}{16\kappa^2k^2}+1\right)^{-1}$$

Now express $(k^2+\kappa^2)/k^2\kappa^2$ in terms of a ratio of energies, $\varepsilon = E/V_0$. k and κ are defined by [7D.17–*269*] and [7D.18–*269*], respectively. The factors in $\hbar$ and m cancel out, leaving $\kappa \propto (V_0 - E)$ and $k \propto E$, which gives

$$\frac{(\kappa^2+k^2)^2}{k^2\kappa^2} = \frac{(E+V_0-E)^2}{E(V_0-E)} = \frac{V_0^2}{E(V_0-E)} = \frac{1}{\varepsilon(1-\varepsilon)}$$

making the transmission probability

$$T = \left(\frac{(\mathrm{e}^{\kappa W}-\mathrm{e}^{-\kappa W})^2}{16\varepsilon(1-\varepsilon)}+1\right)^{-1}$$

When $\kappa W \gg 1$ the negative term inside the parentheses is negligible compared to the positive term, and the 1 is negligible compared to the exponential term, such that

$$T \approx \left(\frac{\mathrm{e}^{2\kappa W}}{16\varepsilon(1-\varepsilon)}\right)^{-1} = \boxed{16\varepsilon(1-\varepsilon)\mathrm{e}^{-2\kappa W}}$$

P7D.14 The probability of the particle being inside the barrier is the integral of the probability density, $|\psi|^2$, within the barrier which extends from $x = 0$ to $x = \infty$

$$P = \int_0^\infty (N\mathrm{e}^{-\kappa x})^2\,\mathrm{d}x = N^2\int_0^\infty \mathrm{e}^{-2\kappa x}\mathrm{d}x = \boxed{N^2/2\kappa}$$

The average penetration depth is interpreted as the expectation values of x, computed inside the barrier. The required integral is of the form of Integral G.2 with $k = 2\kappa$.

$$\langle x\rangle = \int_0^\infty x(N\mathrm{e}^{-\kappa x})^2\,\mathrm{d}x = N^2\int_0^\infty x\mathrm{e}^{-2\kappa x}\mathrm{d}x = \boxed{N^2/(2\kappa)^2}$$

7E Vibrational motion

Answers to discussion questions

D7E.2 For the harmonic oscillator the spacing of the energy levels is constant. Therefore, relative to the energy of the oscillator, the spacing becomes progressively smaller as the quantum number increases. In the limit of very high quantum numbers this spacing becomes negligible compared to the total energy, and effectively the energy can take any value, as in the classical case.

As is shown in Fig. 7E.7 on page 277, as the quantum number becomes large the probability density clusters more and more around the classical turning points of the classical harmonic oscillator (that is, the points at which the kinetic energy is zero). Because the classical oscillator is moving most slowly near these points, they are the displacements at which it is most probable that the oscillator will be found. Again, the quantum and classical results converge at high quantum numbers

Solutions to exercises

E7E.1(b) The zero-point energy of a harmonic oscillator is given by [7E.5–*274*], $E_0 = \frac{1}{2}\hbar\omega$, where the frequency ω is given by [7E.3–*274*], $\omega = (k_f/m)^{1/2}$. For this system,

$$\begin{aligned}E_0 &= \tfrac{1}{2} \times (1.0546 \times 10^{-34}\,\mathrm{J\,s}) \times \left[(285\,\mathrm{N\,m^{-1}})/(5.16 \times 10^{-26}\,\mathrm{kg})\right]^{1/2}\\ &= \boxed{3.92 \times 10^{-21}\,\mathrm{J}}\end{aligned}$$

E7E.2(b) The separation between adjacent energy levels of a harmonic oscillator is [7E.4–*274*], $\Delta E = \hbar\omega$, where the frequency, ω is given by [7E.3–*274*], $\omega = (k_f/m)^{1/2}$. This is rearranged for the force constant as $k_f = m(\Delta E/\hbar)^2$. Evaluating this gives

$$k_f = (2.88 \times 10^{-25}\,\mathrm{kg}) \times \left[(3.17 \times 10^{-21}\,\mathrm{J})/(1.0546 \times 10^{-34}\,\mathrm{J\,s})\right]^2 = \boxed{260\,\mathrm{N\,m^{-1}}}$$

E7E.3(b) The separation between adjacent energy levels of a harmonic oscillator is [7E.4–*274*], $\Delta E = \hbar\omega$, where the frequency, ω is given by [7E.3–*274*], $\omega = (k_f/m)^{1/2}$. The Bohr frequency condition [7A.9–*241*], $\Delta E = h\nu$, can be rewritten in terms of the wavelength as $\Delta E = hc/\lambda$. The wavelength of the photon corresponding to a transition between adjacent energy levels is therefore given by $\hbar\omega = hc/\lambda$, or $\hbar(k_f/m)^{1/2} = hc/\lambda$. Solving for λ gives $\lambda = 2\pi c/(k_f/m)^{1/2}$; with the data given

$$\begin{aligned}\lambda &= \frac{2\pi \times (2.9979 \times 10^{8}\,\mathrm{m\,s^{-1}})}{\left[(544\,\mathrm{N\,m^{-1}})/(15.9949 \times 1.6605 \times 10^{-27}\,\mathrm{kg})\right]^{1/2}}\\ &= \boxed{1.32 \times 10^{-5}\,\mathrm{m}}\end{aligned}$$

E7E.4(b) The wavefunctions are depicted in Fig. 7E.6 on page 276; they are real. Two wavefunctions are orthogonal if $\int \psi_i^*\psi_j\,\mathrm{d}\tau = 0$. In this case the wavefunctions are $\psi_1(y) = N_1 y \mathrm{e}^{-y^2/2}$ and $\psi_2(y) = N_2(y^2 - 1)\mathrm{e}^{-y^2/2}$, and the integration is from $y = -\infty$ to $+\infty$. The integrand is $\psi_2\psi_1 = N_2N_1(y^3 - y)\mathrm{e}^{-y^2}$, which is an odd function, meaning that its value at $-y$ is the negative of its value at $+y$. The integral of an odd function over a symmetric range is zero, hence these wavefunctions are orthogonal.

E7E.5(b) The zero-point energy of a harmonic oscillator is given by [7E.5–*274*], $E_0 = \frac{1}{2}\hbar\omega$, where the frequency ω is given by [7E.3–*274*], $\omega = (k_f/\mu)^{1/2}$. The effective mass μ of a diatomic AB is given by [7E.6–*274*], $\mu = (m_A m_B)/(m_A + m_B)$. In the case of a homonuclear diatomic A_2 this reduces to $\mu = m_A/2$. For this system,

$$\begin{aligned}E_0 &= \tfrac{1}{2} \times (1.0546 \times 10^{-34}\,\text{J s}) \\ &\quad \times \left[(2293.8\,\text{N m}^{-1})/(\tfrac{1}{2} \times 14.0031 \times 1.6605 \times 10^{-27}\,\text{kg})\right]^{1/2} \\ &= \boxed{2.3422 \times 10^{-20}\,\text{J}}\end{aligned}$$

E7E.6(b) The energy levels of a harmonic oscillator are [7E.3–*274*], $E_v = (v + \frac{1}{2})\hbar\omega$, with $\omega = (k_f/m)^{1/2}$ and $v = 0, 1, 2....$ The energy of the state with $v = 1$ is $E_1 = \frac{3}{2}\hbar\omega$.

(i) For the system with $k_f = 1000\,\text{N m}^{-1}$ the energy of the state with $v = 1$ is

$$\begin{aligned}E_1 &= \tfrac{3}{2} \times (1.0546 \times 10^{-34}\,\text{J s}) \times [(1000\,\text{N m}^{-1})/(1 \times 1.6605 \times 10^{-27}\,\text{kg})]^{1/2} \\ &= 1.22... \times 10^{-19}\,\text{J} = \boxed{1.23 \times 10^{-19}\,\text{J}}\end{aligned}$$

The classical turning points of this state occur when $E_1 = \frac{1}{2}k_f x_{tp}^2$. Solving this for x_{tp} leads to $x_{tp} = \pm\sqrt{2E_1/k_f}$, giving a separation of

$$2\sqrt{2E_1/k_f} = 2\sqrt{2 \times (1.22... \times 10^{-19}\,\text{J})/(1000\,\text{N m}^{-1})} = 31.3...\,\text{pm}$$

As a percentage of the typical bond length, 110 pm, this is

$$(31.3...\,\text{pm})/(110\,\text{pm}) \times 100\% = \boxed{28.5\%}$$

(ii) For the system with $k_f = 100\,\text{N m}^{-1}$ the energy of the state with $v = 1$ is

$$\begin{aligned}E_1 &= \tfrac{3}{2} \times (1.0546 \times 10^{-34}\,\text{J s}) \times [(100\,\text{N m}^{-1}/(1 \times 1.6605 \times 10^{-27}\,\text{kg})]^{1/2} \\ &= 3.88... \times 10^{-20}\,\text{J} = \boxed{3.88 \times 10^{-20}\,\text{J}}\end{aligned}$$

The classical turning points of this state occur when $E_1 = \frac{1}{2}k_f x_{tp}^2$. Solving this for x_{tp} leads to $x_{tp} = \pm\sqrt{2E_1/k_f}$, giving a separation of

$$2\sqrt{2E_1/k_f} = 2\sqrt{2 \times (3.88... \times 10^{-20}\,\text{J})/(100\,\text{N m}^{-1})} = 55.7...\,\text{pm}$$

As a percentage of the typical bond length, 110 pm, this is

$$(55.7...\,\text{pm})/(110\,\text{pm}) \times 100\% = \boxed{50.7\%}$$

E7E.7(b) The wavefunctions are depicted in Fig. 7E.6 on page 276. The general form of the harmonic oscillator wavefunctions is $\psi_v = N_v H_v(y) e^{-y^2/2}$, where N_v is a normalization constant and $H_v(y)$ is the Hermite polynomial of order v in the reduced position variable y. Nodes occur when the wavefunction passes through zero. The wavefunction asymptotically approaches zero at $y = \pm\infty$, but as the function does not pass through zero these limits do not count as nodes. The nodes in the wavefunction therefore correspond to the solutions of $H_v(y) = 0$. $H_v(y)$ is a polynomial of order v, meaning that the highest power of y that occurs is y^v; such polynomials in general have v solutions and hence there are v nodes. Therefore (a) the wavefunction with $v = 5$ has $\boxed{5}$ nodes; (b) the wavefunction with $v = 35$ has $\boxed{35}$ nodes.

E7E.8(b) The wavefunction with $v = 3$ is $\psi_3(y) = N_3(y^3 - 3y)e^{-y^2/2}$. Nodes occur when the wavefunction passes through zero; the wavefunction approaches zero at $y = \pm\infty$, but these do not count as nodes as the wavefunction does not pass through zero. It is evident that the nodes occur when $y^3 - 3y = y(y^2 - 3) = 0$ which solves to give nodes at $\boxed{y = 0, \pm\sqrt{3}}$.

E7E.9(b) The wavefunction with $v = 3$ is $\psi_3(y) = N_3(8y^3 - 12y)e^{-y^2/2}$, which gives a probability density of $P(y) = |\psi_3(y)|^2 = N_3^2(8y^3 - 12y)^2e^{-y^2}$. The extrema are located by differentiating the wavefunction, setting the result to 0 and solving for y. The differential is evaluated using the product rule

$$\begin{aligned}\frac{d\psi_3(y)}{dy} &= N_3^2\left(\frac{d(8y^3 - 12y)^2}{dy}e^{-y^2} + (8y^3 - 12y)^2\frac{de^{-y^2}}{dy}\right)\\ &= N_3^2[2(8y^3 - 12y)(24y^2 - 12)e^{-y^2} + (8y^3 - 12y)^2 \times (-2ye^{-y^2})]\end{aligned}$$

It is necessary to use mathematical software to find the solutions of $d\psi_3(y)/dy = 0$; these solutions are

$$0.000 \quad \pm 0.6021 \quad \pm 1.225 \quad \pm 2.0341 \quad \pm\infty$$

It is evident from inspection of the wavefunction that $y = 0$ is a mimimum in the probability density, and that there is also a minimum when $(8y^2 - 12) = 0$, which corresponds to $y = \pm 1.225$. It follows that maxima occur at $\boxed{y = \pm 0.6021}$ and $\boxed{y = \pm 2.034}$.

Solutions to problems

P7E.2 (a) In the case that $m_B \gg m_A$, $m_A + m_B \approx m_B$, and so $\mu_{AB} \approx m_A m_B/m_B = m_A$. The ratio of the vibrational frequencies is then

$$\omega_{A'B} = \omega_{AB}(\mu_{AB}/\mu_{A'B})^{1/2} \approx \omega_{AB}(m_A/m_{A'})^{1/2}$$

If the frequencies are expressed in Hz the analogous result is

$$\nu_{A'B} \approx \nu_{AB}(m_A/m_{A'})^{1/2}$$

(b) Using the previous result gives $\nu_{^2H^{35}Cl} \approx \nu_{^1H^{35}Cl}(m_{^1H}/m_{^2H})^{1/2} = (5.63 \times 10^{14}\ \text{Hz}) \times (1\ m_u/2\ m_u)^{1/2} = \boxed{3.98 \times 10^{14}\ \text{Hz}}$.

(c) Comparing it to the result from *Problem* P7E.1, there is a $\boxed{1.5\%}$ difference, which is relatively small. The assumption of replacing the effective mass by the mass of the lighter nucleus is quite a good approximation.

(d) A C–H vibration in an organic molecule can be thought of as the H atom moving against the rest of the molecule, which has a much greater mass. Therefore, to some rough approximation such vibrations can be modelled by a diatomic X–^{1}H in which $m_X \gg m_H$. In such a situation the analysis in part (a) applies and the vibrational frequency of X–^{2}H is well approximated as $(1\ m_u/2\ m_u)^{1/2} = 0.7$ times that of X–^{1}H.

P7E.4 The vibrational frequency in Hz, ν is given by $\nu = (1/2\pi)(k_f/\mu)^{1/2}$; using this the following table is drawn up

	$^{12}C^{16}O$	$^{13}C^{16}O$	$^{12}C^{18}O$	$^{13}C^{18}O$
μ/m_u	6.85...	7.17...	7.2	7.54...
ν/THz	$\boxed{64.3}$	$\boxed{62.8}$	$\boxed{62.7}$	$\boxed{61.3}$

P7E.6 As in *Problem* P7E.5, the force constant can be found from the wavenumber of the $v = 0 \rightarrow 1$ transition, $k_f = \mu(2\pi\tilde{\nu}c)^2$. This allows the following table to be drawn up

	$^1H^{35}Cl$	$^1H^{81}Br$	$^1H^{127}I$	$^{12}C^{16}O$	$^{14}N^{16}O$
$\tilde{\nu}/\ cm^{-1}$	2990	2650	2310	2170	1904
$\mu/\ m_u$	0.972...	0.987...	0.992...	6.85...	7.46...
$k_f/\ N\,m^{-1}$	$\boxed{512}$	$\boxed{409}$	$\boxed{312}$	$\boxed{1902}$	$\boxed{1595}$

Hence, the order of increasing stiffness is $\boxed{HI<HBr<HCl<NO<CO}$

P7E.8 Assuming that one can identify the CO peak in the infrared spectrum of the complex, taking infrared spectra of each of the isotopic variants of the complexes can show which atom binds to the haem group and determine the C – O force constant. Compare isotopic variants to $^{12}C^{16}O$ as the standard; when an isotope changes but the vibrational frequency does not, then the atom whose isotope was varied is the atom that binds to the haem. (As usual, the better the experimental results agree with the whole set of predictions, the more confidence one would have with the conclusion.)

As it is expected that the force constant for the bond will remain constant, and that the atom that bonds to the haem group will be immobilized, meaning that appropriate mass for this system is the mass of the unbound atom, allows predictions to be made for the wavenumbers of each isotope in the case of C and O binding, using $\tilde{\nu}_2 = \tilde{\nu}_1\sqrt{\mu_1/\mu_2}$, where 1 refers to the free case and 2 to the bound case.

isotopomer	$\tilde{\nu}/\text{cm}^{-1}$ if C binds	$\tilde{\nu}/\text{cm}^{-1}$ if O binds
$^{12}\text{C}^{16}\text{O}$	1421	1640
$^{13}\text{C}^{16}\text{O}$	1421	1576
$^{12}\text{C}^{18}\text{O}$	1339	1640
$^{13}\text{C}^{18}\text{O}$	1339	1576

The force constant is found using $\tilde{\nu} = (1/2\pi c)(k_\text{f}/\mu)^{1/2}$, rearranged to $k_\text{f} = \mu(2\pi\tilde{\nu}c)^2$.

P7E.10 The ground-state wavefunction is found from [7E.7–275] as $\psi_0(y) = N_0\text{e}^{-y^2/2}$. The normalization constant is found by evaluating

$$N_0^2\int_{-\infty}^{+\infty}\text{e}^{-y^2}\,\text{d}y = 2N_0^2\int_0^{+\infty}\text{e}^{-y^2}\,\text{d}y = 2N_0^2\times\left(\tfrac{1}{2}\pi^{1/2}\right) = 1$$

where required integral is of the form of Integral G.1 with $k = 1$. The normalized wavefunction is therefore $\psi_0(y) = \pi^{-1/4}\text{e}^{-y^2/2}$.

(a) For the expectation value of y, the integral to evaluate is

$$\langle y\rangle = \int_{-\infty}^{\infty}\psi_0^* y\,\psi_0\,\text{d}y = \pi^{-1/2}\int_{-\infty}^{\infty} y\,\text{e}^{-y^2}\text{d}y$$

The integrand is an odd function, meaning that its value at $-y'$ is the negative of its value at y', and so when integrated over a symmetrical range about $y = 0$ the result is necessarily zero. Hence $\boxed{\langle y\rangle = 0}$.

(b) To calculate $\langle y^2\rangle$ the required integral is of the form of Integral G.3 with $k = 1$

$$\langle y^2\rangle = \int_{-\infty}^{\infty}\psi_0^* y^2\psi_0\,\text{d}y = \pi^{-1/2}\int_{-\infty}^{\infty} y^2\text{e}^{-y^2}\,\text{d}y$$
$$= 2\pi^{-1/2}\int_0^{\infty} y^2\text{e}^{-y^2}\,\text{d}y = 2\pi^{-1/2}\times\tfrac{1}{4}\pi^{1/2} = \boxed{\tfrac{1}{2}}$$

(c) The first excited state is $\psi_1(y) = N_1 y\text{e}^{-y^2/2}$. The normalization constant is found by evaluating

$$N_1^2\int_{-\infty}^{+\infty} y^2\text{e}^{-y^2}\,\text{d}y = 2N_1^2\int_0^{+\infty} y^2\text{e}^{-y^2}\,\text{d}y = 2N_1^2\times\left(\tfrac{1}{4}\pi^{1/2}\right) = 1$$

where required integral is of the form of Integral G.3 with $k = 1$. The normalized wavefunction is therefore $\psi_1(y) = (4/\pi)^{1/4}y\,\text{e}^{-y^2/2}$.
The expectation value of y is zero for the same reason as in (a). To calculate $\langle y^2\rangle$ the required integral is of the form of Integral G.5 with $k = 1$

$$\langle y^2\rangle = \int_{-\infty}^{\infty}\psi_1^* y^2\psi_1\,\text{d}y = (4/\pi)^{1/2}\int_{-\infty}^{\infty} y^4\text{e}^{-y^2}\,\text{d}y$$
$$= 2(4/\pi)^{1/2}\int_0^{\infty} y^4\text{e}^{-y^2}\,\text{d}y = 2(4/\pi)^{1/2}\times\tfrac{3}{8}\pi^{1/2} = \boxed{\tfrac{3}{2}}$$

P7E.12 In general

$$\langle x^n \rangle_v = \alpha^n \langle y^n \rangle_v = \alpha^n \int_{-\infty}^{\infty} \psi_v^* y^n \psi_v \,\mathrm{d}x = \alpha^{n+1} \int_{-\infty}^{\infty} \psi_v^2 y^n \,\mathrm{d}y$$

as $x = \alpha y$. Then

$$\langle x^3 \rangle_v = \alpha^4 \int_{-\infty}^{\infty} \psi_v^2 y^3 \,\mathrm{d}y = \boxed{0}$$

as the square of the wavefunction always an even function, the integrand is odd.

$$\langle x^4 \rangle_v = \alpha^5 \int_{-\infty}^{\infty} \psi_v y^4 \psi_v \,\mathrm{d}y$$

Consider the term $y^4\psi_v = y^4 N_v H_v \mathrm{e}^{-y^2/2}$. The $y^4 H_v$ term can be rewritten by using the property $yH_v = vH_{v-1} + \frac{1}{2}H_v$ four times, as

$$\begin{aligned}
y^4 H_v &= y^3[yH_v] = vy^3 H_{v-1} + \tfrac{1}{2}y^3 H_v \\
&= y^2[v(v-1)H_{v-2} + (v+\tfrac{1}{2})H_v + \tfrac{1}{4}H_{v+2}] \\
&= y[\tfrac{1}{4}(\tfrac{1}{2}H_{v+3} + (v+2)H_{v+1}) + (v+\tfrac{1}{2})(\tfrac{1}{2}H_{v+1} + vH_{v-1}) \\
&\qquad + v(v-1)(\tfrac{1}{2}H_{v-1} + (v-2)H_{v-3}] \\
&= y\left[\tfrac{1}{8}H_{v+3} + \tfrac{3}{4}(v+1)H_{v+1} + \tfrac{3}{2}v^2 H_{v-1} + v(v-1)(v-2)H_{v-3}\right]
\end{aligned}$$

The only terms from the above that will contribute to the expectation value will be those that produce H_v, due to orthogonality of the hermite polynomials. These are yH_{v-1} and yH_{v+1}. Hence,

$$\begin{aligned}
&= \tfrac{3}{4}y[(v+1)H_{v+1} + 2v^2 H_{v-1}] + \ldots \\
&= \tfrac{3}{4}\left[(v+1)(\tfrac{1}{2}H_{v+2} + (v+1)H_v) + 2v^2(\tfrac{1}{2}H_v + (v-1)H_{v-2})\right] + \ldots \\
&= \tfrac{3}{4}[(v+1)^2 + v^2]H_v + \ldots = \tfrac{3}{4}[2v^2 + 2v + 1]H_v \ldots
\end{aligned}$$

Hence,

$$\langle x^4 \rangle_v = \alpha^4 \tfrac{3}{4}[2v^2 + 2v + 1] \int_{-\infty}^{\infty} (N_v H_v \mathrm{e}^{-y^2/2})^2 \mathrm{d}(\alpha y) = \boxed{\alpha^4 \tfrac{3}{4}[2v^2 + 2v + 1]}$$

For the last step the normalization condition $\int_{-\infty}^{\infty} (N_v H_v \mathrm{e}^{-y^2/2})^2 \mathrm{d}(\alpha y) = 1$ is used.

P7E.14 As is shown in *Example* 7E.3 on page 279, in terms of the dimensionless variable y the classical turning points are at $y_{\mathrm{tp}} = \pm(2v+1)^{1/2}$, where v is the quantum number of the state. The wavefunction of the state with quantum number v is $\psi_v = N_v H_v \mathrm{e}^{-y^2/2}$, where H_v is the Hermite polynomial of order v. The normalization constant N_v is found from

$$N_v^2 \int_{-\infty}^{\infty} H_v^2 \mathrm{e}^{-y^2} \,\mathrm{d}y = 1$$

From Table 7E.1 on page 275 these polynomials have the property $\int_{-\infty}^{\infty} H_v^2 e^{-y^2}\,dy = \pi^{1/2}2^v v!$ so it follows that $N_v^2 = 1/(\pi^{1/2}2^v v!)$. The probability of finding the particle outside the range of the turning points is then

$$\begin{aligned} P_v &= 2\int_{\sqrt{2v+1}}^{\infty} |\psi_v|^2\,dy = \frac{2}{\pi^{1/2}2^v v!}\int_{\sqrt{2v+1}}^{\infty} H_v^2\,e^{-y^2}\,dy \\ &= \frac{1}{\pi^{1/2}2^{v-1}v!}\int_{\sqrt{2v+1}}^{\infty} H_v^2\,e^{-y^2}\,dy \end{aligned}$$

The integral is evaluated using mathematical software to give the results in the following which are plotted in Fig. 7.8. The probability of a classical oscillator being found in a non-classical region is, of course, zero and the correspondence principle indicates that the quantum result must converge to this value as the quantum number becomes large. The results show that P is indeed a decreasing function of v, albeit rather slowly. The probability reduces to about 0.02 for $v = 200$.

v	0	1	2	3	4	5	6	7
P_v	0.157	0.112	0.0951	0.0855	0.0789	0.0740	0.0702	0.0670

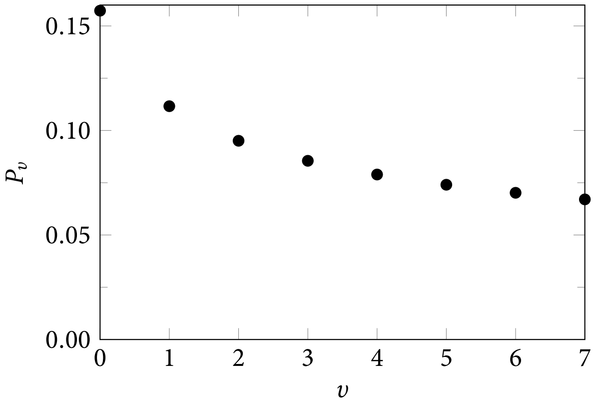


Figure 7.8

P7E.16 Oscillations are expected about a minimum in the potential energy, because this corresponds to the equilibrium arrangement. For a potential of the form $V = V_0\cos 3\phi$, the (first) minimum is when $3\phi = \pi$, that is $\phi = \pi/3$ or 60°. The form of the potential close to the minimum is found by expanding the function in a Taylor series about the point $\phi = \pi/3$

$$\begin{aligned} V/V_0 &= V(\pi/3) + \left(\frac{dV(\phi)}{d\phi}\right)_{\phi=\pi/3}(\phi-\pi/3) + \tfrac{1}{2}\left(\frac{d^2V(\phi)}{d\phi^2}\right)_{\phi=\pi/3}(\phi-\pi/3)^2 \\ &= \cos(\pi) + (-3\sin 3\phi)_{\phi=\pi/3}(\phi-\pi/3) + \tfrac{1}{2}(-9\cos 3\phi)_{\phi=\pi/3}(\phi-\pi/3)^2 \\ &= -1 + \tfrac{1}{2}\times 9(\phi-\pi/3)^2 \end{aligned}$$

Apart from the constant, the leading term is quadratic in the displacement from the minimum at $\phi = \pi/3$. By analogy with the harmonic potential $V = \frac{1}{2}k_f x^2$, the force constant is $9V_0$.

The energy levels are therefore

$$E_v = (v + \tfrac{1}{2})\hbar\omega \qquad \omega = (9V_0/m_{\text{eff}})^{1/2}$$

where m_{eff} is the appropriate effective mass for the motion.

As the energy increases the amplitude of the motion increases and it begins to sample parts of the potential which are no longer well-represented by a quadratic function. Additional terms are needed to describe the potential, and from the form of the cosine function it is evident that these terms will flatten out the potential meaning that it rises less steeply than the quadratic function developed above. As a result the energy levels will get closer together.

P7E.18 The general form of the harmonic wavefunctions are $\psi_v = N_v H_v(y)\mathrm{e}^{-y^2/2}$, where N_v is the normalization constant and $H_v(y)$ is a Hermite polynomial of order v, expressed in terms of the reduced position variable y. Nodes in the wavefunction occur when the wavefunction passes through zero. The wavefunctions go asymptotically to zero at $y = \pm\infty$ on account of the term $\mathrm{e}^{-y^2/2}$, but these do not count as nodes as the wavefunction does not pass through zero. Therefore, nodes in the wavefunction correspond to those values at which $H_v(y) = 0$.

The first six Hermite polynomials are plotted in Figs 7.9 and 7.10; note that the normalizing factors have been included.

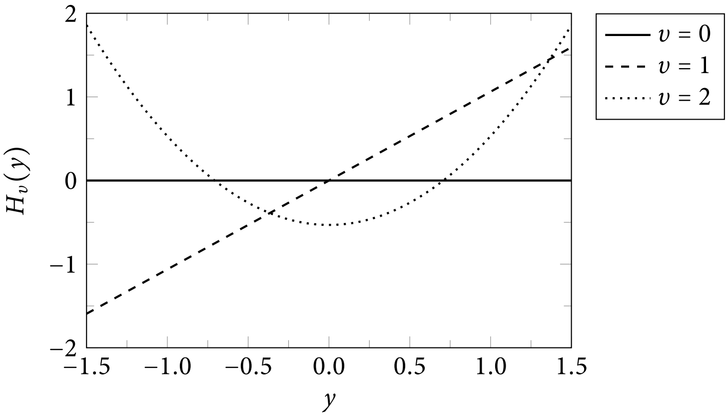


Figure 7.9

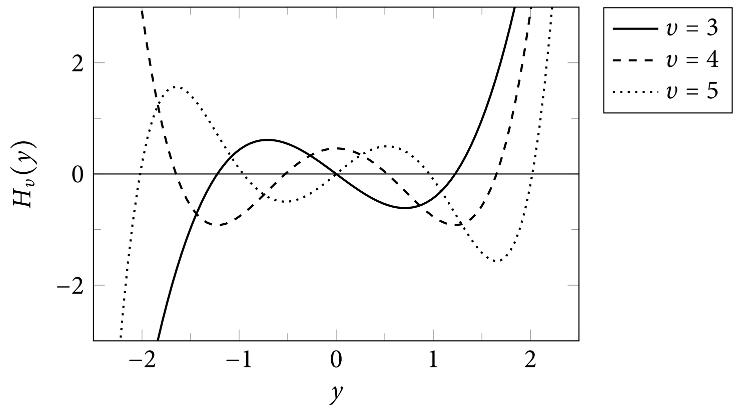


Figure 7.10

7F **Rotational motion**

Answers to discussion questions

D7F.2 Rotational motion on a ring and on a sphere share the following features: (a) quantization arising as a result of the need to satisfy a cyclic boundary condition; (b) energy levels which go inversely with the moment of inertia; (c) the lack of zero-point energy; (d) degeneracy; (e) quantization of the angular momentum about one axis.

Solutions to exercises

E7F.1(b) The magnitude of the angular momentum associated with a wavefunction with angular momentum quantum number l is given by [7F.11–*288*], magnitude $= \hbar[l(l+1)]^{1/2}$. Hence for $l = 2$ the magnitude is $\hbar[2(2+1)]^{1/2} = \boxed{6^{1/2}\hbar}$.

The projection of the angular momentum onto the z-axis is given by [7F.6–*284*], $\hbar m_l$, where m_l is a quantum number that takes values between $-l$ and $+l$ in integer steps, $m_l = -l, -l+1, \ldots + l$. Hence the possible projections onto the z-axis are $\boxed{-2\hbar, -\hbar, 0, \hbar, 2\hbar}$.

E7F.2(b) The wavefunction of a particle on a ring, with quantum number m_l is $\psi_{m_l} = e^{im_l\phi} = \cos(m_l\phi) + i\sin(m_l\phi)$ in the range $0 \le \phi \le 2\pi$. The real and imaginary parts of the wavefunction are therefore $\cos(m_l\phi)$ and $\sin(m_l\phi)$ respectively.

Nodes occur when the function passes through zero, which for trigonometric functions are the same points at which the function is zero. Hence in the real part, nodes occur when $\cos(m_l\phi) = 0$, and so when $m_l\phi = (2n+1)\pi/2$ for integer n, which gives $\phi = (2n+1)\pi/2m_l$. In the imaginary part, nodes occur when $\sin(m_l\phi) = 0$ and so when $m_l\phi = n\pi$ for an integer n, which gives $\phi = n\pi/m_l$.

(i) With $m_l = 1$, nodes in the real part occur at $\boxed{\pi/2, 3\pi/2}$, and in the imaginary part at $\boxed{0, \pi}$. There are $\boxed{2}$ nodes in each of the parts.

(ii) With $m_l = 2$, nodes in the real part occur at $\boxed{\pi/4, 3\pi/4, 5\pi/4, 7\pi/4}$, and in the imaginary part at $\boxed{0, \pi/2, \pi, 3\pi/2}$. There are $\boxed{4}$ nodes in each of the parts.

E7F.3(b) The normalization condition is $\int \psi_{m_l}^* \psi_{m_l}\,\mathrm{d}\tau = 1$. In this case the integral is over ϕ in the range $0 \le \phi \le 2\pi$, and the wavefunction is $\psi_{m_l} = N \cos m_l\phi$, hence

$$N^2 \int \psi_{m_l}^* \psi_{m_l}\,\mathrm{d}\tau = N^2 \int_0^{2\pi} \cos^2(m_l\phi)\,\mathrm{d}\phi$$

The integral is evaluated by using the identity $\cos^2\theta + \sin^2\theta = 1$, hence $\cos^2\theta = 1 - \sin^2\theta$, and then using Intergral T.2 with $a = 2\pi$ and $k = m_l$

$$\begin{aligned} N^2 \int_0^{2\pi} [1 - \sin^2(m_l\phi)]\,\mathrm{d}\phi &= N^2 \int_0^{2\pi} \mathrm{d}\phi - N^2 \int_0^{2\pi} \sin^2(m_l\phi)\,\mathrm{d}\phi \\ &= 2\pi N^2 - N^2\left[\tfrac{1}{2} \times 2\pi - (1/4m_l)\sin(2\pi m_l)\right] \end{aligned}$$

Because $\sin(2\pi m_l) = 0$ for integer m_l it follows that the integral evaluates to πN^2 and hence the normalization factor is $N = \boxed{\pi^{-1/2}}$.

E7F.4(b) The integral to evaluate is $\int_0^{2\pi} \cos(m_l\phi)\cos(m_l'\phi)\mathrm{d}\phi$. Using the identity given in the question, the integral can be rewritten as

$$\begin{aligned} &\frac{1}{2}\int_0^{2\pi} \cos[(m_l + m_l')\phi] + \cos[(m_l - m_l')\phi]\mathrm{d}\phi \\ &= \frac{1}{2}\left.\frac{\sin[(m_l + m_l')\phi]}{m_l + m_l'} + \frac{\sin[(m_l - m_l')\phi]}{m_l - m_l'}\right|_0^{2\pi} \\ &= \frac{1}{2}\left(\frac{\sin[2\pi(m_l + m_l')] - \sin 0}{m_l + m_l'} + \frac{\sin[2\pi(m_l - m_l')] - \sin 0}{m_l - m_l'}\right) \\ &= \boxed{0} \end{aligned}$$

Hence these two wavefunctions are orthogonal.

E7F.5(b) The energy levels on a particle on a ring are [7F.4–*283*], $E_{m_l} = m_l^2\hbar^2/2I$ where I is the momentum of inertia of the system, $I = mr^2$, see *The chemist's toolkit* 20 in Topic 7F on page 282. This is equal to the classical average energy when $\frac{1}{2}kT = m_l^2\hbar^2/2I$. Here $kT = (1.3806 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K}) = 4.11... \times 10^{-21}\,\mathrm{J}$. Solving this for $|m_l|$ gives

$$\begin{aligned} |m_l| &= \left(\frac{kTmr^2}{\hbar^2}\right)^{1/2} \\ &= \frac{[(1.6726 \times 10^{-27}\,\mathrm{kg}) \times (100 \times 10^{-12}\,\mathrm{m})^2(4.11... \times 10^{-21}\mathrm{J})]^{1/2}}{1.0546 \times 10^{-34}\,\mathrm{J\,s}} \\ &= \boxed{2.49} \end{aligned}$$

As m_l must be integral the closest level is $|m_l| = 2$.

E7F.6(b) The energy levels are [7F.10–*287*], $E_l = \hbar^2 l(l+1)/2I$, where I is the moment of inertia. 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, $\Delta E = E_1 - E_0 = (\hbar^2/2I)(1(1+1) - 0(0+1)] = \hbar^2/I$. Evaluating this gives

$$\Delta E = (1.0546 \times 10^{-34}\,\text{J s})^2/(3.07 \times 10^{-47}\,\text{kg m}^2) = \boxed{3.62 \times 10^{-22}\,\text{J}}$$

E7F.7(b) The energy levels are [7F.10–*287*], $E_l = \hbar^2 l(l+1)/2I$, where I is the moment of inertia. So that the excitation energy is $\Delta E = E_2 - E_1 = (\hbar^2/2I)[2(2+1) - 1(1+1)] = 2\hbar^2/I$. Evaluating this gives

$$\Delta E = 2(1.0546 \times 10^{-34}\,\text{J s})^2/(3.07 \times 10^{-47}\,\text{kg m}^2) = \boxed{7.25 \times 10^{-22}\,\text{J}}$$

E7F.8(b) The energy levels are [7F.10–*287*], $E_l = \hbar^2 l(l+1)/2I$, where I is the moment of inertia. The corresponding angular momentum is $\langle l^2\rangle^{1/2} = \hbar\sqrt{l(l+1)}$. Hence, the minimum energy allowed is 0, through this corresponds to zero angular momentum, and so rest and not motion. So the minimum energy of rotation occurs for the state that has $l = 1$. The angular momentum of that state is $\langle l^2\rangle_1^{1/2} = \hbar\sqrt{1(1+1} = \sqrt{2}\hbar = \sqrt{2} \times (1.0546 \times 10^{-34}\,\text{J s}) = \boxed{1.49 \times 10^{-34}\,\text{J s}}$.

E7F.9(b) The diagrams shown in Fig. 7.11 are drawn by forming a vector of length $[l(l+1)]^{1/2}$ and with a projection m_l on the z-axis. For $l = 6$ the vector is of length $\sqrt{42}$ and has possible projections from -6 to $+6$ in integer steps on the z-axis; the vectors are labelled with the value of m_l. Each vector may lie anywhere on a cone described by rotating the vector about the z-axis.

E7F.10(b) Following the pattern shown in Fig. 7F.5 on page 287, the spherical harmonic $Y_{4,0}$ is expected to show four angular nodes. The angle $\theta = 0$ specifies a point on the z-axis; this does not describe an angular node or plane.

E7F.11(b) The real part of the spherical harmonic $Y_{2,+2}$ is $-\frac{1}{2}\sqrt{3/\pi}\sin^2\theta\cos 2\phi$. Angular nodes occur when $\cos 2\phi = 0$, i.e. at $\boxed{\phi = \pi/4, 3\pi/4, 5\pi/4, 7\pi/4}$.

The imaginary part of the same spherical harmonic is $-\frac{1}{2}\sqrt{3/\pi}\sin\theta\sin 2\phi$. This has angular nodes when $\sin 2\phi = 0$, i.e. at $\boxed{\phi = 0, \pi/2, \pi, 3\pi/2}$

E7F.12(b) The rotational energy depends only on the quantum number l [7F.10–*287*], but there are distinct states for every allowed value of m_l, which can range from $-l$ to $+l$ in integer steps. There are $2l+1$ such states, as there are l of these with $m_l > 0$, l of these with $m_l < 0$ and $m_l = 0$. Hence $l = 4$ has a degeneracy of $\boxed{9}$.

E7F.13(b) The diagram shown in Fig. 7.12 is drawn by forming a vector of length $[l(l+1)]^{1/2}$ and with a projection m_l on the z-axis. For $l = 3$ the vector is of length $\sqrt{12}$ and has projection $-3, \ldots +3$ in integer steps on the z-axis. Each vector may lie anywhere on a cone described by rotating the vector about the z-axis. For $l = 0$ the angular momentum is zero, and no vector can be drawn.

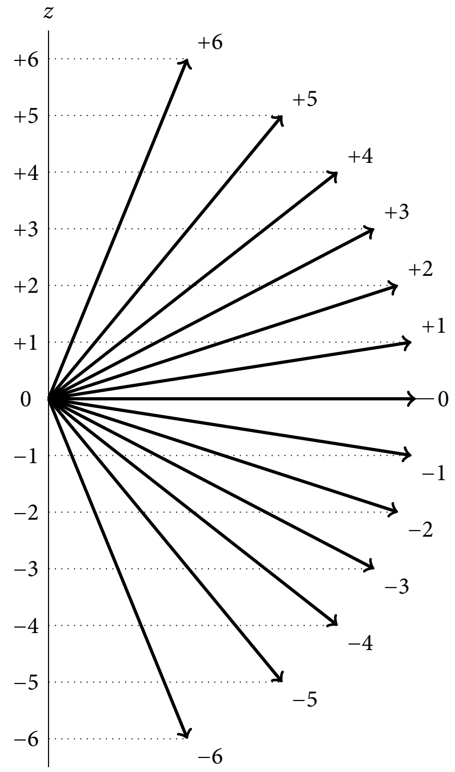


Figure 7.11

E7F.14(b) The angle in question is that between the z-axis and the vector representing the angular momentum. The projection of the vector onto the z-axis is $m_l\hbar$, and the length of the vector is $\hbar\sqrt{l(l+1)}$. Therefore the angle θ that the vector makes to the z-axis is given by $\cos\theta = m_l/\sqrt{l(l+1)}$.

When l is very large, the number of projections onto the z axis, $(2l+1)$, is also very large implying that the angular momentum vector can take any direction. In addition, for $l >> 1$, the vector representing the state with $m_l = l$ makes an angle with the z-axis given by $\cos\theta = l/\sqrt{l(l+1)} \approx l/l = 1$. Thus, in this limit, $\theta = 0$ and the vector may point along the z-axis. Both of these results fit in with the correspondence principle.

Solutions to problems

P7F.2 (a) A function ψ is an eigenfunction of an operator $\hat{\Omega}$ if $\hat{\Omega}\psi = \omega\psi$ where ω is a constant called the eigenvalue.

(i) $\hat{l}_z(e^{i\phi}) = (\hbar/i)d/d\phi(e^{i\phi}) = (\hbar/i) \times ie^{i\phi} = \hbar e^{i\phi}$. Hence $e^{i\phi}$ is an eigenfunction of the operator $(\hbar/i)d/d\phi$, eigenvalue $\boxed{\hbar}$.

(ii) $\hat{l}_z(e^{-2i\phi}) = (\hbar/i)d/d\phi(e^{-2i\phi}) = (\hbar/i) \times -2ie^{-2i\phi} = -2\hbar e^{-2i\phi}$. Hence $e^{-2i\phi}$ is an eigenfunction of the operator $(\hbar/i)d/d\phi$, eigenvalue $\boxed{-2\hbar}$.

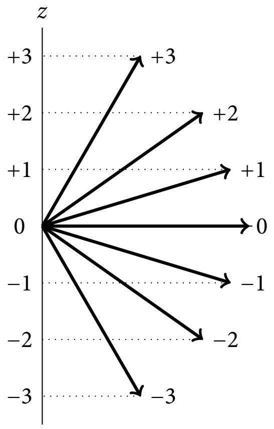


Figure 7.12

(iii) $\hat{l}_z(\cos\phi) = (\hbar/\mathrm{i})\mathrm{d}/\mathrm{d}\phi(\cos\phi) = (\hbar/\mathrm{i}) \times (-\sin\phi) = -(\hbar/\mathrm{i})\sin\phi$. Hence $\cos\phi$ is $\boxed{\text{not an eigenfunction}}$ of the operator $(\hbar/\mathrm{i})\mathrm{d}/\mathrm{d}\phi$.

(iv) $\hat{l}_z(\cos\chi\mathrm{e}^{\mathrm{i}\phi}+\sin\chi\mathrm{e}^{-\mathrm{i}\phi}) = (\hbar/\mathrm{i})(\mathrm{d}/\mathrm{d}\phi)(\cos\chi\mathrm{e}^{\mathrm{i}\phi}+\sin\chi\mathrm{e}^{-\mathrm{i}\phi}) = (\hbar/\mathrm{i})\times(\mathrm{i}\cos\chi\mathrm{e}^{\mathrm{i}\phi} - \mathrm{i}\sin\chi\mathrm{e}^{-\mathrm{i}\phi}) = \hbar(\cos\chi\mathrm{e}^{\mathrm{i}\phi} - \sin\chi\mathrm{e}^{-\mathrm{i}\phi})$. Hence $\cos\chi\mathrm{e}^{\mathrm{i}\phi} - \sin\chi\mathrm{e}^{-\mathrm{i}\phi}$ is $\boxed{\text{not an eigenfunction}}$ of the operator $(\hbar/\mathrm{i})\mathrm{d}/\mathrm{d}\phi$.

(b) For $\psi = \cos\phi$,

$$\langle l_z\rangle = \frac{\int_0^{2\pi}\psi^*\hat{l}_z\psi\,\mathrm{d}\phi}{\int_0^{2\pi}\psi^*\psi\,\mathrm{d}\phi} = \frac{-(\hbar/\mathrm{i})\int_0^{2\pi}\cos\phi\sin\phi\,\mathrm{d}\phi}{\int_0^{2\pi}\cos^2\phi\,\mathrm{d}\phi} = \frac{-(\hbar/2\mathrm{i})\sin 4\pi}{\int_0^{2\pi}\cos^2\phi\,\mathrm{d}\phi} = \boxed{0}$$

where Integral T.7 is used to evaluate the numerator.

For $\psi = \cos\chi\mathrm{e}^{\mathrm{i}\phi} + \sin\chi\mathrm{e}^{-\mathrm{i}\phi}$,

$$\langle l_z\rangle = \frac{\int_0^{2\pi}\psi^*\hat{l}_z\psi\,\mathrm{d}\phi}{\int_0^{2\pi}\psi^*\psi\,\mathrm{d}\phi} = \frac{\int_0^{2\pi}(\cos\chi\mathrm{e}^{-\mathrm{i}\phi} + \sin\chi\mathrm{e}^{\mathrm{i}\phi})\hbar(\cos\chi\mathrm{e}^{\mathrm{i}\phi} - \sin\chi\mathrm{e}^{-\mathrm{i}\phi})\,\mathrm{d}\phi}{\int_0^{2\pi}(\cos\chi\mathrm{e}^{-\mathrm{i}\phi} + \sin\chi\mathrm{e}^{\mathrm{i}\phi})(\cos\chi\mathrm{e}^{\mathrm{i}\phi} + \sin\chi\mathrm{e}^{-\mathrm{i}\phi})\,\mathrm{d}\phi}$$

$$= \frac{\hbar\int_0^{2\pi}\cos^2\chi - \sin^2\chi - \cos\chi\sin\chi\mathrm{e}^{-2\mathrm{i}\phi} + \cos\chi\sin\chi\mathrm{e}^{2\mathrm{i}\phi}\,\mathrm{d}\phi}{\int_0^{2\pi}\cos^2\chi + \sin^2\chi + \cos\chi\sin\chi\mathrm{e}^{-2\mathrm{i}\phi} + \cos\chi\sin\chi\mathrm{e}^{2\mathrm{i}\phi}\,\mathrm{d}\phi}$$

Note that as $\mathrm{e}^{\mathrm{i}n\phi}$ is periodic over 2π for integer n, $\int_0^{2\pi}\mathrm{e}^{\mathrm{i}n\phi}\mathrm{d}\phi = 0$. Hence

$$\langle l_z\rangle = \frac{\hbar 2\pi(\cos^2\chi - \sin^2\chi)}{2\pi(\cos^2\chi + \sin^2\chi)} = \boxed{\hbar\cos 2\chi}$$

(c) (i) For $\psi = \mathrm{e}^{\mathrm{i}\phi}$

$$\hat{T}\psi = -(\hbar^2/2I)\mathrm{d}^2(\mathrm{e}^{\mathrm{i}\phi})/\mathrm{d}\phi^2 = -(\hbar^2/2I)(\mathrm{i})^2\mathrm{e}^{\mathrm{i}\phi} = (\hbar^2/2I)\mathrm{e}^{\mathrm{i}\phi}$$

Hence ψ is an eigenfunction with eigenvalue $\boxed{\hbar^2/2I}$.

(ii) For $\psi = \mathrm{e}^{-2\mathrm{i}\phi}$

$$\hat{T}\psi = -(\hbar^2/2I)\mathrm{d}^2(\mathrm{e}^{-2\mathrm{i}\phi})/\mathrm{d}\phi^2 = -(\hbar^2/2I)(-2\mathrm{i})^2\mathrm{e}^{-2\mathrm{i}\phi} = (4\hbar^2/2I)\mathrm{e}^{-2\mathrm{i}\phi}$$

Hence ψ is an eigenfunction with eigenvalue $\boxed{4\hbar^2/2I}$.

(iii) For $\psi = \cos\phi$

$$\hat{T}\psi = -(\hbar^2/2I)\mathrm{d}^2(\cos\phi)/\mathrm{d}\phi^2 = (\hbar^2/2I)\cos\phi$$

Hence ψ is an eigenfunction with eigenvalue $\boxed{\hbar^2/2I}$.

(iv) For $\psi = \cos\chi\mathrm{e}^{\mathrm{i}\phi} + \sin\chi\mathrm{e}^{-\mathrm{i}\phi}$

$$\begin{aligned}\hat{T}\psi &= -(\hbar^2/2I)\mathrm{d}^2(\cos\chi\mathrm{e}^{\mathrm{i}\phi} + \sin\chi\mathrm{e}^{-\mathrm{i}\phi})/\mathrm{d}\phi^2\\ &= (\hbar^2/2I)(\cos\chi\mathrm{e}^{\mathrm{i}\phi} + \sin\chi\mathrm{e}^{-\mathrm{i}\phi})\end{aligned}$$

Hence ψ is an eigenfunction with eigenvalue $\boxed{\hbar^2/2I}$.

(d) A function is a definite state of a particular variable if it is an eigenfunction of the corresponding operator. Hence, all four wavefunctions are definite kinetic energy states, but only $\mathrm{e}^{\mathrm{i}\phi}$ and $\mathrm{e}^{-2\mathrm{i}\phi}$ are definite angular momentum states.

P7F.4 The rotational energy levels of a free molecule are given by [7F.10–*287*], $E_l = \hbar^2 l(l+1)/2I$, where $l = 0, 1, 2...$ and I is the moment of inertia, which for a diatomic molecule is $I = \mu R^2$, where μ is the reduced mass of the molecule and R is the bond length.

For $^1\mathrm{H}^{127}\mathrm{I}$, the reduced mass is

$$\begin{aligned}\mu &= (1\,m_\mathrm{u})(127\,m_\mathrm{u})/[(1+127)\,m_\mathrm{u}] = 0.992...\,m_\mathrm{u}\\ &= (0.992...\,m_\mathrm{u}) \times (1.6605\times10^{-27}\,\mathrm{kg}) = 1.64...\times10^{-27}\,\mathrm{kg}\end{aligned}$$

This gives the moment of inertia as $I = (1.64...\times10^{-27}\,\mathrm{kg})\times(160\times10^{-12}\,\mathrm{m})^2 = 4.21...\times10^{-47}\,\mathrm{kg\,m^2}$, and so the energy levels become $E_l = (1.0546\times10^{-34}\,\mathrm{J\,s})^2/[2\times 4.21...\times10^{-47}\,\mathrm{kg\,m^2}]\times l(l+1) = l(l+1)\times(1.31...\times10^{-22}\,\mathrm{J})$.

Using this the energies of the first four levels are computed as

$$\boxed{E_0 = 0,\quad E_1 = 2.64\times10^{-22}\,\mathrm{J},\quad E_2 = 7.91\times10^{-22}\,\mathrm{J},\quad E_3 = 1.58\times10^{-21}\,\mathrm{J}}$$

P7F.6 The function $Y_{1,+1} = -\frac{1}{2}\sqrt{3/2\pi}\sin\theta\mathrm{e}^{\mathrm{i}\phi}$. The integral to evaluate is

$$\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} Y_{1,+1}^{*}Y_{1,+1}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$

$Y_{1,+1}$ is complex , and so $Y_{1,+1}^{*} = -\frac{1}{2}\sqrt{3/2\pi}\sin\theta\mathrm{e}^{-\mathrm{i}\phi}$. Hence, the integrand is

$$\begin{aligned}&-\tfrac{1}{2}\sqrt{3/2\pi}\sin\theta\mathrm{e}^{-\mathrm{i}\phi}\times-\tfrac{1}{2}\sqrt{3/2\pi}\sin\theta\mathrm{e}^{\mathrm{i}\phi}\times\sin\theta\\ &= (3/8\pi)\sin^3\theta\mathrm{e}^{\mathrm{i}(\phi-\phi)} = (3/8\pi)\sin^3\theta\end{aligned}$$

Hence,

$$I = \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} Y_{1,+1}^{*}Y_{1,+1}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi = \frac{3}{8\pi}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\sin^3\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$

Because the integrand is a function of θ only, the two integrals can be separated

$$\begin{aligned} I &= \frac{3}{8\pi}\int_0^{2\pi}\mathrm{d}\phi\int_0^{\pi}\sin^3\theta\,\mathrm{d}\theta = \frac{3}{8\pi}\,\phi\big|_0^{2\pi}\times\frac{1}{3}(2-(\sin^2\pi+2)\cos\pi)\\ &= \frac{3}{8\pi}(2\pi-0)\times\frac{2-(0+2)(-1)}{3} = 1 \end{aligned}$$

where Integral T.3 is used to evaluate the integral in θ. It is confirmed that the function is normalized.

P7F.8 (a) The function Y_{l,m_l} is an eigenfunction of the operator $\hat{\Lambda}^2$ with eigenvalue $-l(l+1)$ for any allowed m_l. Hence for $\psi = c_1Y_{l,m_l} + c_2Y_{l,m_l'}$, $\hat{\Lambda}^2\psi = \hat{\Lambda}^2(c_1Y_{l,m_l} + c_2Y_{l,m_l'}) = c_1\hat{\Lambda}^2Y_{1,m_l} + c_2\hat{\Lambda}^2Y_{1,m_l'}$ as $\hat{\Lambda}^2$ is a linear operator. This is equal to $c_1[-l(l+1)]Y_{l,m_l} + c_2[-l(l+1)]Y_{l,m_l'} = -l(l+1)[c_1Y_{l,m_l} + c_2Y_{l,m_l'}] = -l(l+1)\psi$. Hence, this is an eigenfunction, eigenvalue $\boxed{-l(l+1)}$.

(b) The relevant functions are $Y_{1,+1} = -\frac{1}{2}\sqrt{3/2\pi}\sin\theta\mathrm{e}^{\mathrm{i}\phi}$, $Y_{1,-1} = -\frac{1}{2}\sqrt{3/2\pi}\times\sin\theta\mathrm{e}^{-\mathrm{i}\phi}$. This gives the following combinations,

$$\begin{aligned} \psi_a &= -Y_{1,+1} + Y_{1,-1} = \tfrac{1}{2}\sqrt{3/2\pi}\sin\theta\mathrm{e}^{\mathrm{i}\phi} + \tfrac{1}{2}\sqrt{3/2\pi}\sin\theta\mathrm{e}^{-\mathrm{i}\phi}\\ &= N\sqrt{3/2\pi}\sin\theta(\mathrm{e}^{\mathrm{i}\phi}+\mathrm{e}^{-\mathrm{i}\phi})/2 = \sqrt{3/2\pi}\sin\theta\tfrac{1}{2}(\mathrm{e}^{\mathrm{i}\phi}+\mathrm{e}^{-\mathrm{i}\phi})\\ &= \sqrt{3/2\pi}\sin\theta\cos\phi \end{aligned}$$

using $\cos x = \frac{1}{2}(\mathrm{e}^{\mathrm{i}x} + \mathrm{e}^{-\mathrm{i}x})$

$$\begin{aligned} \psi_b &= \mathrm{i}(Y_{1,+1} + Y_{1,-1}) = -(\mathrm{i}/2)\sqrt{3/2\pi}\sin\theta\mathrm{e}^{\mathrm{i}\phi} - (\mathrm{i}/2)\sqrt{3/2\pi}\sin\theta\mathrm{e}^{-\mathrm{i}\phi}\\ &= -\mathrm{i}\sqrt{3/2\pi}\sin\theta(\mathrm{e}^{\mathrm{i}\phi}-\mathrm{e}^{-\mathrm{i}\phi})/2 = -\mathrm{i}\sqrt{3/2\pi}\sin\theta(\mathrm{i}\sin\phi) \end{aligned}$$

using $\sin x = (\mathrm{e}^{\mathrm{i}x} + \mathrm{e}^{-\mathrm{i}x})/2\mathrm{i}$

$$= \sqrt{3/2\pi}\sin\theta\sin\phi$$

$\boxed{\text{Both of which are real functions}}$.

(c) Writing $\psi_a = N_a\sin\theta\cos\phi$ and $\psi_b = N_b\sin\theta\sin\phi$, these are orthogonal if $\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\psi_a^*\psi_b\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi = 0$. As ψ_a is real this integral becomes

$$\begin{aligned} &\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}(N_a\sin\theta\cos\phi)\times(N_b\sin\theta\sin\phi)\times\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\\ &= N_aN_b\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\sin^3\theta\sin\phi\cos\phi\mathrm{d}\theta\mathrm{d}\phi \end{aligned}$$

as the integrand can be written as the product of a function of θ with a function of ϕ, the integral can be separated

$$\begin{aligned}&= N_aN_b\int_0^{2\pi}\sin\phi\cos\phi\,\mathrm{d}\phi\int_0^{\pi}\sin^3\theta\,\mathrm{d}\theta\\&=(N_aN_b/2)\times\sin^2\phi\Big|_0^{2\pi}\times\int_0^{\pi}\sin^3\theta\,\mathrm{d}\theta\\&=(N_aN_b/2)\times[\sin^2(2\pi)-\sin^2(0)]\times\int_0^{\pi}\sin^3\theta\,\mathrm{d}\theta\\&=\boxed{0}\end{aligned}$$

Hence, ψ_a and ψ_b are orthogonal.

(d) The wavefunctions are normalized if

$$\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\psi_a^*\psi_a\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi=1 \text{ and } \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\psi_b^*\psi_b\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi=1$$

Note that both ψ_a and ψ_b are real. For ψ_a this integral is

$$I=\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}(N_a\sin\theta\cos\phi)^2\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi=N_a^2\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\sin^3\theta\cos^2\phi\,\mathrm{d}\theta\,\mathrm{d}\phi$$

This integral can be separated

$$I=N_a^2\int_0^{2\pi}\cos^2\phi\,\mathrm{d}\phi\int_0^{\pi}\sin^3\theta\,\mathrm{d}\theta=N_a^2\int_0^{2\pi}1-\sin^2\phi\,\mathrm{d}\phi\int_0^{\pi}\sin^3\theta\,\mathrm{d}\theta$$

The integral in ϕ can be evaluated using Integral T.3 and the integral in θ using Integral T.2

$$\begin{aligned}I&=N_a^2[2\pi-2\pi/2+(1/4)\sin 2(2\pi)](1/3)[2-(\sin^2\pi+2)\cos\pi]\\&=N_a^2(\pi)(4/3)\end{aligned}$$

The normalizing factor is therefore $\boxed{N_a=\sqrt{3/4\pi}}$.

For ψ_b,

$$I=\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}(N_b\sin\theta\sin\phi)^2\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi=N_b^2\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\sin^3\theta\sin^2\phi\,\mathrm{d}\theta\,\mathrm{d}\phi$$

This integral can be separated

$$I=N_b^2\int_0^{2\pi}\sin^2\phi\,\mathrm{d}\phi\int_0^{\pi}\sin^3\theta\,\mathrm{d}\theta$$

The integral in ϕ is evaluated using Integral T.3 and the integral in θ using Integral T.2

$$\begin{aligned}I&=N_b^2[2\pi+2\pi/2-(1/4)\sin 2(2\pi)](1/3)[2-(\sin^2\pi+2)\cos\pi]\\&=N_b^2(\pi)(4/3)\end{aligned}$$

The normalizing factor is therefore $\boxed{N_b=\sqrt{3/4\pi}}$.

(e) Angular nodes occur when these wavefunctions pass through zero, and so for ψ_a occur when $\cos\phi = 0$, that is when $\boxed{\phi = \pi/2, 3\pi/2}$: this corresponds to the $\boxed{yz \text{ plane}}$. For ψ_b they occur when $\sin\phi = 0$, that is when $\boxed{\phi = 0, \pi}$, which is the $\boxed{xz \text{ plane}}$.

P7F.10 The Hamiltonian for a hydrogen atom is

$$\hat{H} = -\frac{\hbar^2}{2mr}\frac{\partial^2}{\partial r^2}r + \frac{\hbar^2\hat{l}^2}{2mr^2} - \frac{e^2}{4\pi\varepsilon_0 r}$$

The operators $\hat{l}_z$ and $\hat{l}^2$ only operate on the angles θ and ϕ, and so commute with the operators that affect r only, such that

$$[\hat{l}_z, \hat{H}] = \frac{\hbar^2}{2mr^2}[\hat{l}_z, \hat{l}^2] \quad [\hat{l}^2, \hat{H}] = \frac{\hbar^2}{2mr^2}[\hat{l}^2, \hat{l}^2]$$

For the latter, for an arbitrary function f, $[\hat{l}^2, \hat{l}^2]f = \hat{l}^2\hat{l}^2 f - \hat{l}^2\hat{l}^2 f = 0$. Hence, $[\hat{l}^2, \hat{l}^2] = 0$, and so $[\hat{l}^2, \hat{H}] = 0$, meaning that the total angular momentum operator commutes with the Hamiltonian.

For the former, $[\hat{l}_z, \hat{l}^2]f = [\hat{l}_z, \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2]f = [\hat{l}_z, \hat{l}_x^2]f + [\hat{l}_z, \hat{l}_y^2]f + [\hat{l}_z, \hat{l}_z^2]f$. Using the relation given in the question, $[\hat{l}_z, \hat{l}_x^2] = [\hat{l}_z, \hat{l}_x]\hat{l}_x + \hat{l}_x[\hat{l}_z, \hat{l}_x] = \mathrm{i}\hbar\hat{l}_y\hat{l}_x + \mathrm{i}\hbar\hat{l}_x\hat{l}_y$, and $[\hat{l}_z, \hat{l}_y^2] = [\hat{l}_z, \hat{l}_y]\hat{l}_y + \hat{l}_y[\hat{l}_z, \hat{l}_y] = -[\hat{l}_y, \hat{l}_z]\hat{l}_y - \hat{l}_y[\hat{l}_y, \hat{l}_z] = -\mathrm{i}\hbar\hat{l}_y\hat{l}_x - \mathrm{i}\hbar\hat{l}_x\hat{l}_y$. Finally, $[\hat{l}_z, \hat{l}_z^2] = \hat{l}_z\hat{l}_z^2 - \hat{l}_z^2\hat{l}_z = \hat{l}_z^3 - \hat{l}_z^3 = 0$. Hence, $[\hat{l}_z, \hat{l}^2] = \mathrm{i}\hbar\hat{l}_y\hat{l}_x + \mathrm{i}\hbar\hat{l}_x\hat{l}_y - \mathrm{i}\hbar\hat{l}_y\hat{l}_x - \mathrm{i}\hbar\hat{l}_x\hat{l}_y + 0 = 0$, meaning that the z component of the angular momentum operator commutes with the Hamiltonian.

This is important as it implies that all functions that are eigenfunctions of the Hamiltonian of a H atom are also eigenfunctions of $\hat{l}_z$ and $\hat{l}^2$.

P7F.12 (a) Write the solutions $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$, and then the Schrödinger equation, $\hat{H}\psi = E\psi$ becomes

$$-\frac{\hbar^2}{2mr}\frac{\partial^2(rRY)}{\partial r^2} - \frac{\hbar^2}{2mr^2}\hat{\Lambda}^2(RY) = ERY$$

Note that the derivatives in r only affects R, and $\hat{\Lambda}^2$ only operates on Y, such that

$$-\frac{\hbar^2 Y}{2mr}\frac{\partial^2(rR)}{\partial r^2} - \frac{\hbar^2 R}{2mr^2}\hat{\Lambda}^2 Y = ERY$$

Dividing this equation by the function RY then gives

$$-\frac{\hbar^2}{2mrR}\frac{\partial^2(rR)}{\partial r^2} - \frac{\hbar^2}{2mr^2 Y}\hat{\Lambda}^2 Y = E$$

The first term on the left hand side depends only on r, but the second term depends on r and the angles. Hence, to make this equation separable, multiply through by r^2, and rearrange to give

$$-\frac{\hbar^2 r}{2mR}\frac{\partial^2(rR)}{\partial r^2} - Er^2 = \frac{\hbar^2 \hat{\Lambda}^2 Y}{2mY}$$

The left side is dependent only on r and the right side depends only on the angles. Hence, this equation is only true for all r and all angles if both sides are equal to the same constant, arbitrarily called λ. This gives two equations

$$-\frac{\hbar^2 r}{2mR}\frac{\partial^2(rR)}{\partial r^2} - Er^2 = \lambda \qquad \frac{\hbar^2 \hat{\Lambda}^2 Y}{2mY} = \lambda$$

The solutions to the second equation are the spherical harmonics, which are eigenfunctions of the operator $\hat{\Lambda}^2$, with eigenvalue $-l(l+1)$, which gives $-\hbar^2 l(l+1)Y/2mY = \lambda$ and so $\lambda = -\hbar^2 l(l+1)/2m$. This makes the equation in r

$$-\frac{\hbar^2 r}{2mR}\frac{\partial^2(rR)}{\partial r^2} - Er^2 = -\frac{\hbar^2 l(l+1)}{2m}$$

which is rearranged to

$$-\frac{\hbar^2}{2mr^2}\frac{\partial^2(rR)}{\partial r} + \frac{\hbar^2 l(l+1)}{2mr^2}R = ER$$

(b) For the case when $l = 0$, this becomes

$$-\frac{\hbar^2}{2mr}\frac{\partial^2(rR)}{\partial r^2} = ER$$

For the trial solution $R(r) = N\sin(n\pi r/a)/r$, and so $rR = N\sin(n\pi r/a)$

$$-\frac{\hbar^2}{2mr}\frac{\partial^2(N\sin(n\pi r/a))}{\partial r^2} = E\frac{N\sin(n\pi r/a)}{r}$$

Note that $\mathrm{d}^2 \sin ax/\mathrm{d}x^2 = \mathrm{d}a\cos ax/\mathrm{d}x = -a^2\sin ax$

$$-\frac{\hbar^2}{2mr} \times -\left(\frac{n\pi}{a}\right)^2 N\sin(n\pi r/a) = EN\sin(n\pi r/a)/r$$

Which is solved if

$$E = \frac{\hbar^2(n\pi)^2}{2ma^2} = \frac{(h/2)^2 n^2}{2ma^2} = \frac{h^2 n^2}{8ma^2}$$

where $\hbar = h/2\pi$ has been used

(c) As the wavefunction must be zero outside the cavity, and be continuous, the wavefunction must equal zero at $r = a$, for all angles, and so the boundary condition is that $R(a) = 0$. Hence $\sin(n\pi a/a)/a = 0$, which is true if $\sin(n\pi) = 0$, which implies that n must be integral. Hence, the allowed energies are $E_n = n^2h^2/8ma^2$, $n = 1, 2, 3...$

Answers to integrated activities

I7.2 Macroscopic synthesis and material development always contains elements of randomness at the molecular level. Crystal structures are never perfect. A product of organic synthesis is never absolutely free of impurities, although impurities may be at a level that is lower than measurement techniques make possible. Alloys are grainy and slightly non-homogeneous within any particular grain. Furthermore, the random distribution of atomic/molecular positions and orientations within, and between, macroscopic objects causes the conversion of energy to non-useful heat during manufacturing processes. Production efficiencies are difficult to improve. Nanometre technology on the 1 nm to 100 nm scale may resolve many of these problems. Self-organization and production processes by nanoparticles and nanomachines may be able to exclude impurities and greatly improve homogeneity by effective examination and selection of each atom/molecule during nanosynthesis and nanoproduction processes. Higher efficiencies of energy usage may be achievable as nanomachines produce idealized materials at the smaller sizes and pass their products to larger nanomachines for production of larger scale materials.

The directed, non-random, use of atoms and molecules by nanotechniques holds the promise for the production of smaller transistors and wires for the electronics and computer industries. Unusual material strengths, optical properties, magnetic properties, and catalytic properties may be achievable. Higher efficiencies of photo-electronic conversion would have a great impact.

I7.4 (a) The first step is to compute the total energy of the system of N_A particles, which is identified as the internal energy U. The energy levels for a particle in a cubic box of side L are given by [7D.13b–*267*], $E_n = h^2n^2/8mL^2$, where $n^2 = n_1^2 + n_2^2 + n_3^2$. If there are N_A particles, all occupying the level corresponding to a particular value of n, the internal energy of the system is $U = N_A E_n = N_A h^2 n^2/8mL^2$. Using $V = L^3$ the length is written in terms of the volume as $L = V^{1/3}$, hence $L^2 = V^{2/3}$ and therefore $U = N_A h^2 n^2/8mV^{2/3}$.

If the expansion is adiabatic (that is, not heat flows into or out of the system) then from the First Law, $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$, it follows that $\mathrm{d}U = \mathrm{d}w$. The work done on expansion is therefore computed by finding how U changes with volume, specifically by finding $\partial U/\partial V$.

$$\frac{\partial U}{\partial V} = \frac{\partial}{\partial V}\left(\frac{N_A h^2 n^2}{8mV^{2/3}}\right)_{\text{adia}} = \frac{-2}{3} \times \frac{N_A h^2 n^2}{8mV^{5/3}} = -\frac{N_A h^2 n^2}{12mV^{5/3}}$$

The change in internal energy on expansion through $\mathrm{d}V$ will therefore be

$$\mathrm{d}U = \left(\frac{\partial U}{\partial V}\right)_{\text{adia}} \mathrm{d}V = -\overbrace{\frac{N_A h^2 n^2}{12mV^{5/3}}}^{A}\,\mathrm{d}V \qquad (7.2)$$

The work is equal to this change in internal energy. For a finite change the expression is integrated with respect to V between limits V_1 and V_2, with $\Delta V = V_2 - V_1$.

(b) It is evident from eqn 7.2 that $\mathrm{d}U$, and hence the work, goes as n^2.

(c) The work of expansion against an external pressure p_{ex} is given by [2A.5a–39], $\mathrm{d}w = -p_{\mathrm{ex}}\mathrm{d}V$. In eqn 7.2 the term A which multiplies $\mathrm{d}V$ refers to the sample itself, and so must presumably in some way reflect the pressure of the sample, not the external pressure. However, if the expansion is reversible, the external pressure is equal to the internal pressure and the term A can then be identified as the pressure. Therefore, if it is assumed that the expansion is both adiabatic and reversible

$$p = \frac{N_{\mathrm{A}}h^2n^2}{12mV^{5/3}}$$

The expression can be rewritten in terms of the average energy of each particle which, because they all occupy the same level, is simply $E_{\mathrm{av}} = n^2h^2/8mL^2 = n^2h^2/8mV^{2/3}$, hence

$$p = \frac{N_{\mathrm{A}}h^2n^2}{12mV^{5/3}} = \frac{8N_{\mathrm{A}}}{12V}\overbrace{\frac{n^2h^2}{8mV^{2/3}}}^{E_{\mathrm{av}}} = \frac{2N_{\mathrm{A}}E_{\mathrm{av}}}{3V}$$

This expression is reminiscent of the form of the pressure derived using the kinetic theory of gases (Topic 1B): $pV = \frac{1}{3}nMv_{\mathrm{rms}}^2$, where n is the amount in moles, M is the molar mass, and v_{rms} is the root-mean-square speed. Because $M = mN_{\mathrm{A}}$, where m is the mass of a molecule, the expression can be rewritten

$$pV = \tfrac{1}{3}nmN_{\mathrm{A}}v_{\mathrm{rms}}^2 = n\tfrac{2}{3}N_{\mathrm{A}}\overbrace{\tfrac{1}{2}mv_{\mathrm{rms}}^2}^{E_{\mathrm{k}}}$$

The term $\frac{1}{2}mv_{\mathrm{rms}}^2$ is identified as the average kinetic energy of one molecule and, because in the kinetic theory the only energy a molecule possesses is kinetic, E_{k} can further be identified as the average energy, E_{av}. Thus, for one mole ($n = 1$)

$$pV = \tfrac{2}{3}N_{\mathrm{A}}E_{\mathrm{av}} \qquad \text{hence} \qquad p = \frac{2N_{\mathrm{A}}E_{\mathrm{av}}}{3V}$$

The two expressions for the pressure are therefore directly comparable within the restrictions imposed.

(d) For an isothermal expansion heat would have to enter the system in order to maintain its temperature, and this would involve promoting particles to higher energy levels. As the volume increases the energy levels move closer together, so the promotion of particles to higher levels needs to offset this effect as well.

I7.6 (a) In *Problem* P7D.6 and *Problem* P7D.7 it is shown that for a particle in a box in a state with quantum number n

$$\Delta x = L(1/12 - 1/2n^2\pi^2)^{1/2} \quad \text{and} \quad \Delta p_x = nh/2L$$

hence

$$\Delta x \Delta p_x = L(1/12 - 1/2n^2\pi^2)^{1/2} \times nh/2L = (nh/2)(1/12 - 1/2n^2\pi^2)^{1/2}$$

For $n = 1$

$$\Delta x \Delta p_x = L(1/12 - 1/2\pi^2)^{1/2} \times h/2L = (h/2)(1/12 - 1/2\pi^2)^{1/2} \approx 0.57\hbar$$

and for $n = 2$ $\Delta x \Delta p_x \approx 1.7\hbar$. The Heisenberg uncertainty principle is satisfied in both cases, and it is evident that $\Delta x \Delta p_x$ is an increasing function of n. The principle is therefore satisfied for all $n > 1$.

(b) In *Problem* P7E.17 it is shown that for a harmonic oscillator in a state with quantum number υ

$$\Delta x_\upsilon \Delta p_\upsilon = (\upsilon + \tfrac{1}{2})\hbar$$

Therefore, for the ground state with $\upsilon = 0$, $\Delta x \Delta p = \tfrac{1}{2}\hbar$: the Heisenberg uncertainty principle is satisfied with the smallest possible uncertainty. It follow that for $\upsilon > 0$ the principle is also satisfied because $\Delta x_\upsilon \Delta p_\upsilon$ is an increasing function of υ.

8

Atomic structure and spectra

8A Hydrogenic Atoms

Answers to discussion questions

D8A.2 (i) The principal quantum number n determines the energy of a hydrogenic atomic orbital through [8A.8–*306*].

(ii) The azimuthal quantum number l determines the magnitude of the orbital angular momentum, given by $[l(l+1)]^{1/2}\hbar$.

(iii) The magnetic quantum number m_l determines the z-component of the orbital angular momentum, given by $m_l\hbar$.

(iv) The spin quantum number s determines the magnitude of the spin angular momentum, given by $[s(s+1)]^{1/2}\hbar$; for hydrogenic atomic orbitals s can only be $\frac{1}{2}$.

(v) The quantum number m_s determines the z-component of the spin angular momentum, given by $m_s\hbar$; for hydrogenic atomic orbitals m_s can only be $\pm\frac{1}{2}$.

Solutions to exercises

E8A.1(b) The energy of the level of a hydrogenic atom with quantum number n is given by [8A.14–*308*], $E_n = -hc\tilde{R}_H Z^2/n^2$, where Z is the atomic number of the atom. As described in Section 8A.2(d) on page 309, the degeneracy of a state with quantum number n is n^2.

- With $Z = 2$, $E_n = -4hc\tilde{R}_H/n^2$; the state with $E = -4hcR_H$ has $n = 1$, and hence degeneracy $(1)^2 = \boxed{1}$.
- With $Z = 4$, $E_n = -16hc\tilde{R}_H/n^2$; the state with energy $E = -hcR_H/4 = -16hc\tilde{R}_H/(8)^2$ has $n = 8$, and hence degeneracy $(8)^2 = \boxed{64}$.
- With $Z = 5$, $E_n = -25hc\tilde{R}_H/n^2$; the state with energy $E = -hcR_H = -25hc\tilde{R}_H/(5)^2$ has $n = 5$, and hence degeneracy $(5)^2 = \boxed{25}$.

E8A.2(b) The task is to find the value of N such that the integral $\int \psi^*\psi\,\mathrm{d}\tau = 1$, where $\psi = N(2 - r/a_0)\mathrm{e}^{-r/2a_0}$. The integration is over the range $r = 0$ to ∞, $\theta = 0$ to π, and $\phi = 0$ to 2π; the volume element is $r^2 \sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi$. The required integral is therefore

$$N^2 \int_0^\infty \int_0^\pi \int_0^{2\pi} (2 - r/a_0)^2 r^2 \mathrm{e}^{-r/a_0} \sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi$$

The integrand is a product of functions of each of the variables, and so the integral separates into three

$$N^2 \int_0^\infty (2 - r/a_0)^2 r^2 \mathrm{e}^{-r/a_0}\,\mathrm{d}r \int_0^\pi \sin\theta\,\mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi$$

The integral over r is found by first expanding the bracket to give

$$\begin{aligned}\int_0^\infty (2 - r/a_0)^2 r^2 \mathrm{e}^{-r/a_0}\,\mathrm{d}r &= \int_0^\infty (4r^2 - 4r^3/a_0 + r^4/a_0^2)\mathrm{e}^{-r/a_0}\,\mathrm{d}r \\ = 4\frac{2!}{(1/a_0)^3} - \frac{4}{a_0}\frac{3!}{(1/a_0)^4} + \frac{1}{a_0^2}\frac{4!}{(1/a_0)^5} &= 8a_0^3 - 24a_0^3 + 24a_0^3 = 8a_0^3\end{aligned}$$

These integrals are evaluated using Integral E.3 with the appropriate value of n and $k = 1/a_0$. The integrals over the angles are straightforward

$$\int_0^\pi \sin\theta\,\mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi = (-\cos\theta)|_0^\pi \times \phi|_0^{2\pi} = 4\pi$$

The complete integral evaluates to $N^2 \times 4\pi \times 8a_0^3$; setting this equal to 1 gives $\boxed{N = (32\pi a^3)^{-1/2}}$.

E8A.3(b) The wavefunction is given by [8A.12–*307*], $\psi_{n,l,m_l} = Y_{l,m_l}(\theta,\phi)R_{n,l}(r)$; for the state with $n = 3$, $l = 0$, $m_l = 0$ this is

$$\psi_{3,0,0} = Y_{0,0}(\theta,\phi)R_{3,0}(r) = (4\pi)^{-1/2}(243)^{-1/2}(Z/a_0)^{3/2}(6 - 6\rho + \rho^2)\mathrm{e}^{-\rho/2}$$

where the radial wavefunction is taken from Table 8A.1 on page 306, the angular wavefunction (the spherical harmonic) is taken from Table 7F.1 on page 286, and $\rho = 2Zr/na_0$. The probability density is therefore

$$P_{3,0,0} = |\psi_{3,0,0}|^2 = (4\pi)^{-1}(243)^{-1}(Z/a_0)^3(6 - 6\rho + \rho^2)^2\mathrm{e}^{-\rho}$$

The probability density at the nucleus, $\rho = 0$, is then $(4\pi)^{-1}(243)^{-1}(Z/a_0)^3(6)^2 = \boxed{Z^3/(27\pi a^3)}$.

E8A.4(b) The radial wavefunction of a 3s orbital is taken from Table 8A.1 on page 306, $R_{3,0}(r) = N(6 - 6\rho + \rho^2)\mathrm{e}^{-\rho/2}$, where $\rho = 2Zr/na_0$; for $n = 3$, $\rho = 2Zr/3a_0$. The extrema are located by finding the values of ρ for which $\mathrm{d}R_{3,0}/\mathrm{d}\rho = 0$; the product rule is required

$$\begin{aligned}\frac{\mathrm{d}R_{3,0}}{\mathrm{d}\rho} &= N\frac{\mathrm{d}(6 - 6\rho + \rho^2)}{\mathrm{d}\rho}\mathrm{e}^{-\rho} + N(6 - 6\rho + \rho^2)\frac{\mathrm{d}\mathrm{e}^{-\rho/2}}{\mathrm{d}\rho} \\ &= (2\rho - 6)\mathrm{e}^{-\rho/2} - \tfrac{1}{2}\left(6 - 6\rho + \rho^2\right)\mathrm{e}^{-\rho/2} \\ &= -(\rho^2 - 10\rho + 18)\mathrm{e}^{-\rho/2}\end{aligned}$$

Setting the term in the parentheses to zero and solving the resulting quadratic gives $\rho = 5 \pm \sqrt{7}$, so extrema occur at $\boxed{r = (3a_0/2Z)(5 \pm \sqrt{7})}$.

The simplest way to identify the nature of the extrema is to make a plot of $R_{3,0}(\rho)$, from which it is immediately evident that $\rho = 5 - \sqrt{7}$ is a minimum and $\rho = 5 + \sqrt{7}$ is a maximum.

E8A.5(b) Assuming that the electron is in the ground state, the wavefunction is $\psi = N\mathrm{e}^{-r/a_0}$, and so the radial distribution function, given by [8A.17a–*312*], is $R(r) = 4\pi r^2\psi^2 = 4\pi N^2 r^2 \mathrm{e}^{-2r/a_0}$. The first step is to find the value of r at which this is a maximum, and this is done by solving $\mathrm{d}R(r)/\mathrm{d}r = 0$; for such a calculation the constants $4\pi N^2$ can be discarded.

$$\frac{\mathrm{d}R(r)}{\mathrm{d}r} = 2r\,\mathrm{e}^{-2r/a_0} - (2r^2/a_0)\,\mathrm{e}^{-2r/a_0}$$

The derivative is zero at $r = 0$ and $r = a_0$, with the latter being the maximum. The radial distribution function falls to a fraction f of its maximum at radius r' given by $R(r')/R(a_0) = f$, hence

$$f = \frac{R(r')}{R(a_0)} = \frac{4\pi N^2 r'^2 \mathrm{e}^{-2r'/a_0}}{4\pi N^2 a_0^2 \mathrm{e}^{-2a_0/a_0}} = \frac{r'^2 \mathrm{e}^{-2r'/a_0}}{a_0^2 \mathrm{e}^{-2}}$$

The solutions to this equation need to be found numerically using mathematical software. For $f = 0.5$ the solutions are $r' = \boxed{0.381a_0 \text{ and } 2.08a_0}$. For $f = 0.75$ the solutions are $r' = \boxed{0.555a_0 \text{ and } 1.64a_0}$.

E8A.6(b) The radial wavefunction is $R_{4,1} = N(20 - 10\rho + \rho^2)\mathrm{e}^{-\rho/2}$ where $\rho = Zr/2a_0$. Radial nodes occur when the wavefunction passes through 0, which is when $20 - 10\rho + \rho^2 = 0$. The roots of this quadratic equation are at $\rho = 5 \pm \sqrt{5}$ and hence the nodes are at $\boxed{r = (2a_0/Z)(5 \pm \sqrt{5})}$. The wavefunction goes to zero as $\rho \rightarrow \infty$, but this does not count as a node as the wavefunction does not pass through zero.

E8A.7(b) Angular nodes occur when $\sin^2\theta \sin 2\phi = 0$, which occurs when either of $\sin^2\theta$ or $\sin 2\phi$ is equal to zero; recall that the range of θ is $0 \rightarrow \pi$ and of ϕ is $0 \rightarrow 2\pi$.

Although the function is zero for $\theta = 0$ this does not describe a plane, and so is discounted. The function is zero for $\boxed{\phi = 0}$ with any value of θ: this is the xz plane (the solution $\phi = \pi$ corresponds to the same plane). The function is also zero for $\boxed{\phi = \pi/2}$ with any value of θ: this is the yz plane. There are two nodal planes, as expected for a d orbital.

E8A.8(b) The radial distribution function is defined in [8A.17b–*312*], $P(r) = r^2 R(r)^2$. For the 3s orbital $R(r)$ is given in Table 8A.1 on page 306 as $R_{2,0} = N(6 - 6\rho + \rho^2)\mathrm{e}^{-\rho/2}$ where $\rho = 2Zr/na_0$, which for $n = 3$ is $\rho = 2Zr/3a_0$. With the substitution $r^2 = \rho^2(3a_0/2Z)^2$, the radial distribution function is therefore $P(\rho) = N^2(3a_0/2Z)^2\rho^2(6 - 6\rho + \rho^2)^2\mathrm{e}^{-\rho}$.

Mathematical software is used to find the values of ρ for which $\mathrm{d}P(\rho)/\mathrm{d}\rho = 0$, giving the results $\rho = 0, 0.493, 1.27, 2.79, 4.73, 8.72$. The simplest way to identify which of these is a maximum is to plot $P(\rho)$ against ρ, from which it is evident that $\rho = 0.493, 2.79, 8.72$ are all maxima, with the principal maximum being at $\rho = 8.72$. The maximum in the radial distribution function is therefore at $r = \boxed{8.72 \times (3a_0/2Z)}$.

E8A.9(b) The radius at which the electron is most likely to be found is that at which the radial distribution function is a maximum. The radial distribution function is defined in [8A.17b–*312*], $P(r) = r^2R(r)^2$. For the 3p orbital $R(r)$ is given in Table 8A.1 on page 306 as $R_{3,0} = N(4-\rho)\rho e^{-\rho/2}$ where $\rho = 2Zr/na_0$, which for $n = 3$ is $\rho = 2Zr/3a_0$. With the substitution $r^2 = \rho^2(3a_0/2Z)^2$, The radial distribution function is therefore $P(\rho) = N^2(3a_0/2Z)^2(4-\rho)^2\rho^4e^{-\rho}$.

To find the maximum in this function the derivative is set to zero and the resulting equation solved for ρ. Mathematical software gives the following values of ρ: $0, 2, 4, 8$. It is evident that $P(\rho)$ is zero at $\rho = 0$ and $\rho = 4$, and that $P(\rho)$ tends to zero as $\rho \to \infty$. Therefore $\rho = 2$ and $\rho = 8$ must correspond to maxima; a plot of $P(\rho)$ shows that the latter is the principal maximum; this occurs at $r = \boxed{8(3a_0/2Z)}$.

E8A.10(b) The N shell has $n = 4$. The possible values of l (subshells) are 0, corresponding to the s orbital, $l = 1$ corresponding to the p orbitals, $l = 2$ corresponding to the d orbitals, and $l = 3$ corresponding to the f orbitals; there are therefore $\boxed{\text{4 subshells}}$. As there is one s orbital, 3 p orbitals, 5 d orbitals and 7 p orbitals, there are $\boxed{\text{16 orbitals}}$ in total.

E8A.11(b) The magnitude of the orbital angular momentum of an orbital with quantum number l is $\sqrt{l(l+1)}\hbar$. The total number of nodes for an orbital with quantum number n is $n-1$, l of these are angular and so the number of radial nodes is $n-l-1$.

orbital	n	l	ang. mom.	angular nodes	radial nodes
4d	4	2	$\sqrt{6}\hbar$	2	1
2p	2	1	$\sqrt{2}\hbar$	1	0
3p	3	1	$\sqrt{2}\hbar$	1	1

E8A.12(b) All the 3d orbitals have the same value of n and l, and hence have the same radial function, which is given in Table 8A.1 on page 306 as $R_{3,2} = N\rho^2e^{-\rho/2}$ where $\rho = 2Zr/na_0$, which for $n = 3$ is $\rho = 2Zr/3a_0$. Radial nodes occur when the wavefunction passes through zero. The function goes to zero at $\rho = 0$ and as $\rho \to \infty$, but it does not pass through zero at these points so they are not nodes. The number of radial nodes is therefore 0.

Solutions to problems

P8A.2 Two wavefunctions, ψ_1 and ψ_2 are orthogonal if the integral $\int \psi_1^* \psi_2 \,\mathrm{d}\tau$ is equal to zero. In spherical polar coordinates the range of integration is $r = 0$ to ∞, $\theta = 0$ to π and $\phi = 0$ to 2π; with a volume element is $r^2 \sin\theta \,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi$.

(i) Hydrogenic 1s and 2s orbitals take the form $\psi_{1s} = R_{1,0}(r)Y_{0,0}(\theta,\phi)$ and $\psi_{2s} = R_{2,0}(r)Y_{0,0}(\theta,\phi)$. Because the angular function is the same for the two orbitals, the orthogonality must arise from the radial parts, so only these need be considered further. The radial functions are $R_{1,0}(\rho) = N_{1,0}\mathrm{e}^{-\rho/2}$, where $\rho = 2Zr/a_0$ and $R_{2,0}(\rho') = N_{2,0}(2-\rho')\mathrm{e}^{-\rho'/2}$ where $\rho' = Zr/a_0$. The latter is rewritten in terms of ρ by noting that $\rho' = \rho/2$: $R_{2,0}(\rho) = N_{2,0}(2-\rho/2)\mathrm{e}^{-\rho/4}$. The relevant integral is conveniently taken over ρ rather than r. Noting that $r^2 = \rho^2(a_0/2Z)^2$

$$\begin{aligned}\int_0^\infty \rho^2(a_0/2Z)^2 R_{1,0}R_{2,0}\,\mathrm{d}\rho &= \overbrace{(a_0/2Z)^2 N_{1,0}N_{2,0}}^{C}\\ &\quad\times \int_0^\infty \mathrm{e}^{-\rho/2}\,(2-\rho/2)\mathrm{e}^{-\rho/4}\,\rho^2\,\mathrm{d}\rho\\ &= C\int_0^\infty (2\rho^2 - \rho^3/2)\mathrm{e}^{-3\rho/4}\,\mathrm{d}\rho\\ &= 2C\left[\frac{2!}{(3/4)^3}\right] - \tfrac{1}{2}C\left[\frac{3!}{(3/4)^4}\right]\\ &= 2C\times\frac{128}{27} - \tfrac{1}{2}C\times\frac{1536}{81} = 0\end{aligned}$$

The integrals are evaluated using Integral E.3 with $k = 3/4$ and the relevant value of n. The integral is zero and therefore the 1s and 2s orbitals are $\boxed{\text{orthogonal}}$.

(ii) It is explained in Section 8A.2(g) on page 313 that the p_x and p_y orbitals are proportional to x and y respectively. Therefore, in Cartesian coordinates, the integral of the product of these two functions is proportional to $\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} xy\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$. The integrand is an odd function of both x and y, so when evaluated over a symmetrical range the result is zero. These orbitals are therefore $\boxed{\text{orthogonal}}$.

Alternatively, consider the angular parts of the orbitals given in [8A.21–*314*]: $\mathrm{p}_x \propto \sin\theta\cos\phi$ and $\mathrm{p}_y \propto \sin\theta\sin\phi$. The product of these two contains the term $(\cos\phi\sin\phi)$ which is equal to $\frac{1}{2}\sin 2\phi$. The integral of this function over the range $\phi = 0$ to 2π is zero (the integral over two complete sine waves). Therefore the functions are orthogonal.

P8A.4 Ionization of He^+ and Li^{2+} both occur from the ground state, with $n = 1$. The ionization energy is the energy needed to take the electron from its original state to the state with $n = \infty$, which has energy zero by definition. Therefore the ionization energy is simply minus the energy of the ground state. Using [8A.13–*308*] follows that $I = hcZ^2\tilde{R}_\mathrm{N}$. The ratio of the ionization energies of Li^+, $Z = 3$, and He^+, $Z = 2$, is therefore $I_\mathrm{Li}/I_\mathrm{He} = (3/2)^2(\tilde{R}_\mathrm{Li}/\tilde{R}_\mathrm{He})$.

The Rydberg constants for Li and He are in principle different because the reduced masses of the atoms are different. However, this difference is too small to have a significant effect on the result of the present calculation, given the precision of the data. Therefore, it is assumed that $\tilde{R}_{\mathrm{Li}}/\tilde{R}_{\mathrm{He}} = 1$ and hence

$$I_{\mathrm{Li}} = I_{\mathrm{He}}(3/2)^2 = (54.36\ \mathrm{eV}) \times (3/2)^2 = \boxed{122.3\ \mathrm{eV}}$$

P8A.6 From [8A.21–*314*], the wavefunctions for the p_x and p_y orbitals can be written as $\psi_{\mathrm{p}_x} = rf(r)\sin\theta\cos\phi$ and $\psi_{\mathrm{p}_y} = rf(r)\sin\theta\sin\phi$. Then, using the identities $\cos x = (\mathrm{e}^{\mathrm{i}x} + \mathrm{e}^{-\mathrm{i}x})/2$ and $\sin x = (\mathrm{e}^{\mathrm{i}x} - \mathrm{e}^{-\mathrm{i}x})/2\mathrm{i}$, these wavefunctions can be rewritten

$$\psi_{\mathrm{p}_x} = (2)^{-1}rf(r)\sin\theta(\mathrm{e}^{\mathrm{i}\phi} + \mathrm{e}^{-\mathrm{i}\phi}) \quad \psi_{\mathrm{p}_y} = (2\mathrm{i})^{-1}rf(r)\sin\theta(\mathrm{e}^{\mathrm{i}\phi} - \mathrm{e}^{-\mathrm{i}\phi})$$

The form of the operator $\hat{l}_z$ is given in [7F.5b–*284*], $\hat{l}_z = (\hbar/\mathrm{i})\partial/\partial\phi$. To determine whether or not ψ_{p_x} is an eigenfunction of $\hat{l}_z$, the operator is allowed to act on the function

$$\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial\phi}\frac{1}{2}rf(r)\sin\theta(\mathrm{e}^{\mathrm{i}\phi} + \mathrm{e}^{-\mathrm{i}\phi}) = \frac{\hbar}{\mathrm{i}}\frac{1}{2}rf(r)\sin\theta(\mathrm{i}\mathrm{e}^{\mathrm{i}\phi} - \mathrm{i}\mathrm{e}^{-\mathrm{i}\phi})$$

It is evident that the effect of the operator is *not* to regenerate the original function times a constant, so ψ_{p_x} is $\boxed{\text{not}}$ an eigenfunction of the operator. A similar calculation shows that the same is true for ψ_{p_y}.

However, the functions $\mathrm{e}^{\pm\mathrm{i}\phi}$ are eigenfunctions of $\hat{l}_z$, $(\hbar/\mathrm{i})\partial/\partial\phi\,\mathrm{e}^{\pm\mathrm{i}\phi} = \pm\hbar\mathrm{e}^{\pm\mathrm{i}\phi}$. Using the identities $\mathrm{e}^{\pm\mathrm{i}x} = \cos x \pm \mathrm{i}\sin x$, suitable combinations of ψ_{p_x} and ψ_{p_y} are found which are proportional to $\mathrm{e}^{\pm\mathrm{i}\phi}$, and hence which are eigenfunctions of $\hat{l}_z$. There are two such combinations

$$\psi_{\mathrm{p}_x} \pm \mathrm{i}\times\psi_{\mathrm{p}_y} = rf(r)\sin\theta\cos\phi + \mathrm{i}\times rf(r)\sin\theta\sin\phi = rf(r)\sin\theta\,\mathrm{e}^{\pm\mathrm{i}\phi}$$

P8A.8 The expectation value of $1/r$ is given by $\langle 1/r\rangle = \int \psi^* r^{-1}\psi\,\mathrm{d}\tau$. The wavefunction can be written as a product of a radial part and an angular part $\psi = R(r)Y(\theta,\phi)$. As $1/r$ is a function of r only, the integral over the angles can be evaluated separately, and because the $Y(\theta,\phi)$ are normalized with respect to integration over the angles the integral simplifies to $\langle 1/r\rangle = \int_0^\infty R(r)^2(1/r)r^2\,\mathrm{d}r = \int_0^\infty R(r)^2 r\,\mathrm{d}r$.

(a) For a 1s orbital the radial function is $R_{1,0}(r) = 2(Z/a_0)^{3/2}\mathrm{e}^{-Zr/a_0}$ (Table 8A.1) and so

$$\langle r^{-1}\rangle = 4(Z/a_0)^3\int_0^\infty r\mathrm{e}^{-2Zr/a_0}\mathrm{d}r = 4(Z/a)^3[1!/(2Z/a_0)^2] = \boxed{Z/a_0}$$

where the integral is evaluated using Integral E.3 with $n = 1$ and $k = 2Z/a_0$.

(b) For 2s the radial function is $R_{2,0}(r) = 8^{-1/2}(Z/a_0)^{3/2}[2 - Zr/a_0]e^{-Zr/2a_0}$ and so

$$\begin{aligned}\langle r^{-1}\rangle &= 8^{-1}(Z/a_0)^3 \int_0^\infty r(2 - Zr/a_0)^2 e^{-Zr/a_0}\,dr \\ &= 8^{-1}(Z/a_0)^3 \int_0^\infty (4r - 4Zr^2/a_0 + Z^2r^3/a_0^2)e^{-Zr/a_0}\,dr \\ &= 8^{-1}(Z/a_0)^3(a_0/Z)^2(4 - 8 + 6) = \boxed{Z/4a_0}\end{aligned}$$

(c) For a 2p orbital, $R_{2,1}(r) = 24^{-1/2}(Z/a_0)^{3/2}(Zr/a_0)e^{-Zr/2a_0}$ and so

$$\begin{aligned}\langle r^{-1}\rangle &= \int_0^\infty r\left[24^{-1/2}(Z/a_0)^{3/2}(Zr/a_0)e^{-Zr/2a_0}\right]^2\,dr \\ &= (Z^5/24a_0^5)\int_0^\infty r^3 e^{-Zr/a_0}\,dr = (Z^5/24a_0^5) \times 3!/(Z/a_0)^4 = \boxed{Z/4a_0}\end{aligned}$$

The expectation value of $1/r$ is the same for 2s and 2p.

(d) There is no reason to assume that $\langle 1/r\rangle = 1/\langle r\rangle$. To take a specific example, in the case of a 1s orbital $\langle r\rangle = 3a_0/2Z$ and $\langle 1/r\rangle = Z/a_0$.

P8A.10 (a) The main difference between the Bohr and quantum models is that in the Bohr model the trajectory (that is the position) of the electron is precisely defined, whereas in quantum mechanics only the probability distribution of the position can be predicted.

(b) In quantum mechanics the magnitude of the orbital angular momentum of an electron with quantum number l is given by $\hbar\sqrt{l(l+1)}$. In contrast, in the Bohr model the magnitude depends on n and is $n\hbar$. In the Bohr model the ground state, with $n = 1$, has angular momentum $\hbar$, whereas in quantum mechanics the ground state (1s) has zero angular momentum. As has already been commented on, the predicted distribution of the electron is quite different in the two cases.

(c) The angular momentum of the ground state and the spatial distribution of the electron can be probed experimentally by various kinds of spectroscopy.

8B Many-electron atoms

Answers to discussion questions

D8B.2 This is covered in any introductory or general chemistry text.

D8B.4 See Section 8B.4 on page 325.

Solutions to exercises

E8B.1(b) Hydrogenic orbitals are written in the form [8A.12–*307*], $R_{n,l}(r)Y_{l,m_l}(\theta,\phi)$, where the appropriate radial function $R_{n,l}$ is selected from Table 8A.1 on page 306 and the appropriate angular function Y_{l,m_l} is selected from Table 7F.1 on page 286. Using $Z = 2$ for the 1s and $Z = 1$ for the 3s gives

$$\begin{aligned}\psi_{1s}(r) &= R_{1,0}Y_{0,0} = 2(2/a_0)^{3/2}e^{-2r/a_0} \times (4\pi)^{-1/2}\\ \psi_{3s}(r) &= R_{3,0}Y_{0,0}\\ &= (243)^{-1/2}(2/3a_0)^{3/2}[6-6(2r/3a_0)+(2r/3a_0)^2]e^{-r/3a_0} \times (4\pi)^{-1/2}\end{aligned}$$

The overall wavefunction is simply the product of the orbital wavefunctions

$$\Psi(r_1,r_2) = \psi_{1s}(r_1)\psi_{3s}(r_2)$$

E8B.2(b) For a subshell with angular momentum quantum number l there are $2l + 1$ values of m_l, each of which corresponds to a separate orbital. Each orbital can accommodate two electrons, therefore the total number of electrons is $2 \times (2l+1)$. The subshell with $l = 5$ can therefore accommodate $2(10+1) = \boxed{22}$ electrons.

E8B.3(b) All configurations have the [Kr] core. The table shows the ‘accepted’ configurations for the ground states.

Y	Zr	Nb	Mo	Tc
$5s^24d^1$	$5s^24d^2$	$5s^14d^4$	$5s^14d^5$	$5s^24d^5$
Ru	Rh	Pd	Ag	Cd
$5s^14d^7$	$5s^14d^8$	$4d^{10}$	$5s^14d^{10}$	$5s^24d^{10}$

E8B.4(b) $1s^22s^22p^6 = [\mathrm{Ar}]$

E8B.5(b) Across the period the energy of the orbitals generally decreases as a result of the increasing nuclear charge. The second ionization energy corresponds to an electron being removed from the ion M^+. For Li^+ this would involve removing an electron from the 1s orbital, which is much lower in energy (and therefore harder to ionize) than the 2s. For $\boxed{Be^+}$ it is a 2s electron which is ionized, and as this element has the lowest nuclear charge of the remaining elements in Period 2 it is expected to have the highest orbital energy and hence the lowest ionization energy.

Solutions to problems

P8B.2 The electronic configuration of the Y atom is [Kr] $4d^15s^2$ as opposed to $4d^25s^1$. This is due to the 5s orbital being much larger and diffuse than the 4d orbitals, and so the average distance between electrons is larger and so the average repulsion between electrons is much smaller. [Kr] $4d^15s^2$ is therefore the lower energy, more stable configuration.

The Ag atom has the configuration [Kr] $4d^{10}5s^1$, as opposed to [Kr] $4d^95s^2$. The number of both spin up and spin down electrons is the same in both of these configurations, but the number of parallel spin pairs within the 4d subshell is larger for the configuration [Kr] $4d^{10}5s^1$, which means this configuration is lower in energy, as a parallel spin pair is lowest in energy when between two electrons within the same subshell. Also this has fewer electrons in higher energy subshells.

P8B.4 The electronic configuration of Fe is [Ar] $3d^64s^2$, of Fe^{2+} it is [Ar] $3d^6$, and of Fe^{3+} it is [Ar] $3d^5$. Hence, the outermost electron in both ions is in a 3d orbital, with the only difference between these configurations that Fe^{2+} has one of the five 3d orbitals doubly occupied.

There is more repulsion between the 6 3d electrons in Fe^{2+} than the 5 3d electrons in Fe^{3+}, and there is no compensating increase in the atomic number to draw the electrons towards the nucleus, and so the $\boxed{Fe^{2+}}$ ion is expected to be the larger of the two ions.

8C Atomic spectra

Answers to discussion questions

D8C.2 The selection rules are given in [8C.8–*335*]. In part these can be rationalised by noting that a photon has one unit of (spin) angular momentum and that in the spectroscopic transition this angular momentum must be conserved. The selection rule for l, $\Delta l = \pm 1$, can be understood as a single electron in the atom changing angular momentum by one unit in order to accommodate the angular momentum from the photon. This selection is derived in *How is that done?* 8C.1 on page 327 by considering the relevant transition dipole moment. The selection rule for the total spin, $\Delta S = 0$, stems from the fact that the electromagnetic radiation does not affect the spin directly.

The selection rules for multi-electron atoms are harder to rationalise not least because the change in the overall angular momentum (L and J) is affected both by changes in the angular momenta of individual electrons and by the way in which these couple together.

D8C.4 This is discussed in Section 8C.2(b) on page 329.

Solutions to exercises

E8C.1(b) The spectral lines of a hydrogen atom are given by [8A.1–*304*], $\tilde{\nu} = \tilde{R}_H(n_1^{-2} - n_2^{-2})$, where $\tilde{R}_H$ is the Rydberg constant and $\tilde{\nu}$ is the wavenumber of the transition.

The Pfund series corresponds to $n_1 = 5$. The lowest energy transition, which would involve a photon with the longest wavelength, is to the next highest energy level which has $\boxed{n_2 = 6}$. Transitions to higher energy levels involve more an more energy, and the limit of this is the transition to $\boxed{n_2 = \infty}$ which involves the greatest possible energy change and hence the shortest wavelength.

E8C.2(b) he energy levels of a hydrogenic atom are $E_n = -hcZ^2\tilde{R}_{\mathrm{N}}n^{-2}$, where Z is the atomic number; for all but the most precise work it is sufficient to approximate $\tilde{R}_{\mathrm{N}}$ by $\tilde{R}_\infty$. The wavenumber of the transition between states with quantum numbers n_1 and n_2 in the Li^{2+} ion is given by a modified version of [8A.1–*304*], $\tilde{\nu} = Z^2\tilde{R}_\infty(n_1^{-2} - n_2^{-2})$. For the 5 → 4 transition and with $Z = 3$

$$\begin{aligned}
\tilde{\nu} &= 3^2 \times (1.0974 \times 10^5\ \mathrm{cm^{-1}}) \times (4^{-2} - 5^{-2}) = \boxed{2.22 \times 10^5\ \mathrm{cm^{-1}}} \\
\lambda &= \tilde{\nu}^{-1} = 1/[3^2 \times (1.0974 \times 10^5\ \mathrm{cm^{-1}}) \times (4^{-2} - 5^{-2})] \\
&= 4.49... \times 10^{-5}\ \mathrm{cm} = \boxed{450\ \mathrm{nm}} \\
\nu &= c/\lambda = (2.9979 \times 10^8\ \mathrm{m\,s^{-1}})/(4.49... \times 10^{-7}\ \mathrm{m}) = \boxed{666\ \mathrm{THz}}
\end{aligned}$$

E8C.3(b) The selection rules for a many-electron atom are given in [8C.8–*335*]. For a single electron these reduce to $\Delta l = \pm 1$; there is no restriction on changes in n.

(i) 5d $(n = 5, l = 2) \rightarrow$ 2s $(n = 2, l = 0)$ has $\Delta l = -2$, and so is $\boxed{\text{forbidden}}$.

(ii) 5p $(n = 5, l = 1) \rightarrow$ 3s $(n = 1, l = 0)$ has $\Delta l = -1$, and so is $\boxed{\text{allowed}}$.

(iii) 6p $(n = 3, l = 1) \rightarrow$ 4f $(n = 2, l = 3)$ has $\Delta l = +2$, and so is $\boxed{\text{forbidden}}$.

E8C.4(b) The single electron in a f orbital has $l = 3$ and hence $L = 3$, and $s = \frac{1}{2}$ hence $S = \frac{1}{2}$. The spin multiplicity is $2S + 1 = 2$. Using the Clebsh–Gordon series, [8C.5–*332*], the possible values of J are $J = L + S,\ L + S - 1,\ \ldots |L - S| = \frac{7}{2}, \frac{5}{2}$. Hence, the term symbols for the levels are $\boxed{{}^2\mathrm{F}_{7/2},\ {}^2\mathrm{F}_{5/2}}$.

E8C.5(b) For a p electron $l = 1$ and $s = \frac{1}{2}$. Using the Clebsh–Gordon series, [8C.5–*332*], the possible values of j are $l + s,\ l + s - 1,\ \ldots |l - s|$, which in this case are $\boxed{j = \frac{3}{2}, \frac{1}{2}}$.

For an h electron $l = 5$ and $s = \frac{1}{2}$ hence $\boxed{j = \frac{11}{2}, \frac{9}{2}}$.

E8C.6(b) The Clebsch–Gordan series [8C.5–*332*] gives the possible values of J as $J = j_1 + j_2,\ j_1 + j_2 - 1,\ \ldots |j_1 - j_2|$. With $j_1 = 5, j_2 = 3$, the possible values of J are $\boxed{J = 8, 7, 6, 5, 4, 3, 2}$.

E8C.7(b) The symbol F implies that the total orbital angular momentum $\boxed{L = 3}$, the superscript 3 implies that the multiplicity $2S + 1 = 3$, so that the total spin angular momentum $\boxed{S = 1}$. The subscript 4 implies that the total angular momentum $\boxed{J = 4}$.

E8C.8(b) The Clebsch–Gordan series, [8C.5–*332*], is used to combine two spin angular momenta s_1 and s_2 to give $S = s_1 + s_2,\ s_1 + s_2 - 1\ ...,\ |s_1 - s_2|$.

(i) Four electrons are treated by first combing the angular momenta of two electrons, then combining the result with the spin of the third electron, and then with the spin of the fourth. For two electrons, each with $s = \frac{1}{2}$, $S' = 1,\ 0$. Combining $S' = 1$ with $s_3 = \frac{1}{2}$ for the third spin gives $S'' = 1 + \frac{1}{2},\ |1 - \frac{1}{2}| = \frac{3}{2},\ \frac{1}{2}$. Combining $S' = 0$ with $s_3 = \frac{1}{2}$ just gives $S'' = \frac{1}{2}$. The process is continued with the fourth electron: $S'' = \frac{3}{2}$ with $s_4 = \frac{1}{2}$ gives $S = 2,\ 1$; $S'' = \frac{1}{2}$ with $s_4 = \frac{1}{2}$ gives $S = 1,\ 0$. In summary the possible values for the total spin are $\boxed{S = 2,\ 1,\ 0}$, with multiplicities $\boxed{5, 3, 0}$.

(ii) For five electrons the values of S from (i) are combined with a further spin $s_5 = \frac{1}{2}$. For $S = 2$ the result is $\frac{5}{2},\ \frac{3}{2}$; $S = 1$ gives $\frac{3}{2},\ \frac{1}{2}$; and $S = 0$ gives just $\frac{1}{2}$. The possible values for the total spin for five electrons are are $\boxed{S = \frac{5}{2},\ \frac{3}{2},\ \frac{1}{2}}$, with multiplicities $\boxed{6, 4, 2}$.

E8C.9(b) The valence electron configuration of the V^{2+} is [Ar] $3d^3$. With 3 electrons occupying the 5 d orbitals the Pauli principle places no restrictions on the number of parallel spins because the 3 electrons can occupy separate orbitals. The procedure used in *Exercise* E8C.8(b) part (i) can therefore be followed, giving the possible values of S for 3 electrons as $\boxed{S = \frac{3}{2},\ \frac{1}{2}}$. The quantum number M_S, which specifies the z-component of the spin angular momentum, takes values $S,\ (S-1)\ \ldots\ -S$. Therefore for $S = \frac{3}{2}$, $\boxed{M_S = \pm\frac{3}{2},\ \pm\frac{1}{2}}$ and for $S = \frac{1}{2}$, $\boxed{M_S = \pm\frac{1}{2}}$.

E8C.10(b) These electrons are not equivalent, as they are in different subshells, hence all the terms that arise from the vector model and the Clebsch–Gordan series are allowed. The orbital angular momentum of the p and d electrons are $l_1 = 1$ and $l_2 = 2$ respectively, and these are combined using $L = l_1 + l_2,\ l_1 + l_2 - 1,\ ...\ |l_1 - l_2|$ which in this case gives $L = 3,\ 2,\ 1$. The spin angular momenta of each electron is $s_1 = s_2 = \frac{1}{2}$, and these combine in the same way to give $S = 1,\ 0$; these values of S have spin multiplicities of $2S + 1 = 3,\ 1$. The terms which arise are therefore ${}^3F$, ${}^1F$, ${}^3D$, ${}^1D$, ${}^3P$, and ${}^1P$.

The possible values of J are given by $J = L + S,\ L + S - 1,\ ...,\ |L - S|$, and hence for $S = 1$, $L = 3$ the values of J are 4, 3, and 2. For $S = 1$, $L = 2$ the values of J are 3, 2, and 1. For $S = 1$, $L = 1$ the values of J are 2, 1, and 0. For $S = 0$ and any value of L only $J = L$ is possible. The term symbols are therefore $\boxed{{}^3F_4,\ {}^3F_3,\ {}^3F_2,\ {}^3D_3,\ {}^3D_2,\ {}^3D_1,\ {}^3P_2,\ {}^3P_1 \text{ and } {}^3P_0}$, and $\boxed{{}^1F_3,\ {}^1D_2, \text{ and } {}^1P_1}$.

From Hund's rules, described in Section 8C.2(d) on page 335, the lowest energy state is the one with the greatest spin, then the greatest orbital angular momentum and then, because the shell is less than half full, the smallest J. This is $\boxed{{}^3F_2}$.

E8C.11(b) (i) ${}^3D$ has $L = 2$, $S = 1$ and so $\boxed{J = 3,\ 2,\ 1}$ only. There are $2J + 1$ values of M_J, which for these three values of J gives $\boxed{7,\ 5,\ 3}$ states, respectively. (ii) ${}^4D$ has $L = 2$, $S = \frac{3}{2}$, and so $\boxed{J = \frac{7}{2},\ \frac{5}{2},\ \frac{3}{2},\ \frac{1}{2}}$ with $\boxed{8,\ 6,\ 4,\ 2}$ states, respectively. (ii) ${}^2G$ has $L = 4$, $S = \frac{1}{2}$, and so $\boxed{J = \frac{9}{2},\ \frac{7}{2}}$ with $\boxed{10,\ 8}$ states, respectively.

E8C.12(b) Closed shells have total spin and orbital angular momenta of zero, and so do not contribute to the overall values of S and L. (i) $3d^{10}4s^2$ is a closed shell configuration with $L = 0$, $S = 0$, and $J = 0$. The term symbol is $\boxed{^1S_0}$.

(ii) For the configuration $3d^{10}4s^24p^5$ only the p electrons need be considered as the others are in a closed shell. Because of the spin pairing required by the Pauli principle the configuration p^5 has the same terms as p^1: this is often expressed by saying that p^5 is the 'absence' of one electron or a 'hole'. Holes behave just like electrons when it comes to formulating term symbols. Therefore, one 'hole' in a p sub-shell has $l = 1$ and $s = \frac{1}{2}$, so $L = 1$, $S = \frac{1}{2}$, and $J = \frac{3}{2}, \frac{1}{2}$. The term symbols are therefore $\boxed{^2P_{3/2}}$ and $\boxed{^2P_{1/2}}$.

E8C.13(b) The two terms arising from an f^1 configuration are $^2F_{7/2}$, $^2F_{5/2}$, which have $S = \frac{1}{2}, L = 3$ and $J = \frac{7}{2}, \frac{5}{2}$. The energy shift due to spin-orbit coupling is given by [8C.4–*331*], $E_{L,S,J} = \frac{1}{2}hc\tilde{A}[J(J+1) - L(L+1) - S(S+1)]$, where $\tilde{A}$ is the spin-orbit coupling constant. Hence, $E_{3,1/2,7/2} = \boxed{+(3/2)hc\tilde{A}}$, and $E_{3,1/2,5/2} = \boxed{-2hc\tilde{A}}$.

E8C.14(b) The selection rules for a many-electron atom are given in [8C.8–*335*].

(i) $^2P_{3/2}$ $(S = \frac{1}{2}, L = 1, J = \frac{3}{2}) \rightarrow {}^2S_{1/2}$ $(S = \frac{1}{2}, L = 0, J = \frac{1}{2})$ has $\Delta S = 0$, $\Delta L = -1$, $\Delta J = -1$ and so is $\boxed{\text{allowed}}$.

(ii) $^3P_0$ $(S = 1, L = 1, J = 0) \rightarrow {}^3S_1$ $(S = 1, L = 0, J = 1)$ has $\Delta S = 0$, $\Delta L = -1$, $\Delta J = +1$ and so is $\boxed{\text{allowed}}$.

(iii) $^3D_3$ $(S = 1, L = 2, J = 3) \rightarrow {}^1P_1$ $(S = 0, L = 1, J = 1)$ has $\Delta S = -1$, $\Delta L = -1$, $\Delta J = -2$ and so is $\boxed{\text{forbidden}}$ by the S and J selection rules.

Solutions to problems

P8C.2 The wavenumbers of the spectral lines of the H atom for the $n_2 \rightarrow n_1$ transition is given by [8A.1–*304*], $\tilde{\nu} = \tilde{R}_H(n_1^{-2} - n_2^{-2})$, where $\tilde{R}_H$ is the Rydberg constant for Hydrogen, $\tilde{R}_H = 109677\ \text{cm}^{-1}$. Hence, the wavelength of this transition is $\lambda = \tilde{\nu}^{-1} = \tilde{R}_H^{-1}(n_1^{-2} - n_2^{-2})^{-1}$.

The lowest energy, and therefore the longest wavelength transition (the one at $\lambda_{\max} = 656.46\ \text{nm} = 6.5646 \times 10^{-5}\ \text{cm}$) is assumed to correspond to the transition from $n_1 + 1 \rightarrow n_1$

$$\frac{1}{\lambda_{\max}\tilde{R}_H} = \frac{1}{n_1^2} - \frac{1}{(n_1+1)^2} = \frac{(n_1+1)^2 - n_1^2}{n_1^2(n_1+1)^2} = \frac{2n_1+1}{n_1^2(n_1+1)^2}$$

From the given data $(\lambda_{\max}\tilde{R}_H)^{-1} = [(6.5646 \times 10^{-5}\ \text{cm}) \times (109677\ \text{cm}^{-1})]^{-1} = (7.19...)^{-1}$. The value of n_1 is found by seeking an integer value of n_1 for which $n_1^2(n_1+1)^2/(2n_1+1) = 7.19....$ For $n_1 = 2$ the fraction on the left is $4^2 \times 9^2/5 = 7.2$. Therefore, the series is that with $\boxed{n_1 = 2}$.

Therefore the wavelengths of the transitions are given by $\lambda^{-1} = (109677\,\text{cm}^{-1}) \times (2^{-2} - n_2^{-2})$, and $n_2 = 3, 4, 5, 6$; the next line has $n_2 = 7$, and so has a wavelength of

$$\lambda = \left[(109677\,\text{cm}^{-1}) \times (2^{-2} - 7^{-2})\right]^{-1} = 3.97... \times 10^{-5}\,\text{cm} = \boxed{397.13\,\text{nm}}$$

The ionization energy of the atom when it is in the lower state of quoted transitions is the energy to remove electron from the $n = 2$ state, which is the energy for the transition $\infty \rightarrow 2$

$$\begin{aligned} I &= hc\tilde{R}_{\text{H}}(2^{-2} - \infty^{-2}) = \tfrac{1}{4}hc\tilde{R}_{\text{H}} \\ &= \tfrac{1}{4} \times (6.6261 \times 10^{-34}\,\text{J s}) \times (2.9979 \times 10^{10}\,\text{cm s}^{-1}) \times (109677\,\text{cm}^{-1}) \\ &= \boxed{5.4466 \times 10^{-19}\,\text{J}} \text{ or } 3.3995\,\text{eV} \end{aligned}$$

P8C.4 The wavenumbers of transitions between energy levels in hydrogenic atoms are given by a modified version of [8A.1–*304*], $\tilde{\nu} = Z^2\tilde{R}_{\text{Li}}\left(n_1^{-2} - n_2^{-2}\right)$ where Z is the nuclear charge, for $\text{Li}^{2=}$ $Z = 3$, and $\tilde{R}_{\text{N}}$ is the Rydberg constant for Li. The Lyman series all have $n_1 = 1$ so the wavenumber of the transitions are given by

$$\tilde{\nu}_{n_2} = 9\tilde{R}_{\text{Li}}\left(1 - n_2^{-2}\right)$$

If the three lines given correspond to $n_2 = 2, 3, 4$, then using this value for n_2 the fraction $\tilde{\nu}_{n_2}/9(1 - n_2^{-2})$ should be constant, and equal to $\tilde{R}_{\text{Li}}$. This is explored in the following table

n_2	2	3	4
$\tilde{\nu}_{n_2}/\,\text{cm}^{-1}$	740 747	877 924	925 933
$\tilde{\nu}_{n_2}/[9(1 - n_2^{-2})]/\,\text{cm}^{-1}$	109 740	109 741	109 740

The ratio is indeed constant, confirming that the correct value of n_2 has been chosen; the average value of $\tilde{R}_{\text{Li}}$ is $\boxed{109\,740\,\text{cm}^{-1}}$.

The Balmer series all have $n_1 = 2$ so the wavenumber of the transitions are given by

$$\tilde{\nu}_{n_2} = 9\tilde{R}_{\text{Li}}\left(\tfrac{1}{4} - n_2^{-2}\right)$$

The longest wavelength transition has $n_2 = 3$

$$\tilde{\nu}_3 = 9(109\,740\,\text{cm}^{-1})\left(\tfrac{1}{4} - 3^{-2}\right) = \boxed{137\,175\,\text{cm}^{-1}}$$

The next longest has $n_2 = 4$ and a similar calculation gives $\boxed{\tilde{\nu}_4 = 185\,186\,\text{cm}^{-1}}$.

The energy needed to ionize an electron from the ground state, with $n = 1$, is simply minus the energy of this state, which is $9(109\,740\,\text{cm}^{-1}) = 987\,660\,\text{cm}^{-1}$ or $\boxed{122.45\,\text{eV}}$.

P8C.6 The 7p configuration has just one electron outside a closed subshell. That electron has $l = 1, s = 1/2$, and $j = 1/2$ or $3/2$, so the atom has $L = 1, S = 1/2$, and $J = 3/2$ or $1/2$. The term symbols are ${}^{2}2\mathrm{P}_{1/2}$ and ${}^{2}\mathrm{P}_{3/2}$ of which the former has the lower energy. The 6d configuration also has just one electron outside a closed subshell; that electron has $l = 2, s = 1/2$, and $j = 3/2$ or $5/2$, so the atom has $L = 2, S = 1/2$, and $J = 5/2$ or $3/2$. The term symbols are ${}^{2}\mathrm{D}_{5/2}$ and ${}^{2}\mathrm{D}_{3/2}$ of which the former has the lower energy.

The spin-orbit coupling energy can be estimated using [8C.4–*331*], but this gives the energy of ${}^{2}\mathrm{P}_{1/2}$ relative to ${}^{2}\mathrm{P}_{3/2}$, or ${}^{2}\mathrm{D}_{5/2}$ relative to ${}^{2}\mathrm{D}_{3/2}$. The expression cannot be used to compare the energy of ${}^{2}\mathrm{D}$ and ${}^{2}\mathrm{P}$.

P8C.8 The energy levels of a hydrogenic atom are given by [8A.13–*308*], $E_n = -hc\tilde{R}_\mathrm{N}/n^2$, where $\tilde{R}_\mathrm{N}$ is the Rydberg constant for the nucleus in question which in turn is proportional to the reduced mass of the nucleus–electron system [8A.14–*308*], $\mu_\mathrm{N} = m_\mathrm{N}m_\mathrm{e}/(m_\mathrm{N} + m_\mathrm{e})$. The ratio of the wavenumbers of the same transition in two hydrogenic atoms with the same nuclear charge is proportional to the ratio of the Rydberg constants, and hence to the ratio of the reduced masses

$$\frac{\tilde{\nu}_\mathrm{D}}{\tilde{\nu}_\mathrm{H}} = \frac{\tilde{R}_\mathrm{D}}{\tilde{R}_\mathrm{H}} = \frac{\mu_\mathrm{D}}{\mu_\mathrm{H}} = \frac{m_\mathrm{D}m_\mathrm{e}/(m_\mathrm{D} + m_\mathrm{e})}{m_\mathrm{H}m_\mathrm{e}/(m_\mathrm{H} + m_\mathrm{e})} = \frac{m_\mathrm{D}(m_\mathrm{H} + m_\mathrm{e})}{m_\mathrm{H}(m_\mathrm{D} + m_\mathrm{e})}$$

This expression is rearranged to give

$$m_\mathrm{D} = \frac{(\tilde{\nu}_\mathrm{D}/\tilde{\nu}_\mathrm{H})m_\mathrm{H}m_\mathrm{e}}{m_\mathrm{e} + m_\mathrm{H}[1 - (\tilde{\nu}_\mathrm{D}/\tilde{\nu}_\mathrm{H})]}$$

Given the high precision of the data, it is necessary to use an equivalent high precision for the fundamental constants (taken from the inside of the front cover of the text) and to use the mass of the H nucleus as $1.007\,825\ m_\mathrm{u}$. Using such data it is found that $\boxed{m_\mathrm{D} = 3.345\,19 \times 10^{-27}\ \mathrm{kg}}$ or $\boxed{2.014\,52\ m_\mathrm{u}}$.

The ionization energy is simply $hc\tilde{R}_\mathrm{N}$ and because the wavenumbers of the transitions are proportional to the relevant value of $\tilde{R}_\mathrm{N}$ it follows that

$$\frac{I_\mathrm{H}}{I_\mathrm{D}} = \frac{\tilde{R}_\mathrm{H}}{\tilde{R}_\mathrm{D}} = \frac{\tilde{\nu}_\mathrm{H}}{\tilde{\nu}_\mathrm{D}} = \frac{82\,259.098\ \mathrm{cm}^{-1}}{82\,281.476\ \mathrm{cm}^{-1}} = \boxed{0.999\,728}$$

P8C.10 (a) The separation of the lines observed in the spectrum when a magnetic field is applied is a direct reflection of the energy splitting of the energy levels. Therefore, the separation of the lines $\delta\tilde{\nu}$, expressed as a wavenumber, is $hc\delta\tilde{\nu} = \mu_\mathrm{B}\mathcal{B}$.

$$\delta\tilde{\nu} = \frac{\mu_\mathrm{B}\mathcal{B}}{hc} = \frac{(9.274 \times 10^{-24}\,\mathrm{J\,T^{-1}}) \times (2\ \mathrm{T})}{(6.6261 \times 10^{-34}\,\mathrm{J\,s}) \times (2.9979 \times 10^{10}\ \mathrm{cm\,s^{-1}})} = \boxed{0.94\ \mathrm{cm}^{-1}}$$

(b) The first line in the Balmer series ($n = 2 \rightarrow 3$) has wavenumber

$$\tilde{\nu}_{2,3} = \tilde{R}_\mathrm{H}(1/2^2 - 1/3^2) = 15\,233\ \mathrm{cm}^{-1}$$

Therefore the normal Zeeman splitting is $\boxed{\text{very small}}$ compared to the difference in the energy of the states involved in typical transitions.

P8C.12 For a 'red star', with a surface temperature in the range 3 000 K to 4 000 K, the thermal energy is insufficient to cause the excitation of the electron in hydrogen from its ground state: no emission spectra from hydrogen is therefore seen. In contrast, for a 'blue star', with a surface temperature in the range 15 000 K to 20 000 K, the thermal energy is sufficient to cause ionization of the electron. Therefore, neither absorption not emission from hydrogen is seen simply because there are no hydrogen atoms present – they have all been ionized. If the with a surface temperature is in the range 8 000 K to 10 000 K the thermal energy is sufficient to cause excitation of hydrogen atoms, but not sufficient to cause extensive ionization. Intense hydrogen emission lines are seen from such stars.

This explanation can be explored in a more quantitative way be examining how the frequency spectrum of black body radiation changes with temperature, and examining what part of the radiation is at high enough frequencies to cause excitation or ionization. The Planck distribution is given by [11A.5–*420*], $\rho(\nu) = 8\pi h\nu^3 c^{-3}(e^{h\nu/kT} - 1)^{-1}$, and in Fig. 8.1 this is plotted against $h\nu/I$, where I is the ionization energy of hydrogen, for three different temperatures. At 25000 K a significant fraction of the radiation is at frequencies above that needed to ionize hydrogen ($h\nu/I > 1$).

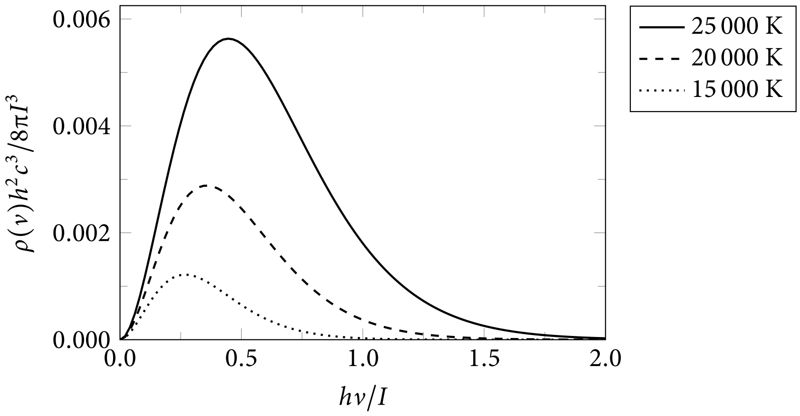


Figure 8.1

Answers to integrated activities

I8.2 (a) The energy levels of a Hydrogen atom (with $Z = 1$) are given by [8A.13–*308*], $E_n = -hc\tilde{R}_H n^{-2}$, where $\tilde{R}_H = 109\,677\ \text{cm}^{-1}$ is the Rydberg constant for the Hydrogen atom. Hence, the separation between between the energy levels n and $n + 1$ is

$$\Delta E = E_{n+1} - E_n = hc\tilde{R}_H\left(\frac{1}{n^2} - \frac{1}{(n+1)^2}\right) = hc\tilde{R}_H\frac{(n+1)^2 - n^2}{n^2(n+1)^2}$$
$$= hc\tilde{R}_H(2n+1)/[n^2(n+1)^2] \approx 2hc\tilde{R}_H/n^3$$

where the approximation is for $n \gg 1$ so that $(2n+1) \approx 2n$ and $(n+1)^2 \approx n^2$

(b) For $n = 100$, this becomes

$$\begin{aligned}\Delta E &= 2hc\tilde{R}_{\mathrm{H}}/100^3\\ &= 2 \times (6.6261 \times 10^{-34}\,\mathrm{J\,s}) \times (2.9979 \times 10^{10}\,\mathrm{cm\,s^{-1}}) \times (109\,677\,\mathrm{cm^{-1}})/100^3\\ &= \boxed{4.357 \times 10^{-24}\,\mathrm{J}}\end{aligned}$$

The average radius of a H 100s orbital ($Z = 1, n = 100, l = 0$) is given by the expression in *Integrated activity* I8.1

$$\langle r \rangle_{100,0,0} = \frac{(100)^2 a_0}{1}\left[1 + \tfrac{1}{2}\left(1 - \frac{0(0+1)}{100^2}\right)\right] = \boxed{15\,000\ a_0}$$

The ionization energy for an electron in the state with $n = 100$ is simply minus the orbital energy

$$\begin{aligned}I &= hc\tilde{R}_{\mathrm{H}}/100^2\\ &= (6.6261 \times 10^{-34}\,\mathrm{J\,s}) \times (2.9979 \times 10^{10}\,\mathrm{cm\,s^{-1}}) \times (109677\,\mathrm{cm^{-1}})/100^2\\ &= \boxed{2.179 \times 10^{-22}\,\mathrm{J}}\end{aligned}$$

(c) The energy available in a collision is of the order of $\frac{1}{2}kT$ (from the equipartition principle), which at 298 K is $\frac{1}{2} \times (1.3806 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K}) = 2.06 \times 10^{-21}\,\mathrm{J}$. This is well in excess of the ionization energy, so a collision could easily result in ionization.

(d) The minimum velocity required for ionization will be when the kinetic energy of the H atom, $E_{\mathrm{k}} = \frac{1}{2}mv^2$ is equal to the ionization energy I; hence $v = (2I/m)^{1/2}$

$$\begin{aligned}v &= (2I/m)^{1/2} = [2 \times (2.179 \times 10^{-22}\,\mathrm{J})/(1.0078 \times 1.6605 \times 10^{-27}\,\mathrm{kg})]^{1/2}\\ &= \boxed{510\,\mathrm{m\,s^{-1}}}\end{aligned}$$

where the mass of H is taken as $1.0078\ m_{\mathrm{u}}$.

(e) The radial wavefunction for a 100s orbital will have a finite value at the nucleus and 99 radial nodes. The exponentially decaying part of the wavefunction, which dominates for sufficiently large distances, is of the form $\mathrm{e}^{-r/100a_0}$.

9

Molecular Structure

9A Valence-bond theory

Answers to discussion questions

D9A.2 Promotion and hybridization are two modifications to the simplest version of valence-bond (VB) theory, adopted to overcome obvious mismatches between predictions of that theory and observations. In its simplest form VB theory assumes that the functions ψ_A and ψ_B that appear in a VB wavefunction, [9A.2–*344*], are orbitals in free atoms occupied by unpaired electrons. For example, such a theory would predict that carbon, with the electronic configuration $2s^2 2p^2$, would form two bonds on account if it having two unpaired electrons. This prediction is at odds with the characteristic valency of four shown by carbon.

To account for the tetravalence of carbon it is supposed that one of the 2s electrons is excited ('promoted') to the empty 2p orbital, giving a configuration of $2s^1 2p^3$. There are now four unpaired electrons (in the 2s and 2p orbitals) available for forming four valence bonds.

Hybrid orbitals are invoked to account for the fact that valence bonds formed from atomic orbitals would have different orientations in space 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 formed by combining the atomic orbitals in such a way that the hybrid orbitals have the required directional properties.

D9A.4 The part of the VB wavefunction that depends on spatial coordinates is given in [9A.2–*344*], $\Psi(1,2)_{\text{space}} = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)$. The complete wavefunction includes a spin part, $\sigma(1,2)$

$$\Psi(1,2) = \{\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)\}\,\sigma(1,2)$$

The Pauli principle requires that the wavefunction must be antisymmetric, that is it must change sign, upon interchange of particle labels: $\Psi(2,1) = -\Psi(1,2)$. The spatial part is symmetric under this interchange of labels $\Psi(2,1)_{\text{space}} = +\Psi(1,2)_{\text{space}}$, therefore the spin part must be antisymmetric $\sigma(2,1) = -\sigma(1,2)$. The antisymmetric spin wavefunction for two spins is the one in which the spins are paired

$$\sigma(2,1) = (1/2)^{1/2}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$$

In summary, the form of the VB wavefunction which results in a the lowering of the energy, and hence bond formation, is symmetric with respect to interchange of the electron labels, and in order to satisfy the Pauli principle the associated spin wavefunction must be anti-symmetric with respect to this exchange. This wavefunction corresponds to one in which the spins are paired.

Solutions to exercises

E9A.1(b) The nitrogen atoms in N_2 are sp hybridized. The σ bond is formed by the overlap of two sp hybrid atomic orbitals oriented towards each other along the internuclear axis. Using [9A.2–*344*], the spatial part of the valence-bond wavefunction of the σ orbital is written $\Psi(1,2) = \psi_{\mathrm{Nsp_A}}(1)\psi_{\mathrm{Nsp_B}}(2) + \psi_{\mathrm{Nsp_A}}(2)\psi_{\mathrm{Nsp_B}}(1)$. This wavefunction is symmetric, therefore it has to be combined with the anti-symmetric two-electron spin wavefunction given by [8B.3–*319*], $\sigma_-(1,2)$. The resulting complete, asymmetric two-electron wavefunction satisfies the Pauli principle and has the form of

$$\Psi_\sigma(1,2) = [\psi_{\mathrm{Nsp_A}}(1)\psi_{\mathrm{Nsp_B}}(2) + \psi_{\mathrm{Nsp_A}}(2)\psi_{\mathrm{Nsp_B}}(1)] \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

The two π orbitals are formed by the side-by-side overlap of two p_x and two p_y orbitals. Following the same logic as above, the valence-bond wavefunction for the $2p_y\pi$ orbital is written as

$$\Psi_\pi(1,2) = [\psi_{\mathrm{Np}_{y_\mathrm{A}}}(1)\psi_{\mathrm{Np}_{y_\mathrm{B}}}(2) + \psi_{\mathrm{Np}_{y_\mathrm{A}}}(2)\psi_{\mathrm{Np}_{y_\mathrm{B}}}(1)] \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

and similarly for the $2p_x\pi$ orbital.

E9A.2(b) The resonance hybrid wavefunction constructed from one two-electron wavefunction corresponding to the purely covalent form of the bond and one two-electron wavefunction corresponding to the ionic form of the bond is given in [9A.3–*346*] as $\Psi = \Psi_{\mathrm{covalent}} + \lambda\Psi_{\mathrm{ionic}}$. Therefore the (unnormalized) resonance hybrid wavefunction of N_2 with two ionic structures is written as $\Psi_{\mathrm{N_2}} = \Psi_{\mathrm{N-N}} + \lambda\Psi_{\mathrm{N^+N^-}} + \kappa\Psi_{\mathrm{N^{2-}N^{2+}}}$.

The valence bond description of the triple bond in N_2 is give in *Example* E9A.1(b). Omitting the spin functions for simplicity, the spatial wavefunction is a product of that for the σ bond, and that for each of the π bonds

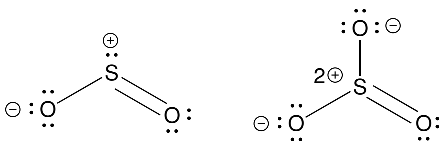
$$\begin{aligned}&[\psi_{\mathrm{Nsp_A}}(1)\psi_{\mathrm{Nsp_B}}(2) + \psi_{\mathrm{Nsp_A}}(2)\psi_{\mathrm{Nsp_B}}(1)]\\ &\quad\times[\psi_{\mathrm{Np}_{y_\mathrm{A}}}(3)\psi_{\mathrm{Np}_{y_\mathrm{B}}}(4) + \psi_{\mathrm{Np}_{y_\mathrm{A}}}(4)\psi_{\mathrm{Np}_{y_\mathrm{B}}}(3)]\\ &\quad\times[\psi_{\mathrm{Np}_{x_\mathrm{A}}}(5)\psi_{\mathrm{Np}_{x_\mathrm{B}}}(6) + \psi_{\mathrm{Np}_{x_\mathrm{A}}}(6)\psi_{\mathrm{Np}_{x_\mathrm{B}}}(5)]\end{aligned}$$

Somewhat arbitrarily electrons 1 and 2 have been assigned to the first valence-bond wavefunction, 3 and 4 to the next and so on.

The ionic structure N^+N^- can be thought of as arising when electrons 5 and 6 are both located in $\mathrm{Np}_{x_\mathrm{B}}$. In this case, the part of the wavefunction in the third bracket becomes $[\psi_{\mathrm{Np}_{x\mathrm{B}}}(5)\psi_{\mathrm{Np}_{x\mathrm{B}}}(6)]$. This is just one possibility: ionic structures also arise when electrons 3 and 4 are on the same atom (leading to a modification of the second bracket), or 1 and 2 are on the same atom (leading to a modification of the first bracket).

The ionic structure $\mathrm{N}^{2-}\mathrm{N}^{2+}$ can be thought of as arising when electrons 5 and 6 are both located in $\mathrm{Np}_{x_\mathrm{A}}$, and electrons 3 and 4 are both located in $\mathrm{Np}_{y_\mathrm{A}}$. In this case, the third bracket becomes $[\psi_{\mathrm{Np}_{x_\mathrm{A}}}(5)\psi_{\mathrm{Np}_{x_\mathrm{A}}}(6)]$ and the second bracket becomes $[\psi_{\mathrm{Np}_{y_\mathrm{A}}}(3)\psi_{\mathrm{Np}_{y_\mathrm{A}}}(4)]$. Similar wavefunctions for $\mathrm{N}^{2-}\mathrm{N}^{2+}$ can be written by rearranging any two of the valence electrons.

E9A.3(b) A good starting point is to construct Lewis structures in which bonded pairs of electrons are identified by a line and lone pairs by the usual double dot; the charges are formal.



A VB wavefunction is written for each bonded pair. It is convenient to assume that sulfur and oxygen atoms are sp^2 hybridized. Each of the S–O σ bonds is formed by the overlap of one sp^2 hybrid on sulfur and one sp^2 hybrid on an oxygen atom projecting towards each other. There is also a π bond formed between the unhybridized 3p atomic orbital on sulfur and an unhybridized 2p atomic orbitals on the oxygen. This π bond is involved in resonance, as it can be between the sulfur and any of the oxygen atoms. The lone pairs on the oxygen atoms are either accommodated in sp^2 orbitals or in an out-of-plane 2p orbitals if the latter is not involved in a π bond. The lone pair on the sulfur atom in $\mathrm{SO_2}$ resides in an sp^2 hybrid atomic orbital.

E9A.4(b) The ground state electronic configuration of phosphorus is $[\mathrm{Ne}]3\mathrm{s}^2 3\mathrm{p}_x^1 3\mathrm{p}_y^1 3\mathrm{p}_z^1$. In the ground state it has three unpaired electrons on the three different 3p orbitals, therefore it is able to form three covalent bonds. Promotion of an electron from 3s orbital to 3d results in the configuration $[\mathrm{Ne}]3\mathrm{s}^1 3\mathrm{p}_x^1 3\mathrm{p}_y^1 3\mathrm{p}_z^1 3\mathrm{d}^1$. These orbitals can then be used to form five hybrids, each of which can form a bond.

E9A.5(b) Carbon atoms C1–C4 in 1,3-pentadiene are sp^2 hybridized, whereas carbon atom C5 is sp^3 hybridized. The σ framework of the molecule consists of C–H and C–C σ bonds. The C–H σ bonds are formed by the overlap of sp^2 or sp^3 hybrid atomic orbitals on the carbon atoms with the 1s atomic orbitals on the corresponding hydrogen atoms. Similarly, the C–C σ bonds are formed by the overlap of sp^2 or sp^3 hybrid atomic orbitals on neighbouring carbon atoms. The two π bonds are formed by the side-by-side overlap of unhybridized 2p orbitals on carbon atoms C1 and C2, and likewise between C3 and C4.

E9A.6(b) The carbon and nitrogen atoms in pyridine are sp^2 hybridized. The C–N and C–C σ bonds are formed by the overlap of sp^2 hybrid atomic orbitals on neighbouring carbon or nitrogen atoms with each other. The C–H σ bonds are formed by the overlap of a carbon sp^2 hybrid atomic orbital with a hydrogen 1s atomic orbitals. Formally there are three π bonds in pyridine. Each of them is a result of the overlap of a pair of unhybridized 2p atomic orbitals on the nitrogen or the carbon atoms. There is a lone pair on nitrogen residing in an sp^2 hybrid atomic orbital.

E9A.7(b) The condition of orthogonality is given by [7C.8–*254*], $\int \Psi_i^* \Psi_j \, d\tau = 0$ for $i \neq j$. The atomic orbitals are all real, therefore $\Psi_i^* = \Psi_i$. The orthogonality condition becomes

$$\begin{aligned}\int h_1^* h_2 \, d\tau &= \int [(\sin\zeta)s + (\cos\zeta)p] \times [(\cos\zeta)s - (\sin\zeta)p] \, d\tau \\ &= \sin\zeta\cos\zeta \overbrace{\int s^2 \, d\tau}^{1} - \sin^2\zeta \overbrace{\int sp \, d\tau}^{0} + \cos^2\zeta \overbrace{\int ps \, d\tau}^{0} \\ &\quad - \cos\zeta\sin\zeta \overbrace{\int p^2 \, d\tau}^{1} = \sin\zeta\cos\zeta - \cos\zeta\sin\zeta = 0\end{aligned}$$

All the integrals of the form $\int sp \, d\tau$ are zero because the s and p orbitals are orthogonal, and all the integrals of the form $\int s^2 \, d\tau$ and $\int p^2 \, d\tau$ are 1 because the orbitals are normalized. The condition for the orthogonality of h_1 and h_2 is satisfied.

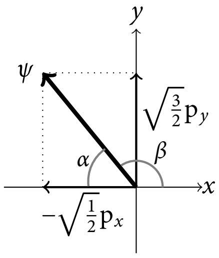
E9A.8(b) A normalized wavefunction satisfies [7B.4c–*248*], $\int \psi^* \psi \, d\tau = 1$. The wavefunction is normalized by finding the values of N_1 and N_2 for which $h_1 = N_1[(\sin\zeta)s + (\cos\zeta)p]$ and $h_2 = N_2[(\cos\zeta)s - (\sin\zeta)p]$ satisfy this condition. The orbital wavefunctions s and p are real, as are N_1 and N_2, therefore, for h_1

$$\begin{aligned}\int h_1^* h_1 \, d\tau &= N_1^2 \int [(\sin\zeta)s + (\cos\zeta)p]^2 \, d\tau \\ &= N_1^2 \left[\sin^2\zeta \overbrace{\int s^2 \, d\tau}^{1} + \cos^2\zeta \overbrace{\int p^2 \, d\tau}^{1} + 2\sin\zeta\cos\zeta \overbrace{\int sp \, d\tau}^{0} \right] \\ &= N_1^2[\sin^2\zeta + \cos^2\zeta] = N_1^2\end{aligned}$$

The integral $\int sp \, d\tau$ is zero because the s and p orbitals are orthogonal. The integrals $\int s^2 \, d\tau$ and $\int p^2 \, d\tau$ are 1 because the s and p orbitals are normalized. The identity $\sin^2\theta + \cos^2\theta = 1$ is used in the last step. The normalization condition is $N_1^2 = 1$, therefore $N_1 = 1$. A similar calculation shows that $N_2 = 1$ also.

Solutions to problems

P9A.2 For the purposes of this problem, the p_x orbital has the same properties as a unit vector along the x-axis and the p_y orbital is likewise a unit vector along the y-axis. The hybrid orbital ψ is represented by a vector resulting from the addition of the vectors representing the p_x and p_y orbitals. The s orbital is spherically symmetric about the origin, therefore it has no effect on the direction of the hybrid.

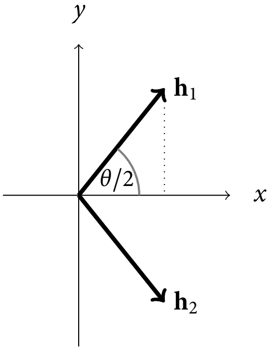


The angle α is calculated as

$$\alpha = \tan^{-1}\left(\sqrt{3/2}/\sqrt{1/2}\right) = \tan^{-1}\sqrt{3} = 60°$$

Therefore the vector representing ψ makes and angle $\beta = 180° - \alpha = 180° - 60° = 120°$ to the x-axis.

P9A.4 Following the same logic as in *Problem* P9A.2 and *Problem* P9A.2, the vector representation of the two hybrid atomic orbitals is as shown below.



It follows from the diagram that for h_1 the contribution from p_x is proportional to $\cos\theta/2$, and the contribution from p_y is proportional to $\sin\theta/2$; for h_2 all that is different is that the sign of the contribution from p_y is reversed. Both hybrids will have a contribution from the s orbital, and so can be written

$$h_1 = \mathrm{s}+\lambda\left(\cos(\theta/2)\,\mathrm{p}_x + \sin(\theta/2)\,\mathrm{p}_y\right) \quad h_2 = \mathrm{s}+\lambda\left(\cos(\theta/2)\,\mathrm{p}_x - \sin(\theta/2)\,\mathrm{p}_y\right)$$

The parameter λ is to be determined, but it is the same for both hybrids as they are equivalent. The value of λ is found by using the requirement that the hybrids are orthogonal, $\int h_1 h_2 \, d\tau = 0$

$$\int [s+\lambda\left(\cos(\theta/2)p_x + \sin(\theta/2)p_y\right)][s+\lambda\left(\cos(\theta/2)p_x - \sin(\theta/2)p_y\right)]\, d\tau = 0$$

Because the atomic orbitals are orthonormal the integral is evaluates to

$$1 + \lambda^2\left(\cos^2(\theta/2) - \sin^2(\theta/2)\right) = 1 + \lambda^2 \cos\theta$$

where the identity $\cos 2x = \cos^2 x - \sin^2 x$ is used. Setting this to zero gives $\boxed{\lambda = \pm(-1/\cos\theta)^{1/2}}$.

The ratio of p to s in a hybrid is given by the ratio of the squares of the coefficients of the contributing atomic orbitals. For these hybrids

$$\frac{\text{p character}}{\text{s character}} = \frac{[\lambda\cos(\theta/2)]^2 + [\pm\lambda\sin(\theta/2)]^2}{1^2} = \lambda^2$$

where the identity $\cos^2 x + \sin^2 x = 1$ is used. Therefore what is usually known as an sp^2 hybrid has $\lambda = \sqrt{2}$, an sp hybrid has $\lambda = 1$, and an sp^3 hybrid has $\lambda = \sqrt{3}$. The plotshown in Fig. 9.1 shows the relationship between λ^2 and the angle between the hybrids.

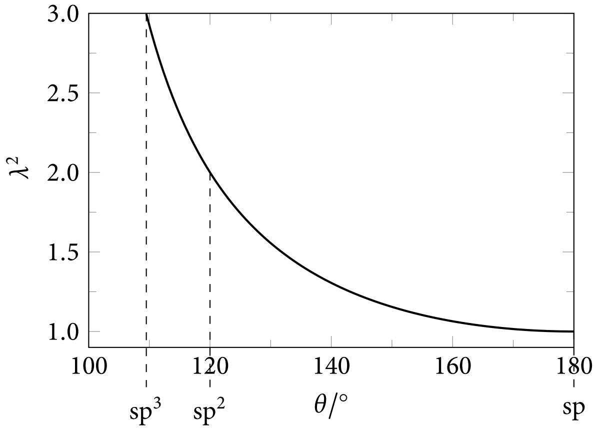


Figure 9.1

9B Molecular orbital theory: the hydrogen molecule-ion

Answer to discussion questions

D9B.2 As described in Section 9B.1(b) on page 353, the reason why the bonding molecular orbital is lower in energy than the atomic orbitals is not entirely clear. However, it is clear that bonding character correlates strongly with molecular orbitals that have an accumulation of electron density between nuclei due to overlap and constructive interference of their component atomic orbitals. A simple and plausible explanation of this correlation is that enhanced electron probability between nuclei lowers the potential energy by putting electrons in a position where they can be attracted to two nuclei at the same time; however, the source of the reduced energy may be more complicated.

Solutions to exercises

E9B.1(b) The normalization condition is given by [7B.4c–*248*], $\int \psi^* \psi \, \mathrm{d}\tau = 1$. The wavefunction is normalized by finding N such that $\psi = N(\psi_\mathrm{A} + \lambda\psi_\mathrm{B} + \lambda'\psi'_\mathrm{B})$ satisfies this condition. The wavefunctions ψ_A, ψ_B and ψ'_B are all real as is N, therefore

$$\begin{aligned}
\int \Psi^* \Psi \, \mathrm{d}\tau &= N^2 \int (\psi_\mathrm{A} + \lambda\psi_\mathrm{B} + \lambda'\psi'_\mathrm{B})^2 \, \mathrm{d}\tau \\
&= N^2 \Big[\overbrace{\int \psi_\mathrm{A}^2 \, \mathrm{d}\tau}^{1} + \lambda^2 \overbrace{\int \psi_\mathrm{B}^2 \, \mathrm{d}\tau}^{1} + \lambda'^2 \overbrace{\int \psi_\mathrm{B}'^{\,2} \, \mathrm{d}\tau}^{1} + 2\lambda \overbrace{\int \psi_\mathrm{A}\psi_\mathrm{B} \, \mathrm{d}\tau}^{S} \\
&\qquad + 2\lambda' \overbrace{\int \psi_\mathrm{A}\psi'_\mathrm{B} \, \mathrm{d}\tau}^{S'} + 2\lambda\lambda' \overbrace{\int \psi_\mathrm{B}\psi'_\mathrm{B} \, \mathrm{d}\tau}^{0} \Big] \\
&= N^2(1 + \lambda^2 + \lambda'^2 + 2\lambda S + 2\lambda' S)
\end{aligned}$$

The integrals $\int \psi_\mathrm{A}^2 \, \mathrm{d}\tau$, $\int \psi_\mathrm{B}^2 \, \mathrm{d}\tau$ and $\int \psi_\mathrm{B}'^{\,2} \, \mathrm{d}\tau$ are 1 because the wavefunctions ψ_A, ψ_B and ψ'_B are normalized; $\int \psi_\mathrm{B}\psi'_\mathrm{B} \, \mathrm{d}\tau = 0$ because the exercise specifies that these are orthogonal. The value of this integral must equal 1, therefore the normalization constant is $\boxed{N = 1/(1 + \lambda^2 + \lambda'^2 + 2\lambda S + 2\lambda' S)^{1/2}}$.

E9B.2(b) The condition of orthogonality is given by [7C.8–*254*], $\int \psi_i^* \psi_j \, \mathrm{d}\tau = 0$ for $i \neq j$. The given molecular orbital, $\psi_i = 0.727A + 0.144B$ is real, therefore $\psi_i^* = \psi_i$. The new linear combination of A and B, which is orthogonal to ψ_i must have the form of $\psi_j = A + \beta B$, where the coefficient of wavefunction A is chosen to be 1 for simplicity. Substitution of these wavefunctions in the condition of orthogonality gives

$$\begin{aligned}
\int \psi_i^* \psi_j \, \mathrm{d}\tau &= \int (0.727A + 0.144B) \times (A + \beta B) \mathrm{d}\tau \\
&= 0.727 \overbrace{\int A^2 \, \mathrm{d}\tau}^{1} + 0.144\beta \overbrace{\int B^2 \, \mathrm{d}\tau}^{1} + (0.727\beta + 0.144) \overbrace{\int AB \, \mathrm{d}\tau}^{S} \\
&= 0.727 + 0.144\beta + (0.727\beta + 0.144)S
\end{aligned}$$

Using $S = 0.117$ the value of the integral becomes $0.744 + 0.229\beta$. This value must be zero for the two wavefunctions to be orthogonal, therefore $\beta = -3.25$ and so $\psi_j = A - 3.25B$.

Normalization of ψ_i follows the same logic as in *Exercise* E9B.1(a). First the wavefunction is written as $\psi_i = N(0.727A + 0.144B)$ and then the normalization constant N is found such that $\int \psi^* \psi \, d\tau = 1$.

$$\int \psi_i^* \psi_i \, d\tau = \int [N(0.727A + 0.144B)]^2 \, d\tau$$

$$= N^2 \left(0.727^2 \overbrace{\int A^2 \, d\tau}^{1} + 0.144^2 \beta \overbrace{\int B^2 \, d\tau}^{1} + (2 \times 0.727 \times 0.144) \overbrace{\int AB \, d\tau}^{S} \right)$$

$$= N^2 (0.549 + 0.209S)$$

Using $S = 0.117$ gives a value of $0.573N^2$ for the integral, therefore $N = 1/\sqrt{0.573} = 1.32$. Therefore the normalized wavefunction is

$$\psi_i = 1.32 \times (0.727A + 0.144B) = \boxed{0.960A + 0.190B}$$

Normalization of ψ_j follows a similar procedure as for ψ_i, giving $N = 0.304$ and therefore $\boxed{\psi_j = 0.304A - 0.989B}$.

E9B.3(b) The energy of the σ^* antibonding orbital in H_2^+ is given by [9B.7–*355*], $E_{\sigma^*} = E_{\text{H1s}} + j_0/R - (j - k)/(1 - S)$. Molecular potential energy curves are usually plotted with respect to the energy of the separated atoms, therefore the energies to be plotted are $E_{\sigma^*} - E_{\text{H1s}} = j_0/R - (j - k)/(1 - S)$. Using [9B.5d–*353*], $j_0/a_0 = 27.21 \text{ eV} = 1 \, E_h$, the energy for $R/a_0 = 1$ is computed as

$$E_{\sigma^*} - E_{\text{H1s}} = \frac{(1 \, E_h)}{1} - \frac{(0.729 \, E_h) - (0.736 \, E_h)}{(1 - 0.858)} = +1.05 \, E_h$$

Similar calculations give the following energies

R/a_0	1	2	3	4
$(E_\sigma^* - E_{\text{H1s}})/E_h$	+1.05	+0.340	+0.132	$+5.52 \times 10^{-2}$

These data are plotted in Fig. 9.2. The data are fitted well by the following cubic

$$(E_\sigma - E_{\text{H1s}})/E_h = -0.0616(R/a_0)^3 + 0.6203(R/a_0)^2 - 2.1385(R/a_0) + 2.6288$$

Note that this cubic equation has no physical meaning, it is only used to draw the line on the plot above.

E9B.4(b) The sketch below shows the bonding and the antibonding face-to-face overlap of two d orbitals, resulting in δ molecular orbitals. The bonding molecular orbital is symmetric with respect to inversion, therefore it is labelled δ_g, whereas the antibonding molecular orbital is antisymmetric with respect to inversion, and is labelled δ_u.

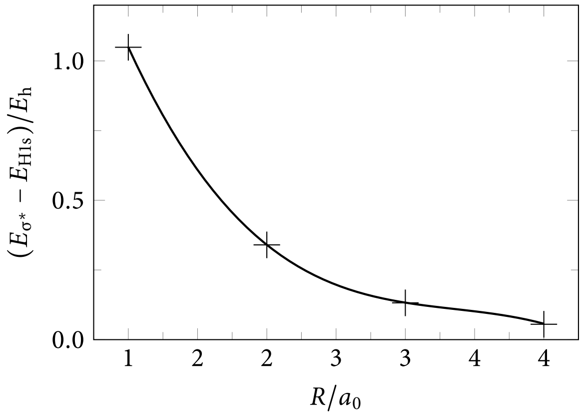
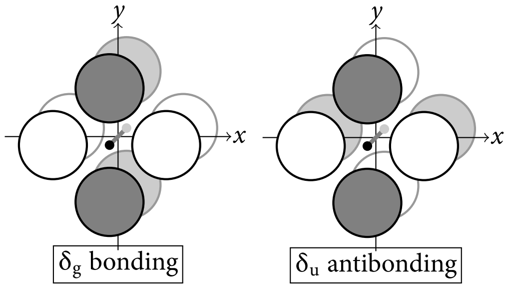


Figure 9.2



Solutions to problems

P9B.2 The bonding and antibonding molecular orbitals resulting from the linear combination of hydrogenic atomic orbitals are given by

$$\begin{aligned}\psi_\pm &= N_\pm(\psi_{\mathrm{H1sA}} \pm \psi_{\mathrm{H1sB}})\\ &= N_\pm\left[\frac{1}{(\pi a_0^3)^{1/2}}\mathrm{e}^{-r_\mathrm{A}/a_0} \pm \frac{1}{(\pi a_0^3)^{1/2}}\mathrm{e}^{-r_\mathrm{B}/a_0}\right]\end{aligned}$$

where r_A and r_B are the distances of the electron from nucleus A and B, respectively. Given that the internuclear separation along the z-axis is R, in Cartesian coordinates r_A and r_B become

$$r_\mathrm{A} = (x^2 + y^2 + z^2)^{1/2} \quad \text{and} \quad r_\mathrm{B} = (x^2 + y^2 + (z - R)^2)^{1/2}$$

Therefore the wavefunction is

$$\psi_\pm = \frac{N_\pm}{(\pi a_0^3)^{1/2}}\left[\mathrm{e}^{-(x^2+y^2+z^2)^{1/2}/a_0} \pm \mathrm{e}^{-(x^2+y^2+(z-R)^2)^{1/2}/a_0}\right]$$

The normalisation constants at the experimental internuclear separation (R = 106 pm = 2.00 a_0) are calculated in *Example* 9B.1 on page 352, giving N_+ =

0.56 and $N_- = 1.10$. Both of the bonding and antibonding wavefunctions are real, therefore $\psi_\pm = \psi_\pm^*$. The square of the wavefunction gives the probability density of finding the electron at a particular position. The volume element δV given in this problem (1.00 pm^3) is small enough that it is assumed that the wavefunction has a constant value over the entire volume element. Therefore the probability is simply $\psi^2\delta V$.

(a) At nucleus A $x = y = z = 0$ the probability is computed as

$$\psi_+^2\delta V = \frac{N_+^2}{(\pi a_0^3)}\left[\mathrm{e}^0 + \mathrm{e}^{-2.00\,a_0/a_0}\right]^2\delta V$$

$$= \frac{0.56^2}{[\pi\times(52.91\text{ pm})^3]}\left[1+\mathrm{e}^{-2.00}\right]^2\times(1.00\text{ pm}^3) = \boxed{8.7\times10^{-7}}$$

(b) The probability of finding the electron at nucleus B must be the same as the probability of finding the electron at nucleus A due to the inherent symmetry of the problem. Therefore $\boxed{P = 8.7\times10^{-7}}$.

(c) The Cartesian coordinates of the position halfway between A and B are $x = y = 0$ and $z = 1.00\,a_0$. At this position the probability is computed as

$$\psi_+^2\delta V = \frac{N_+^2}{(\pi a_0^3)}\left[\mathrm{e}^{-1.00\,a_0/a_0} + \mathrm{e}^{-[((1.00\,a_0)-(2.00\,a_0))^2]^{1/2}/a_0}\right]^2\delta V$$

$$= \frac{0.56^2}{[\pi\times(52.91\text{ pm})^3]}\left[\mathrm{e}^{-1.00}+\mathrm{e}^{-1.00}\right]^2\times(1.00\text{ pm}^3) = \boxed{3.6\times10^{-7}}$$

(d) At 20 pm along the bond from nucleus A and 10 pm perpendicularly the coordinates are $z = 20\text{ pm} = 0.378...\,a_0$ and $x^2+y^2 = (10\text{ pm})^2 = (0.189...\,a_0)^2$. At this position the probability is computed as

$$\psi_+^2\delta V = \frac{N_+^2}{(\pi a_0^3)}\Big[\mathrm{e}^{-[(0.189...\,a_0)^2+(0.378...\,a_0)^2]^{1/2}/a_0}$$

$$+\mathrm{e}^{-[(0.189...\,a_0)^2+((0.378...\,a_0)-(2.00\,a_0))^2]^{1/2}/a_0}\Big]^2\delta V$$

$$= \frac{0.56^2}{[\pi\times(52.91\text{ pm})^3]}\left[\mathrm{e}^{-0.422...}+\mathrm{e}^{-1.63...}\right]^2\times(1.00\text{ pm}^3)$$

$$= \boxed{4.9\times10^{-7}}$$

The calculation of the probabilities when the electron occupies the antibonding orbital follows exactly the same procedure as above, and gives the following results: (a) $P = \boxed{1.9\times10^{-6}}$; (b) $P = \boxed{1.9\times10^{-6}}$; (c) $\boxed{P = 0}$, which is the expected result, as the antibonding orbital has a node going through the point halfway between the two nuclei; (d) $P = \boxed{5.5\times10^{-7}}$

P9B.4 The bonding and antibonding MO wavefunctions are $\psi_\pm = N_\pm(\psi_A \pm \psi_B)$, where $N_\pm$ is the normalizing factor. This factor depends on the distance between the nuclei (*Example* 9B.1 on page 352), but this just scales the orbital without changing any of its key features. Therefore, this normalizing factor, as well as those for ψ_A and ψ_B given in *Brief illustration* 9B.1 on page 352 are simply ignored. Without loss of generality, it is assumed that atom A is located at $z_{A1} = 0$ and atom B at $z_{B1} = R$, the internuclear separation. The requirement is to plot the wavefunction along the z-axis, so $x_{A1} = y_{A1} = 0$, and likewise for atom B. With all of these conditions imposed the function to be plotted is

$$\psi_\pm = e^{-|z|/a_0} \pm e^{-|(z-R)|/a_0}$$

The modulus sign is needed because the argument of the exponential is the distance from the nucleus, which is always positive.

(a) The wavefunction corresponding to the bonding molecular orbital is plotted in Fig. 9.3 for three different internuclear separations. The positions of the nuclei for each wavefunction are indicated by dotted lines. None of the plotted wavefunctions have any nodes. The value of the wavefunctions and hence the electron densities in the internuclear region are larger than the sum of the values of the corresponding wavefunctions describing the hydrogenic atomic orbitals. This feature is responsible for the bonding. However, with increasing internuclear separation this surplus electron density at the internuclear region diminishes, the overall energy of the wavefunction increases and hence the wavefunction becomes less and less bonding.

(b) The wavefunction corresponding to the antibonding molecular orbital at three different internuclear separations is plotted in Fig. 9.4. The wavefunctions have a node halfway between the two nuclei, which results in less electron density in the internuclear region compared to if the wavefunctions were not overlapping. This feature is responsible for the antibonding effect. With increasing internuclear separation this deficiency in electron density at the internuclear region decreases, the overall energy of the wavefunction decreases and hence the wavefunction becomes less and less antibonding.

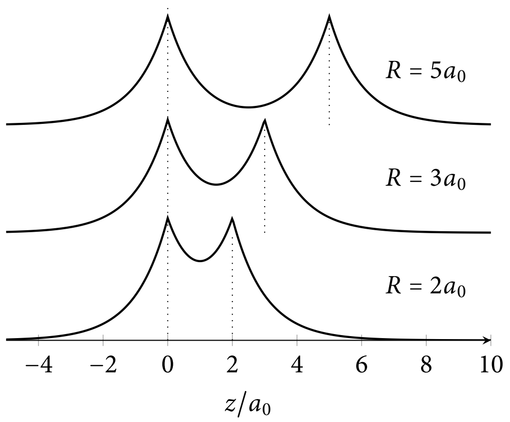


Figure 9.3

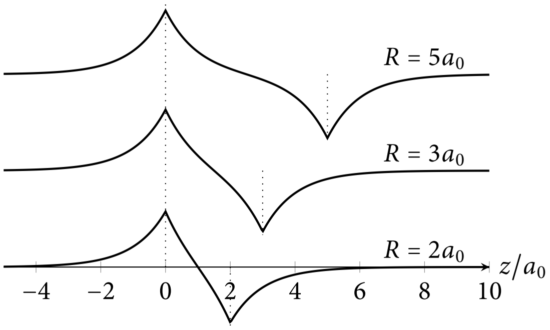


Figure 9.4

9C Molecular orbital theory: homonuclear diatomic molecules

Answer to discussion questions

D9C.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. A diagram of energy levels (orbitals) and degeneracies is needed. For diatomic molecules, these energy levels are either nondegenerate (for σ bonds) or doubly degenerate (for all others). The orbitals are populated with electrons, placing each successive electron in the lowest-energy orbital available, no more than two electrons per orbital. Hund's rule indicates that different degenerate orbitals should be populated first, with electrons that have parallel spins, before pairing two electrons in the same degenerate orbital.

D9C.4 The bond strength is related to the extent to which the occupied bonding molecular orbitals are lowered in energy compared to the constituent atomic orbitals. As described in Topic 9B for the case of H_2^+, this lowering in energy depends on the size of the term k, [9B.5c–*353*], which is a measure of the interaction between a nucleus and the excess electron density in the internuclear region arising from overlap.

The overlap integral, S, is a different quantity than k, but its behaviour with (for example) internuclear distance is quite similar. Thus the overlap integral is often taken as a proxy for k, not least as it much easier to imagine how the overlap varies when the orbital or the internuclear distance is varied. It is therefore common to speak of a bond being strong when 'there is good overlap'. The fact that there is a correlation between overlap and bond strength may, however, simply be fortuitous as the theory does not indicate such a connection.

Solutions to exercises

E9C.1(b) The molecular orbital diagram for O_2^{2-} and F_2^- is shown in Fig. 9C.11 on page 361, and that of N_2 is shown in Fig. 9C.12 on page 361. According to the Pauli principle, up to two valence electrons can be placed in each of the molecular orbitals. First the lowest energy orbital is filled up, then the next lowest and so on, until all the valence electrons are used up.

(i) ${F_2}^-$ has $7+7+1 = 15$ valence electrons (VE) overall, therefore the ground-state electron configuration is $1\sigma_g^2\,1\sigma_u^{*2}\,2\sigma_g^2\,1\pi_u^4\,1\pi_g^{*4}\,2\sigma_u^{*1}$. The bond order is defined in [9C.4–*361*] as $b = \frac{1}{2}(N - N^*)$, therefore $b = \frac{1}{2}(8-7) = \frac{1}{2}$.

(ii) N_2: $5 + 5 = 10$ VE; $1\sigma_g^2\,1\sigma_u^{*2}\,2\sigma_g^2\,1\pi_u^4$; $b = \frac{1}{2}(8-2) = 3$.

(iii) ${O_2}^{2-}$: $6 + 6 + 2 = 14$ VE; $1\sigma_g^2\,1\sigma_u^{*2}\,2\sigma_g^2\,1\pi_u^4\,1\pi_g^{*4}$; $b = \frac{1}{2}(8-6) = 1$.

E9C.2(b) The molecule with the greater bond order is expected to have the larger dissociation energy. Qualitatively Li_2 and Be_2 share the same molecular orbital energy level diagram, shown in Fig. 9C.12 on page 361. Li_2 has $1 + 1 = 2$ valence electrons overall, therefore its ground-state electron configuration is $1\sigma_g^2$. The bond order is defined in [9C.4–*361*] as $b = \frac{1}{2}(N - N^*)$, therefore $b = \frac{1}{2}(2-0) = 1$.

Be_2 has $2 + 2 = 4$ valence electrons, its configuration is $1\sigma_g^2\,1\sigma_u^{*2}$, and the bond order is $b = \frac{1}{2}(2-2) = 0$. Li_2 has greater bond order than Be_2, therefore Li_2 is expected to have the larger bond dissociation energy.

E9C.3(b) The species with the smaller bond order is expected to have larger bond length. The molecular orbital diagram of O_2 and its ions is shown in Fig. 9C.11 on page 361. The ground state electron configuration and the bond order of the species in the order of increasing number of valence electrons, VE, is given below.

${O_2}^+$	$6 + 6 - 1 = 11$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,2\sigma_g^2\,1\pi_u^4\,1\pi_g^{*1}$	$b = \frac{1}{2}(8-3) = \frac{5}{2}$
O_2	$6 + 6 = 12$ VE	$\ldots\,1\pi_g^{*2}$	$b = \frac{1}{2}(8-4) = 2$
${O_2}^-$	$6 + 6 + 1 = 13$ VE	$\ldots\,1\pi_g^{*3}$	$b = \frac{1}{2}(8-5) = \frac{3}{2}$
${O_2}^{2-}$	$6 + 6 + 2 = 14$ VE	$\ldots\,1\pi_g^{*4}$	$b = \frac{1}{2}(8-6) = 1$

The bond order increases in the order ${O_2}^{2-}$, ${O_2}^-$, O_2, ${O_2}^+$, therefore the bond length is expected to increase in the same order.

E9C.4(b) The molecular orbital energy level diagram for Li_2, Be_2, B_2, C_2, N_2 and related ions is shown in Fig. 9C.12 on page 361, and for O_2, F_2, Ne_2 and related ions in Fig. 9C.11 on page 361. Following the same logic as in *Exercise* E9C.1(b) and *Exercise* E9C.2(b) gives

${Li_2}^+$	$1 + 1 - 1 = 1$ VE	$1\sigma_g^1$	$b = \frac{1}{2}(1-0) = \frac{1}{2}$
${Be_2}^+$	$2 + 2 - 1 = 3$ VE	$1\sigma_g^2\,1\sigma_u^{*1}$	$b = \frac{1}{2}(2-1) = \frac{1}{2}$
${B_2}^+$	$3 + 3 - 1 = 5$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,1\pi_u^1$	$b = \frac{1}{2}(3-2) = \frac{1}{2}$
${C_2}^+$	$4 + 4 - 1 = 7$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,1\pi_u^3$	$b = \frac{1}{2}(5-2) = \frac{3}{2}$
${N_2}^+$	$5 + 5 - 1 = 9$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,1\pi_u^4\,2\sigma_g^1$	$b = \frac{1}{2}(7-2) = \frac{5}{2}$
${O_2}^+$	$6 + 6 - 1 = 11$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,2\sigma_g^2\,1\pi_u^4\,1\pi_g^{*1}$	$b = \frac{1}{2}(8-3) = \frac{5}{2}$
${F_2}^+$	$7 + 7 - 1 = 13$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,2\sigma_g^2\,1\pi_u^4\,1\pi_g^{*3}$	$b = \frac{1}{2}(8-5) = \frac{3}{2}$
${Ne_2}^+$	$8 + 8 - 1 = 15$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,2\sigma_g^2\,1\pi_u^4\,1\pi_g^{*4}\,2\sigma_u^{*1}$	$b = \frac{1}{2}(8-7) = \frac{1}{2}$

$\mathrm{Li_2}^-$	$1+1+1=3$ VE	$1\sigma_g^2\,1\sigma_u^{*1}$	$b=\frac{1}{2}(2-1)=\frac{1}{2}$
$\mathrm{Be_2}^-$	$2+2+1=5$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,1\pi_u^1$	$b=\frac{1}{2}(3-2)=\frac{1}{2}$
$\mathrm{B_2}^-$	$3+3+1=7$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,1\pi_u^3$	$b=\frac{1}{2}(5-2)=\frac{3}{2}$
$\mathrm{C_2}^-$	$4+4+1=9$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,1\pi_u^4\,2\sigma_g^1$	$b=\frac{1}{2}(7-2)=\frac{5}{2}$
$\mathrm{N_2}^-$	$5+5+1=11$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,1\pi_u^4\,2\sigma_g^2\,1\pi_g^{*1}$	$b=\frac{1}{2}(8-3)=\frac{5}{2}$
$\mathrm{O_2}^-$	$6+6+1=13$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,2\sigma_g^2\,1\pi_u^4\,1\pi_g^{*3}$	$b=\frac{1}{2}(8-5)=\frac{3}{2}$
$\mathrm{F_2}^-$	$7+7+1=15$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,2\sigma_g^2\,1\pi_u^4\,1\pi_g^{*4}\,2\sigma_u^{*1}$	$b=\frac{1}{2}(8-7)=\frac{1}{2}$
$\mathrm{Ne_2}^-$	$8+8+1=17$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,2\sigma_g^2\,1\pi_u^4\,1\pi_g^{*4}\,2\sigma_u^{*2}\,3\sigma_g^1$	$b=\frac{1}{2}(9-8)=\frac{1}{2}$

Note that the extra electron in $\mathrm{Ne_2}$ is accommodated on a bonding molecular orbital resulting from the overlap of the 3s atomic orbitals.

E9C.5(b) The molecular orbital energy level diagram for $\mathrm{Li_2}$, $\mathrm{Be_2}$, $\mathrm{B_2}$, $\mathrm{C_2}$, $\mathrm{N_2}$ and their ions is shown in Fig. 9C.12 on page 361, and for $\mathrm{O_2}$, $\mathrm{F_2}$, $\mathrm{Ne_2}$ and their ions in Fig. 9C.11 on page 361. The lowest unoccupied molecular orbital (LUMO) is the molecular orbital which is the lowest in energy and is not occupied by any electrons. The LUMO of each of the listed ions is indicated by a box around it.

$\mathrm{Li_2}^+$	$1+1-1=1$ VE	$1\sigma_g^1\,\boxed{1\sigma_u^{*0}}$
$\mathrm{Be_2}^+$	$2+2-1=3$ VE	$1\sigma_g^2\,1\sigma_u^{*1}\,\boxed{1\pi_u^0}$
$\mathrm{B_2}^+$	$3+3-1=5$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,1\pi_u^1\,\boxed{2\sigma_g^0}$
$\mathrm{C_2}^+$	$4+4-1=7$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,1\pi_u^3\,\boxed{2\sigma_g^0}$
$\mathrm{N_2}^+$	$5+5-1=9$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,1\pi_u^4\,2\sigma_g^1\,\boxed{1\pi_g^{*0}}$
$\mathrm{O_2}^+$	$6+6-1=11$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,2\sigma_g^2\,1\pi_u^4\,1\pi_g^{*1}\,\boxed{2\sigma_u^{*0}}$
$\mathrm{F_2}^+$	$7+7-1=13$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,2\sigma_g^2\,1\pi_u^4\,1\pi_g^{*3}\,\boxed{2\sigma_u^{*0}}$
$\mathrm{Ne_2}^+$	$8+8-1=15$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,2\sigma_g^2\,1\pi_u^4\,1\pi_g^{*4}\,2\sigma_u^{*1}\,\boxed{3\sigma_g^0}$

$\mathrm{Li_2}^-$	$1+1+1=3$ VE	$1\sigma_g^2\,1\sigma_u^{*1}\,\boxed{1\pi_u^0}$
$\mathrm{Be_2}^-$	$2+2+1=5$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,1\pi_u^1\,\boxed{2\sigma_g^0}$
$\mathrm{B_2}^-$	$3+3+1=7$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,1\pi_u^3\,\boxed{2\sigma_g^0}$
$\mathrm{C_2}^-$	$4+4+1=9$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,1\pi_u^4\,2\sigma_g^1\,\boxed{1\pi_g^{*0}}$
$\mathrm{N_2}^-$	$5+5+1=11$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,1\pi_u^4\,2\sigma_g^2\,1\pi_g^{*1}\,\boxed{2\sigma_u^{*0}}$
$\mathrm{O_2}^-$	$6+6+1=13$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,2\sigma_g^2\,1\pi_u^4\,1\pi_g^{*3}\,\boxed{2\sigma_u^{*0}}$
$\mathrm{F_2}^-$	$7+7+1=15$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,2\sigma_g^2\,1\pi_u^4\,1\pi_g^{*4}\,2\sigma_u^{*1}\,\boxed{3\sigma_g^0}$
$\mathrm{Ne_2}^-$	$8+8+1=17$ VE	$1\sigma_g^2\,1\sigma_u^{*2}\,2\sigma_g^2\,1\pi_u^4\,1\pi_g^{*4}\,2\sigma_u^{*2}\,3\sigma_g^1\,\boxed{3\sigma_u^{*0}}$

Note that the extra electron in Ne_2 is accommodated on a bonding molecular orbital resulting from the overlap of the 3s atomic orbitals.

E9C.6(b) The energy of the incident photon must equal the sum of the ionization energy of the orbital and the kinetic energy of the ejected photoelectron, [9C.5–*362*], $h\nu = I + \frac{1}{2}m_e v^2$. Therefore the kinetic energy of the photoelectron is E_k = 21 eV − 12 eV = 9 eV, which corresponds to a speed of

$$v = \left(\frac{2E_k}{m_e}\right)^{1/2} = \left(\frac{2 \times (9\,\mathrm{eV}) \times (1.6022 \times 10^{-19}\,\mathrm{J\,eV^{-1}})}{(9.1094 \times 10^{-31}\,\mathrm{kg})}\right)^{1/2} = \boxed{1.78 \times 10^{6}\,\mathrm{m\,s^{-1}}}$$

Solutions to problems

P9C.2 When the internuclear separation is zero the areas of constructive interference get exactly cancelled by the areas of destructive interference, therefore the overlap integral is zero. As the nuclei are moving further away from each other, the area of constructive interference increases at the expense of the area with destructive interference, leading to a maximum value in the overlap integral. At large internuclear separations the overlap of the orbitals becomes insignificant, resulting in zero overlap. Figure 9.5 shows a plot of the overlap integral

$$S = \left(\frac{R}{a_0}\right)\left[1 + \left(\frac{R}{a_0}\right) + \frac{1}{3}\left(\frac{R}{a_0}\right)^2\right] e^{-R/a_0}$$

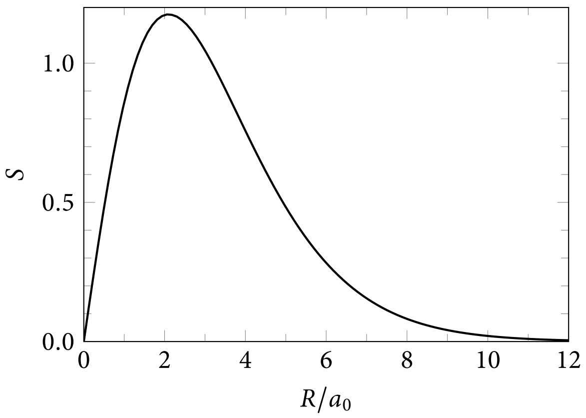


Figure 9.5

The position of the maximum overlap is found by differentiating the overlap integral with respect to $x = R/a_0$ (the product rule is used), and then setting the derivative to zero.

$$\frac{dS}{dx} = \left[1 + 2x + x^2\right] e^{-x} - \left[x + x^2 + \tfrac{1}{3}x^3\right] e^{-x}$$

To find the turning points set $dS/dx = 0$; the factor e^{-x} is cancelled to give

$$1 + 2x + x^2 - \left[x + x^2 + \tfrac{1}{3}x^3\right] = 1 + x - \tfrac{1}{3}x^3 = 0$$

It is the easiest to use mathematical software to solve this equation. The only real solution is $R/a_0 = 2.10$, hence the overlap is maximum at $\boxed{R = 2.10\,a_0}$.

P9C.4 The energy of the incident photon must equal the sum of the ionization energy of the orbital and the kinetic energy of the ejected photoelectron, [9C.5–*362*], $h\nu = \frac{1}{2}m_e v^2 + I$. Rearranging the equation to give the ionisation energy of the orbital gives $I = h\nu - \frac{1}{2}m_e v^2$, therefore the ionisation energy of the orbitals from which the electrons were ejected are

$$I_1 = (21.21\text{ eV}) - (11.01\text{ eV}) = 10.20\text{ eV}$$
$$I_2 = (21.21\text{ eV}) - (8.23\text{ eV}) = 12.98\text{ eV}$$
$$I_3 = (21.21\text{ eV}) - (15.22\text{ eV}) = 5.99\text{ eV}$$

The orbital energies are the negative of the ionisation energies. The molecular orbital energy level diagram is shown in Fig 9.6, the dashed arrows represent the ionisation.

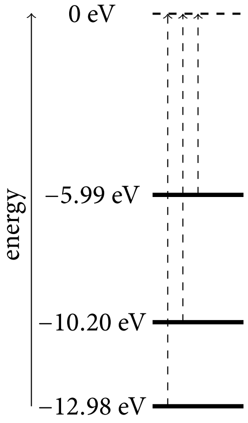


Figure 9.6

9D Molecular orbital theory: heteronuclear diatomic molecules

Answer to discussion questions

D9D.2 In forming a bond an atom must, to some extent, give up electron density to be shared with other atoms in the molecule. The energy needed to do this is connected with the value of the ionization energy of the orbital. Equally, the atom will to some extent acquire additional electron density to interact with, and the energy gained from acquiring this density is connected in some way to the electron affinity. Thus both electron gain and electron loss, in the loosest sense, are involved in the process of bonding. It is for this reason that ionization energy and electron affinity are involved in the estimation of atomic orbital energies for participation in bonding. See Section 9D.2(a) on page 367.

D9D.4 The Coulomb integral is essentially the energy of an electron when it occupies an atomic orbital in the molecule.

The resonance integral is a contribution to the energy of a molecule that can be associated with an electron interacting with more than one nucleus at once.

Solutions to exercises

E9D.1(b) The molecular orbital energy level diagram for a heteronuclear diatomic AB is similar to that for a homonuclear diatomic A_2 (Fig. 9C.11 on page 361 or Fig. 9C.12 on page 361) except that the atomic orbitals on A and B are no longer at the same energies. As a result the molecular orbitals no longer have equal contributions from the orbitals on A and B; furthermore, it is more likely that the s and p orbitals will mix. From simple considerations it it not possible to predict the exact ordering of the resulting molecular orbitals, so the diagram shown Fig. 9.7 is simply one possibility. Note that because the heteronuclear diatomic no longer has a centre of symmetry the g/u labels are not applicable.

The electronic configurations are:
(i) XeF (15 valence electrons) $1\sigma^2\,2\sigma^2\,3\sigma^2\,1\pi^4\,2\pi^4\,4\sigma^1$; (ii) PN (10 valence electrons) $1\sigma^2\,2\sigma^2\,3\sigma^2\,1\pi^4$; (iii) SO^- (13 valence electrons) $1\sigma^2\,2\sigma^2\,3\sigma^2\,1\pi^4\,2\pi^3$.

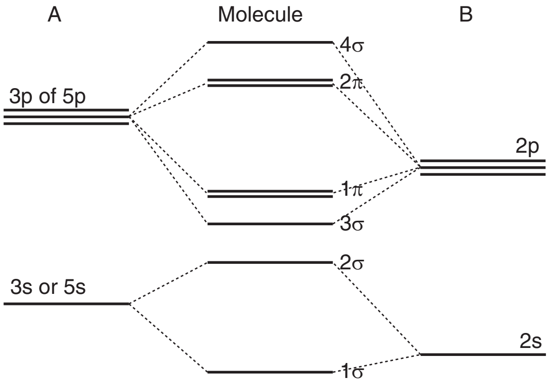


Figure 9.7

E9D.2(b) The molecular orbital diagram of IF is similar to the one shown in the solution to *Exercise* E9D.1(b) where the orbitals on atom A are 5s and 5p. It is not possible to predict the precise energy ordering of the orbitals from simple considerations, so this diagram is simply a plausible suggestion.

IF has $7+7=14$ valence electrons, therefore the ground state electron configuration is $1\sigma^2\,2\sigma^2\,3\sigma^2\,1\pi^4\,2\pi^4$. IF^+ has one fewer electron than IF, therefore it has one fewer electron on the antibonding 2π orbital. IF^- has one more electron than IF, therefore it has one more electron accommodated on the antibonding 4σ orbital. Hence the order of decreasing bond order is IF^+, IF, IF^-, which is expected to be the same as the order of increasing bond length.

E9D.3(b) A suitable MO diagram in shown in the solution to *Exercise* E9D.1(b). The ion with the greater bond order is expected to have the shorter bond length. SO^+ has $6 + 6 - 1 = 11$ valence electrons, therefore the ground state electron configuration is $1\sigma^2\,2\sigma^2\,3\sigma^2\,1\pi^4\,2\pi^1$. SO^- has two more electrons, both accommodated in the antibonding 2π orbital. It follows that SO^+ has a greater bond order than SO^-, therefore SO^+ is expected to have the shorter bond length.

E9D.4(b) The relationship between the Pauling and Mulliken electronegativities is given by [9D.4–*366*], $\chi_{\text{Pauling}} = 1.35\chi_{\text{Mulliken}}^{1/2} - 1.37$. A plot of the Pauling electronegativities of Period 3 atoms against the square root of their Mulliken electronegativities is shown in Fig. 9.8.

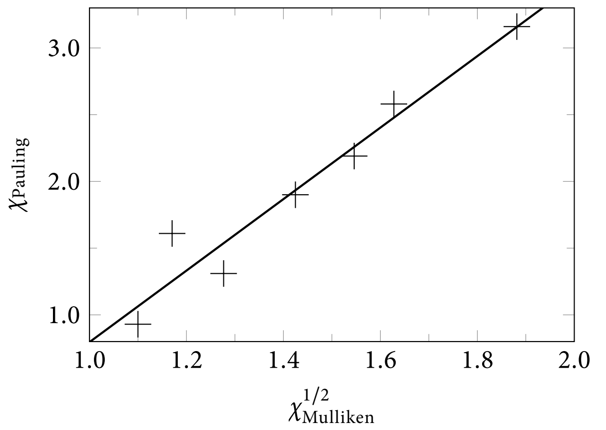


Figure 9.8

The equation of the best fit line is $\chi_{\text{Pauling}} = 2.68\chi_{\text{Mulliken}}^{1/2} - 1.88$, which is very far from the expected relationship.

E9D.5(b) The orbital energy of an atomic orbital in a given atom is estimated using the procedure outlined in *Brief illustration* 9D.2 on page 369, and using data from the *Resource section*. The orbital energy of hydrogen is

$$\alpha_{\text{H}} = -\tfrac{1}{2}[I + E_{\text{ea}}]$$

$$= -\tfrac{1}{2}\times[(1312.0\ \text{kJ mol}^{-1}) + (72.8\ \text{kJ mol}^{-1})]\times\frac{(1\ \text{eV})}{(96.485\ \text{kJ mol}^{-1})} = \boxed{-7.18\ \text{eV}}$$

The conversion factor between kJ mol^{-1} and eV is taken from the front cover of the book. Similarly for bromine

$$\alpha_{\text{Br}} = -\tfrac{1}{2}[I + E_{\text{ea}}]$$

$$= -\tfrac{1}{2}\times[(1139.9\ \text{kJ mol}^{-1}) + (324.5\ \text{kJ mol}^{-1})]\times\frac{(1\ \text{eV})}{(96.485\ \text{kJ mol}^{-1})} = \boxed{-7.59\ \text{eV}}$$

E9D.6(b) The orbital energies of hydrogen ($\alpha_{\mathrm{H}} = -7.18\ \mathrm{eV}$) and bromine ($\alpha_{\mathrm{Br}} = -7.59\ \mathrm{eV}$) are calculated in *Exercise* E9D.5(b). Taking $\beta = -1.0\ \mathrm{eV}$ as a typical value and setting $S = 0$ for simplicity, substitution into [9D.9c–*368*] gives

$$\begin{aligned}E_\pm &= \tfrac{1}{2}(\alpha_{\mathrm{H}} + \alpha_{\mathrm{Br}}) \pm \tfrac{1}{2}(\alpha_{\mathrm{H}} - \alpha_{\mathrm{Br}})\left[1 + \left(\frac{2\beta}{\alpha_{\mathrm{H}} - \alpha_{\mathrm{Br}}}\right)^2\right]^{1/2}\\ &= \tfrac{1}{2}[(-7.18\ \mathrm{eV}) + (-7.59\ \mathrm{eV})]\\ &\qquad \pm \tfrac{1}{2}[(-7.18\ \mathrm{eV}) - (-7.59\ \mathrm{eV})]\left[1 + \left(\frac{(-2.0\ \mathrm{eV})}{(-7.18\ \mathrm{eV}) - (-7.59\ \mathrm{eV})}\right)^2\right]^{1/2}\\ &= (-7.38...\ \mathrm{eV}) \pm (1.02...\ \mathrm{eV})\end{aligned}$$

Therefore the energy of the bonding molecular orbital is $E_- = (-7.38...\ \mathrm{eV}) - (1.02...\ \mathrm{eV}) = \boxed{-8.40\ \mathrm{eV}}$, and the antibonding orbital is at an energy level of $E_+ = (-7.38...\ \mathrm{eV}) + (1.02...\ \mathrm{eV}) = \boxed{-6.36\ \mathrm{eV}}$.

E9D.7(b) The orbital energies of hydrogen ($\alpha_{\mathrm{H}} = -7.18\ \mathrm{eV}$) and bromine ($\alpha_{\mathrm{Br}} = -7.59\ \mathrm{eV}$) are calculated in *Exercise* E9D.5(b). Taking $\beta = -1.0\ \mathrm{eV}$ as a typical value, and setting $S = 0.2$, substitution into [9D.9a–*368*] gives

$$\begin{aligned}E_\pm &= \frac{\alpha_{\mathrm{H}} + \alpha_{\mathrm{Br}} - 2\beta S \pm [(2\beta S - (\alpha_{\mathrm{H}} + \alpha_{\mathrm{Br}}))^2 - 4(1 - S^2)(\alpha_{\mathrm{H}}\alpha_{\mathrm{Br}} - \beta^2)]^{1/2}}{2(1 - S^2)}\\ &= \frac{(-14.3...\ \mathrm{eV}) \pm (1.03...\ \mathrm{eV})}{(1.92)} = (-7.48...\ \mathrm{eV}) \pm (0.539...\ \mathrm{eV})\end{aligned}$$

Therefore the energy of the bonding molecular orbital is $E_- = (-7.48...\ \mathrm{eV}) - (0.539...\ \mathrm{eV}) = \boxed{-8.02\ \mathrm{eV}}$, and the antibonding orbital is at an energy level of $E_+ = (-7.48...\ \mathrm{eV}) + (0.539...\ \mathrm{eV}) = \boxed{-6.95\ \mathrm{eV}}$.

Solutions to problems

P9D.2 (a) The secular equations for a heteronuclear diatomic molecule with one basis orbital per atom are given by [9D.6a–*367*] and [9D.6b–*367*]. In this problem there are two atoms but three basis orbitals, so there are three secular equations which can be generalized from those for the case of two basis orbitals

$$\begin{aligned}(\alpha_{\mathrm{A}} - E)c_{\mathrm{A}} + (\beta_{\mathrm{AB}} - S_{\mathrm{AB}}E)c_{\mathrm{B}} + (\beta_{\mathrm{AC}} - S_{\mathrm{AC}}E)c_{\mathrm{C}} &= 0\\ (\beta_{\mathrm{BA}} - S_{\mathrm{BA}}E)c_{\mathrm{A}} + (\alpha_{\mathrm{B}} - E)c_{\mathrm{B}} + (\beta_{\mathrm{BC}} - S_{\mathrm{BC}}E)c_{\mathrm{C}} &= 0\\ (\beta_{\mathrm{CA}} - S_{\mathrm{CA}}E)c_{\mathrm{A}} + (\beta_{\mathrm{CB}} - S_{\mathrm{CB}}E)c_{\mathrm{B}} + (\alpha_{\mathrm{C}} - E)c_{\mathrm{C}} &= 0\end{aligned}$$

In this case, orbitals B and C are on the same atom. It follows that the resonance integral β_{BC} and the overlap integral S_{BC} are zero, as the atomic orbitals on one atom are orthogonal to each other. Therefore the secular equations simplify to

$$\begin{aligned}(\alpha_{\mathrm{A}} - E)c_{\mathrm{A}} + (\beta_{\mathrm{AB}} - S_{\mathrm{AB}}E)c_{\mathrm{B}} + (\beta_{\mathrm{AC}} - S_{\mathrm{AC}}E)c_{\mathrm{C}} &= 0\\ (\beta_{\mathrm{BA}} - S_{\mathrm{BA}}E)c_{\mathrm{A}} + (\alpha_{\mathrm{B}} - E)c_{\mathrm{B}} &= 0\\ (\beta_{\mathrm{CA}} - S_{\mathrm{CA}}E)c_{\mathrm{A}} + (\alpha_{\mathrm{C}} - E)c_{\mathrm{C}} &= 0\end{aligned}$$

and hence the secular determinant is

$$\begin{vmatrix} \alpha_A - E & \beta_{AB} - S_{AB}E & \beta_{AC} - S_{AC}E \\ \beta_{BA} - S_{BA}E & \alpha_B - E & 0 \\ \beta_{CA} - S_{CA}E & 0 & \alpha_C - E \end{vmatrix}$$

(b) Substituting in the given values of the Coulomb integrals and the resonance integrals gives

$$\begin{vmatrix} (-7.2\text{ eV}) - E & (-1.0\text{ eV}) - S_{AB}E & (-0.8\text{ eV}) - S_{AC}E \\ (-1.0\text{ eV}) - S_{BA}E & (-10.4\text{ eV}) - E & 0 \\ (-0.8\text{ eV}) - S_{CA}E & 0 & (-8.4\text{ eV}) - E \end{vmatrix}$$

(i) If the overlap integrals are set to zero the secular determinant expands to give

$$-E^3 - (26\text{ eV})E^2 - (221.08\text{ eV}^2)E - (613.936\text{ eV}^3)$$

Setting this to zero and finding the roots of the cubic (using mathematical software) gives the energies $\boxed{E_1 = -10.7\text{ eV}}$, $\boxed{E_2 = -8.71\text{ eV}}$ and $\boxed{E_3 = -6.58\text{ eV}}$.

For the case where the overlap is zero the hamiltonian matrix is (expressed in units of eV)

$$\begin{pmatrix} -7.2 & -1.0 & -0.8 \\ -1.0 & -10.4 & 0 \\ -0.8 & 0 & -8.4 \end{pmatrix}$$

The matrix of eigenvectors which diagonalizes this matrix is found using mathematical software as

$$\begin{pmatrix} 0.294 & 0.349 & 0.890 \\ 0.950 & -0.206 & -0.233 \\ 0.102 & 0.914 & -0.392 \end{pmatrix}$$

The entries in each column of this matrix above give the coefficients of the atomic orbitals for the corresponding molecular orbital; the columns correspond to the molecular orbitals in the same order as the energies are quoted above. For example the molecular orbital with $E_1 = -10.7$ eV is $\Psi_1 = 0.294\,\psi_A + 0.950\,\psi_B + 0.102\,\psi_C$.

(ii) If the overlap integrals S_{AB} and S_{AC} are set to 0.2, the secular determinant becomes

$$\begin{vmatrix} (-7.2\text{ eV}) - E & (-1.0\text{ eV}) - 0.2E & (-0.8\text{ eV}) - 0.2E \\ (-1.0\text{ eV}) - 0.2E & (-10.4\text{ eV}) - E & 0 \\ (-0.8\text{ eV}) - 0.2E & 0 & (-8.4\text{ eV}) - E \end{vmatrix}$$
$$= (-0.92)E^3 - (24.528\text{ eV})E^2 - (214.392\text{ eV}^2)E - (613.936\text{ eV}^3)$$

The energies are found by setting the polynomial to zero and then finding the roots using mathematical software. The three roots give the energies $\boxed{E_1 = -10.9\ \text{eV}}$, $\boxed{E_2 = -8.86\ \text{eV}}$ and $\boxed{E_3 = -6.93\ \text{eV}}$. It is seen that the energies are not greatly affected by the including the effect of non-zero overlap.

When the overlap is non-zero, it is not quite so straightforward to find the coefficients of the molecular orbitals. It is necessary to return to the secular equations and, for each energy, to solve them to find the coefficients.

9E Molecular orbital theory: polyatomic molecules

Answer to discussion questions

D9E.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. The 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 of the π electrons between the conjugated molecule with *n* π bonds and the energy of *n* ethene molecules, each of which has one π 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.

D9E.4 Gaussian type orbitals centred on atomic nuclei have the advantage over hydrogenic 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 can be reduced to integrals over two different centres, which are much easier to evaluate numerically; see Section 9E.3(a) on page 378.

Solutions to exercises

E9E.1(b) (i) Without taking the Hückel approximations, the secular determinant of the H_4 molecule is written as

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} - S_{12}E & \beta_{13} - S_{13}E & \beta_{14} - S_{14}E \\ \beta_{21} - S_{21}E & \alpha_2 - E & \beta_{23} - S_{23}E & \beta_{24} - S_{24}E \\ \beta_{31} - S_{31}E & \beta_{32} - S_{32}E & \alpha_3 - E & \beta_{34} - S_{34}E \\ \beta_{41} - S_{41}E & \beta_{42} - S_{42}E & \beta_{43} - S_{43}E & \alpha_4 - E \end{vmatrix}$$

where α_n is the Coulomb integral of the orbital on atom n, β_{nm} is the resonance integral accounting for the interaction between the orbitals on atoms n and m, E is the energy of the molecular orbital and S_{nm} is the overlap integral between the orbtials on atoms n and m.

Within the Hückel approximations the energy of the basis atomic orbitals is taken to be independent of the position of the corresponding atoms in the molecule, therefore all Coulomb integrals are set equal to α (given that there is only one type of basis atomic orbital and only one type of atom is involved in the problem). Interaction between orbitals on non-neighbouring atoms is neglected, that is $\beta_{nm} = 0$ if atoms n and m are not neighbouring. All other resonance integrals are set equal to β. The overlap between atomic orbitals is also neglected, therefore all overlap integrals S_{nm} with $n \neq m$ are set to zero. Hence the secular determinant for linear H_4 is

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix}$$

(ii) In this case hydrogen atoms 1 and 4 are neighbours, therefore $\beta_{14} = \beta$, and the secular determinant is

$$\begin{vmatrix} \alpha - E & \beta & 0 & \beta \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \beta & 0 & \beta & \alpha - E \end{vmatrix}$$

E9E.2(b) (i) The energies of the π molecular orbitals of the allyl system are calculated in *Example* 9E.1 on page 374 as $E = \alpha + 1.41\beta, \alpha, \alpha - 1.41\beta$. Note that α and β are negative quantities, therefore the molecular orbital lowest in energy is the one with energy of $\alpha + 1.41\beta$. The allyl radical has three π electrons and therefore the ground state ic configuration is $\psi_1^2\psi_2^1$. The π-electron binding energy is $E_\pi = 2(\alpha + 1.41\beta) + \alpha = \boxed{3\alpha + 2.82\beta}$.

(ii) The energies of the π molecular orbitals of cyclobutadiene are calculated in *Example* 9E.2 on page 376 as $E = \alpha + 2\beta, \alpha, \alpha, \alpha - 2\beta$. In the cyclobutadiene cation there are three π electrons and the ground state electronic configuration is $\psi_1^2\psi_2^1$. The π-electron binding energy is $E_\pi = 2(\alpha + 2\beta) + \alpha = \boxed{3\alpha + 4\beta}$.

E9E.3(b) The delocalization energy is the energy difference between the π-electron binding energy E_π and the hypothetical π-electron binding energy if the given species had isolated π bonds; $E_{\text{deloc}} = E_\pi - N_\pi(\alpha + \beta)$, where N_π is the number of π electrons. The π-bond formation energy is defined in [9E.12–*376*] as $E_{\text{bf}} = E_\pi - N_\pi\alpha$.

(i) The allyl radical has 3 π electrons and its π-electron binding energy is calculated in *Exercise* E9E.2(b) as $E_\pi = 3\alpha + 2.82\beta$. Therefore $E_{\text{deloc}} = (3\alpha + 2.82\beta) - 3(\alpha + \beta) = \boxed{-0.18\beta}$ and $E_{\text{bf}} = (3\alpha + 2.82\beta) - 3\alpha = \boxed{2.82\beta}$. The calculation of E_{deloc} does not quite work in this case because the third electron in the allyl radical would not be placed in a localized π bonding orbital but in a out-of-plane p orbital, with energy α. The localized energy is therefore $2(\alpha + \beta) + \alpha = 3\alpha + 2\beta$ and hence $E_{\text{deloc}} = 0.82\beta$.

(ii) The cyclobutadiene cation has 3 π electrons and its π-electron binding energy is calculated in *Exercise* E9E.2(b) as $E_\pi = 3\alpha + 4\beta$. Therefore $E_{\text{deloc}} = (3\alpha + 4\beta) - 3(\alpha + \beta) = \boxed{\beta}$ and $E_{\text{bf}} = (3\alpha + 4\beta) - 3\alpha = \boxed{4\beta}$.

E9E.4(b) (i) Following the same logic as in *Exercise* E9E.1(b) and applying the Hückel approximations as explained there the secular determinant for azulene is written as (the numbers in bold refer to the numbering of the carbon atoms in the molecule)

$$\begin{array}{c|cccccccccc|}
 & \mathbf{1} & \mathbf{2} & \mathbf{3} & \mathbf{4} & \mathbf{5} & \mathbf{6} & \mathbf{7} & \mathbf{8} & \mathbf{9} & \mathbf{10} \\
\mathbf{1} & \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta \\
\mathbf{2} & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\mathbf{3} & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 & 0 \\
\mathbf{4} & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 & \beta \\
\mathbf{5} & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 \\
\mathbf{6} & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 \\
\mathbf{7} & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 \\
\mathbf{8} & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 \\
\mathbf{9} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta \\
\mathbf{10} & \beta & 0 & 0 & \beta & 0 & 0 & 0 & 0 & \beta & \alpha-E
\end{array}$$

(ii) Similarly for acenaphthylene

$$\begin{array}{c|cccccccccccc|}
 & \mathbf{1} & \mathbf{2} & \mathbf{3} & \mathbf{4} & \mathbf{5} & \mathbf{6} & \mathbf{7} & \mathbf{8} & \mathbf{9} & \mathbf{10} & \mathbf{11} & \mathbf{12} \\
\mathbf{1} & \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & 0 \\
\mathbf{2} & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\mathbf{3} & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\mathbf{4} & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 & 0 & \beta \\
\mathbf{5} & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 & 0 \\
\mathbf{6} & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 \\
\mathbf{7} & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 \\
\mathbf{8} & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & \beta \\
\mathbf{9} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 \\
\mathbf{10} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 \\
\mathbf{11} & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta \\
\mathbf{12} & 0 & 0 & 0 & \beta & 0 & 0 & 0 & \beta & 0 & 0 & \beta & \alpha-E
\end{array}$$

E9E.5(b) To calculate the π-electron binding energy of the given systems, it is necessary to calculate the energies of the occupied molecular orbitals. This is done by diagonalising the hamiltonian matrix: the diagonal elements of the resulting matrix are the energies of the molecular orbitals. The hamiltonian matrix has the same form as the secular matrix except that the diagonal elements are α instead of $\alpha - E$. Alternatively, the energies can be found my finding the eigenvalues of the hamiltonian matrix, or by multiplying out the secular determinant, setting the resulting polynomial in E to zero and then finding the roots. Mathematical software is needed for all of these approaches.

The secular determinants are derived in *Exercise* E9E.4(b), and from these the form of the hamiltonain matrix is easily found.

(i) The entries of the diagonalized hamiltonian matrix for azulene are $E = \alpha + 2.31\beta$, $\alpha + 1.65\beta$, $\alpha + 1.36\beta$, $\alpha + 0.887\beta$, $\alpha + 0.477\beta$, $\alpha - 0.400\beta$, $\alpha - 0.738\beta$, $\alpha - 1.58\beta$, $\alpha - 1.87\beta$, $\alpha - 2.10\beta$. The π system of azulene accommodates 10 electrons, therefore the 5 lowest energy π molecular orbitals are filled. The π-electron binding energy is therefore $E_\pi = 2(\alpha + 2.31\beta) + 2(\alpha + 1.65\beta) + 2(\alpha + 1.36\beta) + 2(\alpha + 0.887\beta) + 2(\alpha + 0.477\beta) = \boxed{10\alpha + 13.4\beta}$.

(ii) The entries of the diagonalized hamiltonian matrix for acenaphthylene are $E = \alpha + 2.47\beta$, $\alpha + 1.69\beta$, $\alpha + 1.68\beta$, $\alpha + \beta$, $\alpha + 0.831\beta$, $\alpha + 0.638\beta$, $\alpha - 0.285\beta$, $\alpha - \beta$, $\alpha - 1.31\beta$, $\alpha - 1.43\beta$, $\alpha - 1.92\beta$, $\alpha - 2.36\beta$. The π system of acenaphthylene accommodates 12 electrons, therefore the 6 lowest energy π molecular orbitals are filled. The π-electron binding energy is therefore $E_\pi = 2(\alpha + 2.47\beta) + 2(\alpha + 1.69\beta) + 2(\alpha + 1.68\beta) + 2(\alpha + \beta) + 2(\alpha + 0.831\beta) + 2(\alpha + 0.638\beta) = \boxed{12\alpha + 16.6\beta}$.

E9E.6(b) The hamiltonian for a single electron in H_2^+ is given by [9B.1–*351*]. It has a kinetic energy term, $\hat{T} = -(\hbar^2/2m_e)\nabla_1^2$, and a potential energy term, $\hat{V}$. The species LiH^{2+} has two electrons, therefore the kinetic energy term is written as

$$\hat{T} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2$$

The energy of interaction between an electron and a nucleus with charge number Z at distance r is given by $-Ze^2/4\pi\varepsilon_0 r$. The potential energy operator consists of terms for each electron interacting with the H nuclues ($Z = 1$) and the Li nucleus ($Z = 3$)

$$\hat{V} = -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{1H}} + \frac{1}{r_{2H}} + \frac{3}{r_{1Li}} + \frac{3}{r_{2Li}} - \frac{1}{r_{12}}\right)$$

The first term represent the interaction between electron 1 and the H nucleus, and the second is for electron 2 with the same nucleus. The third and fourth terms represent the interactions of the two electrons with the Li nucleus. The last term accounts for the repulsion between the two electrons. The complete electronic hamiltonian is $\hat{H}_{elec} = \hat{T} + \hat{V}$. Because only the electronic hamiltonian is required, the repulsion between the two nuclei is not included.

Solutions to problems

P9E.2 (a) Benzene has six carbon atoms in the ring, $N = 6$, therefore the values k can take are $k = 0, \pm1, \pm2, +3$ and hence the corresponding energies are $E_0 = \alpha + 2\beta$, $E_{\pm1} = \alpha + \beta$, $E_{\pm2} = \alpha - \beta$, and $E_{+3} = \alpha - 2\beta$.

Cyclooctatetraene has eight carbon atoms in the ring, $N = 8$, therefore the values k can take are $k = 0, \pm1, \pm2, \pm3, +4$ and hence the corresponding energies are $E_0 = \alpha + 2\beta$, $E_{\pm1} = \alpha + 1.41\beta$, $E_{\pm2} = \alpha$, $E_{\pm3} = \alpha - 1.41\beta$, and $E_{+4} = \alpha - 2\beta$.

In both cases the molecular orbitals come in degenerate pairs, except for the lowest energy, most bonding molecular orbital, and for the highest energy, most antibonding molecular orbital.

(b) The delocalisation energy is given by $E_{\text{deloc}} = E_\pi - N_\pi(\alpha+\beta)$, where N_π is the number of π electrons. In the ground state of benzene, two electrons occupy the orbital with energy E_0 and four electrons occupy the degenerate pair of orbitals with energy $E_{\pm 1}$. Hence the π-electron binding energy of benzene is $E_\pi = 2E_0 + 4E_{\pm 1} = 2(\alpha+2\beta) + 4(\alpha+\beta) = 6\alpha + 8\beta$. Therefore the delocalization energy is $E_{\text{deloc}} = 6\alpha + 8\beta - 6(\alpha+\beta) = \boxed{2\beta}$.

To calculate the delocalization energy of hexatriene, the energies of the occupied molecular orbitals are required. The six electrons in the π system of hexatriene occupy the three lowest energy orbitals, therefore the π-electron binding energy is

$$\begin{aligned} E_\pi &= 2E_1 + 2E_2 + 2E_3 \\ &= 2[\alpha + 2\beta\cos(\pi/7)] + 2[\alpha + 2\beta\cos(2\pi/7)] + 2[\alpha + 2\beta\cos(3\pi/7)] \\ &= 6\alpha + (6.98...)\beta \end{aligned}$$

Hence the delocalization energy of hexatriene is $E_{\text{deloc}} = 6\alpha + (6.98...)\beta - 6(\alpha+\beta) = \boxed{0.99\beta}$. The lowering in energy as a result of delocalization in benzene in greater than in hexatriene, consistent with the 'aromatic' system in benzene.

(c) The π-electron binding energy in cyclooctatetraene is

$$E_\pi = 2E_0 + 4E_{\pm 1} + 2E_{\pm 2} = 2(\alpha + 2\beta) + 4(\alpha + 1.41\beta) + 2\alpha = 8\alpha + 9.64\beta$$

The delocalization energy is therefore $E_{\text{deloc}} = 8\alpha + 9.64\beta - 8(\alpha+\beta) = \boxed{1.64\beta}$.

The π-electron binding energy in octatetraene is

$$\begin{aligned} E_\pi &= 2E_1 + 2E_2 + 2E_3 + 2E_4 \\ &= 2[\alpha + 2\beta\cos(\pi/9)] + 2[\alpha + 2\beta\cos(2\pi/9)] \\ &\quad + 2[\alpha + 2\beta\cos(3\pi/9)] + 2[\alpha + 2\beta\cos(4\pi/9)] \\ &= 8\alpha + (9.51...)\beta \end{aligned}$$

Therefore the delocalization energy is $E_{\text{deloc}} = 8\alpha + (9.51...)\beta - 8(\alpha+\beta) = \boxed{1.52\beta}$. The difference in delocalization energies between cyclooctatetraene and octatetraene is much smaller than the difference in the values for benzene and hexatriene. This is taken as an result of benzene being 'aromatic' in contrast to cyclooctatetraene which is sometimes described as 'antiaromatic'.

P9E.4 Within the Hückel approximations, the secular determinant of ethene is

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix}$$

The hamiltonian matrix is of the same form, but with diagonal elements α

$$H = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} = \alpha\mathbf{1} + \beta\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

As explained in the text, in order to find the energies it is sufficient to diagonalize the matrix on the right, and this is convenient because most mathematical software packages are only able to diagonalize numerical matrices. The matrix which achieves the diagonalization is

$$\begin{pmatrix} 0.707 & 0.707 \\ 0.707 & -0.707 \end{pmatrix}$$

and the diagonal elements are ±1.00, implying that the energies are $\alpha \pm 1.00\,\beta$.

The secular determinant and hamiltonian matrix for butadiene are

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} \qquad H = \alpha\mathbf{1} + \beta \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

The matrix which achieves the diagonalization is

$$\begin{pmatrix} 0.372 & 0.602 & 0.602 & 0.372 \\ 0.602 & 0.372 & -0.372 & -0.602 \\ 0.602 & -0.372 & -0.372 & 0.602 \\ 0.372 & -0.602 & 0.602 & -0.372 \end{pmatrix}$$

The diagonal elements are ±1.62, and ±0.618, implying that the energies are $\alpha \pm 1.62\,\beta$ and $\alpha \pm 0.618\,\beta$.

The secular determinant and hamiltonian matrix for hexatriene are

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 & 0 \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ 0 & 0 & 0 & 0 & \beta & \alpha - E \end{vmatrix} \qquad H = \alpha\mathbf{1} + \beta \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix}$$

This is diagonalized by the matrix

$$\begin{pmatrix} 0.232 & 0.418 & 0.521 & 0.521 & 0.418 & 0.232 \\ 0.418 & 0.521 & 0.232 & -0.232 & -0.521 & -0.418 \\ 0.521 & 0.232 & -0.418 & -0.418 & 0.232 & 0.521 \\ 0.521 & -0.232 & -0.418 & 0.418 & 0.232 & -0.521 \\ 0.418 & -0.521 & 0.232 & 0.232 & -0.521 & 0.418 \\ 0.232 & -0.418 & 0.521 & -0.521 & 0.418 & -0.232 \end{pmatrix}$$

The diagonal elements are ±1.80, ±1.25, and ±0.445, implying that the energies are $\alpha \pm 1.80\,\beta$, $\alpha \pm 1.25\,\beta$, and $\alpha \pm 0.445\,\beta$

The secular determinant and hamiltonian matrix for octatetraene are

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 & 0 \\ \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 \\ 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 \\ 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 \\ 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 \\ 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 \\ 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta \\ 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E \end{vmatrix} \qquad H = \alpha\mathbf{1}+\beta\begin{pmatrix} 0&1&0&0&0&0&0&0 \\ 1&0&1&0&0&0&0&0 \\ 0&1&0&1&0&0&0&0 \\ 0&0&1&0&1&0&0&0 \\ 0&0&0&1&0&1&0&0 \\ 0&0&0&0&1&0&1&0 \\ 0&0&0&0&0&1&0&1 \\ 0&0&0&0&0&0&1&0 \end{pmatrix}$$

This is diagonalized by the matrix

$$\begin{pmatrix} 0.161 & 0.303 & 0.408 & 0.464 & 0.464 & 0.408 & 0.303 & 0.161 \\ 0.303 & 0.464 & 0.408 & 0.161 & -0.161 & -0.408 & -0.464 & -0.303 \\ 0.408 & 0.408 & 0 & -0.408 & -0.408 & 0 & 0.408 & 0.408 \\ 0.464 & -0.161 & -0.408 & -0.303 & 0.303 & 0.408 & -0.161 & -0.464 \\ 0.464 & -0.161 & -0.408 & 0.303 & 0.303 & -0.408 & -0.161 & 0.464 \\ 0.408 & -0.408 & 0 & 0.408 & -0.408 & 0 & 0.408 & -0.408 \\ 0.303 & -0.464 & 0.408 & -0.161 & -0.161 & 0.408 & -0.464 & 0.303 \\ 0.161 & -0.303 & 0.408 & -0.464 & 0.464 & -0.408 & 0.303 & -0.161 \end{pmatrix}$$

The diagonal elements are ±1.88, ±1.53, ±1.00, and ±0.347, implying that the energies are $\alpha \pm 1.88\,\beta$, $\alpha \pm 1.53\,\beta$, $\alpha \pm 1.00\,\beta$, and $\alpha \pm 0.347\,\beta$.

Each column of the diagonalization matrices gives the coefficients of the atomic orbitals for the corresponding molecular orbitals. For each molecule, the first column gives the coefficients for the lowest energy π molecular orbital. All of these coefficients have positive signs, therefore the lowest energy π molecular orbital has no nodes and the lowest energy π molecular orbital is delocalized over all carbon atoms in the chain. On going to successive columns to the right the energy of the molecular orbital increases and the number of sign changes within a column increases. These sign changes correspond to nodes in the molecular molecular orbitals.

P9E.6 The bonding and antibonding effects of the HOMO and LUMO have to be considered to predict the changes in bond strength that accompany the transition. The ground state electron configuration of butadiene is $1\pi^2\,2\pi^2$, therefore the HOMO of butadiene is the 2π molecular orbital. Looking at Fig. 9E.2 on page 376, this molecular orbital is bonding between carbon atoms C1 and C2 and likewise between C3 and C4, but antibonding between C2 and C3. The LUMO of butadiene is the 3π molecular orbital, which is antibonding between carbon atoms C1 and C2 and likewise between C3 and C4, but bonding between C2 and C3. Therefore promotion of an electron from the HOMO to the LUMO weakens the bonding between C1 and C2 and likewise between C3 and C4, but strengthens the bonding between C2 and C3.

The HOMO of benzene is the e_{1g} orbital and the LUMO is the e_{2u} orbital. One of the e_{1g} orbitals, the one on the right in Fig. 9E.4 on page 377, is bonding between two pairs of neighbouring carbon atoms, and nonbonding between all other pairs of neighbours. One of the e_{2u} orbitals, the one on the left in Fig. 9E.4 on page 377, is antibonding between the same two pairs of neighbouring carbon atoms as above, and nonbonding between all other pairs of neighbours. Therefore promotion of an electron between these two orbitals decreases the bond strength between these two pairs of neighbours, and leaves the bond strength unchanged between all other pairs.

However, the situation is more complicated due to the degeneracy of the HOMO and LUMO. Promotion of an electron between all possible pairs of HOMO and LUMO have to be considered together. Due to the six-fold rotational symmetry of benzene, the bond strength between each pair of atoms is expected to change the same way. The HOMO of benzene is overall bonding, whereas the LUMO is antibonding, therefore promotion of an electron from the HOMO to the LUMO will, in fact, decrease the bond strength between all pairs of neighbouring carbon atoms in the molecule.

P9E.8 To estimate if the given species are stable with respect to dissociation into smaller entities, the standard internal energy change for each dissociation reaction is calculated and its sign examined. This change in internal energy is given by the change in the total electron binding energies (E_{tot}).

The energies of the molecular orbitals are calculated using the expression given in *Problem* P9E.2. The occupied orbitals are identified and with this information it is then possible to calculate the total electron binding energy of the hydrogen ring compounds, as in the table below (VE is the number of valence electrons)

species	VE	energies of occupied MOs	E_{tot}
H_4	4	$\alpha + 2\beta$, α (degenerate)	$4\alpha + 4\beta$
H_5^+	4	$\alpha + 2\beta$, $\alpha + 0.618\beta$ (degenerate)	$4\alpha + 5.24\beta$
H_5^-	6	$\alpha + 2\beta$, $\alpha + 0.618\beta$ (degenerate)	$6\alpha + 6.47\beta$
H_6	6	$\alpha + 2\beta$, $\alpha + \beta$ (degenerate)	$6\alpha + 8\beta$
H_7^+	6	$\alpha + 2\beta$, $\alpha + 1.25\beta$ (degenerate)	$6\alpha + 9\beta$
H_2	2	$\alpha + \beta$	$2\alpha + 2\beta$
H_3^+	2	$\alpha + 2\beta$	$2\alpha + 4\beta$
H^-	2	α	2α

The table includes some other species of interest in these calculations. Note that in *Problem* P9E.7 it is shown that H_3^+ is lower in energy than $H^+ + H_2$, therefore the positively charged hydrogen ring compounds are more likely to dissociate into H_2 and H_3^+, than to H_2 and H^+. The negatively charged hydrogen ring compounds are likely to give H_2 and H^- as dissociation products.

The stability of each species is examined in turn.

(i) The dissociation of H_4 is likely to give two H_2 molecules, $H_4 \longrightarrow 2\,H_2$. Therefore $\Delta_r U^\ominus = E_{\text{tot}}(\text{products}) - E_{\text{tot}}(\text{reactants}) = 2(2\alpha + 2\beta) - (4\alpha +$

$4\beta) = 0$. This means that there is no change in energy on dissociation, but the process is likely to occur because of the increase in entropy that will result.

(ii) The most likely dissociation process for H_5^+ is $H_5^+ \longrightarrow H_2 + H_3^+$. Therefore $\Delta_r U^\ominus = (2\alpha + 2\beta) + (2\alpha + 4\beta) - (4\alpha + 5.24\beta) = 0.76\beta$. This value is negative, hence H_5^+ is likely to be unstable with respect to H_2 and H_3^+.

(iii) The most likely dissociation process for H_5^- is $H_5^- \longrightarrow 2\,H_2 + H^-$. Therefore $\Delta_r U^\ominus = 2(2\alpha + 2\beta) + (2\alpha) - (6\alpha + 6.47\beta) = -0.47\beta$. This value is positive, hence H_5^- is likely to be stable with respect to H_2 and H^-.

(iv) The most likely dissociation process for H_6 is $H_6 \longrightarrow 3\,H_2$. Therefore $\Delta_r U^\ominus = 3(2\alpha + 2\beta) - (6\alpha + 8\beta) = -2\beta$. This value is positive, hence H_6 is likely to be stable with respect to H_2.

(v) The most likely dissociation process for H_7^+ is $H_7^+ \longrightarrow 2\,H_2 + H_3^+$. Therefore $\Delta_r U^\ominus = 2(2\alpha + 2\beta) + (2\alpha + 4\beta) - (7\alpha + 9\beta) = -\beta$. This value is positive, hence H_7^+ is likely to be stable with respect to H_2 and H_3^+.

P9E.10 Data for ethanol (C1 is the oxygen-bearing carbon):

ethanol	AM1*	PM3*	experimental
C1–C2/pm	151.2	151.8	153.0
C1–O/pm	142.0	141.0	142.5
C1–H/pm	112.4	110.8	110
C2–H/pm	111.6	109.7	109
O–H/pm	96.4	94.7	97.1
C2–C1–O/°	107.34	107.81	107.8
C1–O–H/°	106.65	106.74	
H-C1–H/°	108.63	106.98	
H–C2–H/°	108.24	107.24	
$\Delta_f H^\ominus$(g) / kJ mol^{-1}	−262.18	−237.87	−235.10
dipole/D	1.55	1.45	1.69

Both methods give fair agreement with experiment but PM3 gives a better estimate of formation enthalpy.

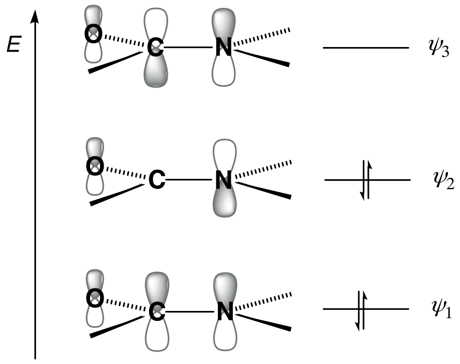
Data for 1,4-dichlorobenzene (C1 is a chlorine-bearing carbon):

1,4-dichlorobenzene	AM1*	PM3*	experimental
C1–C2/pm	139.9	139.4	138.8
C2–C3/pm	139.3	138.9	138.8
C1–Cl/pm	169.9	168.5	173.9
C2–H/pm	110.1	109.6	
Cl–C1–C2/°	119.71	119.42	
C1–C2–H/°	120.40	120.06	
Cl–C1–C2–H/°	0.00	0.00	
$\Delta_f H^\ominus(g)$ / kJ mol^{-1}	33.36	42.31	24.6
dipole/D	0.00	0.00	0.0

Both methods give poor agreement with the experimental formation enthalpy but both methods are in broad agreement with experimental structural values.

Integrated activities

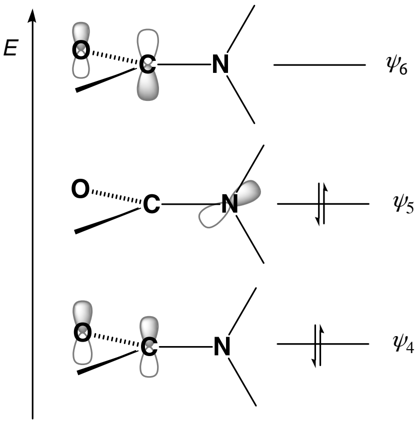
I9.2 (a) All the coefficients of the atomic orbitals for the molecular orbital ψ_1 are positive, therefore it is a fully bonding molecular orbital. The molecular orbital ψ_3 has alternating positive, negative and then positive coefficients, therefore it is a fully antibonding molecular orbital. The molecular orbital ψ_2 is non-bonding, with no interaction between atomic orbitals on adjacent atoms.



(b) The oxygen, carbon and nitrogen atoms all contribute one p orbital (the $2p_z$ atomic orbital) to the π system, therefore they must be sp^2 hybridized. All the σ bonds to an sp^2 hybridized atom must lie in the same plane, therefore all the atoms connected to the oxygen, carbon and nitrogen atoms must lie in the same plane together with the oxygen, carbon and the nitrogen atoms.

(c) The molecular orbital energy level diagram is shown in part (a). There are four electrons in the π system of the peptide link. Two electrons come from the formal π bond between the oxygen and the carbon atoms, and two from the formal lone pair on the nitrogen atom. Hence the two lowest energy molecular orbitals, that is the bonding and the non-bonding molecular orbitals, are filled.

(d) This picture of bonding in the peptide group does not invoke delocalization. The lowest energy, bonding molecular orbital, ψ_4, represents a localized π bond between the oxygen and the carbon atoms. According to this representation, the next highest energy molecular orbital, ψ_5, is the lone pair on nitrogen, a non-bonding molecular orbital. The highest energy molecular orbital, ψ_6 is the antibonding π^* molecular orbital between the oxygen and the carbon atoms. The four electrons in the π system occupy the two lowest energy molecular orbitals.



(e) Assume that the oxygen, carbon and nitrogen atoms are sp^2 hybridized. The p orbital on nitrogen is in the plane in which the oxygen, carbon and their neighbouring atoms are, therefore the two other atoms connected to nitrogen must lie in a plane perpendicular to this one. Therefore the oxygen, carbon, nitrogen and the neighbouring atoms cannot all lie in the same plane.

(f) The bonding molecular orbital ψ_1 must be lower in energy than ψ_4, because ψ_1 extends over three atoms and is bonding between two pairs of atoms, whereas ψ_4 extends over two atoms only and is bonding between one pair of atoms only. Following the same logic, ψ_3 must be higher in energy than ψ_6. Disregarding the small difference in the Coulomb integral of nitrogen and oxygen, the nonbonding orbitals have approximately the same energies.

(g) Only the two lowest energy molecular orbitals are occupied in either case. Occupation of the non-bonding orbital does not result in any difference in the π-electron binding energies. The bonding molecular orbital in the case of the planar peptide link is lower in energy, hence occupation of this orbital results in greater π-electron binding energy when compared with the occupation of the bonding molecular orbital in the non-planar peptide link. Therefore planar geometry is the lower energy conformation of the peptide link.

I9.4 The lower the energy of the vacant orbital, the lower the energy cost of transferring an electron into that orbital. Hence the tendency of the species to accept electrons is greater, and so the standard reduction potential of the given species is also greater. Therefore lower LUMO energy leads to greater standard reduction potential.

I9.6 (a) The table below lists the energy of the HOMO and the LUMO of the relevant molecules calculated using the PM3 method. The energy gap ΔE between the HOMO and LUMO is given in eV, as well as the corresponding wavenumber of the transition.

molecule	E_{LUMO} /eV	E_{HOMO} /eV	ΔE /eV	$(\Delta E/hc)$ $/(10^4\ \text{cm}^{-1})$	$\tilde{\nu}_{\text{obs}}$ $/\text{cm}^{-1}$
C_2H_4	1.23	−10.6	11.8	9.52	61500
C_4H_6	0.263	−9.47	9.73	7.85	46080
C_6H_8	−0.249	−8.90	8.65	6.98	39750
C_8H_{10}	−0.557	−8.58	8.02	6.47	32900
$C_{10}H_{12}$	−0.756	−8.38	7.62	6.15	

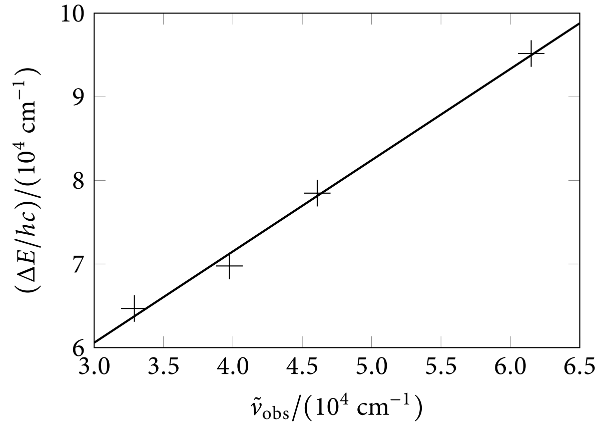


Figure 9.9

(b) A plot of the predicted frequency of the transitions against the observed frequencies is shown in Fig. 9.9. The data points are of a good fit to a straight line. The equation of the best fit line is

$$(\Delta E/hc)/(10^4\ \text{cm}^{-1}) = 1.09\,\tilde{\nu}_{\text{obs}}/(10^4\ \text{cm}^{-1}) + 2.78$$

(c) The HOMO–LUMO energy gap for decapentaene calculated using the PM3 method corresponds $(\Delta E/hc)/(10^4\ \text{cm}^{-1}) = 6.15$, therefore the predicted wavenumber of the transition is given by

$$\tilde{\nu}_{\text{obs}}/(10^4\ \text{cm}^{-1}) = \frac{6.15 - 2.78}{1.09} = 3.09$$

hence the transition is predicted to be at $\boxed{3.09 \times 10^4\ \text{cm}^{-1}}$.

(d) The computational method used in this problem adequately predicts the trend in the transition wavenumber but performs poorly in predicting its absolute value; an error of about 30000 cm^{-1} is typical. The calibration procedure is used to correct the predicted transition wavenumber so that it agrees as closely as possible with the observed values as possible.

10

Molecular symmetry

10A Shape and symmetry

Answers to discussion questions

D10A.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

D10A.4 A molecule may be chiral (optically active) only if it does not possess an axis of improper rotation, S_n.

Solutions to exercises

E10A.1(b) From the table in Section 10A.2(c) on page 393 a molecule belonging to the point group D_{3h}, such as BF_3 (Fig. 10.1), possesses

- the $\boxed{\text{identity } E}$
- a $\boxed{C_3 \text{ axis}}$ perpendicular to the plane of the molecule and passing through the boron atom
- three $\boxed{C_2 \text{ axes}}$, each passing through the boron and one of the fluorine atoms
- a $\boxed{\text{horizontal mirror mirror plane } \sigma_h}$ in the plane of the molecule

In addition

- the elements C_3 and σ_h jointly imply the presence of an $\boxed{S_3}$ axis coincident with the C_3 axis
- the presence of the C_3 axis and three C_2 axes jointly imply the presence of three $\boxed{\text{vertical mirror planes } \sigma_v}$, each containing the C_3 axis and passing through the boron and one of the fluorines

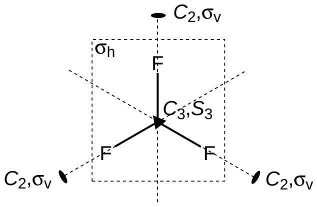


Figure 10.1

E10A.2(b) The point group of the *trans*-difluoroethene molecule is identified by following the flow diagram in Fig. 10A.7 on page 391. Firstly, the molecule is not linear, which leads to the question "*Two or more* C_n, $n > 2$?" There is one C_2 axis perpendicular to the plane of the molecule, but no higher order axes, so the answer to this question is 'No'. However the fact that it does have a C_2 axis means that the answer to the next question "C_n?" is 'Yes'.

This leads to the question "*Select* C_n *with the highest* n*; then, are there* nC_2 *perpendicular to* C_n?" The answer to this is 'No' because the C_2 axis identified so far is the only C_n axis possessed by the molecule; there are therefore no C_2 axes perpendicular to it.

This leads to the question "σ_h?" to which the answer is 'Yes' because there is a horizontal mirror plane in the plane of the molecule, perpendicular to the C_2 axis. This leads to the result C_{nh}, and because the C_n axis with highest n in this molecule is C_2, it follows that the point group is $\boxed{C_{2h}}$.

Alternatively, the point group may be identified from the table in Fig. 10A.8 on page 391 by drawing an analogy between the shape of the *trans*-difluoroethene molecule and the shape that appears in the in the box corresponding to C_{2h}.

From the table in Section 10A.2(c) on page 393 a molecule belonging to the point group C_{2h} such as *trans*-difluoroethene posseses

- the $\boxed{\text{identity } E}$
- a $\boxed{C_2 \text{ axis}}$, perpendicular to the plane of the molecule and passing through the midpoint of the C=C double bond.
- a $\boxed{\text{horizontal mirror plane } \sigma_h}$ in the plane of the molecule

In addition

- The C_2 and σ_h elements jointly imply a $\boxed{\text{centre of inversion } i}$, which lies at the midpoint of the C=C double bond.

These symmetry elements are shown in Fig. 10.2.

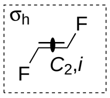


Figure 10.2

E10A.3(b) The objects to be assigned are shown in Fig. 10.3. For clarity not all symmetry elements are shown.

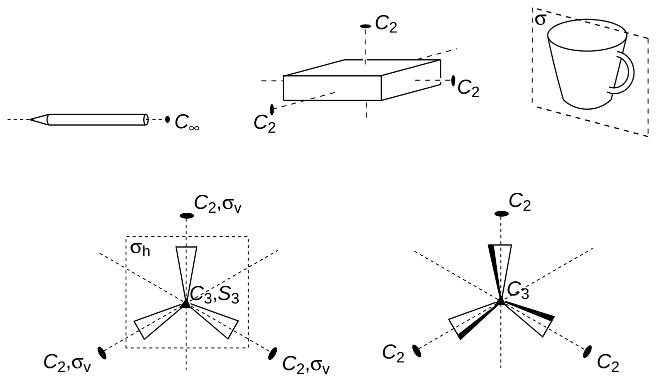


Figure 10.3

(i) A sharpened cylindrical pencil is assigned a point group using the flow diagram in Fig. 10A.7 on page 391, assuming that the main part of the pencil is a perfect cylinder with no lettering or other pattern and that the sharpened tip is a perfect cone. It is linear, in the sense that rotation by any angle around the long axis of the pencil is a symmetry operation so that the pencil possesses a C_∞ axis. However, unless it has been sharpened at both ends, it does not possess a centre of inversion i. From the flow diagram this establishes its point group as $\boxed{C_{\infty\text{v}}}$.

Alternatively the point group may be identified from the summary table in Fig. 10A.8 on page 391 by drawing an analogy between the shape of the pencil and the cone in the cell of the table corresponding to $C_{\infty\text{v}}$.

(ii) Modelling the box as a cuboid with length, width and height all different and ignoring any lettering, pattern, and any means of opening the box, its point group is established using the flow diagram in Fig. 10A.7 on page 391. It has three C_2 axes, each passing through the centre of a pair of opposite faces. It also has three mirror planes, one perpendicular to each of the three C_2 axes. Using the flow diagram this establishes its point group as $\boxed{D_{2\text{h}}}$.

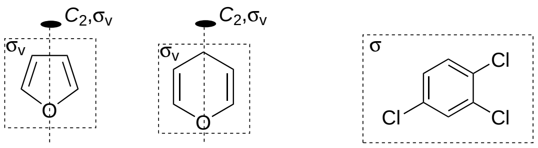
Alternatively the point group may be identified from the summary table in Fig. 10A.8 on page 391 by noting that the symmetry of the box is the same as that of the rectangle in the cell corresponding to $D_{2\text{h}}$.

(iii) An unpatterned coffee mug with a handle has a plane of symmetry that contains the handle, but no other symmetry elements apart from the identity. Using the flow diagram in Fig. 10A.7 on page 391 this identifies its point group as $\boxed{C_\text{s}}$.

(iv) The described propeller has a C_3 axis along the axis of the propeller and a σ_h mirror plane perpendicular to this which contains the three blades. It also has three C_2 axes perpendicular to the C_3 axis, each passing through one of the blades, as well as three σ_v mirror planes and an S_3 axis. Using the flow diagram in Fig. 10A.7 on page 391 these symmetry elements establish the point group as $\boxed{D_{3h}}$.

(v) If the blades on the propeller are twisted then the C_3 axis and the three C_2 axes are retained but the there are no longer any mirror planes. Using the flow diagram in Fig. 10A.7 on page 391 the point group is therefore $\boxed{D_3}$.

E10A.4(b) The molecules to be assigned are shown in Fig. 10.4. For clarity not all symmetry elements are shown.



Furan $\boxed{C_{2v}}$ γ-pyran $\boxed{C_{2v}}$ 1,2,4-trichlorobenzene $\boxed{C_s}$

Figure 10.4

In each case the point group is identified using the flow diagram in Fig. 10A.7 on page 391 having identified the symmetry elements, or by drawing an analogy with one of the shapes in the summary table in Fig. 10A.8 on page 391.

(i) Furan possesses the symmetry elements

- the $\boxed{\text{identity, } E}$
- a $\boxed{C_2}$ axis that lies in the plane of the molecule and passes through the oxygen atom.
- two different $\boxed{\text{vertical mirror planes } \sigma_v}$, both containing the C_2 axis but with one lying in the plane of the molecule and the other perpendicular to it.

The point group is $\boxed{C_{2v}}$.

(ii) Assuming the six-membered ring to be planar, γ-pyran possesses the symmetry elements

- the $\boxed{\text{identity, } E}$
- a $\boxed{C_2}$ axis that lies in the plane of the molecule and passes through the oxygen atom and the opposite carbon
- two different $\boxed{\text{vertical mirror planes } \sigma_v}$, both containing the C_2 axis but with one lying in the plane of the molecule and the other perpendicular to it and containing just the oxygen and the opposite carbon.

The point group is $\boxed{C_{2v}}$.

(iii) 1,2,4-trichlorobenzene has a $\boxed{\text{mirror plane } \sigma}$ in the plane of the molecule but no other symmetry elements apart from the identity. Its point group is therefore $\boxed{C_s}$.

E10A.5(b) The molecules to be assigned are shown in Fig. 10.5 along with some of their symmetry elements. For clarity not all symmetry elements are shown in all cases.

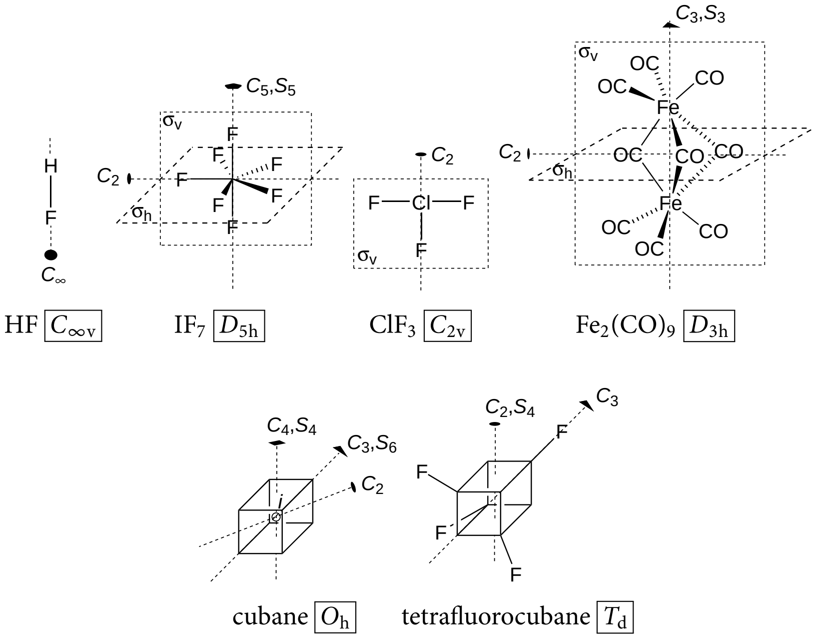


Figure 10.5

(i) HF is a linear molecule and does not possess a centre of inversion. Using the flowchart in Fig. 10A.7 on page 391 this is sufficient to establish the point group as $\boxed{C_{\infty v}}$.

(ii) IF$_7$ possesses a C_5 axis that passes through the iodine and the two axial fluorine atoms, and five C_2 axes perpendicular to the C_5 axis, each of which passes through the iodine and one of the five equatorial fluorine atoms. It also has a σ_h mirror plane containing the iodine and all five equatorial fluorines. These symmetry elements establish the point group as $\boxed{C_{5h}}$. The molecule also has five σ_v mirror planes each containing the iodine, the two axial fluorines and one of the equatorial fluorines, and an S_5 axis coincident with the C_5 axis.

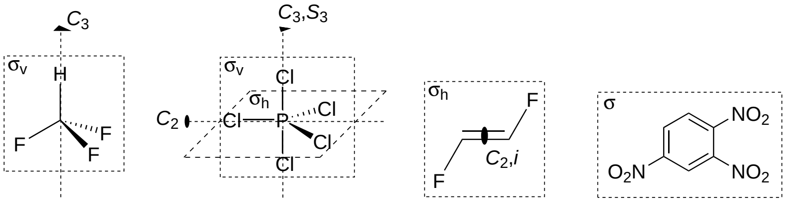
(iii) The T-shaped molecule ClF$_3$ has a C_2 axis that passes through the chlorine and the fluorine at the base of the T. It also has two σ_v mirror planes containing this axis; one of these corresponds to the plane of the molecule and contains all four atoms while the other is perpendicular to it and just contains the chlorine and the fluorine at the base of the T. These symmetry elements establish the point group as $\boxed{C_{2v}}$.

(iv) $Fe_2(CO)_9$ possesses a C_3 axis that passes through the two iron atoms, and a σ_h mirror plane perpendicular to this axis that passes through the three bridging CO groups. There are also three C_2 axes perpendicular to the C_3 axis, each passing through one of the three bridging CO groups. These symmetry elements establish the point group as $\boxed{D_{3h}}$. The molecule also has an S_3 axis coincident with the C_3 axis, and three σ_v planes, each passing through the two iron atoms, one of the bridging CO groups, and one of the terminal CO groups on each iron.

(v) Cubane has the same symmetry as a cube. It has three C_4 axes, each passing through the centre of a pair of opposite faces, and three σ_h mirror planes, one perpendicular to each C_4 axis. It also has four C_3 axes, each passing through a pair of diagonally opposite corners, six C_2 axes which pass through the centres of diagonally opposite edges, and six σ_d mirror planes perpendicular to these six C_2 axes. Finally there are three S_4 axes coincident with the C_4 axes, four S_6 axes coincident with the C_3 axes, and a centre of inversion i. This set of symmetry elements matches that given for the $\boxed{O_h}$ group in the table in Section 10A.2(e) on page 393, and O_h is also the conclusion reached from the flow diagram in Fig. 10A.7 on page 391.

(vi) In tetrafluorocubane, the four C_3 axes which pass through opposite corners of the cube are retained, as are the six σ_d planes. However, the C_4 axes through opposite sides of the cube are replaced by C_2 axes due to the reduced symmetry, and the C_2 axes that were present passing through opposite edges are no longer present. The σ_h mirror planes are also lost, as is the centre of inversion and the S_6 axes, but the three S_4 axes are still present. The set of symmetry elements present matches that given for the $\boxed{T_d}$ group in the table in Section 10A.2(e) on page 393, and T_d is also the conclusion reached from the flow diagram in Fig. 10A.7 on page 391.

E10A.6(b) The molecules are shown in Fig. 10.6 along with their point groups. For clarity not all symmetry elements are shown.



CHF_3, C_{3v} PCl_5, D_{3h} *trans*-$C_2H_2F_2$ C_{2h} 1,2,4-trinitrobenzene C_s

Figure 10.6

As explained in Section 10A.3(a) on page 394, only molecules belonging to the groups C_n, C_{nv}, and C_s may be polar.

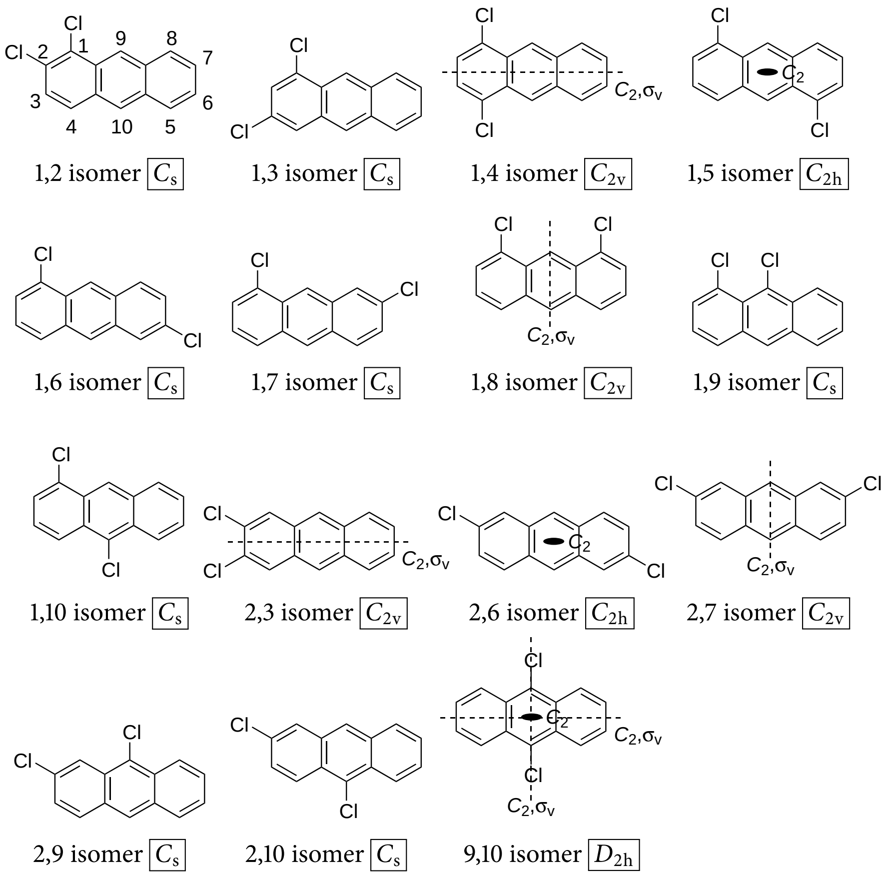
(i) CHF_3, fluoroform, belongs to point group C_{3v} so it $\boxed{\text{may be polar}}$. The dipole must lie along the C_3 axis, which passes through the hydrogen and the carbon.

(ii) PCl_5 has a trigonal bipyramidal shape and belongs to point group D_{3h}. Therefore it $\boxed{\text{may not}}$ be polar.

(iii) *trans*-difluoroethene belongs to point group C_{2h} so it $\boxed{\text{may not}}$ be polar.

(iv) 1,2,4-trinitrobenzene belongs to point group C_s so it $\boxed{\text{may be polar}}$.

E10A.7(b) There are 15 distinct isomers of dichloroanthracene, which are shown in Fig. 10.7 together with their point groups. All isomers have a mirror plane in the plane of the paper; additional symmetry elements are marked.



1,2 isomer $\boxed{C_s}$ 1,3 isomer $\boxed{C_s}$ 1,4 isomer $\boxed{C_{2v}}$ 1,5 isomer $\boxed{C_{2h}}$

1,6 isomer $\boxed{C_s}$ 1,7 isomer $\boxed{C_s}$ 1,8 isomer $\boxed{C_{2v}}$ 1,9 isomer $\boxed{C_s}$

1,10 isomer $\boxed{C_s}$ 2,3 isomer $\boxed{C_{2v}}$ 2,6 isomer $\boxed{C_{2h}}$ 2,7 isomer $\boxed{C_{2v}}$

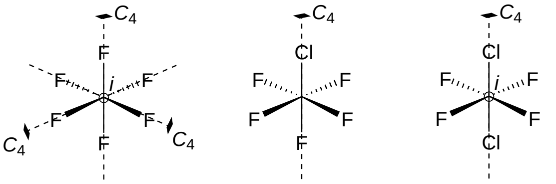
2,9 isomer $\boxed{C_s}$ 2,10 isomer $\boxed{C_s}$ 9,10 isomer $\boxed{D_{2h}}$

Figure 10.7

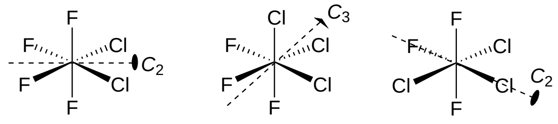
E10A.8(b) As explained in Section 10A.3(b) on page 395, to be chiral a molecule must not possess an axis of improper rotation, S_n. This includes mirror planes, which are the same as S_1, and centres of inversion, which are the same as S_2. The table in Section 10A.2(e) on page 393 shows that a molecule belonging to T_h possesses S_6, i, and σ_h symmetry elements, so such a molecule $\boxed{\text{may not be chiral}}$. Similarly the table in Section 10A.2(e) on page 393 shows that a molecule belonging to T_d possesses S_4 and σ_d symmetry elements, so such a molecule $\boxed{\text{may not be chiral}}$.

Solutions to problems

P10A.2 The molecules are shown in Fig. 10.8 along with some of their key symmetry elements. For clarity the sulfur atoms have been omitted and not all symmetry elements are shown. The point group of each species is determined using the flow diagram in Fig. 10A.7 on page 391. Then, as explained in Section 10A.3(a) on page 394, molecules belonging to C_n, C_{nv}, or C_s may be polar while molecules belonging to all other point groups are not.



SF_6 $\boxed{O_h\text{, not polar}}$ SF_5Cl $\boxed{C_{4v}\text{, polar}}$ *trans*-SF_4Cl_2 $\boxed{D_{4h}\text{, not polar}}$

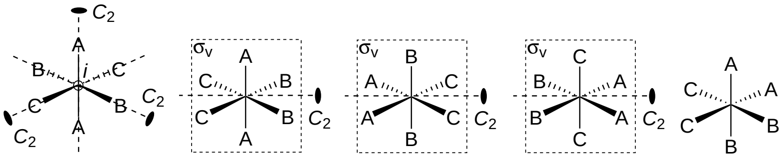


cis-SF_4Cl_2 $\boxed{C_{2v}\text{, polar}}$ *fac*-SF_3Cl_3 $\boxed{C_{3v}\text{, polar}}$ *mer*-SF_3Cl_3 $\boxed{C_{2v}\text{, polar}}$

Figure 10.8

P10A.4 There are five distinct geometric isomers which are shown in Fig. 10.9 together with their point groups and some of their symmetry elements. For clarity not all symmetry elements are shown.

As explained in Section 10A.3(b) on page 395 a molecule is only chiral only if it does not possess an S_n axis; this includes mirror planes σ, which are equivalent to S_1, and centres of inversion i, which are equivalent to S_2. Of the five isomers only the $\boxed{\text{all-}cis}$ isomer, which possesses no symmetry elements apart from the identity and therefore belongs to the point group C_1, is chiral.



all *trans* $\boxed{D_{2h}}$ A *trans* $\boxed{C_{2v}}$ B *trans* $\boxed{C_{2v}}$ C *trans* $\boxed{C_{2v}}$ all *cis* $\boxed{C_1}$

Figure 10.9

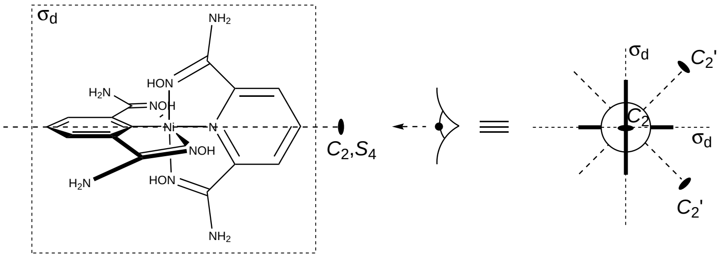


Figure 10.10

P10A.6 The $[\mathrm{Ni(C_7H_9N_5O_2)_2}]^{2+}$ ion is shown in Fig. 10.10.

The complex possesses a C_2 axis which passes through the nickel and the two pyridine nitrogens, and an S_4 axis coincident with this. Viewing the complex down this C_2 axis reveals two C_2' axes and two mirror planes, which are dihedral planes σ_d because they bisect the angle between the C_2' axes. Using the flow diagram in Fig. 10A.7 on page 391 these symmetry elements establish the point group as $\boxed{D_{2d}}$.

10B **Group theory**

Answer to discussion questions

D10B.2 A representative is a mathematical operator, usually taking the form of a matrix, that represents the effect of a particular symmetry operation. It is constructed by considering the effect of the operation on a particular set of basis functions. The set of all these mathematical operators corresponding to all the operations of the group is called a representation.

D10B.4 The process by which a representation is reduced in described in Section 10C.1(b) on page 408.

Solutions to exercises

E10B.1(b) BF_3 belongs to the point group D_{3h}. The C_3 operation corresponds to rotation by 120° around the C_3 axis which passes through the boron atom and is perpendicular to the plane of the molecule.

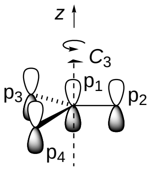


Figure 10.11

Using the orbital numbering shown in Fig. 10.11, a 120° rotation in the direction indicated leaves the boron p orbital p_1 unchanged but permutes the fluorine orbitals: p_2 is converted to p_3, p_3 to p_4, and p_4 to p_2. This effect is written as $(p_1\ p_3\ p_4\ p_2) \leftarrow (p_1\ p_2\ p_3\ p_4)$ which is expressed using matrix multiplication as

$$(p_1\ p_3\ p_4\ p_2) = (p_1\ p_2\ p_3\ p_4)\overbrace{\begin{pmatrix}1&0&0&0\\0&0&0&1\\0&1&0&0\\0&0&1&0\end{pmatrix}}^{\boldsymbol{D}(C_3)} = (p_1\ p_2\ p_3\ p_4)\boldsymbol{D}(C_3)$$

The representative of this operation is therefore

$$\boxed{\boldsymbol{D}(C_3) = \begin{pmatrix}1&0&0&0\\0&0&0&1\\0&1&0&0\\0&0&1&0\end{pmatrix}}$$

E10B.2(b) BF_3 belongs to the point group D_{3h}. The σ_h operation corresponds to a reflection in the plane of the molecule, while the C_3 operation corresponds to rotation by 120° around the C_3 axis which passes through the boron atom and is perpendicular to the plane of the molecule (Fig. 10.12).

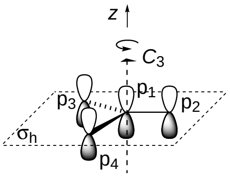


Figure 10.12

Using the orbital numbering shown in Fig. 10.12, the matrix representatives for the σ_h and C_3 operations were found in *Exercise* E10B.1(a) and *Exercise*

E10B.1(b) to be

$$\boldsymbol{D}(\sigma_h) = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \quad \text{and} \quad \boldsymbol{D}(C_3) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

The matrix representative of the operation $C_3\sigma_h$ is found by multiplying the matrix representatives of C_3 and σ_h. Basic information about how to handle matrices is given in *The chemist's toolkit* 24 in Topic 9E on page 373.

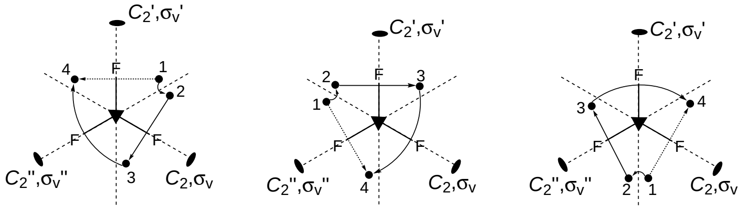
$$\boldsymbol{D}(C_3)\boldsymbol{D}(\sigma_h) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} = \boxed{\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \end{pmatrix}}$$

The operation corresponding to this representative is found by considering its effect on the starting basis

$$\begin{pmatrix} p_1 & p_2 & p_3 & p_4 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \end{pmatrix} = \begin{pmatrix} -p_1 & -p_3 & -p_4 & -p_2 \end{pmatrix}$$

The operation $C_3\sigma_h$ therefore changes the sign of p_1, and converts p_2, p_3 and p_4 into $-p_3$, $-p_4$, and $-p_2$ respectively. This is precisely the same outcome as achieved by the $\boxed{S_3 \text{ operation}}$, that is, a 120° rotation around the C_3 axis followed by a reflection in the σ_h plane. Thus, $\boldsymbol{D}(C_3)\boldsymbol{D}(\sigma_h) = \boldsymbol{D}(S_3)$.

E10B.3(b) Fig. 10.13 shows BF_3, an example of a molecule with D_{3h} symmetry. The three C_2 axes are labelled C_2, C_2' and C_2'', and likewise for the σ_v mirror planes.



$C_2''^{-1}\sigma_v C_2'' = \sigma_v'$ $\quad$ $C_2^{-1}\sigma_v' C_2 = \sigma_v''$ $\quad$ $C_2'^{-1}\sigma_v'' C_2' = \sigma_v$

Figure 10.13

The criteria for two operations R and R' to be in the same class is given by [10B.1–*398*], $R' = S^{-1}RS$ where S is another operation in the group. The task is therefore to find an operation S in D_{3h} such that this equation is satisfied when R and R' are two of the σ_v planes.

Referring to the first diagram in Fig. 10.13, to show that σ_v and σ_v' are in the same class consider the operation $C_2''^{-1}\sigma_v C_2''$. Start at the arbitrary point 1, and recall that the operations are applied starting from the right. The operation C_2'' moves the point to 2, and then σ_v moves the point to 3. The inverse of a C_2 rotation is itself, $C_2''^{-1} = C_2''$, so the effect of $C_2''^{-1}$ is to move the point to 4. From the diagram it can be seen that 4 can be reached by applying σ_v' to point 1, thus demonstrating that $C_2''^{-1}\sigma_v C_2'' = \sigma_v'$ and hence that σ_v and σ_v' belong to the same class.

In a similar way the second diagram in Fig. 10.13 shows that $C_2^{-1}\sigma_v' C_2 = \sigma_v''$ and hence that σ_v' and σ_v'' belong to the same class, while the third diagram shows that σ_v'' and σ_v belong to the same class.

E10B.4(b) The orthonormality of irreducible representations is defined by [10B.7–*402*],

$$\frac{1}{h}\sum_C N(C)\chi^{\Gamma^{(i)}}(C)\chi^{\Gamma^{(j)}}(C) = \begin{cases} 0 & \text{for } i \neq j \\ 1 & \text{for } i = j \end{cases} \tag{10.1}$$

where the sum is over all classes of the group, $N(C)$ is the number of operations in class C, and h is the number of operations in the group (its order). $\chi^{\Gamma^{(i)}}(C)$ is the character of class C in irreducible representation $\Gamma^{(i)}$, and similarly for $\chi^{\Gamma^{(j)}}(C)$.

The character table for the point group D_{3h} is given in the *Resource section*. The operations of the group are $\{E, \sigma_h, 2C_3, 2S_3, 3C_2', 3\sigma_v\}$, and $h = 12$. There are 6 classes and the values of $N(C)$ are the numbers multiplying the operations listed.

The irreducible representation E′ has characters {2, 2, −1, −1, 0, 0}. With $\Gamma^{(i)} =$ E′ and $\Gamma^{(j)} = \mathrm{A}_1'$, which has characters {1, 1, 1, 1, 1, 1}, eqn 10.1 evaluates as

$$\tfrac{1}{12}\{1\times2\times1 + 1\times2\times1 + 2\times(-1)\times1 + 2\times(-1)\times1 + 3\times0\times1 + 3\times0\times1\} = 0$$

With $\Gamma^{(i)} =$ E′ and $\Gamma^{(j)} = \mathrm{A}_2'$, which has characters {1, 1, 1, 1, −1, −1}, the sum is

$$\tfrac{1}{12}\{1\times2\times1 + 1\times2\times1 + 2\times(-1)\times1 + 2\times(-1)\times1 + 3\times0\times(-1) + 3\times0\times(-1)\} = 0$$

With $\Gamma^{(i)} =$ E′ and $\Gamma^{(j)} =$ E″, which has characters {2, −2, −1, 1, 0, 0}, the sum is

$$\tfrac{1}{12}\{1\times2\times2 + 1\times2\times(-2) + 2\times(-1)\times(-1) + 2\times(-1)\times1 + 3\times0\times0 + 3\times0\times0\} = 0$$

These results confirm that the E′ irreducible representation is orthogonal to A_1', A_2', and E″.

E10B.5(b) The D_{4h} character table is given in the *Resource section*. As explained in Section 10B.3(a) on page 402, an s orbital on a central atom always spans the totally symmetric representation of a group, which in D_{4h} is $\boxed{\mathrm{A}_{1g}}$, as it is unchanged under all symmetry operations. The symmetry species of the p and d orbitals are found using the information on the right hand side of the character table. The position of z in the table shows that p_z, which is proportional to $zf(r)$, has symmetry species $\boxed{A_{2u}}$ in D_{4h}. Similarly the positions of x and y in the character table shows that p_x and p_y, which are proportional to $xf(r)$ and $yf(r)$ respectively, jointly span the irreducible representation of symmetry species $\boxed{E_u}$.

In the same way the positions of z^2, x^2-y^2, and xy in the character table show that d_{z^2}, $d_{x^2-y^2}$, and d_{xy} have symmetry species $\boxed{A_{1g}}$, $\boxed{B_{1g}}$, and $\boxed{B_{2g}}$ respectively, while the positions of yz and zx show that d_{yz} and d_{zx} jointly span $\boxed{E_g}$.

E10B.6(b) As explained in Section 10B.3(c) on page 404, the highest dimensionality of irreducible representations in a group is equal to the maximum degree of degeneracy in the group. The highest dimensionality is found by noting the maximum value of $\chi(E)$ in the character table. An icosahedral nanoparticle has I_h symmetry, the character table for which is given in the *Online resource centre*. The maximum value of $\chi(E)$ is 5, corresponding to the H irreducible representations. Therefore the maximum degeneracy of a particle inside an icosahedral nanoparticle is $\boxed{\text{five}}$.

E10B.7(b) As explained in Section 10B.3(c) on page 404, the highest dimensionality of any irreducible representation in a group is equal to the maximum degree of degeneracy in the group. The highest dimensionality is found by noting the maximum value of $\chi(E)$ in the character table. 1,4-dichlorobenzene has D_{2h} symmetry, and from the D_{2h} character table in the *Resource section* the maximum value of $\chi(E)$ is 1, that is, all irreducible representations are one-dimensional. Therefore the maximum degeneracy of the orbitals in 1,4-dichlorobenzene is $\boxed{1}$.

Solutions to problems

P10B.2 Fig. 10.14 shows that a C_2 rotation followed by a reflection in a mirror plane perpendicular to the C_2 axis is equivalent to an inversion i. Hence $\sigma_h C_2 = i$.

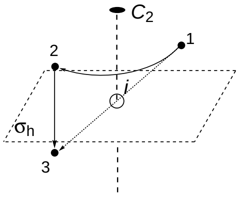


Figure 10.14

Because criterion 3 of the definition of a group given in Section 10B.1 on page 397 specifies that RR' is equivalent to a single member of the group, it follows that if a group has both a C_2 operation and a σ_h operation it must also have the operation $\sigma_h C_2$, which as shown above is i.

P10B.4 The methane molecule and H1s orbitals are shown in Fig. 10.15, along with one operation of each class. Note that different operations in the same class may give different representatives, but these representatives will necessarily all have the same trace.

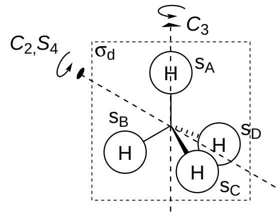


Figure 10.15

The C_3 operation shown in Fig. 10.15 leaves s_A unchanged but converts s_B into s_C, s_C into s_D, and s_D into s_B: $(\, s_A \; s_C \; s_D \; s_B \,) \leftarrow (\, s_A \; s_B \; s_C \; s_D \,)$. This is written using matrix multiplication as

$$(\, s_A \; s_C \; s_D \; s_B \,) = (\, s_A \; s_B \; s_C \; s_D \,)\overbrace{\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}}^{\boldsymbol{D}(C_3)}$$

The matrix $\boldsymbol{D}(C_3)$ is the representative of the C_3 operation in this basis. Similarly, the C_2 operation shown in Fig. 10.15 exchanges s_A and s_B, and also exchanges s_C and s_D. This is written using matrix multiplication as

$$(\, s_B \; s_A \; s_D \; s_C \,) = (\, s_A \; s_B \; s_C \; s_D \,)\overbrace{\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}}^{\boldsymbol{D}(C_2)}$$

The σ_d operation shown in Fig. 10.15 leaves s_A and s_B unchanged and exchanges s_C and s_D; this gives

$$(\, s_A \; s_B \; s_D \; s_c \,) = (\, s_A \; s_B \; s_C \; s_D \,)\overbrace{\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}}^{\boldsymbol{D}(\sigma_d)}$$

The S_4 operation shown in Fig. 10.15 converts $\mathrm{s_A}$ to $\mathrm{s_D}$, $\mathrm{s_B}$ to $\mathrm{s_C}$, $\mathrm{s_C}$ to $\mathrm{s_A}$, and $\mathrm{s_D}$ to $\mathrm{s_B}$, giving

$$\left(\,\mathrm{s_D}\ \mathrm{s_C}\ \mathrm{s_A}\ \mathrm{s_B}\,\right) = \left(\,\mathrm{s_A}\ \mathrm{s_B}\ \mathrm{s_C}\ \mathrm{s_D}\,\right)\overbrace{\begin{pmatrix}0&0&1&0\\0&0&0&1\\0&1&0&0\\1&0&0&0\end{pmatrix}}^{\boldsymbol{D}(S_4)}$$

Finally, the E operation leaves all orbitals unchanged, meaning that its representative is simply the identity matrix

$$\left(\,\mathrm{s_A}\ \mathrm{s_B}\ \mathrm{s_C}\ \mathrm{s_D}\,\right) = \left(\,\mathrm{s_A}\ \mathrm{s_B}\ \mathrm{s_C}\ \mathrm{s_D}\,\right)\overbrace{\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix}}^{\boldsymbol{D}(E)}$$

P10B.6 In the previous exercise, the representatives were found to be

$$\boldsymbol{D}(E)=\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix}\quad \boldsymbol{D}(C_2^x)=\begin{pmatrix}0&0&0&1\\0&0&1&0\\0&1&0&0\\1&0&0&0\end{pmatrix}\quad \boldsymbol{D}(C_2^y)=\begin{pmatrix}0&1&0&0\\1&0&0&0\\0&0&0&1\\0&0&1&0\end{pmatrix}\quad \boldsymbol{D}(C_2^z)=\begin{pmatrix}0&0&1&0\\0&0&0&1\\1&0&0&0\\0&1&0&0\end{pmatrix}$$

$$\boldsymbol{D}(i)=\begin{pmatrix}0&0&1&0\\0&0&0&1\\1&0&0&0\\0&1&0&0\end{pmatrix}\quad \boldsymbol{D}(\sigma^{xy})=\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix}\quad \boldsymbol{D}(\sigma^{yz})=\begin{pmatrix}0&1&0&0\\1&0&0&0\\0&0&0&1\\0&0&1&0\end{pmatrix}\quad \boldsymbol{D}(\sigma^{xz})=\begin{pmatrix}0&0&0&1\\0&0&1&0\\0&1&0&0\\1&0&0&0\end{pmatrix}$$

The group multiplications are verified by multiplying the corresponding matrix representatives

$$\boldsymbol{D}(C_2^z)\boldsymbol{D}(C_2^y) = \overbrace{\begin{pmatrix}0&0&1&0\\0&0&0&1\\1&0&0&0\\0&1&0&0\end{pmatrix}}^{\boldsymbol{D}(C_2^z)}\overbrace{\begin{pmatrix}0&1&0&0\\1&0&0&0\\0&0&0&1\\0&0&1&0\end{pmatrix}}^{\boldsymbol{D}(C_2^y)} = \overbrace{\begin{pmatrix}0&0&0&1\\0&0&1&0\\0&1&0&0\\1&0&0&0\end{pmatrix}}^{\boldsymbol{D}(C_2^x)} = \boldsymbol{D}(C_2^x)$$

$$\boldsymbol{D}(\sigma^{xz})\boldsymbol{D}(C_2^z) = \overbrace{\begin{pmatrix}0&0&0&1\\0&0&1&0\\0&1&0&0\\1&0&0&0\end{pmatrix}}^{\boldsymbol{D}(\sigma^{xz})}\overbrace{\begin{pmatrix}0&0&1&0\\0&0&0&1\\1&0&0&0\\0&1&0&0\end{pmatrix}}^{\boldsymbol{D}(C_2^z)} = \overbrace{\begin{pmatrix}0&1&0&0\\1&0&0&0\\0&0&0&1\\0&0&1&0\end{pmatrix}}^{\boldsymbol{D}(C_2^y)} = \boldsymbol{D}(C_2^y)$$

$$\boldsymbol{D}(i)\boldsymbol{D}(C_2^y) = \overbrace{\begin{pmatrix}0&0&1&0\\0&0&0&1\\1&0&0&0\\0&1&0&0\end{pmatrix}}^{\boldsymbol{D}(i)}\overbrace{\begin{pmatrix}0&1&0&0\\1&0&0&0\\0&0&0&1\\0&0&1&0\end{pmatrix}}^{\boldsymbol{D}(C_2^y)} = \overbrace{\begin{pmatrix}0&0&0&1\\0&0&1&0\\0&1&0&0\\1&0&0&0\end{pmatrix}}^{\boldsymbol{D}(\sigma^{xz})} = \boldsymbol{D}(\sigma^{xz})$$

P10B.8 Performing the matrix multiplications gives

$$\sigma_x\sigma_x = \begin{pmatrix}0&1\\1&0\end{pmatrix}\begin{pmatrix}0&1\\1&0\end{pmatrix} = \begin{pmatrix}1&0\\0&1\end{pmatrix} = \sigma_0 \qquad \sigma_x\sigma_y = \begin{pmatrix}0&1\\1&0\end{pmatrix}\begin{pmatrix}0&-\mathrm{i}\\\mathrm{i}&0\end{pmatrix} = \begin{pmatrix}\mathrm{i}&0\\0&-\mathrm{i}\end{pmatrix} = \mathrm{i}\sigma_z$$

$$\sigma_x\sigma_z = \begin{pmatrix}0&1\\1&0\end{pmatrix}\begin{pmatrix}1&0\\0&-1\end{pmatrix} = \begin{pmatrix}0&-1\\1&0\end{pmatrix} = -\mathrm{i}\sigma_y \qquad \sigma_x\sigma_0 = \begin{pmatrix}0&1\\1&0\end{pmatrix}\begin{pmatrix}1&0\\0&1\end{pmatrix} = \begin{pmatrix}0&1\\1&0\end{pmatrix} = \sigma_x$$

$$\sigma_y\sigma_x = \begin{pmatrix}0&-\mathrm{i}\\\mathrm{i}&0\end{pmatrix}\begin{pmatrix}0&1\\1&0\end{pmatrix} = \begin{pmatrix}-\mathrm{i}&0\\0&\mathrm{i}\end{pmatrix} = -\mathrm{i}\sigma_z \qquad \sigma_y\sigma_y = \begin{pmatrix}0&-\mathrm{i}\\\mathrm{i}&0\end{pmatrix}\begin{pmatrix}0&-\mathrm{i}\\\mathrm{i}&0\end{pmatrix} = \begin{pmatrix}1&0\\0&1\end{pmatrix} = \sigma_0$$

$$\sigma_y\sigma_z = \begin{pmatrix}0&-\mathrm{i}\\\mathrm{i}&0\end{pmatrix}\begin{pmatrix}1&0\\0&-1\end{pmatrix} = \begin{pmatrix}0&\mathrm{i}\\\mathrm{i}&0\end{pmatrix} = \mathrm{i}\sigma_x \qquad \sigma_y\sigma_0 = \begin{pmatrix}0&-\mathrm{i}\\\mathrm{i}&0\end{pmatrix}\begin{pmatrix}1&0\\0&1\end{pmatrix} = \begin{pmatrix}0&-\mathrm{i}\\\mathrm{i}&0\end{pmatrix} = \sigma_y$$

$$\sigma_z\sigma_x = \begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}0&1\\1&0\end{pmatrix} = \begin{pmatrix}0&1\\-1&0\end{pmatrix} = \mathrm{i}\sigma_y \qquad \sigma_z\sigma_y = \begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}0&-\mathrm{i}\\\mathrm{i}&0\end{pmatrix} = \begin{pmatrix}0&-\mathrm{i}\\-\mathrm{i}&0\end{pmatrix} = -\mathrm{i}\sigma_x$$

$$\sigma_z\sigma_z = \begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}1&0\\0&-1\end{pmatrix} = \begin{pmatrix}1&0\\0&1\end{pmatrix} = \sigma_0 \qquad \sigma_z\sigma_0 = \begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}1&0\\0&1\end{pmatrix} = \begin{pmatrix}1&0\\0&-1\end{pmatrix} = \sigma_z$$

$$\sigma_0\sigma_x = \begin{pmatrix}1&0\\0&1\end{pmatrix}\begin{pmatrix}0&1\\1&0\end{pmatrix} = \begin{pmatrix}0&1\\1&0\end{pmatrix} = \sigma_x \qquad \sigma_0\sigma_y = \begin{pmatrix}1&0\\0&1\end{pmatrix}\begin{pmatrix}0&-\mathrm{i}\\\mathrm{i}&0\end{pmatrix} = \begin{pmatrix}0&-\mathrm{i}\\\mathrm{i}&0\end{pmatrix} = \sigma_y$$

$$\sigma_0\sigma_z = \begin{pmatrix}1&0\\0&1\end{pmatrix}\begin{pmatrix}1&0\\0&-1\end{pmatrix} = \begin{pmatrix}1&0\\0&-1\end{pmatrix} = \sigma_z \qquad \sigma_0\sigma_0 = \begin{pmatrix}1&0\\0&1\end{pmatrix}\begin{pmatrix}1&0\\0&1\end{pmatrix} = \begin{pmatrix}1&0\\0&1\end{pmatrix} = \sigma_0$$

The RR' multiplication table is therefore

$R\downarrow\ R'\rightarrow$	σ_x	σ_y	σ_z	σ_0
σ_x	σ_0	$\mathrm{i}\sigma_z$	$-\mathrm{i}\sigma_y$	σ_x
σ_y	$-\mathrm{i}\sigma_z$	σ_0	$\mathrm{i}\sigma_x$	σ_y
σ_z	$\mathrm{i}\sigma_y$	$-\mathrm{i}\sigma_x$	σ_0	σ_z
σ_0	σ_x	σ_y	σ_z	σ_0

The four matrices do $\boxed{\text{not}}$ form a group under multiplication. This is because they do not satisfy criterion 3 in Section 10B.1 on page 397, that the combination RR' must be equivalent to a single member of the collection. For example, $\sigma_x\sigma_y = \mathrm{i}\sigma_z$, but $\mathrm{i}\sigma_z$ is not one of the four matrices.

P10B.10 The two wavefunctions are shown schematically in Fig. 10.16, where the shading indicates the sign of the wavefunction.

It is clear from Fig. 10.16 that a C_4^+ rotation, taken to be 90° anticlockwise, converts $\psi_{2,3}$ into $\psi_{3,2}$ and $\psi_{3,2}$ into $-\psi_{2,3}$: $(\,\psi_{3,2}\ \ -\psi_{2,3}\,) \leftarrow (\,\psi_{2,3}\ \ \psi_{3,2}\,)$. Similarly C_4^- transforms $(\,-\psi_{3,2}\ \ \psi_{2,3}\,) \leftarrow (\,\psi_{2,3}\ \ \psi_{3,2}\,)$, C_2 changes the sign of both wavefunctions, while E leaves both unchanged. Writing these using matrix multiplication gives

$$\psi_{2,3}=\left(\tfrac{2}{L}\right)\sin\left(\tfrac{2\pi x}{L}\right)\sin\left(\tfrac{3\pi y}{L}\right)\qquad \psi_{3,2}=\left(\tfrac{2}{L}\right)\sin\left(\tfrac{3\pi x}{L}\right)\sin\left(\tfrac{2\pi y}{L}\right)$$

Figure 10.16

$$\text{For } E\text{:}\quad (\,\psi_{2,3}\ \psi_{3,2}\,)=(\,\psi_{2,3}\ \psi_{3,2}\,)\overbrace{\begin{pmatrix}1&0\\0&1\end{pmatrix}}^{\boldsymbol{D}(E)}$$

$$\text{For } C_4^+\text{:}\quad (\,\psi_{3,2}\ -\psi_{2,3}\,)=(\,\psi_{2,3}\ \psi_{3,2}\,)\overbrace{\begin{pmatrix}0&-1\\1&0\end{pmatrix}}^{\boldsymbol{D}(C_4^+)}$$

$$\text{For } C_4^-\text{:}\quad (\,-\psi_{3,2}\ \psi_{2,3}\,)=(\,\psi_{2,3}\ \psi_{3,2}\,)\overbrace{\begin{pmatrix}0&1\\-1&0\end{pmatrix}}^{\boldsymbol{D}(C_4^-)}$$

$$\text{For } C_2\text{:}\quad (\,-\psi_{2,3}\ -\psi_{3,2}\,)=(\,\psi_{2,3}\ \psi_{3,2}\,)\overbrace{\begin{pmatrix}-1&0\\0&-1\end{pmatrix}}^{\boldsymbol{D}(C_2)}$$

The characters are

$$\chi(E)=2\quad \chi(C_4^+)=0\quad \chi(C_4^-)=0\quad \chi(C_2)=-2$$

Noting that C_4^+ and C_4^- are in the same class and appear in the column labelled $2C_4$, the C_4 character table in Table 10B.3 on page 405 shows that the basis of $\psi_{2,3}$ and $\psi_{3,2}$ spans the doubly degenerate irreducible representation E. It follows that these two wavefunctions are degenerate.

10C **Applications of symmetry**

Answers to discussion questions

D10C.2 The key point is that only orbitals (or combinations of orbitals) which transform as the same symmetry species (irreducible representation) can overlap to form molecular orbitals. The first step is therefore to classify the valence orbitals according to symmetry. Usually, it is possible to identify sets of such orbitals which are interconverted by the operations of the group and so can be considered separately from other sets. Having classified a set of orbitals according to symmetry the projection operator is then used to construct symmetry-adapted linear combinations (SALCs) each of which transforms as a single symmetry species (irreducible representation). The molecular orbitals are formed from the overlap of these SALCs.

Solutions to exercises

E10C.1(b) As explained in Section 10C.1 on page 406 an integral can only be non-zero if the integrand spans the totally symmetric irreducible representation, which in D_{3h} is A_1'. From Section 10C.1(a) on page 407 the symmetry species spanned by the integrand $p_x z p_z$ is found by the forming the direct product of the symmetry species spanned by p_x, z, and p_z separately. These are read off the D_{3h} character table by looking for the appropriate Cartesian functions listed on the right of the table: x and hence p_x spans E', while z and hence p_z both span A_2''. The direct product required is therefore $E' \times A_2'' \times A_2''$.

The order does not matter, so this is equal to $A_2'' \times A_2'' \times E'$. This is equal to $A_1' \times E'$ because, from the second simplifying feature listed in Section 10C.1(a) on page 407, the direct product of an irreducible representation such as A_2'' with itself is the totally symmetric irreducible representation A_1'. In turn, $A_1' \times E'$ is simply equal to E' because, from the first simplifying feature listed in Section 10C.1(a) on page 407, the direct product of the totally symmetric irreducible representation with any other representation is the latter representation itself: $A_1' \times \Gamma^{(i)} = \Gamma^{(i)}$. The integrand therefore spans E'. This is not the totally symmetric irreducible representation, therefore the integral is $\boxed{\text{zero}}$.

E10C.2(b) As explained in Section 10C.3 on page 411, an electric dipole transition is forbidden if the electric transition dipole moment $\mu_{q,\mathrm{fi}}$ is zero. The transition dipole moment is given by [10C.6–*411*], $\mu_{q,\mathrm{fi}} = -e\int \psi_\mathrm{f}^* q \psi_\mathrm{i}\,\mathrm{d}\tau$ where q is x, y, or z. The integral is only non-zero if the integrand contains the totally symmetric irreducible representation, which from the D_{6h} character table is A_{1g}.

For a transition $A_{1g} \rightarrow E_{2u}$, the symmetry species of the integrand is given by the direct product $A_{1g} \times \Gamma^{(q)} \times E_{2u}$. The order does not matter so this is equal to $A_{1g} \times E_{2u} \times \Gamma^{(q)}$, which is simply equal to $E_{2u} \times \Gamma^{(q)}$ because, from the first simplifying feature listed in Section 10C.1(a) on page 407, the direct product of the totally symmetric irreducible representation with any other representation is the latter representation itself. Therefore $A_{1g} \times E_{2u} = E_{2u}$.

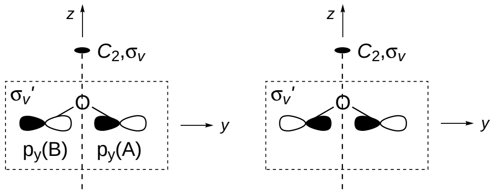
The direct product $E_{2u} \times \Gamma^{(q)}$ contains the totally symmetric irreducible representation only if $\Gamma^{(q)}$ spans E_{2u} because, according to the second simplifying feature listed in Section 10C.1(a) on page 407, the direct product of two irreducible representations contains the totally symmetric irreducible representation only if the two irreducible representations are identical. The D_{6h} character table shows that none of x, y or z span E_{2u}, so it follows that the integrand does not contain A_{1g} and hence the transition is $\boxed{\text{forbidden}}$.

E10C.3(b) As explained in Section 10C.1(a) on page 407 the symmetry species of xyz is determined by forming the direct product between the irreducible representations spanned by x, y and z individually. Inspection of the D_{2h} character table shows that x spans B_{3u} in D_{3h} while y and z span B_{2u} and B_{1u} respectively. The direct product is

	E	C_2^x	C_2^y	C_2^z	i	σ^{xy}	σ^{yz}	σ^{zx}
B_{3u}	1	−1	−1	1	−1	1	−1	1
B_{2u}	1	−1	1	−1	−1	1	1	−1
B_{1u}	1	1	−1	−1	−1	−1	1	1
product	1	1	1	1	−1	−1	−1	−1

The characters in the product row are those of symmetry species A_u, thus confirming that the function xyz has symmetry species A_u in D_{2h}.

E10C.4(b) The OF_2 molecule and the two combinations of p_y orbitals are shown in Fig. 10.17.



$p_y(A) + p_y(B)$ $p_y(A) - p_y(B)$

Figure 10.17

The first combination, $p_y(A) + p_y(B)$, is left unchanged by E and σ_v', but has its sign changed by the C_2 and σ_v operations. Its characters are therefore

$$\chi(E) = 1 \qquad \chi(C_2) = -1 \qquad \chi(\sigma_v) = -1 \qquad \chi(\sigma_v') = 1$$

Inspection of the C_{2v} character table shows that these are the characters of the B_2 irreducible representation, so $p_y(A) + p_y(B)$ spans $\boxed{B_2}$.

The second combination, $p_y(A) - p_y(B)$, is unchanged by all of the operations of the group and therefore spans the totally symmetric irreducible representation $\boxed{A_1}$.

As explained in Section 10C.2(a) on page 409, only orbitals of the same symmetry species may have a nonzero overlap. Inspection of the C_{2v} character table shows that the oxygen $\boxed{2s}$ and $\boxed{2p_z}$ orbitals both have A_1 symmetry, so they can interact with the $p_y(A) - p_y(B)$ combination of fluorine orbitals. The oxygen $\boxed{2p_y}$ orbital has B_2 symmetry, so it can interact with the $p_y(A) + p_y(B)$ combination of fluorine orbitals. The oxygen $2p_x$ orbital has B_1 symmetry, so cannot interact with either combination of fluorine orbitals.

E10C.5(b) As explained in Section 10C.2(a) on page 409, only orbitals of the same symmetry species may have a nonzero overlap. Inspection of the D_{3h} character table shows that the boron 2s and p_z orbitals span A_1' and A_2'' respectively, while the p_x and p_y orbitals jointly span E'. Therefore $\boxed{\mathrm{p}_z}$ can interact with the A_2'' SALC, while none of the boron valence orbitals have the correct symmetry to interact with the E'' SALC.

The character table also shows that d_{z^2} spans A_1', $\mathrm{d}_{x^2-y^2}$ and d_{xy} jointly span E', and d_{yz} and d_{zx} jointly span E''. Therefore the none of the d orbitals have the correct symmetry to interact with the A_2'' SALC, but $\boxed{\mathrm{d}_{yz} \text{ and } \mathrm{d}_{zx}}$ can interact with the E'' SALC.

E10C.6(b) As explained in Section 10C.3 on page 411, a transition from a state with symmetry $\Gamma^{(\mathrm{i})}$ to one with symmetry $\Gamma^{(\mathrm{f})}$ is only allowed if the direct product $\Gamma^{(\mathrm{f})} \times \Gamma^{(q)} \times \Gamma^{(\mathrm{i})}$ contains the totally symmetric irreducible representation, which in $C_{2\mathrm{v}}$ is A_1. In this case $\Gamma^{(\mathrm{i})} = \mathrm{B}_1$ and $\Gamma^{(q)} = \Gamma^{(y)} = \mathrm{B}_2$ because, from the $C_{2\mathrm{v}}$ character table, y spans B_2. The required direct product is therefore $\Gamma^{(\mathrm{f})} \times \mathrm{B}_2 \times \mathrm{B}_1$. The product $\mathrm{B}_2 \times \mathrm{B}_1$ is evaluated by multiplying the characters of the two representations.

	E	C_2	σ_v	σ_v'
B_2	1	−1	−1	1
B_1	1	−1	1	−1
product	1	1	−1	−1

The characters of the product row correspond to those of A_2, therefore $\mathrm{B}_2 \times \mathrm{B}_1 = \mathrm{A}_2$ and hence $\Gamma^{(\mathrm{f})} \times \mathrm{B}_2 \times \mathrm{B}_1 = \Gamma^{(\mathrm{f})} \times \mathrm{A}_2$. If this product is to span A_1 then the symmetry of the upper state $\Gamma^{(\mathrm{f})}$ must be $\boxed{\mathrm{A}_2}$ because, according to the second simplifying feature of direct products listed in Section 10C.1(a) on page 407, the direct product of two irreducible representations only spans the totally symmetric irreducible representation if the two irreducible representations are identical.

E10C.7(b) The number of times $n(\Gamma)$ that a given irreducible representation Γ occurs in a representation is given by [10C.3a–*408*], $n(\Gamma) = (1/h)\sum_C N(C)\chi^{(\Gamma)}(C)\chi(C)$, where h is the order of the group, $N(C)$ is the number of operations in class C, $\chi^{(\Gamma)}$ is the character of class C in the irreducible representation Γ, and $\chi(C)$ is the character of class C in the representation being reduced. In the case of D_2, $h = 4$.

$$\begin{aligned} n(\mathrm{A}_1) &= \tfrac{1}{4}\big(N(E)\times\chi^{(\mathrm{A}_1)}(E)\times\chi(E) \;+\; N(C_2^z)\times\chi^{(\mathrm{A}_1)}(C_2^z)\times\chi(C_2^z) \\ &\qquad + N(C_2^y)\times\chi^{(\mathrm{A}_1)}(C_2^y)\times\chi(C_2^y) \;+\; N(C_2^x)\times\chi^{(\mathrm{A}_1)}(C_2^x)\times\chi(C_2^x)\big) \\ &= \tfrac{1}{4}\left(1\times1\times6 \;+\; 1\times1\times(-2) \;+\; 1\times1\times0 \;+\; 1\times1\times0\right) = 1 \end{aligned}$$

Similarly

$$
\begin{aligned}
n(\mathrm{B_1}) &= \tfrac{1}{4}\left(1\times1\times6 \;+\; 1\times1\times(-2) \;+\; 1\times(-1)\times0 \;+\; 1\times(-1)\times0\right) = 1\\
n(\mathrm{B_2}) &= \tfrac{1}{4}\left(1\times1\times6 \;+\; 1\times(-1)\times(-2) \;+\; 1\times1\times0 \;+\; 1\times(-1)\times0\right) = 2\\
n(\mathrm{B_3}) &= \tfrac{1}{4}\left(1\times1\times6 \;+\; 1\times(-1)\times(-2) \;+\; 1\times(-1)\times0 \;+\; 1\times1\times0\right) = 2
\end{aligned}
$$

The representation therefore spans $\boxed{\mathrm{A_1 + B_1 + 2B_2 + 2B_3}}$.

E10C.8(b) The number of times $n(\Gamma)$ that a given irreducible representation Γ occurs in a representation is given by [10C.3a–*408*], $n(\Gamma) = (1/h)\sum_C N(C)\chi^{(\Gamma)}(C)\chi(C)$, where h is the order of the group, $N(C)$ is the number of operations in class C, $\chi^{(\Gamma)}$ is the character of class C in the irreducible representation Γ, and $\chi(C)$ is the character of class C in the representation being reduced. In the case of O_h, $h = 48$.

Because the representation being reduced has characters of zero for all classes except E, C_4, C_4^2, σ_h and σ_d, only these latter five classes make a non-zero contribution to the sum and therefore only these classes need be considered. The number of times that the irreducible representation $\mathrm{A_{1g}}$ occurs is therefore

$$
\begin{aligned}
n(\mathrm{A_{1g}}) = \tfrac{1}{48}\Big(&N(E)\times\chi^{(\mathrm{A_{1g}})}(E)\times\chi(E) \;+\; N(C_4)\times\chi^{(\mathrm{A_{1g}})}(C_4)\times\chi(C_4)\\
&+\; N(C_4^2)\times\chi^{(\mathrm{A_{1g}})}(C_4^2)\times\chi(C_4^2) \;+\; N(\sigma_\mathrm{h})\times\chi^{(\mathrm{A_{1g}})}(\sigma_\mathrm{h})\times\chi(\sigma_\mathrm{h})\\
&+\; N(\sigma_\mathrm{d})\times\chi^{(\mathrm{A_{1g}})}(\sigma_\mathrm{d})\times\chi(\sigma_\mathrm{d})\Big)\\
= \tfrac{1}{48}\big(&1\times1\times6 \;+\; 6\times1\times2 \;+\; 3\times1\times2 \;+\; 3\times1\times4 \;+\; 6\times1\times2\big) = 1
\end{aligned}
$$

Similarly

$$
\begin{aligned}
n(\mathrm{A_{2g}}) &= \tfrac{1}{48}\left(1\times1\times6+6\times(-1)\times2+3\times1\times2+3\times1\times4+6\times(-1)1\times2\right) = 0\\
n(\mathrm{E_g}) &= \tfrac{1}{48}\left(1\times2\times6+6\times0\times2+3\times2\times2+3\times2\times4+6\times0\times2\right) = 1\\
n(\mathrm{T_{1g}}) &= \tfrac{1}{48}\left(1\times3\times6+6\times1\times2+3\times(-1)\times2+3\times(-1)\times4+6\times(-1)\times2\right) = 0\\
n(\mathrm{T_{2g}}) &= \tfrac{1}{48}\left(1\times3\times6+6\times(-1)\times2+3\times(-1)\times2+3\times1\times4+6\times1\times2\right) = 0\\
n(\mathrm{A_{1u}}) &= \tfrac{1}{48}\left(1\times1\times6+6\times1\times2+3\times1\times2+3\times(-1)\times4+6\times(-1)\times2\right) = 0\\
n(\mathrm{A_{2u}}) &= \tfrac{1}{48}\left(1\times1\times6+6\times(-1)\times2+3\times1\times2+3\times(-1)\times4+6\times1\times2\right) = 0\\
n(\mathrm{E_u}) &= \tfrac{1}{48}\left(1\times2\times6+6\times0\times2+3\times2\times2+3\times(-2)\times4+6\times0\times2\right) = 0\\
n(\mathrm{T_{1u}}) &= \tfrac{1}{48}\left(1\times3\times6+6\times1\times2+3\times(-1)\times2+3\times1\times4+6\times1\times2\right) = 1\\
n(\mathrm{T_{2u}}) &= \tfrac{1}{48}\left(1\times3\times6+6\times(-1)\times2+3\times(-1)\times2+3\times1\times4+6\times(-1)\times2\right) = 0
\end{aligned}
$$

The representation therefore spans $\boxed{\mathrm{A_{1g} + E_g + T_{1u}}}$.

E10C.9(b) As explained in Section 10C.3 on page 411, a transition from a state with symmetry $\Gamma^{(\mathrm{i})}$ to one with symmetry $\Gamma^{(\mathrm{f})}$ is only allowed if the direct product $\Gamma^{(\mathrm{f})}\times$

$\Gamma^{(q)} \times \Gamma^{(i)}$ contains the totally symmetric irreducible representation, which for both molecules is A_{1g}. The ground state is totally symmetric, implying that it transforms as A_{1g}. Therefore the direct product becomes $\Gamma^{(f)} \times \Gamma^{(q)} \times A_{1g}$. This is simply $\Gamma^{(f)} \times \Gamma^{(q)}$ because, from the first simplifying feature of direct products listed in Section 10C.1(a) on page 407, the direct product of the totally symmetric representation A_{1g} with any other representation is the latter representation itself.

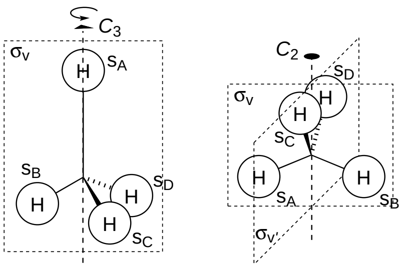
If $\Gamma^{(f)} \times \Gamma^{(q)}$ is to be A_{1g}, then $\Gamma^{(f)}$ must equal $\Gamma^{(q)}$ because, from the second simplifying feature of direct products listed in Section 10C.1(a) on page 407, the direct product of two irreducible representations only contains the totally symmetric irreducible representation if the two irreducible representations are identical.

(i) Anthracene belongs to point group D_{2h}. The D_{2h} character table in the *Resource section* shows that x transforms as B_{3u}, y transforms as B_{2u}, and z transforms as B_{1u}. Therefore anthracene can be excited to $\boxed{B_{3u},\ B_{2u},\ \text{or}\ B_{1u}}$ states by x, y, and z polarised light respectively.

(ii) Coronene belongs to point group D_{6h}. The D_{6h} character table in the *Online resource centre* shows that shows that z transforms as A_{2u}, and x and y together transform as E_{1u}. Therefore light polarized along z can excite coronene to a $\boxed{A_{2u}}$ state, and x or y polarised light can excite it to an $\boxed{E_{1u}}$ state.

Solutions to problems

P10C.2 The distorted molecules are shown in Fig. 10.18 together with some of the symmetry operations.



C_{3v} C_{2v}

Figure 10.18

(a) In the C_{3v} distorted case s_A is unaffected by any of the operations of the group and is not mixed with the other H1s orbitals. It therefore transforms as the totally symmetric irreducible representation A_1.

The irreducible representations spanned by s_B, s_C, and s_D are identified by forming the representatives of the operations with this basis. Only one operation in each class needs to be considered. The C_3 operation converts

s_B into s_C, s_C into s_D, and s_D into s_B: $(\,s_C\ s_D\ s_B\,) \leftarrow (\,s_B\ s_C\ s_D\,)$. This is written using matrix multiplication as

$$(\,s_C\ s_D\ s_B\,) = (\,s_B\ s_C\ s_D\,)\overbrace{\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}}^{\boldsymbol{D}(C_3)}$$

Similarly

$$\text{For } \sigma_v\text{:}\quad (\,s_B\ s_D\ s_C\,) = (\,s_B\ s_C\ s_D\,)\overbrace{\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}}^{\boldsymbol{D}(\sigma_v)}$$

$$\text{For } E\text{:}\quad (\,s_B\ s_C\ s_D\,) = (\,s_B\ s_C\ s_D\,)\overbrace{\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}}^{\boldsymbol{D}(E)}$$

The characters of the representatives are

$$\chi(E) = 3 \quad \chi(C_3) = 0 \quad \chi(\sigma_v) = 1$$

This result can be arrived at much more quickly by noting that: (1) only the diagonal elements of the representative matrix contribute to the trace; (2) orbitals which are unmoved by an operation will result in a 1 on the diagonal; (3) orbitals which are moved to other positions by an operation will result in a 0 on the diagonal. The character is found simply by counting the number of orbitals which do not move. In the present case 3 are unmoved by E, none are unmoved by C_3, and 1 is unmoved by σ_v. The characters are therefore $\{3, 0, 1\}$.

This representation is decomposed using the method described in Section 10C.1(b) on page 408. The number of times $n(\Gamma)$ that a given irreducible representation Γ occurs in a representation is given by [10C.3a–*408*],

$$n(\Gamma) = \frac{1}{h}\sum_C N(C)\chi^{(\Gamma)}(C)\chi(C)$$

where h is the order of the group, $N(C)$ is the number of operations in class C, $\chi^{(\Gamma)}$ is the character of class C in the irreducible representation Γ, and $\chi(C)$ is the character of class C in the representation being reduced. In the case of C_{3v}, $h = 6$. The number of times that the irreducible representation A_1 occurs is

$$\begin{aligned} n(A_1) &= \tfrac{1}{6}\big(N(E)\times\chi^{(A_1)}(E)\times\chi(E) + N(C_3)\times\chi^{(A_1)}(C_3)\times\chi(C_3) \\ &\qquad + N(\sigma_v)\times\chi^{(A_1)}(\sigma_v)\times\chi(\sigma_v)\big) \\ &= \tfrac{1}{6}\left(1\times1\times3 + 2\times1\times0 + 3\times1\times1\right) = 1 \end{aligned}$$

Similarly

$$n(\mathrm{A}_2) = \tfrac{1}{6}\left(1\times1\times3 \;+\; 2\times1\times0 \;+\; 3\times(-1)\times1\right) = 0$$
$$n(\mathrm{E}) = \tfrac{1}{6}\left(1\times2\times3 \;+\; 2\times(-1)\times0 \;+\; 3\times1\times1\right) = 1$$

The three H1s orbitals s_B, s_C, and s_D therefore span $A_1 + E$; adding this to the result from above that s_A spans A_1 gives $2A_1 + E$.

As explained in Section 10C.2(a) on page 409, only orbitals of the same symmetry species may have a nonzero overlap. The C_{3v} character table also shows that the d_{z^2} orbital spans A_1 in C_{3v}, d_{xy} and $d_{x^2-y^2}$ jointly span E, and d_{xz} and d_{yz} also jointly span E. It follows that d_{z^2} can form molecular orbitals with the A_1 combinations of hydrogen orbitals while the other d orbitals can all form molecular orbitals with the E combinations of hydrogen orbitals. So $\boxed{\text{yes}}$, more d orbitals can be involved in forming molecular orbitals than in the case of tetrahedral methane where, as shown in the previous exercise, only d_{xy}, d_{yz} and d_{xz} are able to form molecular orbitals.

(b) The irreducible representations spanned by the H1s orbitals in the C_{2v} distorted molecule, shown in the right-hand side of Fig. 10.18, are found in the same way as above. It is convenient to consider s_A and s_B separately from s_C and s_D. This is because s_A and s_B are mixed with each other but not with s_C or s_D by the operations of the group. Similarly s_C and s_D are mixed with each other but not with s_A or s_B. For s_A and s_B the matrix representatives are

$$\boldsymbol{D}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \boldsymbol{D}(C_2) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$
$$\boldsymbol{D}(\sigma_v) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \boldsymbol{D}(\sigma_v') = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

for which the characters are

$$\chi(E) = 2 \quad \chi(C_2) = 0 \quad \chi(\sigma_v) = 2 \quad \chi(\sigma_v') = 0$$

As before, this result is obtained with much less effort by simply counting the number of orbitals which are not moved by each operation. Using the decomposition formula, or simply by inspection of the C_{2v} character table, this representation decomposes to $A_1 + B_1$. Analysing s_C and s_D in the same way gives the representatives as

$$\boldsymbol{D}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \boldsymbol{D}(C_2) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$
$$\boldsymbol{D}(\sigma_v) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \boldsymbol{D}(\sigma_v') = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

The characters are

$$\chi(E) = 2 \quad \chi(C_2) = 0 \quad \chi(\sigma_v) = 0 \quad \chi(\sigma_v') = 2$$

which decomposes to $A_1 + B_2$.

Combining these results, the four H1s orbitals therefore span $2A_1 + B_1 + B_2$. Inspection of the C_{2v} character table indicates that z^2, and hence d_{z^2}, spans A_1, so this orbital can form molecular orbitals with the A_1 combinations of hydrogen orbitals. Because both x^2 and y^2 span A_1, $x^2 - y^2$ and hence $d_{x^2-y^2}$ also spans A_1 and can therefore also form molecular orbitals with the A_1 combination of hydrogen orbitals. The orbitals d_{zx} and d_{yz} span B_1 and B_2 respectively, so can form molecular orbitals with the B_1 and B_2 combinations of hydrogen orbitals. However, d_{xy} spans A_2 and therefore remains non-bonding because the hydrogen orbitals do not span A_2.

Therefore $\boxed{\text{yes}}$, more d orbitals can form molecular orbitals than for tetrahedral methane, but not as many for the C_{3v} distorted molecule where all five d orbitals could be involved in forming molecular orbitals.

P10C.4 The character table for the I_h point group is available in the *Online resource centre*.

(a) As explained in Section 10C.3 on page 411, a photon-induced transition from a state with symmetry $\Gamma^{(i)}$ to one with symmetry $\Gamma^{(f)}$ is only allowed if the direct product $\Gamma^{(f)} \times \Gamma^{(q)} \times \Gamma^{(i)}$ contains the totally symmetric irreducible representation, A_{1g}. Because the ground state is A_{1g} the direct product becomes $\Gamma^{(f)} \times \Gamma^{(q)} \times A_{1g}$. This is simply $\Gamma^{(f)} \times \Gamma^{(q)}$ because the direct product of the totally symmetric irreducible representation with any other representation is the latter representation itself.

If the product $\Gamma^{(f)} \times \Gamma^{(q)}$ is to be A_{1g}, then $\Gamma^{(f)}$ must equal $\Gamma^{(q)}$ because the direct product of two irreducible representations only contains the totally symmetric irreducible representation if the two irreducible representations are identical. However, inspection of the I_h character table shows that $\Gamma^{(q)} = T_{1u}$, because x, y and z together span the T_{1u} irreducible representation. Because neither of the lowest-lying excited states are of T_{1u} symmetry, photon-induced transitions to these states are $\boxed{\text{not allowed}}$.

(b) If the centre of inversion is removed then the distorted molecule has I symmetry. For this point group the character table in the *Resource section* shows that $\Gamma^{(q)}$ spans T_1. By the same reasoning as above it follows that transitions to an excited state with symmetry $\boxed{T_1 \text{ are allowed}}$ but transitions to a state with symmetry $\boxed{\text{G are not}}$.

P10C.6 As explained in Section 10C.3 on page 411, a photon-induced transition from a state with symmetry $\Gamma^{(i)}$ to one with symmetry $\Gamma^{(f)}$ is only allowed if the direct product $\Gamma^{(f)} \times \Gamma^{(q)} \times \Gamma^{(i)}$ contains the totally symmetric irreducible representation, A_{1g}. For a transition from an A_{1g} ground state to an E_u excited state the direct product becomes $E_u \times \Gamma^{(q)} \times A_{1g}$. This is simply $E_u \times \Gamma^{(q)}$ because the direct product of the totally symmetric irreducible representation A_{1g} with any other representation is the latter representation itself.

This product only contains A_{1g} if $\Gamma^{(q)} = E_u$ because the direct product of two irreducible representations only contains the totally symmetric irreducible representation if the two irreducible representations are identical. Inspection of the D_{4h} character table shows that x and y jointly span E_u, and therefore the transition $\boxed{\text{is allowed}}$ provided $q = (x, y)$, that is with x and y polarised radiation.

P10C.8 The tetrafluoroethene molecule is shown in Fig. 10.19.

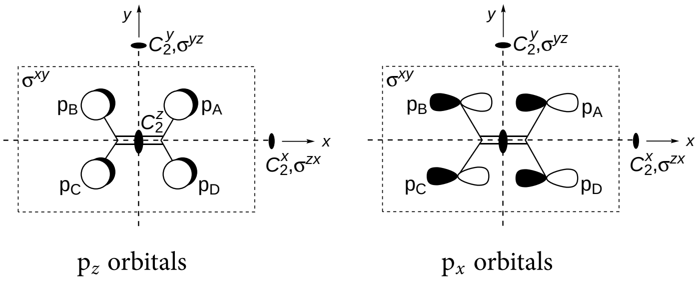


Figure 10.19

(a) The representation for the four p_z orbitals could be determined by finding the representatives using the method in Section 10B.2(a) on page 398, and then finding the traces of each of the representatives. The same result can be arrived at much more quickly by noting that: (1) only the diagonal elements of the representative matrix contribute to the trace; (2) orbitals which are unmoved by an operation will result in a +1 on the diagonal; (3) orbitals which are unmoved by an operation by are changed in sign will result in a −1 on the diagonal; (4) orbitals which are moved to other positions by an operation will result in a 0 on the diagonal. The character is found simply by counting +1 for orbitals which do not move and −1 for orbitals which do not move but which do change sign.

Referring to Fig. 10.19 it is seen that 4 orbitals are unaffected by E, all of the orbitals are moved by each of the C_2 operations and i. The reflections σ^{yz} and σ^{zx} move all of the orbitals, but σ^{xy} leaves all four orbitals unmoved, but with a sign change. The characters are therefore

E	C_2^z	C_2^y	C_2^x	i	σ^{xy}	σ^{yz}	σ^{zx}
4	0	0	0	0	−4	0	0

This representation is decomposed using the method described in Section 10C.1(b) on page 408. The number of times $n(\Gamma)$ that a given irreducible representation Γ occurs in a representation is given by [10C.3a–*408*],

$$n(\Gamma) = (1/h)\sum_C N(C)\chi^{(\Gamma)}(C)\chi(C)$$

where h is the order of the group, $N(C)$ is the number of operations in class C, $\chi^{(\Gamma)}$ is the character of class C in the irreducible representation Γ, and $\chi(C)$ is the character of class C in the representation being reduced. For the point group D_{2h}, $h = 8$. Because the representation to be reduced has characters of zero for all classes except E and σ^{xy}, only these latter two classes will make a non-zero contribution to the sum. The number of times that the irreducible representation $\mathrm{A_g}$ occurs is

$$\begin{aligned} n(\mathrm{A_g}) &= \tfrac{1}{8}\left(N(E)\times\chi^{(\mathrm{A_g})}(E)\times\chi(E) \;+\; N(\sigma^{xy})\times\chi^{(\mathrm{A_g})}(\sigma^{xy})\times\chi(\sigma^{xy})\right) \\ &= \tfrac{1}{8}\left(1\times1\times4+1\times1\times(-4)\right) = 0 \end{aligned}$$

Similarly

$$\begin{aligned} n(B_{1g}) &= \tfrac{1}{8}\left(1\times1\times4 \;+\; 1\times1\times(-4)\right) = 0 \\ n(B_{2g}) &= \tfrac{1}{8}\left(1\times1\times4 \;+\; 1\times(-1)\times(-4)\right) = 1 \\ n(B_{3g}) &= \tfrac{1}{8}\left(1\times1\times4 \;+\; 1\times(-1)\times(-4)\right) = 1 \\ n(A_{u}) &= \tfrac{1}{8}\left(1\times1\times4 \;+\; 1\times(-1)\times(-4)\right) = 1 \\ n(B_{1u}) &= \tfrac{1}{8}\left(1\times1\times4 \;+\; 1\times(-1)\times(-4)\right) = 1 \\ n(B_{2u}) &= \tfrac{1}{8}\left(1\times1\times4 \;+\; 1\times1\times(-4)\right) = 0 \\ n(B_{3u}) &= \tfrac{1}{8}\left(1\times1\times4 \;+\; 1\times1\times(-4)\right) = 0 \end{aligned}$$

The four p_z orbitals therefore span $\boxed{\mathrm{B_{2g}+B_{3g}+A_u+B_{1u}}}$.

(b) The SALCs of $\mathrm{B_{2g}}$, $\mathrm{B_{3g}}$, $\mathrm{A_u}$ and $\mathrm{B_{1u}}$ symmetries are generated by applying the projection operator to the p_A orbital using the method described in Section 10C.2(b) on page 409.

Row		E	C_2^z	C_2^y	C_2^x	i	σ^{xy}	σ^{yz}	σ^{zx}
1	effect on $\mathrm{p_A}$	$\mathrm{p_A}$	$\mathrm{p_C}$	$-\mathrm{p_B}$	$-\mathrm{p_D}$	$-\mathrm{p_C}$	$-\mathrm{p_A}$	$\mathrm{p_B}$	$\mathrm{p_D}$
2	characters for $\mathrm{B_{2g}}$	1	−1	1	−1	1	−1	1	−1
3	row 1 × row 2	$\mathrm{p_A}$	$-\mathrm{p_C}$	$-\mathrm{p_B}$	$\mathrm{p_D}$	$-\mathrm{p_C}$	$\mathrm{p_A}$	$-\mathrm{p_B}$	$\mathrm{p_D}$
4	characters for $\mathrm{B_{3g}}$	1	−1	−1	1	1	−1	1	−1
5	row 1 × row 4	$\mathrm{p_A}$	$-\mathrm{p_C}$	$\mathrm{p_B}$	$-\mathrm{p_D}$	$-\mathrm{p_C}$	$\mathrm{p_A}$	$\mathrm{p_B}$	$-\mathrm{p_D}$
6	characters for $\mathrm{A_u}$	1	1	1	1	−1	−1	−1	−1
7	row 1 × row 6	$\mathrm{p_A}$	$\mathrm{p_C}$	$-\mathrm{p_B}$	$-\mathrm{p_D}$	$\mathrm{p_C}$	$\mathrm{p_A}$	$-\mathrm{p_B}$	$-\mathrm{p_D}$
8	characters for $\mathrm{B_{1u}}$	1	1	−1	−1	−1	−1	1	1
9	row 1 × row 8	$\mathrm{p_A}$	$\mathrm{p_C}$	$\mathrm{p_B}$	$\mathrm{p_D}$	$\mathrm{p_C}$	$\mathrm{p_A}$	$\mathrm{p_B}$	$\mathrm{p_D}$

The SALCs are formed by summing rows 3, 5, 7, and 9 and dividing each by the order of the group ($h = 8$).

$$\begin{aligned}
\text{Row 3: } \psi^{(\mathrm{B_{2g}})} &= \tfrac{1}{8}(\mathrm{p_A} - \mathrm{p_C} - \mathrm{p_B} + \mathrm{p_D} - \mathrm{p_C} + \mathrm{p_A} - \mathrm{p_B} + \mathrm{p_D}) \\
&= \boxed{\tfrac{1}{4}(\mathrm{p_A} - \mathrm{p_B} - \mathrm{p_C} + \mathrm{p_D})} \\
\text{Row 5: } \psi^{(\mathrm{B_{3g}})} &= \tfrac{1}{8}(\mathrm{p_A} - \mathrm{p_C} + \mathrm{p_B} - \mathrm{p_D} - \mathrm{p_C} + \mathrm{p_A} + \mathrm{p_B} - \mathrm{p_D}) \\
&= \boxed{\tfrac{1}{4}(\mathrm{p_A} + \mathrm{p_B} - \mathrm{p_C} - \mathrm{p_D})} \\
\text{Row 7: } \psi^{(\mathrm{A_u})} &= \tfrac{1}{8}(\mathrm{p_A} + \mathrm{p_C} - \mathrm{p_B} - \mathrm{p_D} + \mathrm{p_C} + \mathrm{p_A} - \mathrm{p_B} - \mathrm{p_D}) \\
&= \boxed{\tfrac{1}{4}(\mathrm{p_A} - \mathrm{p_B} + \mathrm{p_C} - \mathrm{p_D})} \\
\text{Row 9: } \psi^{(\mathrm{B_{1u}})} &= \tfrac{1}{8}(\mathrm{p_A} + \mathrm{p_C} + \mathrm{p_B} + \mathrm{p_D} + \mathrm{p_C} + \mathrm{p_A} + \mathrm{p_B} + \mathrm{p_D}) \\
&= \boxed{\tfrac{1}{4}(\mathrm{p_A} - \mathrm{p_B} + \mathrm{p_C} - \mathrm{p_D})}
\end{aligned}$$

(c) The $2\mathrm{p}_x$ orbitals, shown in the right-hand half of Fig. 10.19, are analysed in the same way. The characters are found by noting that under the E operation the four p_x orbitals are not moved so $\chi(E) = 4$. Similarly under the C_2^z operation the orbitals are all moved so $\chi(C_2^z) = 0$. Using this approach the characters are written down as

E	C_2^z	C_2^y	C_2^x	i	σ^{xy}	σ^{yz}	σ^{zx}
4	0	0	0	0	4	0	0

Using the decomposition formula, or simply by inspection of the character table, this is decomposed to $\boxed{\mathrm{A_g} + \mathrm{B_{1g}} + \mathrm{B_{2u}} + \mathrm{B_{3u}}}$. Use of the projection operator then gives

Row		E	C_2^z	C_2^y	C_2^x	i	σ^{xy}	σ^{yz}	σ^{zx}
1	effect on $\mathrm{p_A}$	$\mathrm{p_A}$	$-\mathrm{p_C}$	$-\mathrm{p_B}$	$\mathrm{p_D}$	$-\mathrm{p_C}$	$\mathrm{p_A}$	$-\mathrm{p_B}$	$\mathrm{p_D}$
2	characters for $\mathrm{A_g}$	1	1	1	1	1	1	1	1
3	row 1 × row 2	$\mathrm{p_A}$	$-\mathrm{p_C}$	$-\mathrm{p_B}$	$\mathrm{p_D}$	$-\mathrm{p_C}$	$\mathrm{p_A}$	$-\mathrm{p_B}$	$\mathrm{p_D}$
4	characters for $\mathrm{B_{1g}}$	1	1	−1	−1	1	1	−1	−1
5	row 1 × row 4	$\mathrm{p_A}$	$-\mathrm{p_C}$	$\mathrm{p_B}$	$-\mathrm{p_D}$	$-\mathrm{p_C}$	$\mathrm{p_A}$	$\mathrm{p_B}$	$-\mathrm{p_D}$
6	characters for $\mathrm{B_{2u}}$	1	−1	1	−1	−1	1	1	−1
7	row 1 × row 6	$\mathrm{p_A}$	$\mathrm{p_C}$	$-\mathrm{p_B}$	$-\mathrm{p_D}$	$\mathrm{p_C}$	$\mathrm{p_A}$	$-\mathrm{p_B}$	$-\mathrm{p_D}$
8	characters for $\mathrm{B_{1u}}$	1	−1	−1	1	−1	1	−1	1
9	row 1 × row 8	$\mathrm{p_A}$	$\mathrm{p_C}$	$\mathrm{p_B}$	$\mathrm{p_D}$	$\mathrm{p_C}$	$\mathrm{p_A}$	$\mathrm{p_B}$	$\mathrm{p_D}$

Hence the SALCs are

$$\boxed{\psi^{(\mathrm{A_g})} = \tfrac{1}{4}(\mathrm{p_A} - \mathrm{p_B} - \mathrm{p_C} + \mathrm{p_D})} \quad \boxed{\psi^{(\mathrm{B_{1g}})} = \tfrac{1}{4}(\mathrm{p_A} + \mathrm{p_B} - \mathrm{p_C} - \mathrm{p_D})}$$

$$\boxed{\psi^{(\mathrm{B_{2u}})} = \tfrac{1}{4}(\mathrm{p_A} - \mathrm{p_B} + \mathrm{p_C} - \mathrm{p_D})} \quad \boxed{\psi^{(\mathrm{B_{3u}})} = \tfrac{1}{4}(\mathrm{p_A} + \mathrm{p_B} + \mathrm{p_C} + \mathrm{p_D})}$$

11 Molecular Spectroscopy

11A General features of molecular spectroscopy

Answers to discussion questions

D11A.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. In a gas, molecules have a wide range of speeds in all directions and the detected spectral line is the absorption or emission profile arising from the resulting Doppler shifts. The shape of a Doppler-broadened spectral line reflects the Maxwell distribution of speeds in the sample.

Lifetime broadening. This kind of broadening is a quantum mechanical effect which predicts that for a state with a lifetime τ there is an energy uncertainty δE given by $\delta E \approx \hbar/\tau$. This uncertainty in the energy translates to absorption (or emission) over a range of frequencies and hence a linewidth. The lifetime of a state may be limited by the rate of spontaneous emission from the state, in which case the resulting broadening is called *natural line broadening*.

Collisions between molecules are efficient at changing their rotational and vibrational energies, and therefore the lifetimes of such states are limited by the the collision rate. The resulting line broadening is called *collisional* or *pressure line broadening*.

The rate of spontaneous emission cannot be changed; hence its contribution is the same regardless of phase. Doppler broadening is expected to contribute in a similar way for both gases and liquids. The higher density of liquids compared to gases implies that collisions will be more frequent and hence the collisional line broadening will be greater for a liquid.

Solutions to exercises

E11A.1(b) The ratio A/B is given by [11A.6a–*420*], $A/B = 8\pi h\nu^3/c^3$; the frequency ν is related to the wavelength though $\nu = c/\lambda$.

(i) For radiofrequency radiation with $\nu = 500$ MHz

$$\frac{A}{B} = \frac{8\pi h\nu^3}{c^3} = \frac{8\pi \times (6.6261\times10^{-34}\,\mathrm{J\,s}) \times (500\times10^{6}\,\mathrm{s^{-1}})^3}{(2.9979\times10^{8}\,\mathrm{m\,s^{-1}})^3}$$

$$= \boxed{7.73\times10^{-32}\ \mathrm{J\,s\,m^{-3}}}$$

(ii) For microwave radiation with $\lambda = 3.0$ cm

$$\frac{A}{B} = \frac{8\pi h(c/\lambda)^3}{c^3} = \frac{8\pi h}{\lambda^3} = \frac{8\pi \times (6.6261 \times 10^{-34}\,\mathrm{J\,s})}{(3.0 \times 10^{-2}\,\mathrm{m})^3} = \boxed{6.2 \times 10^{-28}\,\mathrm{J\,s\,m^{-3}}}$$

E11A.2(b) The Beer–Lambert law [11A.8–*421*], $I = I_0 10^{-\varepsilon[\mathrm{J}]L}$ relates the intensity of the transmitted light I to that of the incident light I_0.

$$\begin{aligned} I/I_0 &= 10^{-\varepsilon[\mathrm{J}]L} = 10^{-(227\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}})\times(2.52\times10^{-3}\,\mathrm{mol\,dm^{-3}})\times(0.200\,\mathrm{cm})} \\ &= 0.768... \end{aligned}$$

Using this, the percentage reduction in intensity is calculated as $100(I_0 - I)/I_0 = 100(1 - I/I_0) = 100(1 - 0.768...) = \boxed{23.2\%}$. Note the conversion of L to cm and [J] to mol dm^{-3} in order to match the units of ε.

E11A.3(b) The Beer–Lambert law [11A.8–*421*], $I = I_0 10^{-\varepsilon[\mathrm{J}]L}$ relates the intensity of the transmitted light I to that of the incident light I_0. If a fraction T of the incident light is transmitted through the sample, $I = TI_0$ and hence $I/I_0 = T$; T is the transmittance. It follows that $\log T = -\varepsilon[\mathrm{J}]L$ hence $\varepsilon = -(\log T)/[\mathrm{J}]L$. If 61.5% of the light is transmitted, $T = 0.615$

$$\begin{aligned} \varepsilon &= -(\log T)/[\mathrm{J}]L = -[\log(0.615)]/(0.717 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}) \times (0.250\,\mathrm{cm}) \\ &= 1.17... \times 10^3\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}} \end{aligned}$$

Note the conversion of L to cm and [J] to mol dm^{-3} in order to give the usual units of ε. To convert the molar absorption coefficient to cm^2 mol^{-1} simply multiply the above value by 10^3 to convert dm^3 to cm^3. The units are then cm^3 mol^{-1} cm^{-1} = cm^2 mol^{-1}. Hence $\boxed{\varepsilon = 1.18 \times 10^6\,\mathrm{cm^2\,mol^{-1}}}$.

E11A.4(b) The Beer–Lambert law [11A.8–*421*], $I = I_0 10^{-\varepsilon[\mathrm{J}]L}$ relates the intensity of the transmitted light I to that of the incident light I_0. If a fraction α is absorbed, then a fraction $T = 1 - \alpha$ of the incident light passes through the sample, $I = TI_0$ and hence $I/I_0 = T$; T is the transmittance. It follows that $\log T = -\varepsilon[\mathrm{J}]L$ hence $[\mathrm{J}] = -(\log T)/\varepsilon L$. If 48.3% of the light is absorbed, $\alpha = 0.483$ and $T = 1 - 0.483 = 0.517$

$$\begin{aligned} [\mathrm{J}] &= -(\log T)/\varepsilon L = -[\log(0.517)]/(423\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}) \times (0.650\,\mathrm{cm}) \\ &= 1.04... \times 10^{-3}\,\mathrm{mol\,dm^{-3}} = \boxed{1.04\,\mathrm{mM}} \end{aligned}$$

Note the use of L in cm.

E11A.5(b) The transmittance T is the ratio I/I_0, hence the Beer–Lambert law [11A.8–*421*] can be written $T = I/I_0 = 10^{-\varepsilon[\mathrm{J}]L}$. It follows that $\log T = -\varepsilon[\mathrm{J}]L$ and hence $\varepsilon = -(\log T)/[\mathrm{J}]L$. With this, the following table is drawn up, with $L = 0.250$ cm.

$[\text{dye}]/(\text{mol dm}^{-3})$	0.0010	0.0050	0.0100	0.0500
$T/\%$	68	18	3.7	1.03×10^{-5}
T	0.68	0.18	0.037	1.03×10^{-7}
$\varepsilon/(\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1})$	670	596	573	559

The molar absorption coefficient is clearly not independent of the concentration; this may indicate that the dye molecules are interacting with one another at higher concentrations.

E11A.6(b) The transmittance T is the ratio I/I_0, hence the Beer–Lambert law [11A.8–*421*] can be written $T = I/I_0 = 10^{-\varepsilon[\text{J}]L}$. It follows that $\log T = -\varepsilon[\text{J}]L$ and hence $\varepsilon = -(\log T)/[\text{J}]L$. With the given data, $T = 0.29$ and $L = 0.500$ cm, the molar absorption coefficient is calculated as

$$\varepsilon = -(\log 0.29)/[(18.5\times10^{-3}\,\text{mol dm}^{-3})\times(0.500\,\text{cm})] = 58.1...\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}$$

The molar absorption coefficient is therefore $\boxed{\varepsilon = 58\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}}$. For a path length of 0.250 cm the transmittance is

$$T = 10^{-(58.1...\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1})\times(0.250\,\text{cm})\times(18.5\times10^{-3}\,\text{mol dm}^{-3})} = 0.538...$$

Hence $\boxed{T = 54\%}$. Note the conversion of the concentration to mol dm^{-3}.

E11A.7(b) The ratio of the incident to the transmitted intensities of light after passing through a sample of length L, molar concentration $[\text{J}]$, and molar absorption coefficient ε is given by [11A.8–*421*], $T = I/I_0 = 10^{-\varepsilon[\text{J}]L}$. It follows that $\log T = -\varepsilon[\text{J}]L$, which rearranges to give $L = -(\log T)/\varepsilon[\text{J}]$.

The missing piece of information (in fact misplaced to *Exercise* E11A.7(a)) is that the concentration of the absorber is 10 mmol dm^{-3}. The light intensity is reduced to half when $T = 0.5$, hence the thickness of the sample is calculated as

$$L = -(\log 0.5)/[(30\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1})\times(0.010\,\text{mol dm}^{-3})] = \boxed{1.0\,\text{cm}}$$

The light intensity is reduced to one tenth when $T = 0.1$

$$L = -(\log 0.1)/[(30\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1})\times(0.010\,\text{mol dm}^{-3})] = \boxed{3.3\,\text{cm}}$$

E11A.8(b) The integrated absorption coefficient is given by [11A.10–*423*], $\mathcal{A} = \int_{\text{band}} \varepsilon(\tilde{\nu})\,\mathrm{d}\tilde{\nu}$, where the integration is over the band, and $\tilde{\nu} = \lambda^{-1}$ is the wavenumber. The band extends from 167 nm, corresponding to $\tilde{\nu} = (167\times10^{-7}\,\text{cm})^{-1} = 5.98...\times10^4\,\text{cm}^{-1}$, peaking at 200 nm, $\tilde{\nu} = (200\times10^{-7}\,\text{cm})^{-1} = 5.00\times10^4\,\text{cm}^{-1}$, and ending at 250 nm, $\tilde{\nu} = (250\times10^{-7}\,\text{cm})^{-1} = 4.00\times10^4\,\text{cm}^{-1}$.

The given equation of the parabolic lineshape, $\varepsilon(\tilde{\nu}) = \varepsilon_{\text{max}}[1 - k(\tilde{\nu} - \tilde{\nu}_{\text{max}})^2]$ is conveniently rewritten as $\varepsilon(x) = \varepsilon_{\text{max}}[1 - kx^2]$, where $x = \tilde{\nu} - \tilde{\nu}_{\text{max}}$. The edges of the lineshape are at the wavenumber at which $\varepsilon(x) = 0$

$$0 = \varepsilon_{\text{max}}[1 - kx^2] \qquad \text{hence} \qquad x = \pm k^{-1/2}$$

The area under the lineshape is therefore

$$\begin{aligned}\mathcal{A} &= \int_{-k^{-1/2}}^{+k^{-1/2}} \varepsilon_{\text{max}}(1 - kx^2)\,\mathrm{d}x = \varepsilon_{\text{max}}\ (x - kx^3/3)\big|_{-k^{-1/2}}^{+k^{-1/2}} \\ &= \varepsilon_{\text{max}}(2k^{-1/2} - (2/3)k \times k^{-3/2}) = (4/3)\varepsilon_{\text{max}}k^{-1/2}\end{aligned}$$

For the specified lineshape, $\varepsilon(\tilde{\nu})$ goes to zero at $5.98... \times 10^4\ \text{cm}^{-1}$ and at $4.00 \times 10^4\ \text{cm}^{-1}$. It follows that $2k^{-1/2} = (5.98... - 4.00) \times 10^4\ \text{cm}^{-1}$ and hence

$$\begin{aligned}\mathcal{A} &= (4/3) \times (3.35 \times 10^4\ \text{dm}^3\ \text{mol}^{-1}) \\ &\qquad \times \tfrac{1}{2} \times [(5.98... - 4.00) \times 10^4\ \text{cm}^{-1}] \\ &= \boxed{4.44 \times 10^8\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}}\end{aligned}$$

E11A.9(b) The Doppler linewidth is given by [11A.12a–*424*], $\delta\nu_{\text{obs}} = (2\nu_0/c)(2kT\ln 2/m)^{1/2}$; division of both sides by the speed of light converts $\delta\nu_{\text{obs}}$ and ν_0 to wavenumbers, allowing the expression to be written $\delta\tilde{\nu}_{\text{obs}} = (2\tilde{\nu}_0/c)(2kT\ln 2/m)^{1/2}$. The mass of $^1\text{H}^{127}\text{I}$ is taken as $128\ m_\text{u}$. With these data the linewidth is calculated as

$$\begin{aligned}\delta\tilde{\nu}_{\text{obs}} &= \frac{2 \times 2308\ \text{cm}^{-1}}{2.9979 \times 10^8\ \text{m s}^{-1}} \times \left(\frac{2 \times (1.3806 \times 10^{-23}\ \text{J K}^{-1}) \times (400\ \text{K}) \times \ln 2}{128 \times 1.6605 \times 10^{-27}\ \text{kg}}\right)^{1/2} \\ &= \boxed{2.92 \times 10^{-3}\ \text{cm}^{-1}}\end{aligned}$$

where $1\ \text{J} = 1\ \text{kg m}^2\ \text{s}^{-2}$ is used.

E11A.10(b) If a light source of frequency ν_0 is approached at a speed s, the Doppler shifted frequency ν_a is [11A.11a–*423*],

$$\nu_\text{a} = \nu_0 \left(\frac{1 + s/c}{1 - s/c}\right)^{1/2}$$

Writing the frequencies in terms of the wavelength as $\nu = c/\lambda$ and then inverting before sides gives

$$\lambda_\text{a} = \lambda_0 \left(\frac{1 - s/c}{1 + s/c}\right)^{1/2}$$

Solving this for the speed s leads to

$$s = c\left(\frac{1 - (\lambda_\text{a}/\lambda_0)^2}{1 + (\lambda_\text{a}/\lambda_0)^2}\right)$$

Hence, to achieve a doppler shifted wavelength of 530 nm, the speed needs to be

$$s = c \times \frac{1 - (530\ \text{nm}/680\ \text{nm})^2}{1 + (530\ \text{nm}/680\ \text{nm})^2} = (0.244...) \times c$$

Hence, for this large Doppler shift, the speed of approach needs to be at 24.4% of the speed of light, which is $\boxed{7.31 \times 10^7\ \text{m s}^{-1}}$.

E11A.11(b) The uncertainty in the energy of a state with lifetime τ is $\delta E \approx \hbar/\tau$. Therefore a spectroscopic transition involving this state has an uncertainty in its frequency, and hence a linewidth, of the order of $\delta\nu = \delta E/h \approx (2\pi\tau)^{-1}$. This expression is rearranged to give the lifetime as $\tau = (2\pi\delta\nu)^{-1}$; expressing the linewidth as a wavenumber gives $\tau = (2\pi\delta\tilde{\nu}c)^{-1}$.

(i) For $\delta\nu = 200$ MHz

$$\tau = [2\pi \times (200 \times 10^6\ \text{Hz})]^{-1} = 7.95... \times 10^{-10}\ \text{s} = \boxed{796\ \text{ps}}$$

(ii) For $\delta\tilde{\nu} = 2.45\ \text{cm}^{-1}$

$$\tau = [2\pi \times (2.45\ \text{cm}^{-1}) \times (2.9979 \times 10^{10}\ \text{cm s}^{-1})]^{-1} = 2.16... \times 10^{-12}\ \text{s}$$
$$= \boxed{2.17\ \text{ps}}$$

E11A.12(b) The uncertainty in the energy of a state with lifetime τ is $\delta E \approx \hbar/\tau$. Therefore a spectroscopic transition involving this state has an uncertainty in its frequency, and hence a linewidth, of the order of $\delta\nu = \delta E/h \approx (2\pi\tau)^{-1}$. If each collision deactivates the molecule, the lifetime is 1/(collision frequency), but if only 1 in N of the collisions deactivates the molecule, the lifetime is N/(collision frequency). Thus $\tau = N/z$, where z is the collision frequency. The linewidth is therefore $\delta\nu = (2\pi N/z)^{-1}$.

(i) If each collision is effective at deactivation, $N = 1$ and with the data given

$$\delta\nu = [2\pi \times 1/(1.0 \times 10^9\ \text{s}^{-1})]^{-1} = 1.59 \times 10^8\ \text{Hz} = \boxed{0.16\ \text{GHz}}$$

(ii) If only 1 in 10 collisions are effective at deactivation, $N = 10$

$$\delta\nu = [2\pi \times 10/(1.0 \times 10^9\ \text{s}^{-1})]^{-1} = 1.59 \times 10^7\ \text{Hz} = \boxed{16\ \text{MHz}}$$

Solutions to problems

P11A.2 The argument takes the same steps as in *How is that done?* 11A.1 on page 421 up to the derivation of $\text{d}I/I = -\kappa[\text{J}]\,\text{d}x$. This expression is integrated as before, but instead of [J] being constant, it is given by $[\text{J}] = [\text{J}]_0 \text{e}^{-x/x_0}$

$$\int_{I_0}^{I} (1/I)\,\text{d}I = \int_0^L -\kappa[\text{J}]_0 \text{e}^{-x/x_0}\,\text{d}x$$
$$\ln(I/I_0) = -\kappa[\text{J}]_0(-x_0\text{e}^{-x/x_0})\Big|_0^L = -\kappa[\text{J}]_0 x_0(1 - \text{e}^{-L/x_0})$$
$$\text{hence}\ \lg(I/I_0) = -(\kappa/\ln 10)[\text{J}]_0 x_0(1 - \text{e}^{-L/x_0})$$

For this case the Beer–Lambert law is $\boxed{\lg(I/I_0) = -\varepsilon[\mathrm{J}]_0 x_0(1 - \mathrm{e}^{-L/x_0})}$, where $\varepsilon = \kappa/\ln 10$.

In the limit $L \gg x_0$, $\mathrm{e}^{-L/x_0} \rightarrow 0$ and hence $\boxed{\lg(I/I_0) = -\varepsilon[\mathrm{J}]_0 x_0}$. In this limit the absorption is independent of the length of the sample. If $x_0 \gg L$ then the exponential may be expanded up to the linear term to give $(1 - \mathrm{e}^{-L/x_0}) \approx (1 - 1 + L/x_0) \approx L/x_0$. Then $\boxed{\lg(I/I_0) = -\varepsilon[\mathrm{J}]_0 L}$, which is the form of the Beer–Lambert law for a constant concentration.

P11A.4 Suppose that species A and B associate to give a complex AB according to the equilibrium: $\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{AB}$. Suppose that species A absorbs at a particular wavelength with absorption coefficient ε_A, and that species AB absorbs at the same wavelength but with absorption coefficient ε_AB; B does not absorb at this wavelength. The absorbance at this wavelength is

$$A_\lambda = \varepsilon_\mathrm{A}[\mathrm{A}]L + \varepsilon_\mathrm{AB}[\mathrm{AB}]L$$

If the initial amount of A is $[\mathrm{A}]_0$ and at equilibrium the amount of AB is $[\mathrm{AB}]_\mathrm{e}$, mass balance requires $[\mathrm{A}] = [\mathrm{A}]_0 - [\mathrm{AB}]_\mathrm{e}$. It follows that

$$A_\lambda = \varepsilon_\mathrm{A}\left([\mathrm{A}]_0 - [\mathrm{AB}]_\mathrm{e}\right)L + \varepsilon_\mathrm{AB}[\mathrm{AB}]_\mathrm{e}L = \underbrace{\varepsilon_\mathrm{A}[\mathrm{A}]_0 L}_{\text{term 1}} + \underbrace{(\varepsilon_\mathrm{AB} - \varepsilon_\mathrm{A})[\mathrm{AB}]_\mathrm{e}L}_{\text{term 2}}$$

As the amount of added B is changed, term 1 remains the same, but in general term 2 will change because of the resulting change in $[\mathrm{AB}]_\mathrm{e}$. However, if the wavelength is chosen such that $\varepsilon_\mathrm{AB} = \varepsilon_\mathrm{A}$, term 2 will go to zero and the absorbance will be invariant to the amount of B added. This is the isosbestic point.

P11A.6 Because only the area under the absorption band is of interest it can be assumed, without loss of generality, that the band is centred on $\tilde{\nu} = 0$. The bandshape is then given by $\varepsilon(\tilde{\nu}) = \varepsilon_\mathrm{max}\mathrm{e}^{-a\tilde{\nu}^2}$, where the parameter a determines the width. This parameter is found by finding the wavenumbers $\tilde{\nu}_{1/2}$ at which ε has fallen to half its maximum value

$$\begin{aligned}\tfrac{1}{2}\varepsilon_\mathrm{max} &= \varepsilon_\mathrm{max}\mathrm{e}^{-a(\tilde{\nu}_{1/2})^2}\\ \text{hence } \ln\tfrac{1}{2} &= -a(\tilde{\nu}_{1/2})^2\\ \text{hence } (\tilde{\nu}_{1/2})^2 &= \ln 2/a\end{aligned}$$

where to go to the last line $\ln\frac{1}{2} = -\ln 2$ is used. The wavenumbers of the points at which ε has fallen to half its maximum value are therefore $\pm(\ln 2/a)^{1/2}$, and hence the separation between these is $2(\ln 2/a)^{1/2}$. This separation is the width at half-height $\Delta\tilde{\nu}_{1/2}$

$$\Delta\tilde{\nu}_{1/2} = 2(\ln 2/a)^{1/2} \quad \text{hence} \quad a = \frac{4\ln 2}{(\Delta\tilde{\nu}_{1/2})^2}$$

Having established the relationship between the parameter a and the width at half-height, the integral over the band is computed

$$\mathcal{A} = \int_{-\infty}^{+\infty} \varepsilon(\tilde{\nu})\,\mathrm{d}\tilde{\nu} = \int_{-\infty}^{+\infty} \varepsilon_{\max}\mathrm{e}^{-a\tilde{\nu}^2}\,\mathrm{d}\tilde{\nu} = \varepsilon_{\max}(\pi/a)^{1/2}$$

The integral needed is of the form of Integral G.1 with $k = a$. Now the expression for a derived above is used to give

$$\begin{aligned}\mathcal{A} &= \varepsilon_{\max}\left(\frac{\pi(\Delta\tilde{\nu}_{1/2})^2}{4\ln 2}\right)^{1/2} = \varepsilon_{\max}\left(\frac{\pi}{4\ln 2}\right)^{1/2}\Delta\tilde{\nu}_{1/2}\\ &= \varepsilon_{\max}(1.0645)\Delta\tilde{\nu}_{1/2}\end{aligned}$$

Making measurements from the plot in the text gives $\varepsilon_{\max} = 9.8\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$ and $\Delta\tilde{\nu}_{1/2} = 4500\ \mathrm{cm^{-1}}$, hence $\mathcal{A} = 4.7\times10^4\ \mathrm{dm^3\ mol^{-1}\ cm^{-2}}$. If several points are measured from the plot these can be used as the input data to a non-linear least-squares fitting procedure, most conveniently done using mathematical software. With such an approach the best-fit gaussian line is (omitting units for clarity)

$$\varepsilon(\tilde{\nu}) = 9.704\,\mathrm{e}^{-(1.405\times10^{-7})\times(\tilde{\nu}-2.814\times10^4)^2}$$

Integrating this function gives $\mathcal{A} = 4.5\times10^4\ \mathrm{dm^3\ mol^{-1}\ cm^{-2}}$. A better fit is obtained by using the sum of two gaussians, each with separate parameters:

$$\varepsilon(\tilde{\nu}) = 5.757\,\mathrm{e}^{-(1.310\times10^{-7})\times(\tilde{\nu}-2.916\times10^4)^2} + 5.807\,\mathrm{e}^{-(3.180\times10^{-7})\times(\tilde{\nu}-2.725\times10^4)^2}$$

Integrating this function gives $\mathcal{A} = 4.6\times10^4\ \mathrm{dm^3\ mol^{-1}\ cm^{-2}}$.

P11A.8 (a) The lines from the star are all at longer wavelength, and hence lower frequency, than for the Earth-bound observations, therefore the object is $\boxed{\text{receding}}$. The ratio f is computed as $f = \nu_\mathrm{r}/\nu = \lambda/\lambda_\mathrm{r}$ because the frequency is inversely proportional to the wavelength. Writing $x = s/c$ gives

$$f = \left(\frac{1-x}{1+x}\right)^{1/2} \quad \text{hence} \quad f^2(1+x) = (1-x) \quad \text{hence} \quad x = \frac{1-f^2}{1+f^2}$$

It follows that $s = c[1-(\lambda/\lambda_\mathrm{r})^2]/[1+(\lambda/\lambda_\mathrm{r})^2]$. With this expression s is computed for each of the lines

$\lambda_\mathrm{r}/\mathrm{nm}$	438.882	441.000	442.020
λ/nm	438.392	440.51	441.510
$s/(10^5\ \mathrm{m\,s^{-1}})$	3.34894	3.33285	3.46095

The average of these measurements is $\boxed{3.38\times10^5\ \mathrm{m\,s^{-1}}}$. The spread of values is much larger than the apparent precision of the data.

(b) The radial velocity of the star with respect to the Sun could be computed if the Earth's speed with respect to the Sun along the Sun-star vector at the time of the spectral observation is known. This could be estimated from quantities available through astronomical observation: the Earth's orbital velocity times the cosine of the angle between that velocity vector and the Earth-star vector at the time of the spectral observation. (The Earth-star direction, which is observable by Earth-based astronomers, is practically identical to the Sun-star direction, which is technically the direction needed.) Alternatively, repeat the experiment half a year later. At that time, the Earth's motion with respect to the Sun is approximately equal in magnitude and opposite in direction compared to the original experiment. Averaging f values over the two experiments would yield f values in which the Earth's motion is effectively averaged out.

P11A.10 The Doppler lineshape is given in *How is that done?* 11A.2 on page 423: $I = Ae^{-mc^2(\nu-\nu_0)^2/2\nu_0^2kT}$, where A is a constant of proportionality. It is convenient to rewrite this in terms of the dimensionless parameter $x = (\nu - \nu_0)/\nu_0$, to give $I = Ae^{-mc^2x^2/2kT}$. The derivative lineshape, $D(x)$ is

$$D(x) = \frac{\mathrm{d}I}{\mathrm{d}x} = A\frac{-2xmc^2}{2kT}\mathrm{e}^{-mc^2x^2/2kT} = -A\frac{mc^2}{kT}\,x\,\mathrm{e}^{-mc^2x^2/2kT}$$

It is convenient to define $\alpha = mc^2/kT$, giving

$$D(x) = -A\alpha\,x\,\mathrm{e}^{-\alpha x^2/2}$$

This lineshape is plotted in Fig 11.1 for different values of α. The lineshape goes to zero as $x \to \pm\infty$ on account of the exponential term, is zero at $x = 0$, and has a negative-going minimum at positive x and a positive-going maximum, symmetrically placed, at negative x. As T increases (α decreases) the maximum and minimum decrease in size and the line becomes broader.

The positions of the maximum and minimum are found by differentiating once more with respect to x and setting the result equal to zero.

$$\frac{\mathrm{d}D(x)}{\mathrm{d}x} = -A\alpha\,\mathrm{e}^{-\alpha x^2/2} + A\alpha^2x^2\mathrm{e}^{-\alpha x^2/2}$$

This derivative is zero when $x = \pm\alpha^{-1/2}$: these values correspond to the positions of maximum and minimum. The separation between these two is $2\alpha^{-1/2}$: this goes as $T^{1/2}$.

P11A.12 Figure 11.2 shows plots the interferogram which would arise from a monochromatic beam sampled at different distance increments δ (expressed as a multiple of $\tilde{\nu}p$). The solid line shows the underlying continuous function which, for the values chosen, goes through three complete cycles.

The points indicated with open and closed triangles indicate the values which would be recorded for the two smallest increments. These points on their own

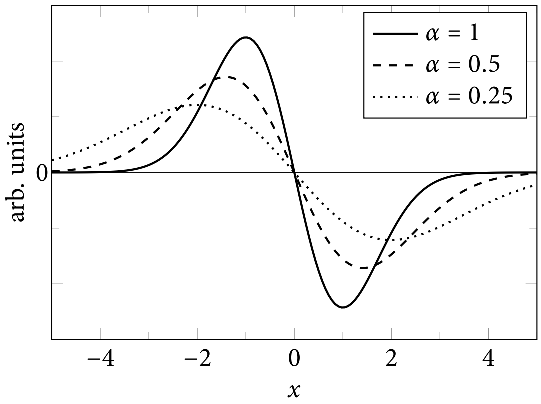


Figure 11.1

provide a pretty good approximation to the curve: the minima and maxima are sufficiently well defined that it is clear that there are three cycles, and so the wavenumber is correctly represented.

The points indicated by the open circles just capture the minima and maxima, and no other detail; they are just sufficient to imply that there are three cycles. In fact these measurements correspond to the *Nyquist condition* which states that at least two data points are required per cycle in order to measure the wavenumber correctly. The filled circles have the largest value of the increment, and it is clear from the digram that they are spaced too widely to represent the waveform correctly – in fact they are consistent with a curve at one third of the wavenumber shown by the complete curve.

This diagram illustrates that in order to infer the wavenumber correctly it is necessary to sample the interferogram such that there are at least two data points per cycle. Therefore, the upper limit on the wavenumber which can be correctly measured using an interferometer is set by the amount by which the mirror is moved in each step.

11B Rotational spectroscopy

Answers to discussion questions

D11B.2 Centrifugal distortion increases the moment of inertia and hence decreases the rotational constant. Therefore, the separation between levels is decreased.

D11B.4 This is discussed in Section 11B.2(a) on page 435.

D11B.6 BeF_2 is linear; ^{19}F has spin $\frac{1}{2}$ and is therefore a fermion. The argument is therefore exactly the same as for $^{1}H_2$, and so the molecule does indeed exist in *ortho* and *para* forms. The Be atom has no effect on the argument as it is at the centre of symmetry.

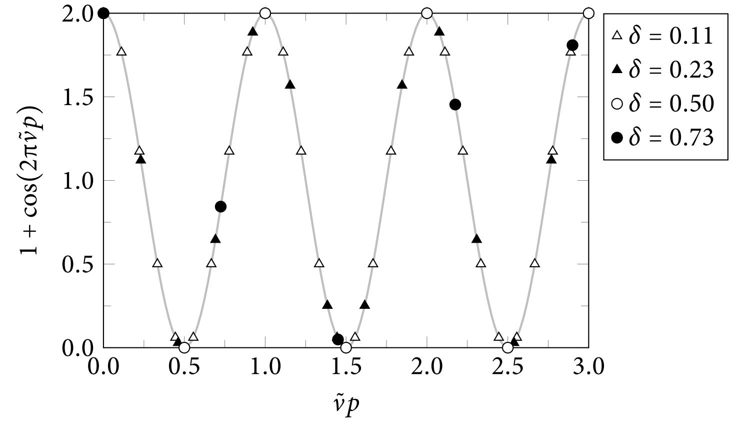


Figure 11.2

D11B.8 $^1H_2$ molecules can exist in two forms: the *para* form has antisymmetric nuclear spin wavefunctions and the *ortho* form has symmetric nuclear spin wavefunctions. As discussed in Section 11B.4 on page 439, it follows that because of these arrangements of the nuclear spins the *ortho* form must have rotational wavefunctions restricted to odd J values. *Ortho* hydrogen therefore cannot exist in the $J = 0$ state and hence it always has some rotational energy: that is, it has rotational zero-point energy.

Solutions to exercises

E11B.1(b) Expressions for the moments of inertia are given in Table 11B.1 on page 431; PH_3 is a symmetric rotor and the second entry under symmetric rotors is the required one. The moment or inertia about the threefold axis is $I_{||}$

$$\begin{aligned} I_{||} &= 2m_{\mathrm{H}}(1-\cos\theta)R^2 \\ &= 2[(1.0078)\times(1.6605\times10^{-27}\,\mathrm{kg})]\times(1-\cos 93.5°)\times(142\times10^{-12}\,\mathrm{m})^2 \\ &= 7.16...\times10^{-47}\,\mathrm{kg\,m^2} = \boxed{7.16\times10^{-47}\,\mathrm{kg\,m^2}} \end{aligned}$$

The corresponding rotational constant is given by [11B.13b–*433*]

$$\begin{aligned} \tilde{A} &= \frac{\hbar}{4\pi c I_{||}} = \frac{1.0546\times10^{-34}\,\mathrm{J\,s}}{4\pi\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})\times(7.16...\times10^{-47}\,\mathrm{kg\,m^2})} \\ &= \boxed{3.91\,\mathrm{cm^{-1}}} \end{aligned}$$

E11B.2(b) There is an error in the *Exercise*: the molecule is AB_4, not AB_3. The required expressions are the first listed under symmetric rotors in Table 11B.1 on page

431

$$\begin{aligned}
I_\perp &= m_A f_1(\theta)R^2 + \frac{m_A(m_B+m_A)}{m} f_2(\theta)R^2 \\
&\quad + \frac{m_C}{m}\left\{(3m_A+m_B)R' + 6m_A R\left[\tfrac{1}{3}f_2(\theta)\right]^{1/2}\right\}R' \\
I_{||} &= 2m_A f_1(\theta)R^2
\end{aligned}$$

Note that the molecule described by these relationships is BA_3C, which becomes BA_4 by letting C=A; the question refers to a molecule AB_4, but for consistency with the main text the exercise will be continued with BA_4. Let $m_C = m_A$ and $R' = \rho R$ to give

$$\begin{aligned}
I_\perp &= m_A f_1(\theta)R^2 + \frac{m_A(m_B+m_A)}{m} f_2(\theta)R^2 \\
&\quad + \frac{m_A}{m}\left\{(3m_A+m_B)\rho R + 6m_A R\left[\tfrac{1}{3}f_2(\theta)\right]^{1/2}\right\}\rho R
\end{aligned}$$

with $m = m_B + 4m_A$. At the tetrahedral angle $\cos\theta_{\text{tet}} = -\tfrac{1}{3}$; hence $f_1(\theta_{\text{tet}}) = \tfrac{4}{3}$ and $f_2(\theta_{\text{tet}}) = \tfrac{1}{3}$; this gives

$$\begin{aligned}
I_\perp &= m_A\tfrac{4}{3}R^2 + \frac{m_A(m_B+m_A)}{m}\tfrac{1}{3}R^2 \\
&\quad + \frac{m_A}{m}\left\{(3m_A+m_B)\rho R + 6m_A R\left[\tfrac{1}{3}\times\tfrac{1}{3}\right]^{1/2}\right\}\rho R \\
&= m_A\tfrac{4}{3}R^2 + \frac{m_A(m_B+m_A)}{m}\tfrac{1}{3}R^2 + \frac{m_A}{m}\left\{(3m_A+m_B)\rho R + 2m_A R\right\}\rho R \\
I_{||} &= 2m_A\tfrac{4}{3}R^2
\end{aligned}$$

To simplify the expression somewhat let $m_B = \alpha m_A$. This gives $m = \alpha m_A + 4m_A = (4+\alpha)m_A$

$$\begin{aligned}
I_\perp &= m_A\tfrac{4}{3}R^2 + \frac{m_A^2(\alpha+1)}{(4+\alpha)m_A}\tfrac{1}{3}R^2 \\
&\quad + \frac{m_A}{(4+\alpha)m_A}\left\{(3+\alpha)\rho m_A R + 2m_A R\right\}\rho R \\
I_\perp/(m_A R^2) &= \tfrac{4}{3} + \frac{(\alpha+1)}{(4+\alpha)}\tfrac{1}{3} + \frac{1}{(4+\alpha)}\left\{(3+\alpha)\rho + 2\right\}\rho \\
&= \frac{4(4+\alpha) + (1+\alpha) + 3[(3+\alpha)\rho + 2\rho]}{3(4+\alpha)} = \frac{17 + 5\alpha + 15\rho + 3\rho\alpha}{3(4+\alpha)} \\
I_{||}/(m_A R^2) &= \tfrac{8}{3}
\end{aligned}$$

A useful check at this point is to set $\rho = 1$ which gives $I_\perp/(m_A R^2) = \tfrac{8}{3}$, the expected values for a tetrahedral BA_4 molecule.

The variation of the moments of inertia with ρ are shown in Fig. 11.3; $I_\perp$ is shown for three representative values of α. As expected, $I_\perp$ and $I_{||}$ converge onto the same value when $\rho = 1$. $I_{||}$ is independent of ρ as this axis passes along the bond with length R', and so the moment of inertia is unaffected by variations in R'.

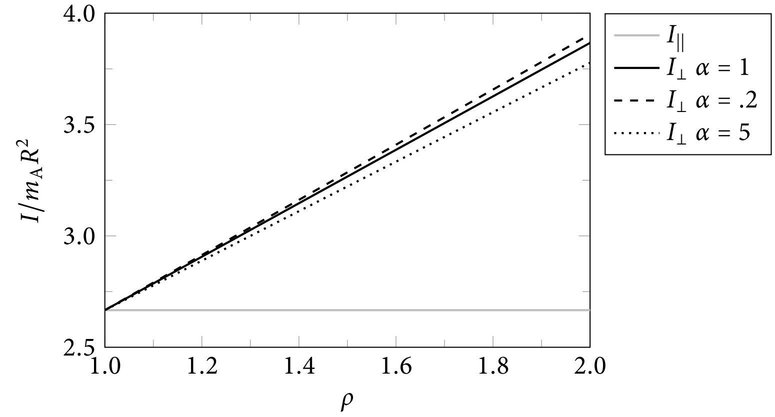


Figure 11.3

E11B.3(b) To be a symmetric rotor a molecule most possess an n-fold axis with $n > 2$. (i) Ethene has three two-fold axes, but no axes with $n > 2$ and so is an asymmetric rotor. (ii) SO_3 is trigonal planar; it has a three-fold axis and so is a symmetric rotor. (iii) ClF_3 is 'T-shaped' and has a two-fold axis; it is an asymmetric rotor. (iv) N_2O is a linear rotor.

E11B.4(b) In order to determine two unknowns, data from two independent experiments are needed. In this exercise two values of B for two isotopologues of OCS are given; these are used to find two moments of inertia. The moment of inertia of a linear triatomic is given in Table 11B.1 on page 431, and if it is assumed that the bond lengths are unaffected by isotopic substitution, the expressions for the moment of inertia of the two isotopologues can be solved simultaneously to obtain the two bond lengths.

The rotational constant in wavenumber is given by [11B.7–*432*], $\tilde{B} = \hbar/4\pi c I$; multiplication by the speed of light gives the rotational constant in frequency units $B = \hbar/4\pi I$, which rearranges to $I = \hbar/4\pi B$

$$I_{\text{OCS}} = (1.0546 \times 10^{-34}\,\text{J s})/[4\pi \times (6081.5 \times 10^6\,\text{Hz})] = 1.37... \times 10^{-45}\,\text{kg m}^2$$
$$I_{\text{OCS}'} = (1.0546 \times 10^{-34}\,\text{J s})/[4\pi \times (5932.8 \times 10^6\,\text{Hz})] = 1.41... \times 10^{-45}\,\text{kg m}^2$$

In these expressions the isotopologue with ^{32}S is denoted S and that with ^{34}S is denoted S′. It is somewhat more convenient for the subsequent manipulations to express the moments of inertia in units of the atomic mass constant m_u and nm.

$$\begin{aligned} I_{\text{OCS}} &= (1.37... \times 10^{-45}\,\text{kg}\,\text{m}^2) \times \left(\frac{10^9\,\text{nm}}{1\,\text{m}}\right)^2 \times \frac{1\,m_\text{u}}{1.6605 \times 10^{-27}\,\text{kg}} \\ &= 0.831...\,m_\text{u}\,\text{nm}^2 \\ I_{\text{OCS}'} &= (1.41... \times 10^{-45}\,\text{kg}\,\text{m}^2) \times \left(\frac{10^9\,\text{nm}}{1\,\text{m}}\right)^2 \times \frac{1\,m_\text{u}}{1.6605 \times 10^{-27}\,\text{kg}} \\ &= 0.851...\,m_\text{u}\,\text{nm}^2 \end{aligned}$$

Using the expressions from Table 11B.1 on page 431, the moments of inertia are expressed in terms of the masses and bond lengths, where the former are expressed as multiples on m_u. In this case A = ^{16}O, B = ^{12}C and C = ^{32}S or ^{34}S

$$\begin{aligned} I_{\text{OCS}} &= m_\text{O}R^2 + m_\text{S}R'^2 - \frac{(m_\text{O}R - m_\text{S}R')^2}{m_\text{O} + m_\text{C} + m_\text{S}} \\ &= 15.9949R^2 + 31.9721R'^2 - \frac{(15.9949R - 31.9721R')^2}{15.9949 + 12.0000 + 31.9721} \\ &= 15.9949R^2 + 31.9721R'^2 - \frac{(15.9949R - 31.9721R')^2}{59.967} \\ I_{\text{OCS}'} &= m_\text{O}R^2 + m_{\text{S}'}R'^2 - \frac{(m_\text{O}R - m_{\text{S}'}R')^2}{m_\text{O} + m_\text{C} + m_{\text{S}'}} \\ &= 15.9949R^2 + 33.9679R'^2 - \frac{(15.9949R - 33.9679R')^2}{15.9949 + 12.0000 + 33.9679} \\ &= 15.9949R^2 + 33.9679R'^2 - \frac{(15.9949R - 33.9679R')^2}{61.9628} \end{aligned}$$

These two equations need to be solved simultaneously for R and R', but because they are quadratics this is a very laborious process by hand: it is best achieved using mathematical software. This gives the resulting bondlengths as $\boxed{R = R_\text{OC} = 0.1161\text{ nm}}$ and $\boxed{R' = R_\text{CS} = 0.1561\text{ nm}}$.

E11B.5(b) The centrifugal distortion constant is given by [11B.16–*434*], $\tilde{D}_J = 4\tilde{B}^3/\tilde{\nu}^2$. With the given data $\tilde{D}_J = 4(0.0809\text{ cm}^{-1})^3/(323.2\text{ cm}^{-1})^2 = \boxed{2.028 \times 10^{-8}\text{ cm}^{-1}}$.

The rotational constant is inversely proportional to the moment of inertia of the molecule, $I = m_\text{eff}R^2$ where R is the bond length and m_eff is the effective mass. Assuming that isotopic substitution does not affect the bond length, it follows that $\tilde{B} \propto m_\text{eff}^{-1}$. Assuming that isotopic substitution does not affect the force constant, the vibrational frequency is proportional to $m_\text{eff}^{-1/2}$. Thus $\tilde{D} \propto (m_\text{eff}^{-1})^3/(m_\text{eff}^{-1/2})^2 = m_\text{eff}^{-2}$. For this estimation it is sufficient to use integer masses, and because a ratio is involved these can be expressed as multiples of m_u.

$$\tilde{D}_{^{81}\text{Br}_2}/\tilde{D}_{^{81}\text{Br}^{79}\text{Br}} = (m_{\text{eff}\,^{81}\text{Br}^{79}\text{Br}}/m_{\text{eff}\,^{81}\text{Br}_2})^2 = \left(\frac{79 \times 81}{79 + 81} \times \frac{81 + 81}{81 \times 81}\right)^2 = \boxed{0.98}$$

E11B.6(b) For a molecule to show a pure rotational (microwave) absorption spectrum is must have a permanent dipole moment. $\boxed{\text{All}}$ of the molecules given satisfy this requirement.

E11B.7(b) The wavenumbers of the lines in the rotational spectrum are given by [11B.20a–*436*], $\tilde{\nu}(J) = 2\tilde{B}(J+1)$; the $J = 2 \leftarrow 1$ transition is therefore at $\tilde{\nu}(1) = 2\tilde{B}(1+1) = 4\tilde{B}$. The rotational constant is given by [11B.7–*432*], $\tilde{B} = \hbar/4\pi cI$, and the moment of inertia is given by $m_{\text{eff}}R^2$, where $m_{\text{eff}} = m_1m_2/(m_1+m_2)$.

$$I = \frac{(12.0000 \times 15.9949)m_{\text{u}}^2}{(12.0000 + 15.9949)m_{\text{u}}} \times \frac{1.6605 \times 10^{-27}\,\text{kg}}{1\,m_{\text{u}}} \times (112.81 \times 10^{-12}\,\text{m})^2$$
$$= 1.44... \times 10^{-46}\,\text{kg}\,\text{m}^2$$
$$\tilde{B} = \frac{\hbar}{4\pi cI} = \frac{1.0546 \times 10^{-34}\,\text{J}\,\text{s}}{4\pi \times (2.9979 \times 10^{10}\,\text{cm}\,\text{s}^{-1}) \times (1.44... \times 10^{-46}\,\text{kg}\,\text{m}^2)}$$
$$= 1.93...\,\text{cm}^{-1}$$

The transition occurs at $4\tilde{B} = 4 \times (1.93...\,\text{cm}^{-1}) = \boxed{7.729\,\text{cm}^{-1}}$. Expressed in frequency units this is $4c\tilde{B} = 4 \times (2.9979 \times 10^{10}\,\text{cm}\,\text{s}^{-1}) \times (1.93...\,\text{cm}^{-1}) = 2.31... \times 10^{11}\,\text{Hz} = \boxed{231.7\,\text{GHz}}$.

Centrifugal distortion will lower the frequency.

E11B.8(b) The wavenumbers of the lines in the rotational spectrum are given by [11B.20a–*436*], $\tilde{\nu}(J) = 2\tilde{B}(J+1)$. The $J = 1 \leftarrow 0$ transition is therefore at $\tilde{\nu}(0) = 2\tilde{B}(0+1) = 2\tilde{B}$, hence $\tilde{B} = (16.93/2)\,\text{cm}^{-1}$. The rotational constant is given by [11B.7–*432*], $\tilde{B} = \hbar/4\pi cI$, and the moment of inertia is given by $m_{\text{eff}}R^2$, where $m_{\text{eff}} = m_1m_2/(m_1+m_2)$. It follows that $R = (\hbar/4\pi c m_{\text{eff}}\tilde{B})^{1/2}$.

$$m_{\text{eff}} = \frac{(1.0078 \times 80.9163)m_{\text{u}}^2}{(1.0078 + 80.9163)m_{\text{u}}} \times \frac{1.6605 \times 10^{-27}\,\text{kg}}{1\,m_{\text{u}}} = 1.65\ldots \times 10^{-27}\,\text{kg}$$

$$R = \left(\frac{1.0546 \times 10^{-34}\,\text{J}\,\text{s}}{4\pi \times (2.9979 \times 10^{10}\,\text{cm}\,\text{s}^{-1}) \times (1.65... \times 10^{-27}\,\text{kg}) \times [(16.93/2)\text{cm}^{-1}]}\right)^{1/2}$$
$$= \boxed{141.4\,\text{pm}}$$

E11B.9(b) The wavenumbers of the lines in the rotational spectrum are given by [11B.20a–*436*], $\tilde{\nu}(J) = 2\tilde{B}(J+1)$; the lines are therefore spaced by $2\tilde{B}$, it therefore follows that $\tilde{B} = (1.033/2)\,\text{cm}^{-1}$. The rotational constant is given by [11B.7–*432*], $\tilde{B} = \hbar/4\pi cI$, and the moment of inertia is given by $m_{\text{eff}}R^2$, where $m_{\text{eff}} = m_1m_2/(m_1+m_2)$. It follows that $I = \hbar/4\pi c\tilde{B}$ and $R = (I/m_{\text{eff}})^{1/2}$.

$$I = \hbar/4\pi c\tilde{B}$$
$$= \frac{1.0546 \times 10^{-34}\,\text{J}\,\text{s}}{4\pi \times (2.9979 \times 10^{10}\,\text{cm}\,\text{s}^{-1}) \times [(1.033/2)\,\text{cm}^{-1}]} = \boxed{5.420 \times 10^{-46}\,\text{kg}\,\text{m}^2}$$

$$m_{\text{eff}} = \frac{(34.9688 \times 18.9984)m_{\text{u}}^2}{(34.9688 + 18.9984)m_{\text{u}}} \times \frac{1.6605 \times 10^{-27}\,\text{kg}}{1\,m_{\text{u}}} = 2.04... \times 10^{-26}\,\text{kg}$$

$$\begin{aligned} R &= (I/m_{\text{eff}})^{1/2} = [(5.420... \times 10^{-46}\,\text{kg}\,\text{m}^2)/(2.04... \times 10^{-26}\,\text{kg})]^{1/2} \\ &= \boxed{162.8\,\text{pm}} \end{aligned}$$

E11B.10(b) The most occupied J state is given by [11B.15–*434*], $J_{\max} = (kT/2hc\tilde{B})^{1/2} - \frac{1}{2}$.

(i) At 25 °C, 298 K, this gives

$$\begin{aligned} &J_{\max} = \\ &\left(\frac{(1.3806 \times 10^{-23}\,\text{J}\,\text{K}^{-1}) \times (298\,\text{K})}{2 \times (6.6261 \times 10^{-34}\,\text{J}\,\text{s}) \times (2.9979 \times 10^{10}\,\text{cm}\,\text{s}^{-1}) \times (0.0809\,\text{cm}^{-1})}\right)^{1/2} - \tfrac{1}{2} \\ &= \boxed{35} \end{aligned}$$

(ii) At 100 °C, 373 K, this gives

$$\begin{aligned} &J_{\max} = \\ &\left(\frac{(1.3806 \times 10^{-23}\,\text{J}\,\text{K}^{-1}) \times (373\,\text{K})}{2 \times (6.6261 \times 10^{-34}\,\text{J}\,\text{s}) \times (2.9979 \times 10^{10}\,\text{cm}\,\text{s}^{-1}) \times (0.0809\,\text{cm}^{-1})}\right)^{1/2} - \tfrac{1}{2} \\ &= \boxed{40} \end{aligned}$$

E11B.11(b) For a molecule to show a pure rotational Raman spectrum it must have an anisotropic polarizability. With the exception of spherical rotors, all molecules satisfy this requirement. Therefore $\boxed{\text{CH}_2\text{Cl}_2,\ \text{CH}_3\text{CH}_3\ \text{and N}_2\text{O}}$ all give rotational Raman spectra.

E11B.12(b) The Stokes lines appear at wavenumbers given by [11B.24a–*438*], $\tilde{\nu}(J+2 \leftarrow J) = \tilde{\nu}_{\text{i}} - 2\tilde{B}(2J+3)$, where the wavenumber of the incident radiation is $\tilde{\nu}_{\text{i}}$, and J is the quantum number of the initial state. With the given data

$$\tilde{\nu}(4 \leftarrow 2) = 20\,623\,\text{cm}^{-1} - 2 \times (1.4457\,\text{cm}^{-1})(2 \times 2 + 3) = \boxed{20\,603\,\text{cm}^{-1}}$$

E11B.13(b) The Stokes lines appear at wavenumbers given by [11B.24a–*438*], $\tilde{\nu}(J+2 \leftarrow J) = \tilde{\nu}_{\text{i}} - 2\tilde{B}(2J+3)$, where the wavenumber of the incident radiation is $\tilde{\nu}_{\text{i}}$, and J is the quantum number of the initial state. It therefore follows that the separation between adjacent lines is $4\tilde{B}$, hence $\tilde{B} = (3.5312/4)\,\text{cm}^{-1}$.

The rotational constant is given by [11B.7–*432*], $\tilde{B} = \hbar/4\pi c I$, and the moment of inertia is given by $m_{\text{eff}}R^2$, where $m_{\text{eff}} = m_1 m_2/(m_1 + m_2)$. It follows that $I = \hbar/4\pi c\tilde{B}$ and $R = (I/m_{\text{eff}})^{1/2}$.

$$\begin{aligned} I &= \hbar/4\pi c\tilde{B} \\ &= \frac{1.0546 \times 10^{-34}\,\text{J}\,\text{s}}{4\pi \times (2.9979 \times 10^{10}\,\text{cm}\,\text{s}^{-1}) \times [(3.5312/4)\,\text{cm}^{-1}]} = 3.17... \times 10^{-46}\,\text{kg}\,\text{m}^2 \end{aligned}$$

For a homonuclear diatomic the effective mass is simply $m_{\text{eff}} = \frac{1}{2}m$

$$R = (I/m_{\text{eff}})^{1/2} = \left(\frac{3.17... \times 10^{-46}\ \text{kg m}^2}{\frac{1}{2} \times 18.9984 \times (1.6605 \times 10^{-27}\ \text{kg})}\right)^{1/2}$$
$$= \boxed{141.79\ \text{pm}}$$

E11B.14(b) $^{12}C^{32}S_2$ is a linear molecule; the carbon atom has no effect on the nuclear statistics as it is at the centre. ^{32}S has spin zero, so the behaviour is analogous to that of $^{12}C^{16}O_2$: only even J levels are permissible.

Changing the carbon to ^{13}C has not effect as this atom is at the centre.

Solutions to problems

P11B.2 Suppose that the centre of mass is at a distance x from B, and therefore $(R-x)$ from A and $(R'+x)$ from C. Balancing moments gives

$$m_A(R-x) = m_B x + m_C(R'+x) \quad \text{hence } x = \frac{m_A R - m_C R'}{m}$$

where the total mass is $m = m_A + m_B + m_C$, the moment of inertia is therefore

$$I = m_A(R-x)^2 + m_B x^2 + m_C(R'+x)^2$$

first gather terms in powers of x

$$= m_A R^2 + m_C R'^2 - 2x(m_A R - m_C R') + x^2(m_A + m_B + m_C)$$
$$= m_A R^2 + m_C R'^2 - 2x(m_A R - m_C R') + x^2 m$$

the substitute for x

$$I = m_A R^2 + m_C R'^2 - 2(m_A R - m_C R')(m_A R - m_C R')/m$$
$$+ (m_A R - m_C R')^2 m/m^2$$
$$= m_A R^2 + m_C R'^2 - 2(m_A R - m_C R')^2/m + (m_A R - m_C R')^2/m$$
$$= m_A R^2 + m_C R'^2 - (m_A R - m_C R')^2/m$$

P11B.4 The wavenumbers of the lines expected for a diatomic are given by [11B.20a–*436*], $\tilde{\nu}(J) = 2\tilde{B}(J+1)$; the separation of the lines is $2\tilde{B}$. The spacing between adjacent lines in the given data is not constant, but varies between 20.3 cm^{-1} and 20.8 cm^{-1}, with an average of 20.5 cm^{-1}; a reasonable first guess at the value of $\tilde{B}$ is therefore $\frac{1}{2} \times (20.5\ \text{cm}^{-1}) = 10.25\ \text{cm}^{-1}$. With this estimate it is then possible to *assign* the lines, that is determine the value of J associated with each. From $\tilde{\nu} = 2\tilde{B}(J+1)$ it follows that $J = \tilde{\nu}/2\tilde{B} - 1$. For the first line $J = (83.32\ \text{cm}^{-1})/(20.5\ \text{cm}^{-1}) - 1 = 3.1$ which indicates that this is likely to be the line $\tilde{\nu}(3)$; similar calculations for the other lines indicates that they are $\tilde{\nu}(4)\ldots\tilde{\nu}(10)$.

The variation in the spacing is attributed to the effects of centrifugal distortion. In this case the wavenumbers of the lines are given by [11B.20b–*436*], $\tilde{\nu}(J) = 2\tilde{B}(J+1) - 4\tilde{D}_J(J+1)^3$. Division of both side of this expression by $(J+1)$ indicates that a plot of $\tilde{\nu}(J)/(J+1)$ against $(J+1)^2$ should be a straight line with slope $-4\tilde{D}_J$ and intercept $2\tilde{B}$

$$\frac{\tilde{\nu}(J)}{J+1} = \overbrace{2\tilde{B}}^{\text{intercept}} \overbrace{-4\tilde{D}_J}^{\text{slope}} (J+1)^2$$

The data are tabulated below; $\tilde{\delta}$ is the difference between successive lines. The plot is shown in Fig. 11.4.

$\tilde{\nu}(J)/\text{cm}^{-1}$	$\tilde{\delta}/\text{cm}^{-1}$	J	$[\tilde{\nu}(J)/(J+1)]/\text{cm}^{-1}$	$(J+1)^2$
83.32		3	20.83	16
104.13	20.81	4	20.83	25
124.73	20.60	5	20.79	36
145.37	20.64	6	20.77	49
165.89	20.52	7	20.74	64
186.23	20.34	8	20.69	81
206.60	20.37	9	20.66	100
226.86	20.26	10	20.62	121

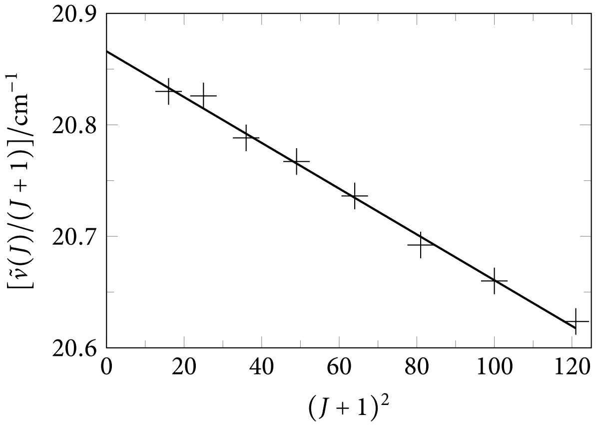


Figure 11.4

The data are quite a good fit to the line

$$[\tilde{\nu}(J)/(J+1)]/\text{cm}^{-1} = -2.0534\times10^{-3}\times(J+1)^2 + 20.866$$

The value of the rotational constant is found from the intercept: $(\tilde{B}/\text{cm}^{-1}) = \frac{1}{2}\times$ intercept. Some elementary statistics on the best-fit line indicates an error of about 0.005 cm^{-1} in the intercept, so the best estimate for the rotational constant is $\tilde{B} = 10.433 \pm 0.002\ \text{cm}^{-1}$. The slope is $(-4\tilde{D}_J/\text{cm}^{-1})$, hence $\tilde{D}_J = 5.13 \times 10^{-4}\ \text{cm}^{-1}$.

The rotational constant is given by [11B.7–*432*], $\tilde{B} = \hbar/4\pi c I$; it follows that $I = \hbar/4\pi c\tilde{B}$

$$I = \frac{1.0546 \times 10^{-34}\ \text{J s}}{4\pi \times (2.9979 \times 10^{10}\ \text{cm s}^{-1}) \times (10.433\ \text{cm}^{-1})} = \boxed{2.6832 \times 10^{-47}\ \text{kg m}^2}$$

The moment of inertia is $I = m_{\text{eff}}R^2$, where m_{eff} is the effective mass, $m_{\text{eff}} = m_{\text{H}}m_{\text{Cl}}/(m_{\text{H}} + m_{\text{Cl}})$. It therefore follows that

$$R = (I/m_{\text{eff}})^{1/2} = \left(\frac{I(m_{\text{H}} + m_{\text{Cl}})}{m_{\text{H}}m_{\text{Cl}}}\right)^{1/2}$$

$$= \left(\frac{(2.6832 \times 10^{-47}\ \text{kg m}^2) \times (1.0078 + 34.9688)}{(1.0078 \times 34.9688) \times (1.6605 \times 10^{-27}\ \text{kg})}\right)^{1/2} = \boxed{128.4\ \text{pm}}$$

Note the factor 1 $m_{\text{u}} = 1.6605 \times 10^{-27}$ kg used to convert the masses to kg. If the average spacing is used as an estimate for $\tilde{B}$ the resulting bond length is 129.6 pm, which is significantly different.

To predict the corresponding lines in the spectrum of $^{2}\text{H}^{35}\text{Cl}$ it is necessary to know the values of the rotational constant and the centrifugal distortion constant. The rotational constant is inversely proportional to the effective mass. Therefore, assuming that the bond length is the same in the isotopologues, $\tilde{B}$ for $^{2}\text{H}^{35}\text{Cl}$ is computed from ratio of effective masses

$$\begin{aligned}
\tilde{B}_{^2\text{H}^{35}\text{Cl}}/\tilde{B}_{^1\text{H}^{35}\text{Cl}} &= m_{\text{eff},^1\text{H}^{35}\text{Cl}}/m_{\text{eff},^2\text{H}^{35}\text{Cl}} \\
\tilde{B}_{^2\text{H}^{35}\text{Cl}} &= \tilde{B}_{^1\text{H}^{35}\text{Cl}} \times m_{\text{eff},^1\text{H}^{35}\text{Cl}}/m_{\text{eff},^2\text{H}^{35}\text{Cl}} \\
&= \tilde{B}_{^1\text{H}^{35}\text{Cl}} \times \frac{m_{^1\text{H}}m_{^{35}\text{Cl}}}{m_{^1\text{H}} + m_{^{35}\text{Cl}}} \times \frac{m_{^2\text{H}} + m_{^{35}\text{Cl}}}{m_{^2\text{H}}m_{^{35}\text{Cl}}} \\
&= (10.433\ \text{cm}^{-1}) \times \frac{1.0078 \times 34.9688}{1.0078 + 34.9688} \times \frac{2.0140 + 34.9688}{2.0140 \times 34.9688} \\
&= 5.367\ \text{cm}^{-1}
\end{aligned}$$

As explained in *Exercise* E11B.5(b), the $\tilde{D}_J \propto m_{\text{eff}}^{-2}$. Because this term only has a small effect it is sufficient to assume that the values of the effective masses of ^{1}HCl and ^{2}HCl are dominated by the much lighter ^{1}H or ^{2}H to give $m_{\text{eff},^1\text{H}^{35}\text{Cl}} \approx 1\ m_{\text{u}}$ and $m_{\text{eff},^2\text{H}^{35}\text{Cl}} \approx 2\ m_{\text{u}}$, thus

$$\tilde{D}_{J,^2\text{H}^{35}\text{Cl}} = \tilde{D}_{J,^1\text{H}^{35}\text{Cl}} \times (1/2)^2 = (5.13 \times 10^{-4}\ \text{cm}^{-1}) \times \tfrac{1}{4} = 1.28 \times 10^{-4}\ \text{cm}^{-1}$$

With these values of $\tilde{B}$ and $\tilde{D}_J$ the wavenumbers of the lines in the spectrum of $^{2}\text{H}^{35}\text{Cl}$ are computed using $\tilde{\nu}(J) = 2\tilde{B}(J+1) - 4\tilde{D}_J(J+1)^3$ to give the following

J	3	4	5	6	7	8	9	10
$\tilde{\nu}(J)/\text{cm}^{-1}$	42.90	53.61	64.29	74.96	85.61	96.23	106.83	117.39

P11B.6 The wavenumbers of the lines expected for a diatomic are given by [11B.20a–*436*], $\tilde{\nu}(J) = 2\tilde{B}(J+1)$; the separation of the lines is $2\tilde{B}$. From the data given the average spacing is 6027.69 MHz, and hence $\boxed{B = 3013.8\ \text{MHz}}$. The precision of this value is likely to be lower than the apparent precision of data: for example, the two separations measurable from the spectrum differ by 0.2 MHz, indicating that there must be some scatter on the data at this level.

The rotational constant is given by [11B.7–*432*], $\tilde{B} = \hbar/4\pi cI$. Expressed in frequency units this is $B = \hbar/4\pi I$. It follows that $I = \hbar/4\pi B$

$$I = \hbar/4\pi B = \frac{1.0546 \times 10^{-34}\ \text{J s}}{4\pi \times (3013.8... \times 10^{6}\ \text{Hz})} = 2.78... \times 10^{-45}\ \text{kg m}^2$$

The effective mass is

$$m_{\text{eff}} = \frac{m_{^{63}\text{Cu}} m_{^{79}\text{Br}}}{m_{^{63}\text{Cu}} + m_{^{79}\text{Br}}} = \frac{62.9296 \times 78.9183}{62.9296 + 78.9183} = 35.0114\ m_{\text{u}}$$

Because $I = m_{\text{eff}}R^2$ it follows that

$$\begin{aligned} R &= (I/m_{\text{eff}})^{1/2} \\ &= \left\{(2.78... \times 10^{-45}\ \text{kg m}^2)/(35.0114 \times [1.6605 \times 10^{-27}\ \text{kg}])\right\}^{1/2} = \boxed{219\ \text{pm}} \end{aligned}$$

P11B.8 The data are tabulated below and the plot is shown in Fig. 11.5.

$\tilde{\nu}(J)/\text{cm}^{-1}$	J	$[\tilde{\nu}(J)/2(J+1)]/\text{cm}^{-1}$	$(J+1)^2$
3.845 033	0	1.922 517	1
7.689 919	1	1.922 480	4
11.534 510	2	1.922 418	9
15.378 662	3	1.922 333	16
19.222 223	4	1.922 222	25

The data are a good fit to the line

$$[\tilde{\nu}(J)/(J+1)]/\text{cm}^{-1} = -1.225\,660 \times 10^{-5} \times (J+1)^2 + 1.922\,529$$

The value of the rotational constant is found from the intercept: $(\tilde{B}/\text{cm}^{-1})$ = intercept. Some elementary statistics on the best-fit line indicates an error of about 10^{-7} cm^{-1} in the intercept (which seems improbably small); using this, the rotational constant is quoted as $\boxed{\tilde{B} = 1.922\,529\ \text{cm}^{-1}}$. The slope is related to the centrifugal distortion constant as $(-2\tilde{D}_J/\text{cm}^{-1})$, and the error is about 10^{-8} cm^{-1} hence $\boxed{\tilde{D}_J = 6.128 \times 10^{-6}\ \text{cm}^{-1}}$.

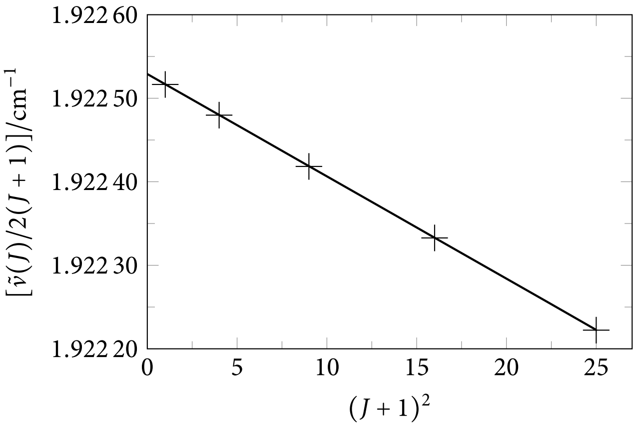


Figure 11.5

P11B.10 (a) The selection rules are $\Delta J = \pm 1$, $\Delta K = 0$. An allowed absorption transition from (J, K) to $(J+1, K)$ has wavenumber

$$\begin{aligned}
\tilde{\nu} &= \tilde{F}(J+1, K) - \tilde{F}(J, K)\\
&= \tilde{B}(J+1)(J+2) + (\tilde{A} - \tilde{B})K^2 - \tilde{D}_J(J+1)^2(J+2)^2\\
&\quad - \tilde{D}_{JK}(J+1)(J+2)K^2 - \tilde{D}_K K^4\\
&\qquad - \Big[\tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2 - \tilde{D}_J J^2(J+1)^2\\
&\qquad - \tilde{D}_{JK}J(J+1)K^2 - \tilde{D}_K K^4\Big]\\
&= 2\tilde{B}(J+1) - \tilde{D}_J[(J+1)^2(J+2)^2 - J^2(J+1)^2]\\
&\quad - \tilde{D}_{JK}K^2[(J+1)(J+2) - J(J+1)]\\
&= 2\tilde{B}(J+1) - \tilde{D}_J[(J^2+2J+1)(J^2+4J+4) - J^2(J^2+2J+1)]\\
&\quad - \tilde{D}_{JK}K^2[J^2+3J+2-J^2-J]\\
&= 2\tilde{B}(J+1) - \tilde{D}_J[4+12J+12J^2+4J^3] - \tilde{D}_{JK}K^2[2J+2]\\
&= 2\tilde{B}(J+1) - \tilde{D}_J 4(J+1)^3 - \tilde{D}_{JK}2K^2(J+1)
\end{aligned}$$

The wavenumber of the lines in the absorption spectrum are given by

$$\boxed{\tilde{\nu}(J, K) = 2\tilde{B}(J+1) - 4\tilde{D}_J(J+1)^3 - 2\tilde{D}_{JK}(J+1)K^2} \qquad (11.1)$$

(b) It is first helpful to compute the separation between the lines

$$51.0718 \underbrace{\qquad}_{51.069} 102.1408 \underbrace{\qquad}_{0.0018} 102.1426 \underbrace{\qquad}_{51.065} 153.2076 \underbrace{\qquad}_{0.0027} 153.2103$$

Recall that $B \gg D$. The separation of about 51 GHz is likely to correspond to $2B$; if this is so then, ignoring centrifugal distortion, the expectation is $\nu(0) = 2B = 51$ GHz, $\nu(1) = 4B = 102$ GHz, and $\nu(2) = 6B = 153$ GHz.

From eqn 11.1 it is seen that for each transition $(J+1 \leftarrow J)$ there are separate lines for each value of K^2. The K quantum number takes values from $-J$ to $+J$ in integer steps, and so has $(2J+1)$ values. However, the energy goes as K^2, of which there are only $(J+1)$ distinct values. The transition $1 \leftarrow 0$ has $J=0$ and hence $K=0$ only: there is one line. The transition $2 \leftarrow 1$ has $J=1$ and hence $K=0,\ 1$: there are two lines, and because the term in K^2 is negative, the line for $K=1$ is at lower frequency that that for $K=0$. The transition $3 \leftarrow 2$ has $J=2$ and hence $K=0,\ 1,\ 2$: there are three lines, running to lower frequency as K increases.

The following table indicates the quantum numbers for each line and their frequencies expressed in terms of the various constants.

line	observed freq./GHz	J	K	$\nu(J,K)$
1	51.0718	0	0	$2B-4D_J$
2	102.1408	1	1	$4B-32D_J-4D_{JK}$
3	102.1426	1	0	$4B-32D_J$
	not given	2	2	$6B-108D_J-24D_{JK}$
4	153.2076	2	1	$6B-108D_J-6D_{JK}$
5	153.2103	2	0	$6B-108D_J$

The assignment of lines 4 and 5 needs some comment. With the assignment given the separation of lines 4 and 5 is $6D_{JK}$, and the separation of lines 2 and 3 is $4D_{JK}$; these separations are therefore expected to be in the ratio $6/4=1.5$. From the data the ratio is $(153.2103-153.2076)/(102.1426-102.1408)=1.5$, which is consistent with the assignment. Such consistency is not achieved with any other values of K for lines 4 and 5.

With this assignment it is possible to find the constants but taking differences between multiples of the frequencies of different lines from the table:

$$\text{line } 3 - \text{line } 2 = 4D_{JK} = 102.1426 - 102.1408 = 0.0018 \text{ GHz}$$

hence $D_{JK} = \frac{1}{4} \times 0.0018 \text{ GHz} = \boxed{0.45 \text{ MHz}}$.

$$\text{line } 3 - 2 \times \text{line } 1 = -24D_J = 102.1426 - 2 \times 51.0718 = -0.0010 \text{ GHz}$$

hence $D_J = \frac{1}{24} \times 0.0010 \text{ GHz} = \boxed{0.042 \text{ MHz}}$. A different choice gives a different value, indicating that the accuracy of the data is perhaps lower than it appears

$$\begin{aligned} 2 \times \text{line } 5 - 3 \times \text{line } 3 = -120D_J &= 2 \times 153.2103 - 3 \times 102.1426 \\ &= -0.0072 \text{ GHz} \end{aligned}$$

hence $D_J = \frac{1}{120} \times 0.0072 \text{ GHz} = \boxed{0.060 \text{ MHz}}$.

$$\text{line } 3 - 8 \times \text{line } 1 = -12B = 102.1426 - 8 \times 51.0718 = -306.43 \text{ GHz}$$

$$\text{hence } B = \frac{1}{12} \times 306.4 \text{ GHz} = \boxed{25.536 \text{ GHz}}$$

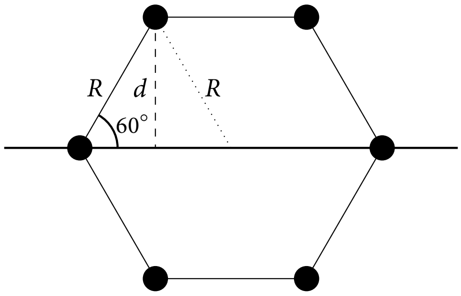
It is not possible to find A, nor is it possible to find D_K, as these constants do not affect the frequencies of the lines.

P11B.12 The issue here is whether or not the rotational transitions of the molecule have wavenumbers which overlap the range for which the black-body radiation is significant. The cosmic microwave background corresponds to about 2.7 K, and the wavelength of the maximum radiation density can be found using Wien's law, [7A.1–*238*], $\lambda_{\max} T = 2.9 \times 10^{-3}$ m T. Expressing this as a wavenumber gives

$$1/\lambda_{\max} = T/(2.9 \times 10^{-3} \text{ m T}) = (2.7 \text{ K})/(2.9 \times 10^{-3} \text{ m T}) = 931 \text{ m}^{-1}$$

The peak in the energy density of the black body is therefore at around 9.31 cm^{-1}. The rotational constant of CN is 1.891 cm^{-1}, so the first line occurs at $2\tilde{B} = 3.782 \text{ cm}^{-1}$, and subsequent lines at 7.564 cm^{-1}, 11.346 cm^{-1} and so on. The first few of these fall conveniently close to the maximum of the black-body radiation. In contrast, for CH the first line is at 28.38 cm^{-1}, which is already at a much higher wavenumber than the maximum of the black-body radiation. Thus, in order to study the energy distribution by looking at the lines from a molecule, CN is much more useful than CH as the CN spectrum overlaps the region of interest.

P11B.14 The first step is to find an expression for the moment of inertia of benzene about any axis in the plane; as long as the axis lies in the plane and passes through the centre its location can be chosen freely. Consider the arrangement shown below in which the axis (shown by the horizontal line) is chosen to pass through two carbon atoms on opposite sides of the ring. Recall that the distance from the centre to the vertices is equal to the length of the sides; let this length be R. The perpendicular distance d from one atom to the axis is $R \sin 60° = R\sqrt{3}/2$. The four carbon atoms which are away from the axis are all at the same distance and so their contribution to the moment of inertia is therefore $4m_C(3/4)R^2 = 3m_C R^2$; the other two atoms lie on the axis and so make no contribution.



Now consider the six hydrogen atoms. These also form a hexagon, but with a larger side, which is denoted R'. Starting from the centre, the distance to a carbon atom is R, and the distance to a hydrogen atom in the same direction is R'. It follows that $R_{\text{CH}} = R' - R$, and as has already been established $R_{\text{CC}} = R$.

The contribution that the hydrogen atoms make to the moment of inertia is, by analogy with the discussion above, $3m_\text{H}R'^2$. Therefore $I_\text{H} = 3m_\text{C}R^2 + 3m_\text{H}R'^2$ and $I_\text{D} = 3m_\text{C}R^2 + 3m_\text{D}R'^2$.

To find R multiply I_H by m_D, and I_D by m_H to give

$$m_\text{D}I_\text{H} = 3m_\text{D}m_\text{C}R^2 + 3m_\text{D}m_\text{H}R'^2 \qquad m_\text{H}I_\text{D} = 3m_\text{H}m_\text{C}R^2 + 3m_\text{H}m_\text{D}R'^2$$

Then, subtract the two expressions and rearrange

$$m_\text{D}I_\text{H} - m_\text{H}I_\text{D} = 3m_\text{D}m_\text{C}R^2 - 3m_\text{H}m_\text{C}R^2 \quad \text{hence} \quad R^2 = \frac{m_\text{D}I_\text{H} - m_\text{H}I_\text{D}}{3m_\text{C}(m_\text{D} - m_\text{H})}$$

With the data given

$$\begin{aligned} R^2 &= \frac{(2.0140) \times (1.4759 \times 10^{-45}\,\text{kg m}^2) - (1.0078) \times (1.7845 \times 10^{-45}\,\text{kg m}^2)}{3 \times (12.0000) \times (2.0140 - 1.0079) \times (1.6605 \times 10^{-27}\,\text{kg})} \\ &= 1.95... \times 10^{-20}\,\text{m}^2 \end{aligned}$$

Therefore the CC bond length is $\boxed{139.7\,\text{pm}}$.

The value of R' is obtained by subtracting I_H from I_D so as to eliminate the term in R^2

$$I_\text{D} - I_\text{H} = 3R'^2(m_\text{D} - m_\text{H}) \quad \text{hence} \quad R'^2 = \frac{I_\text{D} - I_\text{H}}{3(m_\text{D} - m_\text{H})}$$

With the data given

$$\begin{aligned} R'^2 &= \frac{(1.7845 \times 10^{-45}\,\text{kg m}^2) - (1.4759 \times 10^{-45}\,\text{kg m}^2)}{3 \times (2.0140 - 1.0079) \times (1.6605 \times 10^{-27}\,\text{kg})} \\ &= 6.15... \times 10^{-20}\,\text{m}^2 \end{aligned}$$

Therefore $R' = 248.1$ pm and hence $R_\text{CH} = R' - R = 248.1 - 139.7 = \boxed{108.4\,\text{pm}}$

11C Vibrational spectroscopy of diatomic molecules

Answers to discussion questions

D11C.2 The rotational constant depends inversely on the moment of inertia, which in turn depends on the square of the bond length. However, because the molecule is vibrating, the bond length is constantly changing. Vibration is much faster than rotation, so for the purposes of calculating the moment of inertia it is generally a good approximation to take an average over the vibrational motion and use $\langle R^2 \rangle$ in place of R^2. It follows that $B \propto 1/\langle R^2 \rangle$.

If the vibration is assumed to be harmonic $\langle R^2 \rangle$ increases with increasing vibrational energy. However, for a typical anharmonic vibration there is a much greater effect on $\langle R^2 \rangle$ arising from the asymmetry of the potential. Put simply, instead of the molecule oscillating symmetrically about the equilibrium position, the bond stretches more than it is compressed, resulting in the average bond length increasing. As the vibrational energy increases the potential curve becomes shallower for bond extension and the average bond length increases further.

The value of $1/\langle R^2 \rangle$ therefore decreases as the vibrational quantum number v increases, and as a result the rotational constant B is a decreasing function of the v. For typical molecules, this effect of the anharmonicity is dominant, and it is not unusual for the rotational constant to decrease by 1–2 per cent when going from the $v = 0$ to the $v = 1$ vibrational level.

D11C.4 Because bonding is principally a matter resulting from electrostatic interactions, the addition of a neutral particle to the nucleus is not expected to alter the geometry of a molecule (bond lengths, bond angles), nor is it expected to alter the force constants which describe the stretching of bonds. However, rotational spectra, and the rotational fine structure which is associated with vibrational spectra, depend on the rotational constants, and in turn these depend on the effective mass. Likewise, vibrational frequencies also depend on the effective mass, and so they too will be affected.

Different isotopes may have different nuclear spins and this can affect the pattern of intensities of lines arising from different rotational states.

Solutions to exercises

E11C.1(b) The vibrational frequency of a harmonic oscillator is given by [7E.3–*274*], $\omega = (k_\mathrm{f}/m)^{1/2}$; ω is an angular frequency, so to convert to frequency in Hz, ν, use $\omega = 2\pi\nu$. Therefore $2\pi\nu = (k_\mathrm{f}/m)^{1/2}$. Rearranging this gives the force constant as $k_\mathrm{f} = m(2\pi\nu)^2$

$$k_\mathrm{f} = (0.0010\ \mathrm{kg}) \times (2\pi \times 10.0\ \mathrm{Hz})^2 = \boxed{3.95\ \mathrm{N\,m^{-1}}}$$

where $1\ \mathrm{N} = 1\ \mathrm{kg\,m\,s^{-2}}$ and $1\ \mathrm{Hz} = 1\ \mathrm{s^{-1}}$ are used.

E11C.2(b) The vibrational frequency, expressed as a wavenumber, of a harmonic oscillator is given by [11C.4b–*443*], $\tilde{\nu} = (1/2\pi c)(k_\mathrm{f}/m_\mathrm{eff})^{1/2}$, where m_eff is the effective mass, given by $m_\mathrm{eff} = m_1 m_2/(m_1 + m_2)$. Assuming that the force constants of the two isotopologues are the same, $\tilde{\nu}$ simply scales as $(m_\mathrm{eff})^{-1/2}$. The fractional change is therefore

$$\begin{aligned}\frac{\tilde{\nu}_{^1\mathrm{H}^{35}\mathrm{Cl}} - \tilde{\nu}_{^2\mathrm{H}^{37}\mathrm{Cl}}}{\tilde{\nu}_{^1\mathrm{H}^{35}\mathrm{Cl}}} &= 1 - \frac{\tilde{\nu}_{^2\mathrm{H}^{37}\mathrm{Cl}}}{\tilde{\nu}_{^1\mathrm{H}^{35}\mathrm{Cl}}} = 1 - \left(\frac{m_{\mathrm{eff},\,^1\mathrm{H}^{35}\mathrm{Cl}}}{m_{\mathrm{eff},\,^2\mathrm{H}^{37}\mathrm{Cl}}}\right)^{1/2} \\ &= 1 - \left(\frac{1.0078 \times 34.9688}{1.0078 + 34.9688} \times \frac{2.0140 + 36.9651}{2.0140 \times 36.9651}\right)^{1/2} = 0.283...\end{aligned}$$

The fractional change, expressed as a percentage, is therefore $\boxed{28.38\%}$.

E11C.3(b) The wavenumber of the fundamental vibrational transition is simply equal to the vibrational frequency expressed as a wavenumber. This is given by [11C.4b–*443*], $\tilde{\nu} = (1/2\pi c)(k_f/m_{\text{eff}})^{1/2}$, where m_{eff} is the effective mass, given by $m_{\text{eff}} = m_1 m_2/(m_1 + m_2)$. It follows that $k_f = m_{\text{eff}}(2\pi c\tilde{\nu})^2$. With the data given

$$\begin{aligned} k_f &= \frac{78.9183 \times 80.9163}{78.9183 + 80.9163} \times (1.6605 \times 10^{-27}\,\text{kg}) \\ &\qquad \times [2\pi \times (2.9979 \times 10^{10}\,\text{cm s}^{-1}) \times (323.2\,\text{cm}^{-1})]^2 \\ &= \boxed{245.9\,\text{N m}^{-1}} \end{aligned}$$

Note the conversion of the mass to kg.

E11C.4(b) The wavenumber of the fundamental vibrational transition is simply equal to the vibrational frequency expressed as a wavenumber. This is given by [11C.4b–*443*], $\tilde{\nu} = (1/2\pi c)(k_f/m_{\text{eff}})^{1/2}$, where m_{eff} is the effective mass, given by $m_{\text{eff}} = m_1 m_2/(m_1 + m_2)$. Assuming that the force constants of the two isotopologues are the same, $\tilde{\nu}$ simply scales as $(m_{\text{eff}})^{-1/2}$. Therefore

$$\frac{\tilde{\nu}_{^2\text{HX}}}{\tilde{\nu}_{^1\text{HX}}} = \left(\frac{m_{\text{eff},^1\text{HX}}}{m_{\text{eff},^2\text{HX}}}\right)^{1/2} \quad \text{hence} \quad \tilde{\nu}_{^2\text{HX}} = \tilde{\nu}_{^1\text{HX}} \times \left(\frac{m_{\text{eff},^1\text{HX}}}{m_{\text{eff},^2\text{HX}}}\right)^{1/2}$$

Using these relationships, the following table is drawn up

	$^n\text{H}^{19}\text{F}$	$^n\text{H}^{35}\text{Cl}$	$^n\text{H}^{81}\text{Br}$	$^n\text{H}^{127}\text{I}$
$\tilde{\nu}_{^1\text{HX}}/\text{cm}^{-1}$	4141.3	2988.9	2649.7	2309.5
$m_{\text{eff},^1\text{HX}}/m_u$	0.9570	0.9796	0.9954	0.9999
$m_{\text{eff},^2\text{HX}}/m_u$	1.8210	1.9043	1.9651	1.9825
$\tilde{\nu}_{^2\text{HX}}/\text{cm}^{-1}$	3002.3	2143.7	1885.8	1640.1

E11C.5(b) The terms (energies expressed as wavenumbers) of the harmonic oscillator are given by [11C.4b–*443*], $\tilde{G}(v) = (v + \frac{1}{2})\tilde{\nu}$; these are wavenumbers and so can be converted to energy by multiplying by hc to give $E(v) = (v + \frac{1}{2})hc\tilde{\nu}$. The first excited state has $v = 1$, and the second has $v = 2$. The relative population of these levels is therefore given by the Boltzmann distribution, $n_2/n_1 = e^{-(E_2-E_1)/kT}$. The energy difference $E_2 - E_1 = hc\tilde{\nu}$, and hence $n_2/n_1 = e^{-hc\tilde{\nu}/kT}$. It is convenient to compute the quantity $hc\tilde{\nu}/k$ first to give

$$\begin{aligned} hc\tilde{\nu}/k &= \frac{(6.6261 \times 10^{-34}\,\text{J s}) \times (2.9979 \times 10^{10}\,\text{cm s}^{-1}) \times (321\,\text{cm}^{-1})}{1.3806 \times 10^{-23}\,\text{J K}^{-1}} \\ &= 461.8...\,\text{K} \end{aligned}$$

It follows that $n_2/n_1 = e^{-(461.8...\,\text{K})/T}$

(i) At 298 K, $n_2/n_1 = e^{-(461.8...\,\text{K})/(298\,\text{K})} = \boxed{0.212}$

(ii) At 800 K, $n_2/n_1 = e^{-(461.8...\,\text{K})/(800\,\text{K})} = \boxed{0.561}$

As expected, the relative population of the upper level increases with temperature.

E11C.6(b) *Note: the data in the Exercise are in error, the transitions should be at 2329.91* cm^{-1}, *4631.20* cm^{-1}, *and 6903.69* cm^{-1}.

Taking $y_e = 0$ is equivalent to using the terms for the Morse oscillator, which are given in [11C.8–*444*], $\tilde{G}(v) = (v + \frac{1}{2})\tilde{\nu} - (v + \frac{1}{2})^2\tilde{\nu}x_e$. The transition $v \leftarrow 0$ has wavenumber

$$\begin{aligned}\Delta\tilde{G}(v) &= \tilde{G}(v) - \tilde{G}(0)\\ &= [(v+\tfrac{1}{2})\tilde{\nu} - (v+\tfrac{1}{2})^2\tilde{\nu}x_e] - [(0+\tfrac{1}{2})\tilde{\nu} - (0+\tfrac{1}{2})^2\tilde{\nu}x_e]\\ &= v\tilde{\nu} - v(v+1)\tilde{\nu}x_e\end{aligned}$$

Data on three transitions are provided, but only two are needed to obtain values for $\tilde{\nu}$ and x_e. The $\Delta\tilde{G}(v)$ values for the first two transitions are

$$\begin{aligned}1 \leftarrow 0 &\qquad \tilde{\nu} - 2\tilde{\nu}x_e = 2329.91\ \text{cm}^{-1}\\ 2 \leftarrow 0 &\qquad 2\tilde{\nu} - 6\tilde{\nu}x_e = 4631.20\ \text{cm}^{-1}\end{aligned}$$

Multiplying the first expression by 3 and subtracting the second gives

$$3(\tilde{\nu} - 2\tilde{\nu}x_e) - (2\tilde{\nu} - 6\tilde{\nu}x_e) = \tilde{\nu}$$

$$\text{hence } \tilde{\nu} = 3 \times (2329.91\ \text{cm}^{-1}) - (4631.20\ \text{cm}^{-1}) = \boxed{2358.5\ \text{cm}^{-1}}$$

This value for $\tilde{\nu}$ is used in the first equation, which is then solved for x_e to give $x_e = \frac{1}{2} - (2329.91\ \text{cm}^{-1})/[2 \times (2358.53\ \text{cm}^{-1})] = \boxed{6.07 \times 10^{-3}}$.

E11C.7(b) The strategy here is to see if the data can be modelled by the energy levels of the Morse oscillator. This is tested by using the result from [11C.9b–*445*], $\Delta\tilde{G}_{v+1/2} = \tilde{\nu} - 2(v+1)x_e\tilde{\nu}$, where $\Delta\tilde{G}_{v+1/2} = \tilde{G}(v+1) - \tilde{G}(v)$. This implies that a plot of $\Delta\tilde{G}_{v+1/2}$ against $(v+1)$ will have slope $-2x_e\tilde{\nu}$ and intercept $\tilde{\nu}$. The data are shown in the table and the plot in Fig. 11.6.

v	$\tilde{G}_v/\text{cm}^{-1}$	$\Delta\tilde{G}_{v+1/2}/\text{cm}^{-1}$	$v+1$
0	1 144.83	2 230.07	1
1	3 374.90	2 150.61	2
2	5 525.51	2 071.15	3
3	7 596.66	1 991.69	4
4	9 588.35		

The data are a good fit to the line

$$\Delta\tilde{G}_{v+1/2}/\text{cm}^{-1} = -79.46 \times (v+1) + 2\,309.5$$

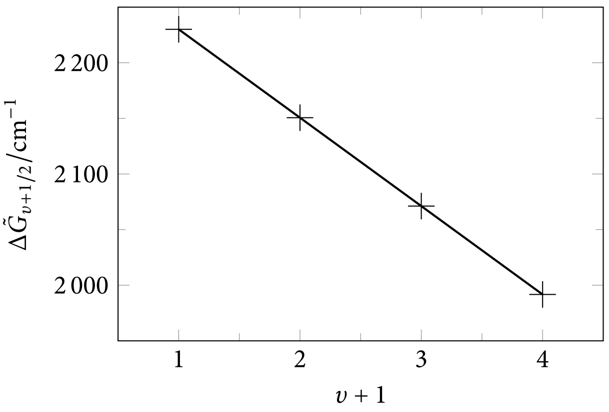


Figure 11.6

This confirms that the data are well-described by the Morse levels. From the slope

$$x_e\tilde{\nu}/\text{cm}^{-1} = -\tfrac{1}{2}\times\text{slope} = -\tfrac{1}{2}(-79.46) \quad \text{hence} \quad x_e\tilde{\nu} = 39.73\ \text{cm}^{-1}$$

and from the intercept

$$\tilde{\nu}/\text{cm}^{-1} = \text{intercept} = 2\,309.5 \quad \text{hence} \quad \tilde{\nu} = 2\,309.5\ \text{cm}^{-1}$$

The depth of the well, $\tilde{D}_e$ is then found using [11C.8–*444*], $x_e = \tilde{\nu}/4\tilde{D}_e$ rearranged to $\tilde{D}_e = \tilde{\nu}/4x_e = \tilde{\nu}^2/4\tilde{\nu}x_e$. The dissociation energy is $\tilde{D}_0 = \tilde{D}_e - \tilde{G}(0)$ (Fig. 11C.3 on page 444), hence

$$\begin{aligned}\tilde{D}_0 = \tilde{D}_e - \tilde{G}(0) &= \frac{\tilde{\nu}^2}{4\tilde{\nu}x_e} - \tilde{G}(0)\\ &= \frac{(2309.5\ \text{cm}^{-1})^2}{4\times(39.73\ \text{cm}^{-1})} - (1144.83\ \text{cm}^{-1}) = \boxed{3.24\times10^4\ \text{cm}^{-1}}\end{aligned}$$

To convert to eV, the conversion 1 eV = 8065.5 cm^{-1} from inside the front cover is used to give $\boxed{D_0 = 4.02\ \text{eV}}$.

The result is only quoted to modest precision because in effect the dissociation limit is extrapolated from just a few levels near to the bottom of the potential energy well.

E11C.8(b) The wavenumber of the transition arising from the rotational state J in the P branch ($\Delta J = -1$) of the fundamental transition ($v = 1 \leftarrow v = 0$) is given by [11C.13a–*447*], $\tilde{\nu}_P(J) = \tilde{\nu} - 2\tilde{B}J$. In this case $\tilde{\nu} = 2648.98\ \text{cm}^{-1}$ and $\tilde{B} = 8.465\ \text{cm}^{-1}$ hence

$$\tilde{\nu}_R(2) = (2648.98\ \text{cm}^{-1}) - 2\times(8.465\ \text{cm}^{-1})\times 2 = \boxed{2615.1\ \text{cm}^{-1}}$$

Solutions to problems

P11C.2 The potential energy function for a Morse oscillator is given by [11C.7–*444*], $V(x) = hc\tilde{D}_e(1-e^{-ax})^2$, and the force constant is defined in [11C.2b–*442*] as $k_f = (d^2V/dx^2)_0$.

$$\frac{d}{dx}hc\tilde{D}_e(1-e^{-ax})^2 = 2hc\tilde{D}_e(1-e^{-ax})(ae^{-ax}) = 2hc\tilde{D}_e a(e^{-ax}-e^{-2ax})$$
$$\frac{d^2}{dx^2}V(x) = \frac{d}{dx}2hc\tilde{D}_e a(e^{-ax}-e^{-2ax}) = 2hc\tilde{D}_e a(-ae^{-ax}+2ae^{-2ax})$$

Evaluation the second derivative at $x = 0$ gives

$$k_f = (d^2V/dx^2)_0 = 2hc\tilde{D}_e a(-a+2a) = \boxed{2hc\tilde{D}_e a^2}$$

P11C.4 The quoted vibrational terms, $\tilde{G}(\upsilon) = (\upsilon+\frac{1}{2})\tilde{\nu} - (\upsilon+\frac{1}{2})^2 x_e\tilde{\nu}$, are those of a Morse oscillator. Therefore [11C.9b–*445*] applies, $\Delta\tilde{G}_{\upsilon+1/2} = \tilde{\nu} - 2(\upsilon+1)x_e\tilde{\nu}$, where $\Delta\tilde{G}_{\upsilon+1/2} = \tilde{G}(\upsilon+1) - \tilde{G}(\upsilon)$, applies. It is therefore expected that a plot of $\Delta\tilde{G}_{\upsilon+1/2}$ against $(\upsilon+1)$ will have slope $-2x_e\tilde{\nu}$ and intercept $\tilde{\nu}$. The data are shown in the table and the plot in Fig. 11.7.

υ	$\tilde{G}_\upsilon/\text{cm}^{-1}$	$\Delta\tilde{G}_{\upsilon+1/2}/\text{cm}^{-1}$	$\upsilon+1$
0	142.81	284.50	1
1	427.31	283.00	2
2	710.31	281.50	3
3	991.81		

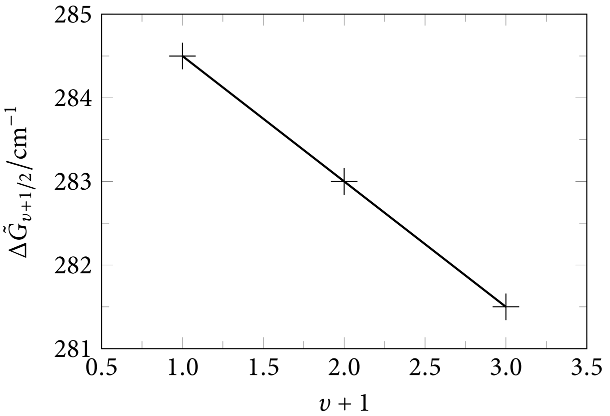


Figure 11.7

The data are a good fit to the line

$$\Delta\tilde{G}_{\upsilon+1/2}/\text{cm}^{-1} = -1.500\times(\upsilon+1) + 286.00$$

This confirms that the data are well-described by the Morse levels. From the slope

$$x_e\tilde{\nu}/\text{cm}^{-1} = -\tfrac{1}{2} \times \text{slope} = -\tfrac{1}{2}(-1.500) \quad \text{hence} \quad x_e\tilde{\nu} = 0.750\ \text{cm}^{-1}$$

and from the intercept

$$\tilde{\nu}/\text{cm}^{-1} = \text{intercept} = 286.00 \quad \text{hence} \quad \tilde{\nu} = 286.00\ \text{cm}^{-1}$$

The zero-point energy is $\tilde{G}(0)$, which is, from the data given, $\boxed{142.81\ \text{cm}^{-1}}$.

The depth of the well, $\tilde{D}_e$ is then found using [11C.8–*444*], $x_e = \tilde{\nu}/4\tilde{D}_e$ rearranged to $\tilde{D}_e = \tilde{\nu}/4x_e = \tilde{\nu}^2/4\tilde{\nu}x_e$. The dissociation energy is $\tilde{D}_0 = \tilde{D}_e - \tilde{G}(0)$ (Fig. 11C.3 on page 444), hence

$$\begin{aligned}\tilde{D}_0 = \tilde{D}_e - \tilde{G}(0) &= \frac{\tilde{\nu}^2}{4\tilde{\nu}x_e} - \tilde{G}(0)\\ &= \frac{(286.00\ \text{cm}^{-1})^2}{4 \times (0.750\ \text{cm}^{-1})} - (142.81\ \text{cm}^{-1}) = \boxed{2.71 \times 10^4\ \text{cm}^{-1}}\end{aligned}$$

To convert to eV, the conversion 1 eV = 8065.5 cm^{-1} from inside the front cover is used to give $\boxed{D_0 = 3.36\ \text{eV}}$. The result is only quoted to modest precision because in effect the dissociation limit is extrapolated from just a few levels near to the bottom of the potential energy well.

In the harmonic limit the vibrational frequency is given by [11C.4b–*443*], $\tilde{\nu} = (1/2\pi c)(k_f/m_{\text{eff}})^{1/2}$, with the effective mass given by $m_{\text{eff}} = m_1m_2/(m_1+m_2)$. It follows that $k_f = m_{\text{eff}}(2\pi c\tilde{\nu})^2$.

$$\begin{aligned}k_f &= \frac{22.9898 \times 126.9045}{22.9898 + 126.9045} \times (1.6605 \times 10^{-27}\ \text{kg})\\ &\quad \times [2\pi \times (2.9979 \times 10^{10}\ \text{cm s}^{-1}) \times (286.00\ \text{cm}^{-1})]^2\\ &= \boxed{93.8\ \text{N m}^{-1}}\end{aligned}$$

P11C.6 The Morse potential is given by [11C.7–*444*], $V(x) = hc\tilde{D}_e(1 - e^{-ax})^2$, where $a = (m_{\text{eff}}\omega^2/2hc\tilde{D}_e)^{1/2}$. The task is to relate the constant a to the given values of $\tilde{\nu}$ and $\tilde{\nu}x_e$. This is done by starting with [11C.8–*444*], $x_e = \tilde{\nu}/4\tilde{D}_e$, hence $\tilde{D}_e = \tilde{\nu}/4x_e$; using $\tilde{\nu} = \omega/(2\pi c)$ this becomes $\tilde{D}_e = \omega/8\pi c x_e$. This is then used in the expression for a to give

$$\begin{aligned}a &= \left(\frac{m_{\text{eff}}\omega^2}{2hc\tilde{D}_e}\right)^{1/2} = \left(\frac{m_{\text{eff}}\omega^2}{2hc} \times \frac{8\pi c x_e}{\omega}\right)^{1/2}\\ &= \left(\frac{m_{\text{eff}}4\pi x_e\omega}{h}\right)^{1/2} = \left(\frac{m_{\text{eff}}4\pi x_e(2\pi c\tilde{\nu})}{h}\right)^{1/2} = \left(\frac{8\pi^2 c m_{\text{eff}} x_e\tilde{\nu}}{h}\right)^{1/2}\end{aligned}$$

where $\omega = 2\pi c\tilde{\nu}$ is used once more. With the data given

$$m_{\text{eff}} = \frac{84.9118 \times 1.0078}{84.9118 + 1.0078} \times (1.6605 \times 10^{-27}\ \text{kg}) = 1.65... \times 10^{-27}\ \text{kg}$$

$$\begin{aligned}a &= \left(\frac{8\pi^2(2.9979 \times 10^{10}\ \text{cm s}^{-1}) \times (1.65... \times 10^{-27}\ \text{kg}) \times (14.15\ \text{cm}^{-1})}{6.6261 \times 10^{-34}\ \text{J s}}\right)^{1/2}\\ &= 9.14... \times 10^9\ \text{m}^{-1} = 9.14...\ \text{nm}^{-1}\end{aligned}$$

The well depth $\tilde{D}_e$ is computed using $\tilde{D}_e = \tilde{\nu}/4x_e = \tilde{\nu}^2/4x_e\tilde{\nu}$; with the given data $\tilde{D}_e = (936.8\ \text{cm}^{-1})^2/(4 \times [14.15\ \text{cm}^{-1}]) = 15\,505\ \text{cm}^{-1}$. With these values of a and D_e, and using $x = R - R_e$, the potential is plotted in Fig. 11.8.

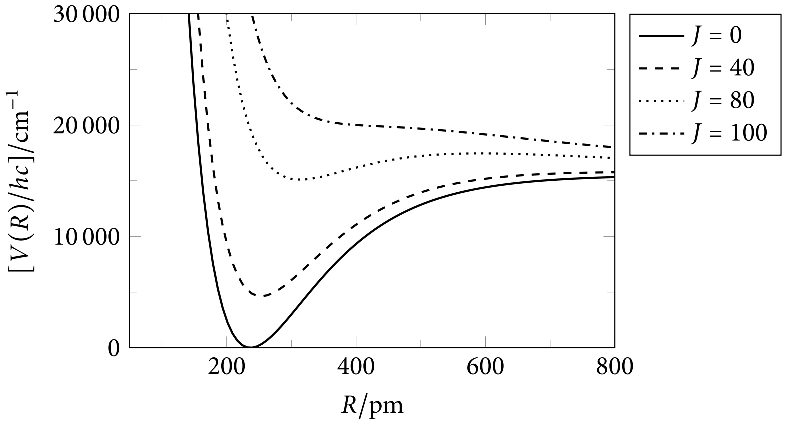


Figure 11.8

If rotation is included the potential is modified to $V^* = V + hc\tilde{B}J(J+1)$, which is conveniently rewritten as $V^*/hc = V/hc + \tilde{B}J(J+1)$ so that the value of V^*/hc is plotted as a wavenumber. Because $\tilde{B} \propto R^{-2}$, the value of $\tilde{B}$ at any R is related to its value at the equilibrium bond length as

$$\frac{\tilde{B}(R)}{\tilde{B}(R_e)} = \frac{R_e^2}{R^2} \quad \text{hence} \quad \tilde{B}(R) = \tilde{B}(R_e)\frac{R_e^2}{R^2}$$

The effective potential function to plot is therefore

$$V^*/hc = \tilde{D}_e(1 - e^{-a(R-R_e)})^2 + \tilde{B}(R_e)\frac{R_e^2}{R^2}J(J+1)$$

This is plotted in Fig. 11.8 for the indicated values of J. It is seen that as J increases the depth of the potential well decreases, and that for $J = 100$ there is no minimum in the potential, implying that the molecule is not bound.

P11C.8 The vibrational terms of the Morse oscillator are [11C.8–*444*], $\tilde{G}(\upsilon) = (\upsilon + \frac{1}{2})\tilde{\nu} - (\upsilon + \frac{1}{2})^2 x_e\tilde{\nu}$. Because of the term in x_e, which goes as υ^2, the energy levels get closer together and eventually the spacing goes to zero at the dissociation limit. This spacing is given by [11C.9b–*445*], $\Delta\tilde{G}_{\upsilon+1/2} = \tilde{\nu} - 2(\upsilon + 1)x_e\tilde{\nu}$, where $\Delta\tilde{G}_{\upsilon+1/2} = \tilde{G}(\upsilon + 1) - \tilde{G}(\upsilon)$. The quantum number of the state at which the spacing goes to zero is therefore found by solving $\Delta\tilde{G}_{\upsilon_{\text{max}}+1/2} = 0$

$$\tilde{\nu} - 2(\upsilon_{\text{max}} + 1)x_e\tilde{\nu} = 0 \quad \text{hence} \quad \boxed{\upsilon_{\text{max}} = 1/2x_e - 1}$$

An alternative approach is say that $\tilde{G}(v)$ reaches a maximum value at the dissociation limit, and therefore to find this limit by solving $\mathrm{d}\tilde{G}(v)/\mathrm{d}v = 0$

$$\frac{\mathrm{d}}{\mathrm{d}v}\left[(v+\tfrac{1}{2})\tilde{\nu} - (v+\tfrac{1}{2})^2 x_e\tilde{\nu}\right] = \tilde{\nu} - 2(v+\tfrac{1}{2})x_e\tilde{\nu}$$

$$\text{solving}\quad 0 = \tilde{\nu} - 2(v_{\max}+\tfrac{1}{2})x_e\tilde{\nu} \quad \text{gives} \quad \boxed{v_{\max} = 1/2x_e - \tfrac{1}{2}}$$

The difference between this result and that previously obtained is not significant because $v_{\max}$ is an integer, whereas both of the expressions derived treat v as a continuous variable; it will therefore be necessary to round to the nearest integer.

Yet another approach is to seek the value of v at which the energy of the term reaches $\tilde{D}_e$

$$(v_{\max}+\tfrac{1}{2})\tilde{\nu} - (v_{\max}+\tfrac{1}{2})^2 x_e\tilde{\nu} = \tilde{D}_e$$

This is most easily solved by letting $y = (v_{\max}+\tfrac{1}{2})$ to give the quadratic

$$0 = y^2 x_e\tilde{\nu} - y\tilde{\nu} + \tilde{D}_e$$

$$\text{hence}\quad y = (1/2x_e\tilde{\nu})\left[\tilde{\nu} \pm (\tilde{\nu}^2 - 4x_e\tilde{\nu}\tilde{D}_e)^{1/2}\right]$$

Using $x_e = \tilde{\nu}/4\tilde{D}_e$ from [11C.8–*444*] gives

$$y = (1/2x_e\tilde{\nu})\left[\tilde{\nu} \pm (\tilde{\nu}^2 - \tilde{\nu}^2)^{1/2}\right] = 1/2x_e$$

hence $\boxed{v_{\max} = 1/2x_e - \tfrac{1}{2}}$.

P11C.10 The rotational constant is given by [11B.7–*432*], $\tilde{B} = \hbar/4\pi c I$, and the moment of inertia is given by $m_{\text{eff}}R^2$, with $m_{\text{eff}} = m_1 m_2/(m_1+m_2)$. It follows that $R = (\hbar/4\pi c m_{\text{eff}}\tilde{B})^{1/2}$.

$$m_{\text{eff}} = \frac{12.0000 \times 15.9949}{12.0000 + 15.9949} \times (1.6605\times 10^{-27}\ \text{kg}) = 1.13... \times 10^{-26}\ \text{kg}$$

For the $v = 0$ state $\tilde{B} = 1.9314\ \text{cm}^{-1}$ and hence

$$\begin{aligned} R &= (\hbar/4\pi c m_{\text{eff}}\tilde{B})^{1/2} \\ &= \left(\frac{1.0546\times 10^{-34}\ \text{J s}}{4\pi \times (2.9979\times 10^{10}\ \text{cm s}^{-1}) \times (1.13...\times 10^{-26}\ \text{kg}) \times (1.9314\ \text{cm}^{-1})}\right)^{1/2} \\ &= \boxed{112.8\ \text{pm}} \end{aligned}$$

Repeating the calculation for the $v = 1$ state $\tilde{B} = 1.6116\ \text{cm}^{-1}$ gives $\boxed{123.5\ \text{pm}}$.

In fact the data are in error: the rotational constant for $v = 0$ is $1.9225\ \text{cm}^{-1}$ giving $R = 113.1$ pm, and for $v = 1$ it is $1.9050\ \text{cm}^{-1}$ giving $R = 113.6$ pm. This variation by a fraction of a percent is more typical.

P11C.12 The expectation is that the separation between the lines in the P and R branches will be approximately constant at $2\tilde{B}$; however the separation of the first line of the R branch, $\tilde{\nu}_R(0)$, from the first line of the P branch, $\tilde{\nu}_P(1)$, is approximately $4\tilde{B}$. Examination of the data shows that the separation between the lines at 2906.25 cm^{-1} and at 2865.14 cm^{-1} is approximately twice that between the other lines. Therefore 2906.25 cm^{-1} is assigned as the first line of the R branch, the transition $J = 1 \leftarrow 0$, and 2865.14 cm^{-1} is assigned as the first line of the P branch, the transition $J = 0 \leftarrow 1$. The assignment of the other lines follows by working out from these.

In the method of combination differences, lines sharing a common upper (or lower) J level are identified and a plot is made of the difference between the wavenumbers of these pairs of lines against J. According to [11C.15b–*448*] a plot of $\tilde{\nu}_R(J) - \tilde{\nu}_P(J)$ against $(J + \frac{1}{2})$ will have slope $4\tilde{B}_1$, and according to [11C.15a–*448*] a plot of $\tilde{\nu}_R(J-1) - \tilde{\nu}_P(J+1)$ against $(J + \frac{1}{2})$ will have slope $4\tilde{B}_0$. The data are shown in the tables and the corresponding lines are plotted in Fig. 11.9.

J	$\tilde{\nu}_R(J)/\text{cm}^{-1}$	$\tilde{\nu}_P(J)/\text{cm}^{-1}$	$[\tilde{\nu}_R(J) - \tilde{\nu}_P(J)]/\text{cm}^{-1}$	$J + \frac{1}{2}$
0	2 906.25			0.5
1	2 925.92	2 865.14	60.78	1.5
2	2 944.99	2 843.63	101.36	2.5
3	2 963.35	2 821.59	141.76	3.5
4	2 981.05	2 799.00	182.05	4.5
5	2 998.05			

J	$\tilde{\nu}_R(J)/\text{cm}^{-1}$	$\tilde{\nu}_P(J)/\text{cm}^{-1}$	$[\tilde{\nu}_R(J-1) - \tilde{\nu}_P(J+1)]/\text{cm}^{-1}$	$J + \frac{1}{2}$
0	2 906.25			0.5
1	2 925.92	2 865.14	62.62	1.5
2	2 944.99	2 843.63	104.33	2.5
3	2 963.35	2 821.59	145.99	3.5
4	2 981.05	2 799.00		4.5
5	2 998.05			

Both plots show good straight lines. For the plot of $\tilde{\nu}_R(J) - \tilde{\nu}_P(J)$ the slope is 40.42 and hence $\tilde{B}_1 = (\text{slope}/4)\ \text{cm}^{-1} = \boxed{10.11\ \text{cm}^{-1}}$. For the second plot of $\tilde{\nu}_R(J-1) - \tilde{\nu}_P(J+1)$ the slope is 41.68 and hence $\tilde{B}_0 = (\text{slope}/4)\ \text{cm}^{-1} = \boxed{10.42\ \text{cm}^{-1}}$.

P11C.14 For a harmonic potential the virial theorem ([7E.14–*278*]) states that $\langle V\rangle = \langle E_k\rangle$. The total energy is the sum of the kinetic and potential energies, therefore $E_{\text{tot}} = \langle V\rangle + \langle E_k\rangle$. It therefore follows that $E_{\text{tot}} = 2\langle V\rangle$.

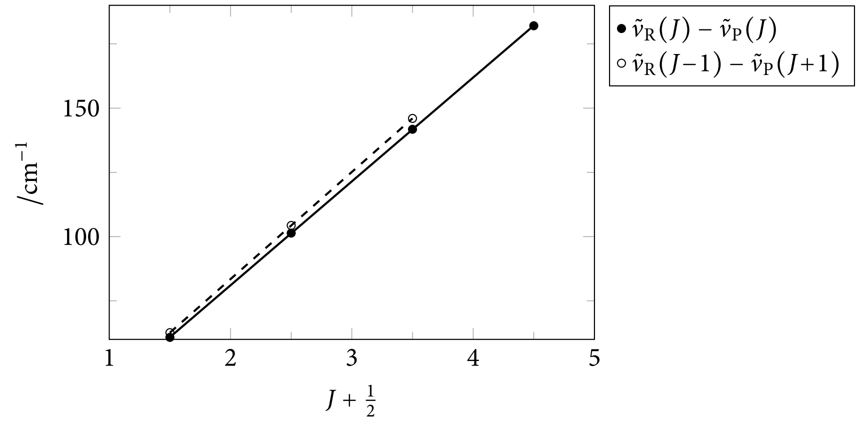


Figure 11.9

For a harmonic oscillator $E_{\text{tot}} = (v+\frac{1}{2})\hbar(k_f/m)^{1/2}$ and $V = \frac{1}{2}k_f x^2$ hence

$$\begin{aligned} 2\times\langle\tfrac{1}{2}k_f x^2\rangle &= (v+\tfrac{1}{2})\hbar(k_f/m)^{1/2} \\ \text{hence } \langle x^2\rangle &= k_f^{-1}\hbar(v+\tfrac{1}{2})(k_f/m)^{1/2} \\ &= (v+\tfrac{1}{2})\hbar(1/k_f m)^{1/2} \end{aligned}$$

The average of x^2 therefore increases with the vibrational energy (is indicated by the quantum number v).

The rotational constant is given by $\tilde{B} = \hbar/4\pi cI = \hbar/4\pi c m_{\text{eff}}R^2$. Because the bond is vibrating much faster than the molecule is rotating, the term R^2 is replaced by the average $\langle R^2\rangle$ over a vibration. It is shown in *Problem* P11C.13 that $\langle R^2\rangle = R_e^2 + \langle x^2\rangle$. Therefore, because $\langle x^2\rangle$ increases with v, so does $\langle R^2\rangle$ and therefore the rotational constant $\tilde{B}$ decreases with v.

If the potential is anharmonic the vibration is no longer symmetric about the equilibrium separation: the average of R is greater than R_e because the bond stretches more than it compresses. The greater the vibrational energy, the more asymmetric the vibration becomes and hence the greater $\langle R\rangle$ becomes. As a result the rotational constant decreases with increasing vibrational quantum number. Usually this effect is much greater than that expected for a harmonic potential.

P11C.16 If the centrifugal force balances exactly the force due to extending the bond from R_e to R_c, the following applies

$$k_f(R_c - R_e) = m_{\text{eff}}\omega^2 R_c \quad \text{hence} \quad (R_c - R_e) = m_{\text{eff}}\omega^2 R_c/k_f \qquad (11.2)$$

It is helpful to recall the steps for converting a classical expression for the rotational energy into the corresponding quantum expression. The (kinetic) energy of a body with moment of inertia I rotating at (angular) velocity ω is $E = \frac{1}{2}I\omega^2$. The rotational angular momentum $\mathcal{J}$ is given by $\mathcal{J} = I\omega$. It therefore follows that $E = \frac{1}{2}(I\omega)^2/I = \mathcal{J}^2/2I$.

The classical angular momentum $\mathcal{J}$ is then replaced by the quantum expression $[J(J+1)]^{1/2}\hbar$ to give $E = J(J+1)\hbar^2/2I$, where J is the rotational quantum number. This expression is written $E = J(J+1)hB$ where $B = \hbar/4\pi I = h/8\pi^2 I$, the rotational constant in frequency units.

The aim of the derivation is to generate an expression which can be compared with $E(J) = hBJ(J+1) - hD_J J^2(J+1)^2$; the first term is recognised as originating from a classical term $\mathcal{J}^2$ (as in the above discussion), and the second term is recognised as originating from a classical term $\mathcal{J}^4$.

The first step is to write the rotational energy as a sum of two terms

$$E = \overbrace{\frac{\mathcal{J}^2}{2I}}^{E_1} + \overbrace{\tfrac{1}{2}k_\mathrm{f}(R_\mathrm{c} - R_\mathrm{e})^2}^{E_2} \tag{11.3}$$

The first term is the rotational energy of a rigid rotor, the second term is the energy that arises from stretching the bond from R_e to R_c: it is simply the harmonic potential energy. From now on attention is focused on this second term. The expression for $(R_\mathrm{c} - R_\mathrm{e})$ from eqn 11.2 is inserted to give

$$E_2 = \tfrac{1}{2}k_\mathrm{f}(R_\mathrm{c} - R_\mathrm{e})^2 = \tfrac{1}{2}k_\mathrm{f}\frac{m_\mathrm{eff}^2\omega^4R_\mathrm{c}^2}{k_\mathrm{f}^2} = \frac{m_\mathrm{eff}^2\omega^4R_\mathrm{c}^2}{2k_\mathrm{f}}$$

Because the aim is to generate a term of the form $\mathcal{J}^4 = (I\omega)^4$, rewrite ω^4 as $(I\omega)^4/I^4$. Then recognise that $I = m_\mathrm{eff}R_\mathrm{c}^2$ and cancel one factor of I

$$E_2 = \frac{m_\mathrm{eff}^2(I\omega)^4R_\mathrm{c}^2}{2k_\mathrm{f}I^4} = \frac{m_\mathrm{eff}(I\omega)^4(m_\mathrm{eff}R_\mathrm{c}^2)}{2k_\mathrm{f}I^4} = \frac{m_\mathrm{eff}(I\omega)^4}{2k_\mathrm{f}I^3}$$

For a harmonic oscillator the vibrational frequency is given by $\omega_\mathrm{HO} = (k_\mathrm{f}/m_\mathrm{eff})^{1/2}$, hence $(m_\mathrm{eff}/k_\mathrm{f}) = 1/\omega_\mathrm{HO}^2$; using this gives

$$E_2 = \frac{(I\omega)^4}{2\omega_\mathrm{HO}^2I^3} = \frac{\mathcal{J}^4}{2\omega_\mathrm{HO}^2I^3}$$

To create the quantum expression replace $\mathcal{J}$ with $[J(J+1)]^{1/2}\hbar$ to give

$$E_2 = \frac{J^2(J+1)^2\hbar^4}{2\omega_\mathrm{HO}^2I^3} = J^2(J+1)^2\underbrace{\left(\frac{\hbar^2}{2I}\right)^3}_{(hB)^3}\frac{8}{2\hbar^2\omega_\mathrm{HO}^2} = J^2(J+1)^2\frac{4(hB)^3}{\hbar^2\omega_\mathrm{HO}^2}$$

To write the expression in wavenumbers, divide both sides by hc to give

$$\tilde{E}_2 = E_2/hc = J^2(J+1)^2\frac{4(hB)^3}{\hbar^2\omega_\mathrm{HO}^2 \times hc} = J^2(J+1)^2\frac{4(hB)^3}{ch^3\omega_\mathrm{HO}^2/4\pi^2}$$

Finally, note that the harmonic frequency can be expressed as a wavenumber: $\tilde{\nu} = \omega_{\mathrm{HO}}/2\pi c$, hence $\omega_{\mathrm{HO}}^2 = 4\pi^2 c^2 \tilde{\nu}^2$, and that the rotational constant can also be expressed as a wavenumber $B = c\tilde{B}$

$$\tilde{E}_2 = J^2(J+1)^2 \frac{4(hc\tilde{B})^3}{ch^3(4\pi^2c^2\tilde{\nu}^2)/4\pi^2} = J^2(J+1)^2 \frac{4\tilde{B}^3}{\tilde{\nu}^2}$$

If follows that $\tilde{D}_J = 4\tilde{B}^3/\tilde{\nu}^2$, as required.

For completeness it is necessary to consider the term E_1 in eqn 11.3 in some more detail. This term contains the moment of inertia which, as a result of the stretching of the bond, is given by $I = m_{\mathrm{eff}} R_{\mathrm{c}}^2$.

$$E_1 = \frac{\mathcal{J}^2}{2I} = \frac{\mathcal{J}^2}{2m_{\mathrm{eff}} R_{\mathrm{c}}^2}$$

From eqn 11.2 $R_{\mathrm{c}} = R_{\mathrm{e}}/(1 - m_{\mathrm{eff}}\omega^2/k_{\mathrm{f}})$. It therefore follows that

$$= \frac{\mathcal{J}^2}{2m_{\mathrm{eff}}} \frac{(1 - m_{\mathrm{eff}}\omega^2/k_{\mathrm{f}})^2}{R_{\mathrm{e}}^2}$$

If it is assumed that $m_{\mathrm{eff}}\omega^2/k_{\mathrm{f}} \ll 1$ (which is the case for typical molecules), then this term may be ignored and hence

$$E_1 = \frac{\mathcal{J}^2}{2m_{\mathrm{eff}} R_{\mathrm{e}}^2} = \frac{\mathcal{J}^2}{2I_{\mathrm{eq}}}$$

where I_{eq} is the moment of inertia corresponding to the equilibrium separation – that is, in the absence of any centrifugal distortion.

P11C.18 According to [11C.15b–*448*] $\tilde{\nu}_{\mathrm{R}}(J) - \tilde{\nu}_{\mathrm{P}}(J) = 4\tilde{B}_1(J+\frac{1}{2})$, and according to [11C.15a–*448*] $\tilde{\nu}_{\mathrm{R}}(J-1) - \tilde{\nu}_{\mathrm{P}}(J+1) = 4\tilde{B}_0(J+\frac{1}{2})$. Hence

$$\tilde{\nu}_{\mathrm{R}}(1) - \tilde{\nu}_{\mathrm{P}}(1) = 6\tilde{B}_1 \quad \text{and} \quad \tilde{\nu}_{\mathrm{R}}(0) - \tilde{\nu}_{\mathrm{P}}(2) = 6\tilde{B}_0$$

Therefore

$$\tilde{B}_1 = [(2150.858\ \mathrm{cm}^{-1}) - (2139.427\ \mathrm{cm}^{-1})]/6 = \boxed{1.905\ \mathrm{cm}^{-1}}$$
$$\tilde{B}_0 = [(2147.084\ \mathrm{cm}^{-1}) - (2135.548\ \mathrm{cm}^{-1})]/6 = \boxed{1.923\ \mathrm{cm}^{-1}}$$

Because only data from a few lines have been used, high precision is not warranted.

11D Vibrational spectroscopy of polyatomic molecules

Answers to discussion questions

D11D.2 The gross selection rule for vibrational Raman scattering is that for a particular normal mode to be active the vibration must result in a change in the polarizability as the molecule vibrates about the equilibrium position. The origin of this rule is that such an change in the polarizability will result in the dipole induced in the molecule by the electric field of the incident radiation being altered as the molecule vibrates. It is this modulation of the dipole that results in Raman scattering.

Solutions to exercises

E11D.1(b) With the exception of homonuclear diatomics, all molecules have at least one infrared active normal mode. Of the molecules listed, $\boxed{CH_3CH_3, CH_4,}$ and $\boxed{CH_3Cl}$ have infrared active modes.

E11D.2(b) According to [11D.1–*451*], a non-linear molecule has $3N-6$ vibrational normal modes, where N is the number of atoms in the molecule; a linear molecule has $3N-5$ normal modes.

(i) C_6H_6 is non-linear, has $N=12$ and hence $\boxed{30}$ normal modes.

(ii) $C_6H_5CH_3$ is non-linear, has $N=15$ and hence $\boxed{39}$ normal modes.

(iii) $HC\equiv C-C\equiv CH$ is linear, has $N=6$ and hence $\boxed{13}$ normal modes.

E11D.3(b) According to [11D.1–*451*], a linear molecule has $3N-5$ normal modes, where N is the number of atoms in the molecule. There are 36 atoms in this linear molecule, and so there are $3(36)-5=\boxed{103}$ normal modes.

E11D.4(b) According to [11D.1–*451*], a non-linear molecule has $3N-6$ vibrational normal modes, where N is the number of atoms in the molecule; therefore SO_2 has 3 normal modes. The terms (energies expressed as wavenumbers) for normal mode q are given by [11D.2–*452*], $\tilde{G}_q(v)=(v_q+\frac{1}{2})\tilde{\nu}_q$, where v_q is the quantum number for that mode and $\tilde{\nu}_q$ is the wavenumber of the vibration of that mode. These terms are additive, so the ground state term corresponds to each mode having $v_q=0$

$$\tilde{G}_1(0)+\tilde{G}_2(0)+\tilde{G}_3(0)=\boxed{\tfrac{1}{2}(\tilde{\nu}_1+\tilde{\nu}_2+\tilde{\nu}_3)}$$

E11D.5(b) A planar AB_3 molecule has no permanent dipole moment, but in the normal mode in which the central atom is displaced vertically out of the plane of the molecule, a dipole will be induced in this direction. During the vibration, the A atom passes back and forth through the plane of the molecule, resulting in an oscillating dipole: the normal mode will therefore be $\boxed{\text{infrared active}}$.

This mode is in fact $\boxed{\text{not Raman active}}$, something which is best deduced using the symmetry arguments discussed in Topic 11E. The rule of mutual exclusion does not apply.

E11D.6(b) The benzene molecule has a centre of symmetry, so the rule of mutual exclusion applies. The molecule has no permanent dipole moment but if it is distorted into a boat-like shape the expectation is that there will be an induced dipole and that therefore the mode will be $\boxed{\text{infrared active}}$.

According to the rule of mutual exclusion, such a mode is $\boxed{\text{not Raman active}}$.

E11D.7(b) The exclusion rule applies only to molecules with a centre of symmetry. C_2H_4 does possess such symmetry, and so the exclusion rule $\boxed{\text{does apply}}$.

Solutions to problems

P11D.2 $NO_2{}^+$ is isoelectronic with CO_2, so the molecule is linear. Around the central N there are four electron pairs, arranged as two double bonds.

The normal modes of $NO_2{}^+$ are analogous to those of CO_2 shown in Fig. 11D.2 on page 452. The one Raman active normal mode at 1400 cm^{-1} is the symmetric stretch (ν_1). The lowest frequency mode at 540 cm^{-1} is the (doubly degenerate) bend (ν_3): typically, bends are a lower frequencies than stretches. The infrared active mode at 2360 cm^{-1} is the asymmetric stretch (ν_2).

The weak absorption at 3735 cm^{-1} is likely to be either an overtone or a combination band. The most likely candidate is for one quantum to be excited into each of the modes ν_1 and ν_2; such a transition would have wavenumber $1400\ \text{cm}^{-1} + 2360\ \text{cm}^{-1} = 3760\ \text{cm}^{-1}$. The numbers do not agree exactly due to the effects of anharmonicity.

11E Symmetry analysis of vibrational spectroscopy

Answer to discussion question

Solutions to exercises

E11E.1(b) Note that there is an error in the *Exercise*: the displacements span $A_{1g} + 2A_{1u} + 2E_{1u} + E_{1g}$.

The displacements include translations and rotations. For the point group $D_{\infty h}$, (x, y) and z transform as E_{1u} and A_{1u}, respectively. The rotations (R_x, R_y) transform as E_{1g}; for a linear molecule there is no rotation about the internuclear axis and so the symmetry species for R_z is not taken away. Taking these symmetry species away leaves just the symmetry species of the normal modes as $\boxed{A_{1g} + A_{1u} + E_{1u}}$. Theses correspond to 4 normal modes, which is the number expected for a linear triatomic (the E_{1u} is doubly degenerate).

E11E.2(b) A mode is infrared active if it has the same symmetry species as one of the functions x, y, and z; in this point group these span $E_{1u} + A_{1u}$. A mode is Raman active if it has the same symmetry as a quadratic form; in this group such forms span $A_{1g} + E_{1g} + E_{2g}$.

Therefore the $\boxed{A_{1u} \text{ and } E_{1u}}$ normal modes are $\boxed{\text{infrared active}}$, and the $\boxed{A_{1g}}$ mode is $\boxed{\text{Raman active}}$. The rule of mutual exclusion applies.

E11E.3(b) (i) H_2O belongs to the point group C_{2v}. Rather than considering all 9 displacement vectors together it is convenient to consider them in sub-sets of displacement vectors which are mapped onto one another by the operations of the group. The x, y, and z vectors on the oxygen are not mapped onto the displacements of the H atoms and so can be considered separately. In fact, because these displacement vectors are attached to the principal axis, they transform as the cartesian functions x, y, and z as listed in the character table: that is as $B_1 + B_2 + A_1$.

Assuming the same axis system as in Fig. 11E.1 on page 456, the two x displacements on the H atoms map onto one another, as do the two y displacements, as do the two z displacements: however, the x, y, and z displacements are not mixed with one another. For the two z displacements the operation E leaves both unaffected so the character is 2; the C_2 operation swaps the two displacements so the character is 0; the $\sigma_v(xz)$ operation swaps the two displacements so the character is 0; the $\sigma'_v(yz)$ operation leaves the two displacements unaffected so the character is 2. The representation is therefore $(2, 0, 0, 2)$, which is easily reduced by inspection to $A_1 + B_2$. For the two y displacements the argument is essentially the same, resulting in the representation $(2, 0, 0, 2)$, which reduces to $A_1 + B_2$.

For the two x displacements the operation E leaves both unaffected so the character is 2; the C_2 operation swaps the two displacements so the character is 0; the $\sigma_v(xz)$ operation swaps the two displacements so the character is 0; the $\sigma'_v(yz)$ operation leaves the two displacements in the same position by changes their direction, so the character is -2. The representation is therefore $(2, 0, 0, -2)$, which is easily reduced by inspection to $A_2 + B_1$.

The 9 displacements therefore transform as $3A_1 + A_2 + 2B_1 + 3B_2$.

The displacements include translations and rotations. For the point group C_{2v}, x, y, and z transform as B_1, B_2, and A_1, respectively. The rotations R_x, R_y, and R_z transform as B_2, B_1, and A_2, respectively. Taking these symmetry species away leaves just the normal modes as $\boxed{2A_1 + B_2}$.

A mode is Raman active if it has the same symmetry as a quadratic form; in this group such forms span $A_1 + A_2 + B_1 + B_2$. Therefore $\boxed{\text{all}}$ of the normal modes are Raman active.

(ii) H_2CO is a straightforward extension of the case of H_2O as both molecules belong to the point group C_{2v}. The H_2C portion lies in the same position as H_2O, with the carbonyl O atom lying on the z axis (the principal axis). The analysis therefore includes three more displacement vectors for the

O, and as they are connected to the principal axis they transform as the cartesian functions x, y, and z, that is as $B_1 + B_2 + A_1$. The tally of normal modes is therefore those for H_2O plus these three in addition: $\boxed{3A_1 + B_1 + 2B_2}$. All these modes are Raman active.

Solutions to problems

P11E.2 It is helpful to tabulate the given data

band in infrared/cm^{-1}	870	1370			2869	3417
band in Raman/cm^{-1}	877		1408	1435		3407

Bands which are are described as deriving from the same normal mode are listed in the same column. It is evident that the rule of mutual exclusion does not apply, therefore the molecule cannot have a centre of symmetry.

(i) If the molecule were linear it would have $3 \times 4 - 5 = \boxed{7}$ normal modes.

(ii) Assuming **1** is planar the molecule possesses a centre of symmetry, a mirror plane in which the molecule lies, and a C_2 axis perpendicular to the plane of the molecule and passing through the mid-point of the O–O bond. The point group is therefore $\boxed{C_{2h}}$.

Assuming **2** is planar the molecule possesses: a C_2 axis lying in the plane of the molecule, passing through the mid-point of the O–O bond and perpendicular to this bond; and two mirror planes, one in the plane of the molecule and one perpendicular to this and containing the C_2 axis. The point group is therefore $\boxed{C_{2v}}$.

3 has a C_2 axis passing through the mid-point of the O–O bond and bisecting the dihedral angle formed between the two O–H bonds. The point group is therefore $\boxed{C_2}$.

(iii) This part of the question can be answered without determining the symmetry species of the normal modes in each case. As has already been noted, the data indicate that the rule of mutual exclusion is not obeyed, so this immediately rules out structure **1**.

In the point group C_2, (x, y, z) span the symmetry species A and B, and the quadratic forms span the same species. Therefore all normal modes (which have to transform as either A or B, the only two symmetry species in the group) are in principle both Raman and infrared active. This is inconsistent with the data, which shows modes which are only seen in either the Raman or the infrared.

In the point group C_{2v}, (x, y, z) span the symmetry species $A_1 + B_1 + B_2$, but the quadratic forms span $A_1 + A_2 + B_1 + B_2$. This means that any mode active in the infrared is also active in the Raman, which is again inconsistent with the data.

The data do not appear to be consistent with any of the three structures. However, it must be kept in mind that the prediction of whether or not a normal mode is active in the infrared or Raman is simply a prediction *in* *principle*. It may be that for other reasons a particular normal mode gives a band with such low intensity that it cannot be detected. The consensus view for H_2O_2 is that it has structure **3**.

For reference the symmetry species of the normal modes are: **1** $3A_g + A_u + 2B_u$; **2** $3A_1 + A_2 + 2B_2$; **3** $4A + 2B$.

11F **Electronic spectra**

Answers to discussion questions

D11F.2 This is explained in Section 11F.1(c) on page 462. A progression is set of transitions arising from a common vibrational level in one electronic state to successive vibrational levels in another electronic state. If the potential energy curve of the upper electronic state is displaced to a shorter or longer equilibrium bond length than that of the ground state, then the Franck–Condon factors are likely to make it possible to see a vibrational progression arising from the $v = 0$ level in the ground electronic state (for small molecules only this level is likely to be populated).

D11F.4 Colour can arise by the emission, absorption, or scattering of electromagnetic radiation by an object. Many molecules have electronic transitions that have wavelengths in the visible portion of the electromagnetic spectrum. When a substance emits radiation, the perceived colour of the object will be that of the emitted radiation, and it may be an additive colour resulting from the emission of more than one wavelength of radiation. When a substance absorbs radiation its colour is determined by the subtraction of those wavelengths from white light. For example, absorption of red light results in the object being perceived as green. Scattering, including the diffraction that occurs when light falls on a material with a grid of variation in texture or refractive index having dimensions comparable to the wavelength of light (for example, the plumage of a bird), may also form colour.

D11F.6 The electronic configuration of Zn^{2+} is ... $3s^2\,3p^6\,3d^{10}$. The 3d sub-shell is full, so no transitions involving the rearrangement of these electrons is possible.

Solutions to exercises

E11F.1(b) The term symbol indicates $|\Lambda| = 1$, which means that one electron must have $\lambda = 0$ and one have $\lambda = \pm1$, implying that one electron is in a σ and one in a π orbital. The total spin, S, is 1, meaning that the two electrons must have parallel spins. The overall symmetry with respect to inversion is u, which implies one electron has g and one has u symmetry. The configuration is therefore $\boxed{\sigma_g^1\,\pi_u^1}$.

E11F.2(b) Filled orbitals make no contribution to Λ and S, and so can be ignored. The electronic configuration of O_2 is ... $1\pi_g^2$, so that of $O_2{}^-$ is ... $1\pi_g^3$. With three electrons in a pair of degenerate orbitals two of the spins must be paired, so the overall spin S is $\frac{1}{2}$, and hence $(2S+1) = 2$. The degenerate π orbitals have $\lambda = \pm 1$. Therefore two electrons are in the orbital with $\lambda = +1$ and one in the orbital with $\lambda = -1$ to give $\Lambda = +1+1-1 = +1$, or two have $\lambda = -1$ and one has $\lambda = +1$ to give $\Lambda = -1-1+1 = -1$. Overall, $\Lambda = \pm 1$, which is represented by Π. The symmetry with respect to inversion is g × g × g = g. The term symbol is therefore $\boxed{{}^2\Pi_g}$.

E11F.3(b) The electronic configuration given is $1\sigma_g^2\,1\sigma_u^2\,1\pi_u^2\,1\pi_g^2$. The filled orbitals, $1\sigma_g^2$ and $1\sigma_u^2$, make no contribution to Λ and S, and so can be ignored. With two electrons in a pair of degenerate π_u orbitals, the spins may either be paired or parallel. Likewise, the two electrons in the degenerate π_g orbitals may either be paired or parallel. The overall result is that the maximum number of parallel spins is $4 \times \frac{1}{2} = 2$, corresponding to $S = 2$; it is also possible for all the spins to be paired up giving $S = 0$. The intermediate value $S = 1$ is also possible. The spin multiplicities are therefore $\boxed{5}$, $\boxed{3}$ and $\boxed{0}$.

The two electrons in the π_u have overall symmetry with respect to inversion (parity) u × u = g. The two electrons in the π_g have overall symmetry with respect to inversion (parity) g × g = g. Thus the overall symmetry with respect to inversion is $\boxed{\mathrm{g}}$.

E11F.4(b)
(i) Allowed
(ii) Allowed
(iii) Symmetry forbidden

E11F.5(b) *Note:* there is an error in the *Exercise*. The second function should be $\psi_1' = N_1(x-x_0)e^{-a(x-x_0)^2/2}$.

To evaluate the normalizing factor for the function $e^{-ax^2/2}$ requires the integral

$$\int_{-\infty}^{+\infty} e^{-ax^2}\,dx$$

which is of the form of Integral G.1 with $k = a$ and evaluates to $(\pi/a)^{1/2}$. The normalizing factor is therefore $N_0 = (a/\pi)^{1/4}$.

To evaluate the normalizing factor for the function $(x-x_0)e^{-a(x-x_0)^2/2}$ requires the integral

$$\int_{-\infty}^{+\infty} (x-x_0)^2 e^{-a(x-x_0)^2}\,dx$$

The substitution $y = x - x_0$ makes this of the form of Integral G.3 with $k = a$ and evaluates to $\frac{1}{2}(\pi/a^3)^{1/2}$. The normalizing factor is therefore $N_1 = (4a^3/\pi)^{1/4}$.

The Franck–Condon factor is given by [11F.5–*464*] and involves the square of integral of the product of the two wavefunctions

$$\begin{aligned}
I &= N_1N_0\int_{-\infty}^{+\infty} \mathrm{e}^{-ax^2/2}(x-x_0)\mathrm{e}^{-a(x-x_0)^2/2}\,\mathrm{d}x\\
&= (a/\pi)^{1/4}(4a^3/\pi)^{1/4}\int_{-\infty}^{+\infty}(x-x_0)\mathrm{e}^{-a[x^2/2+(x-x_0)^2/2]}\,\mathrm{d}x\\
&= (2a^2/\pi)^{1/2}\int_{-\infty}^{+\infty}(x-x_0)\mathrm{e}^{-a[x^2/2+x^2/2-xx_0+x_0^2/2]}\,\mathrm{d}x\\
&= (2a^2/\pi)^{1/2}\int_{-\infty}^{+\infty}(x-x_0)\mathrm{e}^{-a[x^2-xx_0+x_0^2/2]}\,\mathrm{d}x\\
&= (2a^2/\pi)^{1/2}\int_{-\infty}^{+\infty}(x-x_0)\mathrm{e}^{-a(x-x_0/2)^2}\mathrm{e}^{-ax_0^2/4}\,\mathrm{d}x
\end{aligned}$$

the final equality above is verified by expanding out the square and recombining the terms. The next step is to take out the constant factors and split the integral into two using $(x-x_0)=(x-x_0/2)-x_0/2$

$$\begin{aligned}
I &= (2a^2/\pi)^{1/2}\mathrm{e}^{-ax_0^2/4}\int_{-\infty}^{+\infty}(x-x_0)\mathrm{e}^{-a(x-x_0/2)^2}\,\mathrm{d}x\\
&= (2a^2/\pi)^{1/2}\mathrm{e}^{-ax_0^2/4}\\
&\quad\times\Big[\int_{-\infty}^{+\infty}(x-x_0/2)\mathrm{e}^{-a(x-x_0/2)^2}\,\mathrm{d}x-(x_0/2)\int_{-\infty}^{+\infty}\mathrm{e}^{-a(x-x_0/2)^2}\,\mathrm{d}x\Big]
\end{aligned}$$

The first integral is of an odd function over a symmetric interval and so is zero. The second integral is of the form of Integral G.1 with $k=a$ and evaluates to $(\pi/a)^{1/2}$ (it does not matter that it is centred at x_0 rather than 0). Hence

$$I=-(2a^2/\pi)^{1/2}\mathrm{e}^{-ax_0^2/4}(x_0/2)(\pi/a)^{1/2}=-(2a)^{1/2}(x_0/2)\mathrm{e}^{-ax_0^2/4}$$

The Franck–Condon factor is $\boxed{I^2=(ax_0^2/2)\mathrm{e}^{-ax_0^2/2}}$. As expected, this factor is zero when $x_0=0$ as then the two wavefunctions align and have zero overlap on account of one being even and one being odd. By taking the derivative of I^2 with respect to x_0 it is easily shown that the Franck–Condon factor is a maximum at $x_0=\pm(2/a)^{1/2}$.

E11F.6(b) The Franck–Condon factor is given by [11F.5–*464*] and involves the square of integral of the product of the two wavefunctions. The region over which both wavefunctions are non-zero is from $L/2$ to L: this is the domain of integration

$$I=(2/L)\int_{L/2}^{L}\sin(\pi x/L)\sin(\pi[x-L/2]/L)\,\mathrm{d}x$$

Note that $\sin(\pi[x-L/2]/L)=\sin(\pi x/L-\pi/2)=-\cos(\pi x/L)$, this gives a useful simplification

$$I=-(2/L)\int_{L/2}^{L}\sin(\pi x/L)\cos(\pi x/L)\,\mathrm{d}x$$

Next define $\theta = \pi x/L$ so that the limits are $\theta = \pi/2$ to $\theta = \pi$, and $\mathrm{d}x = (L/\pi)\mathrm{d}\theta$

$$= -(2/L)(L/\pi)\int_{\pi/2}^{\pi} \sin\theta\cos\theta\,\mathrm{d}\theta$$

The integral is evaluated by noting that $\mathrm{d}/\mathrm{d}\theta(\sin^2\theta) = 2\sin\theta\cos\theta$

$$= -(2/L)(L/\pi)\tfrac{1}{2}\left|\sin^2\theta\right|_{\pi/2}^{\pi} = -(2/L)(L/\pi)\tfrac{1}{2}(0-1) = 1/\pi$$

The Franck–Condon factor is $\boxed{I^2 = 1/\pi^2}$; numerically this is 0.318.

E11F.7(b) The wavenumbers of the lines in the R branch are given in [11F.7–*465*], $\tilde{\nu}_{\mathrm{R}}(J) = \tilde{\nu} + (\tilde{B}' + \tilde{B})(J+1) + (\tilde{B}' - \tilde{B})(J+1)^2$. The band head is located by finding the value of J which gives the largest wavenumber, which can be inferred by solving $\mathrm{d}\tilde{\nu}_{\mathrm{R}}(J)/\mathrm{d}J = 0$.

$$\frac{\mathrm{d}}{\mathrm{d}J}\left[\tilde{\nu} + (\tilde{B}' + \tilde{B})(J+1) + (\tilde{B}' - \tilde{B})(J+1)^2\right] = (\tilde{B}' + \tilde{B}) + 2(J+1)(\tilde{B}' - \tilde{B})$$

Setting the derivative to zero and solving for J gives

$$J_{\text{head}} = \frac{-(\tilde{B}' + \tilde{B})}{2(\tilde{B}' - \tilde{B})} - 1 = \boxed{\frac{\tilde{B} - 3\tilde{B}'}{2(\tilde{B}' - \tilde{B})}}$$

A band head only occurs in the R branch if $\tilde{B}' < \tilde{B}$.

E11F.8(b) Because $\tilde{B}' > \tilde{B}$ a band head will occur in the P branch.

The wavenumbers of the lines in the P branch are given in [11F.7–*465*], $\tilde{\nu}_{\mathrm{P}}(J) = \tilde{\nu} - (\tilde{B}' + \tilde{B})J + (\tilde{B}' - \tilde{B})J^2$. The band head is located by finding the value of J which gives the smallest wavenumber, which can be inferred by solving $\mathrm{d}\tilde{\nu}_{\mathrm{P}}(J)/\mathrm{d}J = 0$.

$$\frac{\mathrm{d}}{\mathrm{d}J}\left[\tilde{\nu} - (\tilde{B}' + \tilde{B})J + (\tilde{B}' - \tilde{B})J^2\right] = -(\tilde{B}' + \tilde{B}) + 2J(\tilde{B}' - \tilde{B})$$

Setting the derivative to zero and solving for J gives

$$J_{\text{head}} = \frac{\tilde{B}' + \tilde{B}}{2(\tilde{B}' - \tilde{B})}$$

With the data given

$$J_{\text{head}} = \frac{10.470 + 10.308}{2(10.470 - 10.308)} = 64.1$$

Assuming that it is satisfactory simply to round this to the nearest integer the band head occurs at $\boxed{J = 64}$.

E11F.9(b) The fact that a band head is seen in the P branch implies that $\tilde{B}' > \tilde{B}$. It is shown in *Exercise* E11F.7(a) that the band head in the P branch occurs at

$$J_{\text{head}} = \frac{\tilde{B}' + \tilde{B}}{2(\tilde{B}' - \tilde{B})} \tag{11.4}$$

This rearranges to

$$\tilde{B}' = \tilde{B} \times \frac{2J+1}{2J-1} \tag{11.5}$$

A band head at $J = 25$ might arise from a value of J determined from eqn 11.4 anywhere in the range 24.5 to 25.5, followed by subsequent rounding. Using these non-integer values of J in eqn 11.5 gives $\tilde{B}'$ in the range $\boxed{5.65\text{ cm}^{-1}}$ to $\boxed{5.66\text{ cm}^{-1}}$.

The bond length in the upper state is $\boxed{\text{shorter}}$ than that in the lower state (a shorter bond means a smaller moment of inertia and hence a larger rotational constant).

E11F.10(b) Assuming that the transition corresponds to that between the two sets of d orbitals which are split as a result on the interaction with the ligands (Section 11F.2(a) on page 467), the energy of the transition is the value of Δ_o. Hence $\tilde{\Delta}_o = 1/(305 \times 10^{-7}\text{ cm}) = \boxed{3.28 \times 10^4\text{ cm}^{-1}}$ or $\boxed{4.07\text{ eV}}$. This value is very approximate as it does not take into account the energy involved in rearranging the electron spins.

E11F.11(b) A rectangular wavefunction with value h between $x = 0$ and $x = a$ is normalized if the area under the square of the wavefunction is equal to 1: in this case $1 = ah^2$, hence $h = a^{-1/2}$. For the wavefunction which is non-zero between $x = ca$ and $x = a$ the height is likewise $h' = [a(1-c)]^{-1/2}$. The region where the wavefunctions are both non-zero is $x = ca$ to $x = a$ (because $c < 1$); this is the domain of integration. The transition moment is

$$\begin{aligned}\int_{ca}^{a} \psi_i x \psi_f \,dx &= \left(\frac{1}{a \times a(1-c)}\right)^{1/2} \int_{ca}^{a} x \,dx \\ &= \left(\frac{1}{a^2(1-c)}\right)^{1/2} \left|\tfrac{1}{2}x^2\right|_{ca}^{a} = \left(\frac{1}{a^2(1-c)}\right)^{1/2} \tfrac{1}{2}(a^2 - c^2a^2) \\ &= \boxed{\frac{1-c^2}{(1-c)^{1/2}}\frac{a}{2}}\end{aligned}$$

For $c \ll 1$ it is possible to approximate $1 - c^2 \approx 1$ and $(1-c)^{-1/2} \approx 1 + c/2$. The transition moment is then given by $(1 + c/2)(a/2)$. The moment is $a/2$ when $c = 0$, that is when the two wavefunctions are the same; for small c the moment increases linearly with c.

As c approaches 1 the evaluation of the transition moment is made easier by the following manipulations

$$\frac{1-c^2}{(1-c)^{1/2}} = \frac{(1-c^2)(1+c)^{1/2}}{(1-c)^{1/2}(1+c)^{1/2}} = \frac{(1-c^2)(1+c)^{1/2}}{[(1-c)(1+c)]^{1/2}} = \frac{(1-c^2)(1+c)^{1/2}}{(1-c^2)^{1/2}}$$
$$= (1-c^2)^{1/2}(1+c)^{1/2} = (1-c)^{1/2}(1+c)^{1/2}(1+c)^{1/2} = (1-c)^{1/2}(1+c)$$

In the limit that $c = 1$ this term, and hence the transition moment, goes to zero. The value of c for which the moment is a maximum is found by differentiation

$$\frac{\mathrm{d}}{\mathrm{d}c}(1-c)^{1/2}(1+c) = -\tfrac{1}{2}(1-c)^{-1/2}(1+c) + (1-c)^{1/2}$$

setting the derivative to zero and multiplying by $(1-c)^{1/2}$ gives

$$0 = -\tfrac{1}{2}(1+c) + (1-c) \quad \text{hence} \quad c = \tfrac{1}{3}$$

The maximum transition moment occurs at $c = \frac{1}{3}$, and has the value $(8/27)^{1/2}a \approx 0.54\,a$.

E11F.12(b) The Gaussian functions are written $\mathrm{e}^{-\alpha x^2/2}$, where the parameter α determines the width. To evaluate the normalizing factor for the function $\mathrm{e}^{-\alpha x^2/2}$ requires the integral

$$\int_{-\infty}^{+\infty} \mathrm{e}^{-\alpha x^2}\,\mathrm{d}x$$

which is of the form of Integral G.1 with $k = \alpha$ and evaluates to $(\pi/\alpha)^{1/2}$. The normalizing factor is therefore $N = (\alpha/\pi)^{1/4}$. The other Gaussian has half the width of the first, so is of the form $\mathrm{e}^{-4\alpha x^2/2}$, and the normalizing factor is $N' = (4\alpha/\pi)^{1/4}$.

The transition moment is given by the integral

$$I = (2\alpha/\pi)^{1/2}\int_{-\infty}^{+\infty} x\mathrm{e}^{-\alpha x^2/2}\mathrm{e}^{-4\alpha x^2/2}\,\mathrm{d}x$$
$$= (2\alpha/\pi)^{1/2}\int_{-\infty}^{+\infty} x\mathrm{e}^{-5\alpha x^2/2}\,\mathrm{d}x$$

The integrand is odd and the integral is over a symmetric interval, therefore the integral, and hence the transition moment is $\boxed{\text{zero}}$.

E11F.13(b) The absorption at 320 nm is likely to be due to an $\pi^* \leftarrow \mathrm{n}$ transition. The wavelength is typical for such transitions, and they are weak because they are symmetry forbidden.

The absorption at 213 nm is likely to be due to a $\pi^* \leftarrow \pi$ transition. Of the two transitions it is the stronger and it is at a somewhat longer wavelength than for an isolated π bond as a result of the conjugation with the carbonyl π bond.

Solutions to problems

P11F.2 The relevant selection rules are $\Delta S = 0$, $\Delta\Lambda = 0, \pm 1$, $+ \leftrightarrow +$, $- \leftrightarrow -$, $\mathrm{u} \leftrightarrow \mathrm{g}$.

The ground state has $S = \frac{1}{2}$, $\Lambda = 0$, + symmetry, and has parity u (that is, it is odd with respect to inversion). Transitions to other doublet states with $\Lambda =$ 0 or 1, with + symmetry (where relevant), and parity g are allowed, therefore. Thus the allowed transitions are to $\boxed{{}^2\Sigma_\mathrm{g}^+}$ and to $\boxed{{}^2\Pi_\mathrm{g}}$.

P11F.4 The dissociation energy of the upper state is found using a Birge–Sponer extrapolation (Section 11C.3(b) on page 445). Figure 11.10 shows that the difference between two successive lines of the progression from $v = 0$ corresponds to the quantity $\Delta\tilde{G}_{v'+1/2}$ identified in Fig. 11C.5 on page 446:

$$\Delta\tilde{G}_{v'+1/2} = \tilde{\nu}_{0,v'+1} - \tilde{\nu}_{0,v'}$$

Having found these values of $\Delta\tilde{G}_{v'+1/2}$ they are plotted against $v' + \frac{1}{2}$ and the line extrapolated until it intersects the horizontal axis, as in Fig. 11C.6 on page 446. The enclosed area is $\tilde{D}_0'$, the dissociation energy of the upper state. The data are given in the following table and the Birge–Sponer plot is shown in Fig. 11.11.

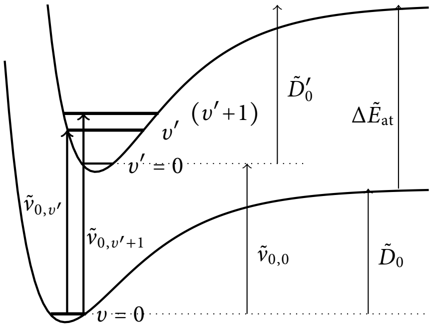


Figure 11.10

v'	$\tilde{\nu}_{0,v'}/\mathrm{cm}^{-1}$	$\Delta\tilde{G}_{v'+1/2}/\mathrm{cm}^{-1}$	$v' + 1/2$
0	50 062.6	662.8	0.5
1	50 725.4	643.6	1.5
2	51 369.0	619.6	2.5
3	51 988.6	590.4	3.5
4	52 579.0	564.4	4.5
5	53 143.4	536.2	5.5
6	53 679.6	497.4	6.5
7	54 177.0	464.8	7.5
8	54 641.8	436.4	8.5
9	55 078.2	381.8	9.5
10	55 460.0	343.1	10.5
11	55 803.1	304.2	11.5
12	56 107.3	253.0	12.5
13	56 360.3	209.7	13.5
14	56 570.0		

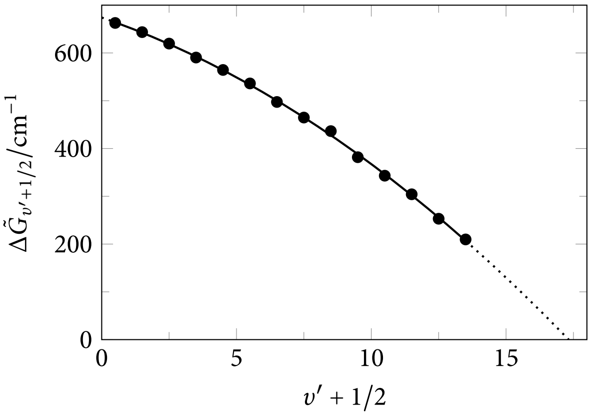


Figure 11.11

The data are a good fit to the quadratic

$$\Delta\tilde{G}_{v'+1/2}/\mathrm{cm}^{-1} = -1.1247 \times (v+1/2)^2 - 19.423 \times (v+1/2) + 674.16$$

The extrapolation is shown by the dotted curve, and by setting the above quadratic to zero it is found that the intersection with the horizontal axis is at $(v'+1/2) =$ 17.33. The area under the curve, $\tilde{D}'_0$, is found from the integral

$$\tilde{D}'_0 = \int_0^{17.33} [-1.1247 \times (v+1/2)^2 - 19.423 \times (v+1/2) + 674.16]\, \mathrm{d}(v+1/2)$$

which evaluates to $\boxed{\tilde{D}'_0 = 6815\ \mathrm{cm}^{-1} = 0.8450\ \mathrm{eV}}$.

Figure 11.10 also shows the relationship between the dissociation energy of the ground electronic state, that of the excited electronic state, the energy difference $\Delta\tilde{E}_{\text{at}}$ between the atomic states into which the two electronic states dissociate, and the energy of the $\tilde{\nu}_{0,0}$ transition. It follows from the diagram that

$$\begin{aligned}
\tilde{D}_0 + \Delta\tilde{E}_{\text{at}} &= \tilde{\nu}_{0,0} + \tilde{D}_0' \\
\text{hence } \tilde{D}_0 &= \tilde{\nu}_{0,0} + \tilde{D}_0' - \Delta\tilde{E}_{\text{at}} \\
&= (50\,062.6\ \text{cm}^{-1}) + (6815\ \text{cm}^{-1}) \\
&\quad - (190\times10^{3}\ \text{J mol}^{-1})\times\frac{1\ \text{cm}^{-1}}{(1.9864\times10^{-23}\ \text{J})\times(6.0221\times10^{23}\ \text{mol}^{-1})} \\
&= \boxed{4.10\times10^{4}\ \text{cm}^{-1} = 5.08\ \text{eV}}
\end{aligned}$$

where the conversion factor between cm^{-1} and J from inside the front cover is used.

P11F.6 (a) The photoelectron spectrum involves a transition from the ground state of the molecule to an electronic state of the molecular ion. The energy needed for the transition is measured indirectly by measuring the energy of the ejected electron, but in all other respects the spectrum is interpreted in the same way as electronic absorption spectra.

A spacing of 0.41 eV corresponds to $(0.41\ \text{eV})\times(8065.5\ \text{cm}^{-1})/(1\ \text{eV}) = 3307\ \text{cm}^{-1}$. This is comparable to the vibrational frequency of the symmetric stretch in neutral H_2O, so the observed spacing in the band can be associated with a vibrational progression involving transitions to excited states of this normal mode. That such transitions are observed implies that they have favourable Franck–Condon factors, and this means that the equilibrium geometry of the ion must be different from that of the molecule. In particular it implies that the change in geometry is at least in part similar to the change in geometry associated with the symmetric stretch. From this it is possible to infer that the electron which has been ionized is responsible for bonding along the direction of the symmetric stretch – presumably O–H σ-type bonding. (In fact only a modest vibrational progression is seen for this band, indicating that the electron which is ionized has only a small effect on the bonding).

(b) A spacing of 0.125 eV corresponds to $(0.125\ \text{eV})\times(8065.5\ \text{cm}^{-1})/(1\ \text{eV}) = 1008\ \text{cm}^{-1}$. This is roughly comparable to the vibrational frequency of the bending mode in neutral H_2O, so the observed spacing in the band can be associated with a vibrational progression involving transitions to excited states of this normal mode. In contrast to (a), for this band there is a long vibrational progression which implies that the geometry of the ion must be significantly different to that of the neutral molecule. Furthermore, this change must involve a change in the equilibrium bond angle as this is the change in geometry associated with the bending mode. The implication is that the electron which is ionized is a bonding electron, and from an orbital which has a strong influence on the bond angle.

The fact that the vibrational frequency is lower in the ion than in the neutral molecule is a result of the removal of a bonding electron: the ion is less tightly held, and so has lower vibrational frequencies.

P11F.8 The energy levels of a particle in a one-dimensional box are $E_n = n^2\hbar^2\pi^2/2mL^2$. The linear triene has 6 π electrons which will occupy levels 1, 2 and 3 (pairwise), so the HOMO–LUMO transition is from $n = 3$ to $n = 4$. If the average C–C bond length is taken as d, then the triene is modelled as a box of length $L = 5d$. The transition energy is therefore

$$\Delta E_{\text{lin}} = E_4 - E_3 = \frac{(4^2 - 3^2)\hbar^2\pi^2}{2m_e(5d)^2} = \frac{7\hbar^2\pi^2}{50m_e d^2}$$

The energy levels of a particle on a ring of radius R are given by [7F.4–*283*], $E_m = m^2\hbar^2/2mR^2$, where $m = 0, \pm1, \pm2 \ldots$. The cyclic triene has 6 π electrons which will occupy levels 0, ±1 (pairwise), so the HOMO–LUMO transition is from $m = 1$ to $m = 2$. If the average C–C bond length is taken as d, then the radius of the circle into which a hexagon with this side can be inscribed is also d. The transition energy is therefore

$$\Delta E_{\text{cyc}} = E_2 - E_1 = \frac{(2^2 - 1^2)\hbar^2}{2m_e d^2} = \frac{3\hbar^2}{2m_e d^2}$$

The ratio between the transition energies is

$$\frac{\Delta E_{\text{cyc}}}{\Delta E_{\text{lin}}} = \frac{3\hbar^2}{2m_e d^2} \times \frac{50m_e d^2}{7\hbar^2\pi^2} = \frac{75}{7\pi^2} \approx 1.09$$

On going from the linear to the cyclic polyene the energy gap therefore $\boxed{\text{increases}}$.

P11F.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.

P11F.12 (a) The ground state of O_2 is a spin triplet, with $S_{\text{mol}} = 1$. An oxygen atom has the configuration ... $2p^4$, which means that two of the electrons must be paired up in a single p orbital, but that the other two can be arranged to have parallel spins, $S = 1$, or paired spins $S = 0$.

According to the Clebsch–Gordon series, [8C.6–*333*], combining $S_{\text{atom},1} = 1$ with $S_{\text{atom},2} = 1$ gives an overall spin of 2, 1, 0. Thus, the two oxygen atoms could both have $S = 1$ and combine to give $S_{\text{mol}} = 1$ for the molecule.

Similarly, combining $S_{\text{atom},1} = 1$ with $S_{\text{atom},2} = 0$ gives an overall spin of 1 only. Thus, one of the oxygen atoms could have $S = 1$ and one could have $S = 0$, and give $S_{\text{mol}} = 1$ for the molecule.

The molecule could dissociate into atoms which are a $\boxed{\text{singlet and a triplet}}$ or into $\boxed{\text{two triplets}}$.

(b) The ground state of N_2 is a spin singlet, with $S_{\text{mol}} = 0$. A nitrogen atom has the configuration ... $2p^3$; these electrons can be configured to give a total spin of $S = \frac{3}{2}$ or $S = \frac{1}{2}$.

According to the Clebsch–Gordon series, [8C.6–*333*], combining $S_{\text{atom},1} = \frac{3}{2}$ with $S_{\text{atom},2} = \frac{3}{2}$ gives an overall spin of $3, 2, 1, 0$. Thus, the two nitrogen atoms could both have $S = \frac{3}{2}$ and combine to give $S_{\text{mol}} = 0$ for the molecule.

Similarly, combining $S_{\text{atom},1} = \frac{1}{2}$ with $S_{\text{atom},2} = \frac{1}{2}$ gives an overall spin of $1, 0$. Thus, the two nitrogen atoms could both have $S = \frac{1}{2}$. However, combining $S_{\text{atom},1} = \frac{1}{2}$ with $S_{\text{atom},2} = \frac{3}{2}$ gives an overall spin of $2, 1$, but not zero.

The molecule could dissociate into atoms which are $\boxed{\text{two quartets}}$ or into a $\boxed{\text{two doublets}}$.

11G Decay of excited states

Answers to discussion questions

D11G.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; (3) it occurs at longer wavelength (lower frequency) than the exciting 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.

D11G.4 Referring to Fig. 11G.8 on page 473 it is seen that the point at which predissociation starts (and the spectrum becomes blurred) is at the energy at which the dissociative electronic state crosses the bound electronic state. The observation of the wavenumber of this point gives the energy separation between the lower electronic state and this crossing point.

Solutions to exercises

E11G.1(b) Naphthalene does not absorb at 360 nm, but benzophenone does (as stated in *Exercise* E11G.1(a)). Presumably in the solid solution there are interactions between the benzophenone and naphthalene molecules which allow the transfer of energy from electronically excited benzophenone to naphthalene. The latter then emits photons as it returns to its ground state: this is the phosphorescent transition.

E11G.2(b) This observed increase in the linewidth is a result of predissociation, as illustrated in Fig. 11G.8 on page 473. Where the dissociative ${}^1\Sigma_u^+$ state crosses the bound upper electronic state the possibility exists that molecules in the upper electronic state will undergo radiationless transitions to the dissociative state leading to subsequent dissociation. This process reduces the lifetime of the excited states and so increases the linewidth of the associated transitions (lifetime broadening, see Section 11A.2(b) on page 425).

Solutions to problems

P11G.2 (a) The Beer–Lambert law is [11A.8–*421*], $I = I_0 10^{-\varepsilon[\mathrm{J}]L}$. It follows that

$$\begin{aligned}I_{\mathrm{abs}}(\tilde{\nu}) &= I_0(\tilde{\nu}) - I(\tilde{\nu})\\ &= I_0(\tilde{\nu}) - I_0(\tilde{\nu})10^{-\varepsilon(\tilde{\nu})[\mathrm{J}]L} = I_0(\tilde{\nu})[1 - 10^{-\varepsilon(\tilde{\nu})[\mathrm{J}]L}]\end{aligned}$$

(b) The problem states that the intensity of fluorescence $I(\tilde{\nu}_{\mathrm{f}})$ is proportional to ϕ_{f} and $I_{\mathrm{abs}}(\tilde{\nu})$, hence

$$I(\tilde{\nu}_{\mathrm{f}}) \propto \phi_{\mathrm{f}} I_0(\tilde{\nu}) \left\{1 - 10^{-\varepsilon(\tilde{\nu})[\mathrm{J}]L}\right\}$$

For weak absorbance, $\varepsilon(\tilde{\nu})[\mathrm{J}]L \ll 1$, the expansion $10^{-x} \approx 1 - x\ln(10)$ is used to give

$$\begin{aligned}I(\tilde{\nu}_{\mathrm{f}}) &\propto \phi_{\mathrm{f}} I_0(\tilde{\nu}) \{1 - 1 + \ln(10)\varepsilon(\tilde{\nu})[\mathrm{J}]L\}\\ &\propto \phi_{\mathrm{f}} I_0(\tilde{\nu})\varepsilon(\tilde{\nu})[\mathrm{J}]L\end{aligned}$$

which is the required result

P11G.4 (a) The coherence length is given by $l_{\mathrm{C}} = \lambda^2/2\Delta\lambda$. With the data given

$$l_{\mathrm{C}} = \frac{(633 \times 10^{-9}\ \mathrm{m})^2}{2 \times 2.0 \times 10^{-12}\ \mathrm{m}} = \boxed{0.10\ \mathrm{m}}$$

This is very much larger than the coherence length for a light bulb.

(b) In the limit that $\Delta\lambda \to 0$ the coherence length becomes infinite.

P11G.6 Each photon with wavelength λ has energy hc/λ, therefore N such photons have energy Nhc/λ. If the laser delivers a power P for time t, the energy is Pt. Equating these two expressions gives $Pt = Nhc/\lambda$ and hence $t = Nhc/\lambda P$. With the data given

$$t = \frac{10^6 \times (6.6261 \times 10^{-34}\ \mathrm{J\,s}) \times (2.9979 \times 10^8\ \mathrm{m\,s^{-1}})}{(488 \times 10^{-9}\ \mathrm{m}) \times (1.0 \times 10^{-3}\ \mathrm{W})} = \boxed{0.41\ \mathrm{ns}}$$

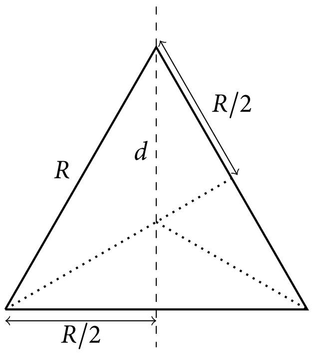


Figure 11.12

Integrated activities

I11.2 (a) The geometry of the molecule is illustrated in Fig. 11.12.

The moment of inertia about the axis parallel to the symmetry axis, that is the axis passing through the middle of the molecule and perpendicular to the plane of the molecule, is given by

$$I_{||} = \sum_i m_i r_i^2 = 3m_H d^2$$

where r_i is the perpendicular distance from the axis to mass m_i. From the diagram is follows that $(R/2)/d = \cos 30° = \sqrt{3}/2$, hence $d = R/\sqrt{3}$

$$I_{||} = 3m_H(R/\sqrt{3})^2 = \boxed{m_H R^2}$$

The moment of inertia perpendicular to the symmetry axis is independent of where this axis is located provided it passes through the centre of the molecule and lies in the plane of the molecule: one such convenient choice is the dashed line shown in the figure.

$$I_\perp = 2m_H(R/2)^2 = \boxed{\tfrac{1}{2}m_H R^2}$$

As expected, $I_{||} = 2I_\perp$.

(b) The moment of inertia is related to the rotational constant through [11B.7–*432*], $\tilde{B} = \hbar/4\pi c I_\perp$; note that the rotational constant $\tilde{B}$ is always associated with the moment of inertia perpendicular to the symmetry axis. It follows that $I_\perp = \hbar/4\pi c\tilde{B}$ and hence, using the result above, $\frac{1}{2}m_H R^2 = \hbar/4\pi c\tilde{B}$. This rearranges to give the following expression for R

$$\begin{aligned} R &= \left(\frac{\hbar}{2\pi m_H c\tilde{B}}\right)^{1/2} \\ &= \left(\frac{1.0546\times10^{-34}\ \text{J s}}{2\pi(1.67...\times10^{-27}\ \text{kg})\times(2.9979\times10^{10}\ \text{cm s}^{-1})\times(43.55\ \text{cm}^{-1})}\right)^{1/2} \\ &= \boxed{87.64\ \text{pm}} \end{aligned}$$

where the mass in kg is given by $(1.0079\,m_u)\times(1.6605\times10^{-27}\,\text{kg})/(1\,m_u) = 1.67...\times10^{-27}$ kg. An alternative value for R is found from the other rotational constant. Here $\tilde{C} = \hbar/4\pi c I_{||}$ and hence $m_H R^2 = \hbar/4\pi c\tilde{C}$.

$$R = \left(\frac{\hbar}{4\pi m_H c\tilde{C}}\right)^{1/2}$$

$$= \left(\frac{1.0546\times10^{-34}\,\text{J s}}{4\pi(1.67...\times10^{-27}\,\text{kg})\times(2.9979\times10^{10}\,\text{cm s}^{-1})\times(20.71\,\text{cm}^{-1})}\right)^{1/2}$$

$$= \boxed{89.87\ \text{pm}}$$

(c) With the given value of R, the rotational constant is computed from $\tilde{B} = \hbar/4\pi c I_{\perp} = \hbar/2\pi m_H c R^2$

$$\tilde{B} = \frac{1.0546\times10^{-34}\,\text{J s}}{2\pi(1.67...\times10^{-27}\,\text{kg})\times(2.9979\times10^{10}\,\text{cm s}^{-1})\times(87.32\times10^{-12}\,\text{m})^2}$$

$$= \boxed{43.87\ \text{cm}^{-1}}$$

The other rotational constant is just half of this, $\boxed{\tilde{C} = 21.94\ \text{cm}^{-1}}$

(d) For a harmonic oscillator the vibrational frequency goes as $m_{\text{eff}}^{-1/2}$, where m_{eff} is the effective mass. The value of the effective mass depends on the vibration in question, but in this case as all the atoms are the same it is reasonable to assume that the effective mass of H_3^+ will be proportional to m_H, and that of D_3^+ will be proportional to m_D. It therefore follows that

$$\tilde{\nu}_D = \tilde{\nu}_H\left(\frac{m_H}{m_D}\right)^{1/2}$$

$$= (2521.6\,\text{cm}^{-1})\times\left(\frac{1.0079}{2.0140}\right)^{1/2} = \boxed{1783.8\ \text{cm}^{-1}}$$

The rotational constants are inversely proportional to the moment of inertia, and for this molecule all the atoms are the same so the rotational constant goes as m^{-1}.

$$\tilde{B}_D = \tilde{B}_H\frac{m_H}{m_D}$$

$$= (43.55\,\text{cm}^{-1})\times\frac{1.0079}{2.0140} = \boxed{21.79\ \text{cm}^{-1}}$$

A similar calculation gives $\boxed{\tilde{C}_D = 10.36\ \text{cm}^{-1}}$.

I11.4 (a) For a harmonic oscillator the vibrational frequency goes as $m_{\text{eff}}^{-1/2}$, where m_{eff} is the effective mass; for a diatomic the effective mass is simply $\frac{1}{2}m$. It therefore follows that

$$\tilde{\nu}_{^{18}O_2} = \tilde{\nu}_{^{16}O_2}\left(\frac{m_{^{16}O}}{m_{^{18}O}}\right)^{1/2}$$

$$= (844\,\text{cm}^{-1})\times\left(\frac{15.9949}{17.9992}\right)^{1/2} = \boxed{796\ \text{cm}^{-1}}$$

(b) The bond order of O_2 is 2, and to form the anions electrons are added to the anti-bonding π_g molecular orbital, thereby decreasing the bond order to 1.5 for $O_2{}^-$ and 1 for $O_2{}^{2-}$. The steady decrease in the bond order is matched by the steady decrease in the vibrational frequency. There is thus a correlation between bond strength and vibrational frequency, as expected.

(c) The observed vibrational frequency of O_2 bound to haemerythrin most closely matches that for $O_2{}^{2-}$, so of the alternatives offered $\boxed{Fe_2^{3+}O_2{}^{2-}}$ seems the most likely.

(d) The observation of two bands attributable to O–O stretching implies that the O_2 is bound is such a way that the two oxygen atoms are no longer equivalent. If this is the case, when the isotopologue $^{16}O^{18}O$ is used, two different frequencies will result because the two ends of the oxygen molecule are now distinguished. This eliminates structures **7** and **8**.

I11.6 Expressed in terms of the absorbance A the Beer–Lambert law is given by [11A.9c–*422*], $A = \varepsilon[J]L$. To convert the given absorbance into a molar absorption coefficient requires [J] in mol dm^{-3}, which is computed using the perfect gas law, $pV = nRT$, rearranged to $n/V = p/RT$. Assuming that the quoted composition of CO_2, '2.1 per cent', refers to a mole per cent, $x_{CO_2} = 0.021$, so $p_{CO_2} = 0.021 \times (1.00\ \text{bar}) = 0.021$ bar. In the calculation of n/V it is convenient to use $R = 8.3145 \times 10^{-2}$ dm^3 bar K^{-1} mol^{-1}

$$\frac{n}{V} = \frac{p}{RT} = \frac{0.021\ \text{bar}}{(8.3145\times10^{-2}\ \text{dm}^3\ \text{bar K}^{-1}\ \text{mol}^{-1})\times(298\ \text{K})}$$
$$= 8.47... \times 10^{-4}\ \text{mol dm}^{-3}$$

The given expression for $A(\tilde{\nu})$ is therefore converted to an expression for the molar absorption coefficient using

$$\varepsilon(\tilde{\nu}) = A(\tilde{\nu})/[J]L = A(\tilde{\nu})/[(8.47...\times10^{-4}\ \text{mol dm}^{-3})\times(10\ \text{cm})]$$
$$= (1.17...\times10^{2}\ \text{mol}^{-1}\ \text{dm}^{3}\ \text{cm}^{-1})\times A(\tilde{\nu})$$

(a) Graphs of $A(\tilde{\nu})$ and $\varepsilon(\tilde{\nu})$ are shown in Fig. 11.13. This band is likely to be due to the fundamental transition of the antisymmetric stretching normal mode of CO_2, which has $\tilde{\nu}_2 = 2349\ \text{cm}^{-1}$. The broad features are the unresolved P and R branches; no Q branch is expected for this mode. The principal contribution to the linewidth of an infrared transition is likely to be pressure broadening.

(b) Expressions for the wavenumbers of the lines in the P and R branches are given in [11C.13a–*447*] and [11C.13c–*447*]

$$\tilde{\nu}_P(J) = \tilde{\nu} - 2\tilde{B}J \qquad \tilde{\nu}_R(J) = \tilde{\nu} + 2\tilde{B}(J+1)$$

Here $\tilde{\nu} = 2349\ \text{cm}^{-1}$. As described in Section 11B.4 on page 439, because ^{16}O is a boson, only even rotational states are occupied (and, in fact, odd rotational states in the first excited vibrational state of the anti-symmetric

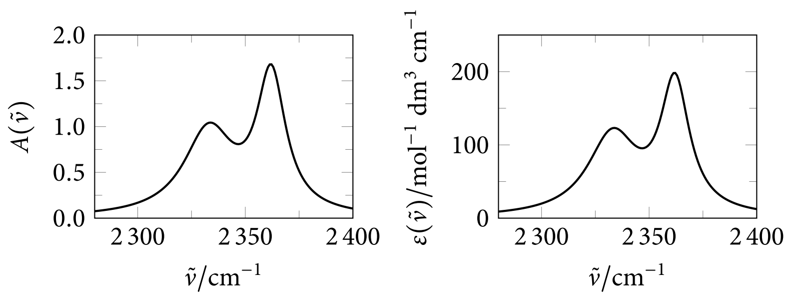


Figure 11.13

stretch), so in the above expression J takes the values 0, 2, 4 …. The rotational constant is computed from [11B.7–*432*], $\tilde{B} = \hbar/4\pi cI$, where $I = 2m_\text{O}R^2$. With the data given

$$\begin{aligned}I &= 2 \times (15.9949\, m_\text{u}) \times (1.6605 \times 10^{-27}\,\text{kg}) \times (116.2 \times 10^{-12}\,\text{m})^2/(1\, m_\text{u})\\ &= 7.17... \times 10^{-46}\,\text{kg m}^2\end{aligned}$$

$$\tilde{B} = \frac{1.0546 \times 10^{-34}\,\text{J s}}{4\pi \times (2.9979 \times 10^{10}\,\text{cm s}^{-1}) \times (7.17... \times 10^{-46}\,\text{kg m}^2)} = 0.3903\,\text{cm}^{-1}$$

The intensity of the transition from level J is proportional to the population of that level, taking into account the degeneracy

$$\text{intensity} \propto (2J+1)\text{e}^{-hc\tilde{B}/kT}$$

Using these expressions the positions and intensities of the lines in the P and R branches are computed and a synthetic spectrum constructed by assuming a linewidth and lineshape (here arbitrarily taken as a Gaussian). Two such spectra are shown in Fig. 11.14: in (a) the linewidth has been chosen so that the lines are well resolved; in (b) a much wider line is used so that the lines in the P and R branches merge into a broad contour. The spectrum in (b) is roughly similar to that in Fig. 11.13, but the asymmetry between the two branches is not reproduced by the calculation.

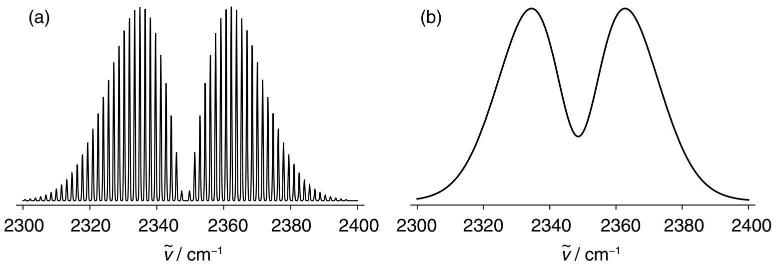


Figure 11.14

(c) The transmittance T is defined as I/I_0 and hence from the Beer–Lambert law [11A.8–*421*], $T = \text{e}^{-\varepsilon[J]L}$; it follows that $\log T = -A$. The concentration of CO_2 is computed as in (a) using $[CO_2] = x_{CO_2}p_{atm}/RT$; both the atmospheric pressure and temperature vary with the height, and therefore so will the concentration. The pressure varies with height according to $p(h) = p_0e^{-h/H}$, where the scale height H is about 8000 m. The total absorbance up to height h_0 is therefore given by integral

$$\begin{aligned}A &= \int_0^{h_0} \varepsilon[CO_2]\,dh = \varepsilon\int_0^{h_0}\frac{x_{CO_2}p}{RT}\,dh\\ &= \varepsilon\int_0^{h_0}\frac{x_{CO_2}p_0e^{-h/H}}{R(288-0.0065h)}\,dh\\ &= \varepsilon x_{CO_2}p_0\int_0^{h_0}\frac{e^{-h/H}}{R(288-0.0065h)}\,dh\end{aligned}$$

where h is in m.

This integral cannot be solved by hand, but some work with mathematical software and a typical value of ε shows that the absorbance exceeds 1 by the time $h_0 = 30$ m. Over such a small height it is safe to assume that the pressure and temperature are constant, in which case the calculation of the absorbance is much simpler

$$\begin{aligned}A &= \varepsilon[CO_2]h_0 = \varepsilon\frac{x_{CO_2}p}{RT}h_0\\ &= [\varepsilon/(\text{mol}^{-1}\,\text{dm}^3\,\text{cm}^{-1})]\\ &\quad\times\frac{(3.3\times10^{-4})\times(1\,\text{bar})}{(8.3145\times10^{-2}\,\text{dm}^3\,\text{bar}\,\text{K}^{-1}\,\text{mol}^{-1})\times(288\,\text{K})}\times(h_0/\text{cm})\\ &= (1.378\times10^{-5})\times[\varepsilon/(\text{mol}^{-1}\,\text{dm}^3\,\text{cm}^{-1})]\times(h_0/\text{cm})\end{aligned}$$

The transmittance is $T = 10^{-A}$.

Figure 11.15 shows plots of the transmittance as a function of height for some representative values of the molar absorption coefficient. For the maximum value of ε seen in this absorption band (refer to Fig. 11.13) the transmittance drops to 0.1 after less than 5 m. For a value of ε more typical of the average (say $\varepsilon = 100\ \text{mol}^{-1}\,\text{dm}^3\,\text{cm}^{-1}$), the transmission drops to 0.1 after about 7.5 m. Even for values of ε typical of the extremities of the band, the transmission has fallen to 0.1 within 20 m or so. A surface plot of the transmission as a function of both wavenumber and height is shown in Fig. 11.16.

I11.8 The electronic ground state of a closed-shell molecule transforms as the totally symmetric irreducible representation. This is because all of the orbitals are doubly occupied by spin paired electrons. The overall symmetry of a filled orbital is found from the direct product $\Gamma^{(i)}\times\Gamma^{(i)}$, where $\Gamma^{(i)}$ is the irreducible representation as which the orbital transforms. When multiplied out, such a

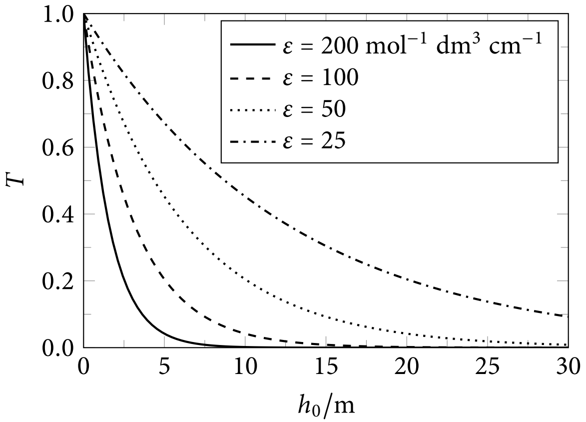


Figure 11.15

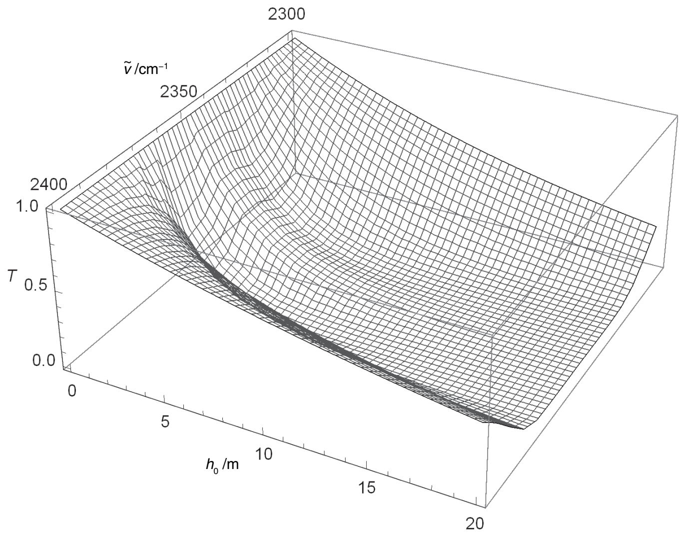


Figure 11.16

product always includes the totally symmetric irreducible representation and it is this symmetry species which needs to be combined with the anti-symmetric spin function for two spin-paired electrons.

(a) Ethene belongs to the point group D_{2h}: assume that the molecule lies in the xy-plane, with the C–C bond along x. The π bonding molecular orbital transforms in the same way as the cartesian function z, that is as B_{1u}. The π* anti-bonding molecular orbital transforms in the same way as the cartesian function xz, that is as B_{2g}. The excited state $(\pi)^1(\pi^*)^1$ therefore has symmetry $B_{1u} \times B_{2g} = B_{3u}$ (the direct product is found by multiplying together the characters of the two irreducible representations, as described in Section 10C.1(a) on page 407).

The transition moment is given by $\int \psi_f{*}\hat{\mu}\psi_i\,d\tau$, and the symmetry species of the integrand is found using the direct product; $\hat{\mu}$ transforms as x, y, or z, which in this case is B_{3u}, B_{2u}, or B_{1u}. The integral is only non-zero if the integrand transforms as the totally symmetric irreducible representation, which is the case here when the component of the dipole is along x

$$\overbrace{B_{3u}}^{\psi_f} \times \overbrace{B_{3u}}^{\hat{\mu}_x} \times \overbrace{A_g}^{\psi_i} = A_g$$

Thus the $\pi \rightarrow \pi^*$ transition is $\boxed{\text{symmetry allowed}}$, with the transition dipole along $\boxed{x}$.

(b) A carbonyl group (as exemplified by that in methanal) is assumed to belong to the point group C_{2v}: assume that the H_2CO fragment lies in the xz-plane, with the C–O bond along z. The π^* anti-bonding molecular orbital transforms in the same way as the cartesian function y, that is as B_2.

A non-bonding electron on oxygen is usually considered to be in a $2p_x$ orbital which transforms as B_1. When an electron is promoted from n to π^*, the excited state has symmetry $B_2 \times B_1 = A_2$. The symmetry of the integrand for the transition moment is

$$\overbrace{A_2}^{\psi_f} \times \overbrace{\Gamma_{x,y,z}}^{\hat{\mu}} \times \overbrace{A_1}^{\psi_i} = A_2 \times \Gamma_{x,y,z}$$

Because $\Gamma_{x,y,z} \neq A_2$ this product is never A_1, so the integral is zero and the transition is $\boxed{\text{forbidden}}$.

I11.10 The energy of the HOMO, E_{HOMO}, is reported in the table below, based on calculations performed with Spartan 10 using the DFT/B3LYP/6-31G* method. The experimentally determined energy of the I_2–aromatic hydrocarbon charge transfer bands is also given.

Figure 11.17 shows a plot of E_{HOMO} against $h\nu_{\text{max}}$; the best-fit straight line is also shown. There is a modest correlation between the two quantities.

hydrocarbon	$h\nu_{\text{max}}$/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

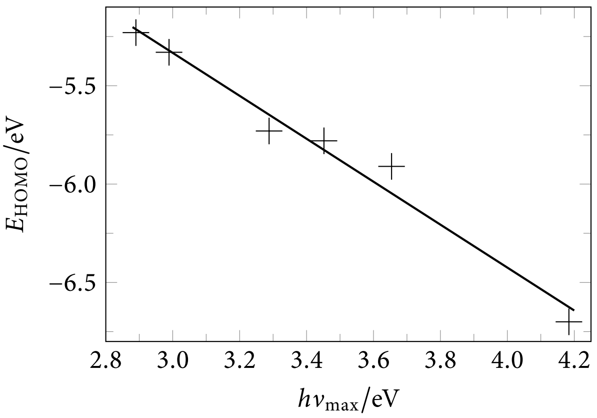


Figure 11.17

12

Magnetic resonance

12A General principles

Answers to discussion questions

D12A.2 The energy levels associated with the interaction between magnetic nuclei and an applied magnetic field scale directly with the field, with the constant of proportion depending on the identity of the nucleus. The interaction between an electron and an applied magnetic field behaves in the same way, but the interaction is much greater, by a factor of the order of 1000.

Solutions to exercises

E12A.1(b) The nuclear g-factor g_I is given by [12A.4c–*489*], $g_I = \gamma_\mathrm{N}\hbar/\mu_\mathrm{N}$, where μ_N is the nuclear magneton $(5.051\times10^{-27}\ \mathrm{J\,T^{-1}})$ and γ_N is the nuclear magnetogyric ratio, the value of which depends on the identity of the nucleus. The units of $\hbar$ are J s and g_I is a dimensionless number, so the nuclear magnetogyric ratio γ_N has units $(\mathrm{J\,T^{-1}})/(\mathrm{J\,s}) = \mathrm{T^{-1}\,s^{-1}}$.

In SI units, $1\ \mathrm{T} = 1\ \mathrm{kg\,s^{-2}\,A^{-1}}$ hence γ_N has units $(\mathrm{kg\,s^{-2}\,A^{-1}})^{-1}\times(\mathrm{s^{-1}}) = \boxed{\mathrm{A\,s\,kg^{-1}}}$.

E12A.2(b) The magnitude of the angular momentum is given by $[I(I+1)]^{1/2}\hbar$ where I is the nuclear spin quantum number. For a $^{14}\mathrm{N}$ nucleus, $I = 1$, hence the magnitude of the angular momentum is $[1(1+1)]^{1/2}\hbar = \boxed{\sqrt{2}\hbar}$.

The component of the angular momentum along the z-axis is $m_I\hbar$ where $m_I = I, I-1, \dots, -I$. For a $^{14}\mathrm{N}$ nucleus, the components along the z-axis are $\boxed{0, \pm\hbar}$ and the angle between angular momentum vector and the z-axis takes the values

$$\theta = 0, \pm\cos^{-1}\left(\frac{\pm\hbar}{\sqrt{2}\hbar}\right) = \boxed{0, \pm0.7854\ \mathrm{rad}\ (\text{or } 0^\circ, \pm45.00^\circ)}$$

E12A.3(b) The NMR frequency is equal to the Larmor precession frequency, ν_L, which is given by [12A.7–*489*], $\nu_\mathrm{L} = \gamma_\mathrm{N}\mathcal{B}_0/2\pi$, where $\mathcal{B}_0$ is the magnitude of the magnetic field and γ_N is the nuclear magnetogyric ratio. Use Table 12A.2 on page 289 in the *Resource section* for the value of γ_N. Hence,

$$\nu_\mathrm{L} = \frac{\gamma_\mathrm{N}\mathcal{B}_0}{2\pi} = \frac{(25.177\times10^{7}\ \mathrm{T^{-1}\,s^{-1}})\times(17.1\ \mathrm{T})}{2\pi} = 6.85\times10^{8}\ \mathrm{Hz} = \boxed{685\ \mathrm{MHz}}$$

E12A.4(b) The energies of the nuclear spin states in a magnetic field are given by [12A.4d–*489*], $E_{m_I} = -g_I\mu_N\mathcal{B}_0 m_I$ where g_I is the nuclear g-factor, μ_N is the nuclear magneton, $\mathcal{B}_0$ is the magnitude of the magnetic field, and the component of the angular momentum on a specified axis is $m_I\hbar$ where $m_I = I, I-1, ..., -I$. Therefore, since the possible values of m_I are 0, ±1, the energies of nuclear spin states are

$$\begin{aligned} E_{m_I} &= -g_I\mu_N\mathcal{B}_0 m_I \\ &= -(0.404) \times (5.0508 \times 10^{-27}\,\mathrm{J\,T^{-1}}) \times (10.50\,\mathrm{T}) \times m_I \\ &= (-2.14... \times 10^{-26}\,\mathrm{J}) \times m_I \end{aligned}$$

Hence $\boxed{E_0 = 0 \text{ and } E_{\pm 1} = \mp 2.14 \times 10^{-26}\,\mathrm{J}}$.

E12A.5(b) The energy level separation is $\Delta E = h\nu$ where $\nu = \gamma_N\mathcal{B}_0/2\pi$, [12A.6–*489*]. Hence, in megahertz, the frequency separation is

$$\nu = 10^{-6} \times \frac{\gamma_N\mathcal{B}_0}{2\pi} = 10^{-6} \times \frac{(1.93 \times 10^7\,\mathrm{T^{-1}\,s^{-1}}) \times (14.4\,\mathrm{T})}{2\pi} = \boxed{44.2\,\mathrm{MHz}}$$

E12A.6(b) For nuclei the energy level separation is $\Delta E = h\nu$ where $\nu = \gamma_N\mathcal{B}_0/2\pi$, [12A.6–*489*]. For the same magnetic field the Larmor frequencies, and hence the energy separations, of the two nuclei are in the ratio of their magnetogyric ratios

$$\frac{\nu_{^{14}\mathrm{N}}}{\nu_{^{1}\mathrm{H}}} = \frac{\Delta E(^{14}\mathrm{N})}{\Delta E(^{1}\mathrm{H})} = \frac{\gamma_N(^{14}\mathrm{N})}{\gamma_N(^{1}\mathrm{H})}$$

hence

$$\Delta E(^{14}\mathrm{N}) = \Delta E(^{1}\mathrm{H}) \times \frac{\gamma_N(^{14}\mathrm{N})}{\gamma_N(^{1}\mathrm{H})} = h\nu_{^{1}\mathrm{H}} \times \frac{\gamma_N(^{14}\mathrm{N})}{\gamma_N(^{1}\mathrm{H})}$$

With the values given

$$\begin{aligned} \Delta E(^{14}\mathrm{N}) &= (6.6261 \times 10^{-34}\,\mathrm{J\,s}) \times (600 \times 10^6\,\mathrm{Hz}) \times \frac{(1.93 \times 10^7\,\mathrm{T^{-1}\,s^{-1}})}{(26.75 \times 10^7\,\mathrm{T^{-1}\,s^{-1}})} \\ &= \boxed{2.87 \times 10^{-26}\,\mathrm{J}} \end{aligned}$$

The energies of the electron spin states in a magnetic field are given by [12A.11c–*492*], $E_{m_s} = g_e\mu_B\mathcal{B}_0 m_s$ where $g_e = 2.0023$ is the g-value of the free electron, $\mathcal{B}_0$ is the magnitude of the magnetic field, $m_s = \pm\frac{1}{2}$, and μ_B is the Bohr magneton. The energy separation is therefore

$$\begin{aligned} \Delta E = E_{+1/2} - E_{-1/2} &= (\tfrac{1}{2}g_e\mu_B\mathcal{B}_0) - (-\tfrac{1}{2}g_e\mu_B\mathcal{B}_0) = g_e\mu_B\mathcal{B}_0 \\ &= (2.0023) \times (9.2740 \times 10^{-24}\,\mathrm{J\,T^{-1}}) \times (0.300\,\mathrm{T}) \\ &= \boxed{5.57 \times 10^{-24}\,\mathrm{J}} \end{aligned}$$

Hence the energy level separation of the electron is $\boxed{\text{much greater}}$ than that of the ^{14}N nucleus under the conditions given.

E12A.7(b) The ground state has $m_I = +\frac{1}{2}$ (α spin) and population N_α, and the upper state has $m_I = -\frac{1}{2}$ (β spin) and population N_β. The total population N is $N = N_\alpha + N_\beta$, and the population difference is $N_\alpha - N_\beta$. The Boltzmann distribution gives $N_\beta/N_\alpha = \mathrm{e}^{-\Delta E/kT}$, where ΔE is the energy difference between the two states: $\Delta E = \gamma_N \hbar \mathcal{B}_0$. It follows that $N_\beta = N_\alpha \mathrm{e}^{-\Delta E/kT}$. With these results

$$\frac{N_\alpha - N_\beta}{N} = \frac{N_\alpha - N_\beta}{N_\alpha + N_\beta} = \frac{N_\alpha(1-\mathrm{e}^{-\Delta E/kT})}{N_\alpha(1+\mathrm{e}^{-\Delta E/kT})} = \frac{1-\mathrm{e}^{-\Delta E/kT}}{1+\mathrm{e}^{-\Delta E/kT}}$$

Because $\Delta E \ll kT$ the exponential $\mathrm{e}^{-\Delta E/kT}$ is approximated as $1 - \Delta E/kT$ to give

$$\frac{N_\alpha - N_\beta}{N} \approx \frac{1-(1-\Delta E/kT)}{1+(1-\Delta E/kT)} = \frac{\Delta E/kT}{2+\Delta E/kT} = \frac{\Delta E}{2kT} = \frac{\gamma_N \hbar \mathcal{B}_0}{2kT}$$

For a ^{13}C nucleus and at 298 K

$$\frac{N_\alpha - N_\beta}{N} = \frac{\gamma_N \hbar \mathcal{B}_0}{2kT} = \frac{(6.73\times10^{7}\,\mathrm{T^{-1}\,s^{-1}})\times(1.0546\times10^{-34}\,\mathrm{J\,s})\times\mathcal{B}_0}{2\times(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}$$
$$= 3.42...\times10^{-6}\times(\mathcal{B}_0/\mathrm{T})$$

For $\mathcal{B}_0 = 0.50$ T, $(N_\alpha - N_\beta)/N = \boxed{4.3\times10^{-7}}$; for $\mathcal{B}_0 = 2.5$ T, the ratio is $\boxed{2.2\times10^{-6}}$; for $\mathcal{B}_0 = 15.5$ T, the ratio is $\boxed{1.34\times10^{-5}}$.

E12A.8(b) The population difference for a collection of N spin-$\frac{1}{2}$ nuclei is given by [12A.8b–*491*], $(N_\alpha - N_\beta) \approx N\gamma_N\hbar\mathcal{B}_0/2kT$, where N_α is the number of spins in the lower energy state and N_β is the number of spins in the higher energy state. At constant magnetic field, $(N_\alpha - N_\beta)/N \propto T^{-1}$. Hence, for the relative population difference to be increased by a factor of 5, the temperature must decreased by this same factor – that is the temperature must by multiplied by factor of $\boxed{0.2}$.

For many samples this is simply not a feasible way of increasing the sensitivity as the solvent would freeze long before the temperature had been lowered by this amount. High-resolution spectra require the sample to remain in a liquid solution.

E12A.9(b) The resonance frequency ν_{NMR} in an NMR spectrometer is given by [12A.6–*489*], $h\nu_{\mathrm{NMR}} = \gamma_N\hbar\mathcal{B}_0$, where γ_N is the nuclear magnetogyric ratio and $\mathcal{B}_0$ is the magnetic field strength. The EPR resonance frequency ν_{EPR} is given by [12A.12b–*492*], $h\nu_{\mathrm{EPR}} = g_e\mu_B\mathcal{B}_0$, where g_e is the magnetogyric ratio of the electron.

The EPR resonance frequency in a magnetic field for which the NMR frequency for ^{1}H nuclei is ν_{NMR} is calculated by taking the ratio of the two resonance conditions, assuming $\mathcal{B}_0$ is equal for both systems. Hence,

$$\frac{h\nu_{\mathrm{EPR}}}{h\nu_{\mathrm{NMR}}} = \frac{g_e\mu_B\mathcal{B}_0}{\gamma_N\hbar\mathcal{B}_0} \quad \text{hence} \quad \frac{\nu_{\mathrm{EPR}}}{\nu_{\mathrm{NMR}}} = \frac{g_e\mu_B}{\gamma_N\hbar}$$

With the data given

$$\begin{aligned}\nu_{\mathrm{EPR}} &= \nu_{\mathrm{NMR}} \times \frac{g_e\mu_B}{\gamma_N\hbar}\\ &= (500\times10^6\ \mathrm{Hz})\times\frac{2.0023\times(9.2740\times10^{-24}\,\mathrm{J\,T^{-1}})}{(26.75\times10^7\ \mathrm{T^{-1}\,s^{-1}})\times(1.0546\times10^{-34}\,\mathrm{J\,s})}\\ &= 3.3\times10^{11}\ \mathrm{Hz} = \boxed{0.33\ \mathrm{GHz}}\end{aligned}$$

Solutions to problems

P12A.2 The relative sensitivity of NMR spectroscopy R is proportional to $I(I+1)\gamma_N^3$. Relative to that of ^{1}H, the sensitivity is

$$S = \frac{R(\text{nuclide})}{R(^1\mathrm{H})} = \frac{I(I+1)\gamma_N^3}{(\frac{1}{2})(\frac{3}{2})\gamma_N^3(^1\mathrm{H})} = \tfrac{4}{3}I(I+1)\left(\frac{\gamma_N}{\gamma_N(^1\mathrm{H})}\right)^3$$

Taking account of the natural abundance A of each isotope, the sensitivity ratio becomes

$$S' = S\times\frac{A(\text{nuclide})}{A(^1\mathrm{H})} = \tfrac{4}{3}I(I+1)\left(\frac{\gamma_N}{\gamma_N(^1\mathrm{H})}\right)^3\times\frac{A(\text{nuclide})}{A(^1\mathrm{H})}$$

For ^{15}N, $\gamma_N = -2.712\times10^7\ \mathrm{T^{-1}\,s^{-1}}$, and the natural abundance is 0.365%.

nuclide	$A/\%$	I	S	S'
^{1}H	99.9844	$\frac{1}{2}$	1	1
^{2}H	0.0156	1	9.65×10^{-3}	1.51×10^{-6}
^{13}C	1.108	$\frac{1}{2}$	1.59×10^{-2}	1.76×10^{-4}
^{14}N	99.635	1	1.01×10^{-3}	1.00×10^{-3}
^{15}N	0.365	$\frac{1}{2}$	1.04×10^{-3}	3.80×10^{-6}
^{11}B	80.4	$\frac{3}{2}$	0.165	0.133

P12A.4 The NMR signal intensity, I, is proportional to the number of protons in a slice of width δ_z at horizontal distance z from the centre of the disk, as shown in Fig 12.1. The number of protons in the slice is proportional to the volume of the slice, which is proportional to the cross-sectional area of the slice. This area is $2r\sin\theta\times\delta_z$, which implies that the intensity is proportional to the length of the slice and thus $\propto\ 2r\sin\theta$. Noting that $\cos\theta = z/r$ it follows that $\boxed{I\propto 2\sin[\cos^{-1}(z/r)]}$. Figure 12.2 shows the expected line shape from the disc; the horizontal axis corresponds to the distance from the centre, but because of the field gradient it is also a frequency axis.

12B Features of NMR spectra

Answers to discussion questions

D12B.2 These are discussed in Section 12B.2 on page 496.

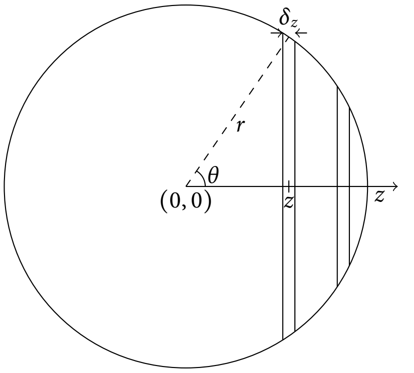


Figure 12.1

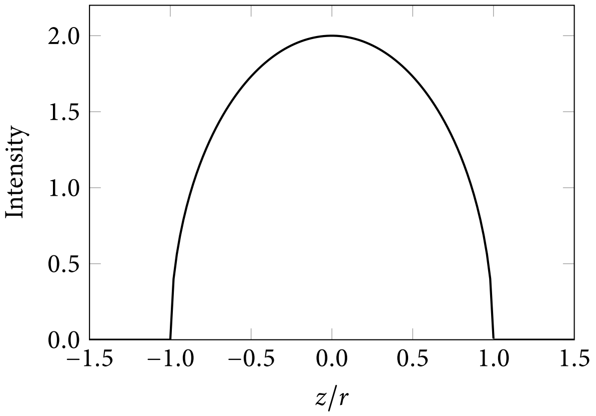


Figure 12.2

D12B.4 This is discussed in detail in Section 12B.3(d) on page 503. In summary, two nuclei are chemically equivalent if they are related by a symmetry operation of the molecule. Such nuclei will have the same resonance frequency, that is, the same chemical shift. Examples are the protons in benzene, and H-2 and H-6 in 4-nitrophenol. In benzene the protons are related by a C_6 operation (as well as others) and in 4-nitrophenol the protons are related by reflection in a mirror plane perpendicular to the plane of the ring and passing through C-1 and C-4.

Two chemically equivalent nuclei A and A′ are magnetically equivalent if the coupling between A and any other magnetic nucleus in the molecule, say Z, is the same as the coupling between A′ and Z. If Z itself is to be magnetically equivalent to Z′, then the couplings A–Z, A–Z′, A′–Z, and A′–Z′ must all be equal: that is, the couplings between any member of a group of equivalent spins with any member of another group of equivalent spins must be the same in order for the groups each to be magnetically equivalent.

For example, in PF_5, which has a trigonal bi-pyramidal structure, the three equatorial fluorines are magnetically equivalent, as are the two axial fluorines.

A second example is 1,2,3-trichlorobenzene: H–4 and H–6 are magnetically equivalent as they both have the same coupling to H-5. Chemical equivalence does not imply magnetic equivalence. In the case of 4-nitrophenol, 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

E12B.1(b) The δ scale is defined by [12B.4a–*494*], $\delta = (\nu - \nu^\circ) \times 10^6/\nu^\circ$, where δ is the chemical shift of the peak, ν is the resonance frequency of the peak, and ν° is the resonance frequency of the standard. Hence

$$\delta = \frac{\nu - \nu^\circ}{\nu^\circ} \times 10^6 = \frac{(125.148750\ \text{MHz}) - (125.130000\ \text{MHz})}{(125.130000\ \text{MHz})} \times 10^6 = \boxed{150}$$

E12B.2(b) The δ scale is defined by [12B.4a–*494*], $\delta = (\nu - \nu^\circ) \times 10^6/\nu^\circ$, where δ is the chemical shift of the peak, ν is the resonance frequency of the peak, and ν° is the resonance frequency of the standard. Hence

$$\delta = \frac{\nu - \nu^\circ}{\nu^\circ} \times 10^6 = \frac{-1875\ \text{Hz}}{(125.130000 \times 10^6\ \text{Hz})} \times 10^6 = \boxed{-14.98}$$

E12B.3(b) The resonance frequency ν is given by [12B.5–*494*], $\nu = \nu^\circ + (\nu_{\text{spect}}/10^6)\delta$, where ν° is the resonance frequency of the standard. The frequency separation of the two peaks, $\Delta\nu$, is

$$\begin{aligned}\Delta\nu = \nu_2 - \nu_1 &= [\nu^\circ + \left(\frac{\nu_{\text{spect}}}{10^6}\right)\delta_2] - [\nu^\circ + \left(\frac{\nu_{\text{spect}}}{10^6}\right)\delta_1] = \left(\frac{\nu_{\text{spect}}}{10^6}\right)(\delta_2 - \delta_1)\\ &= \left(\frac{100.130000 \times 10^6\ \text{Hz}}{10^6}\right)(50.0 - 25.5) = \boxed{2450\ \text{Hz}}\end{aligned}$$

E12B.4(b) The resonance frequency ν is given by [12B.5–*494*], $\nu = \nu^\circ + (\nu_{\text{spect}}/10^6)\delta$, where ν° is the resonance frequency of the standard. The frequency separation of the two peaks, $\Delta\nu$ is

$$\Delta\nu = \nu_2 - \nu_1 = \left[\nu^\circ + \left(\frac{\nu_{\text{spect}}}{10^6}\right)\delta_2\right] - \left[\nu^\circ + \left(\frac{\nu_{\text{spect}}}{10^6}\right)\delta_1\right] = \left(\frac{\nu_{\text{spect}}}{10^6}\right)(\delta_2 - \delta_1)$$

Rearrange to make $\Delta\delta$ the subject.

$$\Delta\delta = \delta_2 - \delta_1 = \Delta\nu \times \left(\frac{10^6}{\nu_{\text{spec}}}\right) = (25000\ \text{Hz}) \times \frac{10^6}{200.130000 \times 10^6\ \text{Hz}} = \boxed{125}$$

E12B.5(b) The combination of [12B.1–*494*], $\mathcal{B}_{\text{loc}} = \mathcal{B}_0 + \delta\mathcal{B}$, and [12B.2–*494*], $\delta\mathcal{B} = -\sigma\mathcal{B}_0$, gives the relationship $\mathcal{B}_{\text{loc}} = (1 - \sigma)\mathcal{B}_0$. For $|\sigma^\circ| << 1$, [12B.6–*495*] gives $\delta = (\sigma^\circ - \sigma) \times 10^6$. Hence,

$$\Delta\delta = \delta_2 - \delta_1 = (\sigma^\circ - \sigma_2)\times 10^6 - (\sigma^\circ - \sigma_1)\times 10^6 = -(\sigma_2 - \sigma_1)\times 10^6 = -(\Delta\sigma)\times 10^6$$

$$\Delta\mathcal{B}_{\text{loc}} = (1 - \sigma_2)\mathcal{B}_0 - (1 - \sigma_1)\mathcal{B}_0 = -(\sigma_2 - \sigma_1)\mathcal{B}_0 = -(\Delta\sigma)\mathcal{B}_0$$

Substituting for $\Delta\sigma$ gives $\Delta\mathcal{B}_{\text{loc}} = (\Delta\delta/10^6)\mathcal{B}_0$.

(i) For $\mathcal{B}_0 = 1.5$ T, $\Delta\mathcal{B}_{\text{loc}} = [(3.36 - 1.16)/10^6] \times (1.9\ \text{T}) = 4.2 \times 10^{-6}\ \text{T} = \boxed{4.2\ \mu\text{T}}$.

(ii) For $\mathcal{B}_0 = 15$ T, $\Delta\mathcal{B}_{\text{loc}} = [(3.36 - 1.16)/10^6] \times (16.5\ \text{T}) = 3.63 \times 10^{-5}\ \text{T} = \boxed{36.3\ \mu\text{T}}$.

E12B.6(b) The resonance frequency ν is given by [12B.5–*494*], $\nu = \nu^\circ + (\nu_{\text{spect}}/10^6)\delta$, where ν° is the resonance frequency of the standard. The resonance from TMS is taken as the origin so $\nu^\circ = 0$.

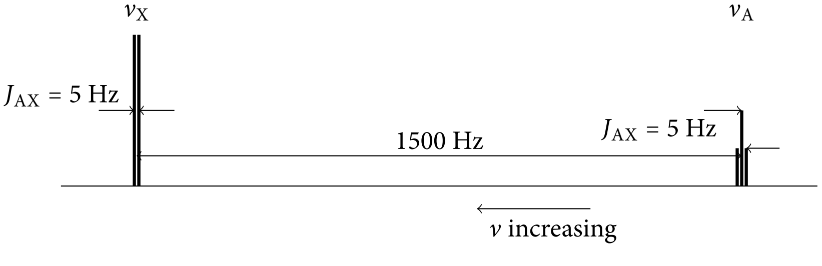
For ^{1}H nuclei, $I = \frac{1}{2}$ and so the signal due to nucleus A is split into $2nI + 1 = 2\times 2\times\frac{1}{2}+1 = 3$ peaks, with a splitting equal to the coupling constant $J_{\text{AX}} = 5$ Hz, and with intensity ratio 1:2:1. Similarly, the signal due to nucleus X is split into $2nI + 1 = 2 \times 1 \times \frac{1}{2} + 1 = 2$ peaks with a splitting equal to the coupling constant $J_{\text{AX}} = 5$ Hz.

For a spectrometer operating at 500 MHz,

$$\nu_{\text{A}} = \nu^\circ + \left(\frac{\nu_{\text{spect}}}{10^6}\right)\delta = 0 + \frac{500 \times 10^6\ \text{Hz}}{10^6} \times 1.50 = 750\ \text{Hz}$$

$$\nu_{\text{X}} = \nu^\circ + \left(\frac{\nu_{\text{spect}}}{10^6}\right)\delta = 0 + \frac{500 \times 10^6\ \text{Hz}}{10^6} \times 4.50 = 2250\ \text{Hz}$$

For the A spin there will be three lines at 745 Hz, 750 Hz, and 755 Hz; for X spin there will be two lines at 2247.5 Hz, and 2252.5 Hz. The integrated intensity of the X spin multiplet will be twice that of the A spin multiplet.



E12B.7(b) ^{19}F NMR: the four ^{19}F nuclei are equivalent and so all have the same shift. This resonance is split by coupling to the single ^{11}B nucleus into $2nI + 1$ lines; here $n = 1$ and $I = 3/2$ so there are 4 lines of equal intensity. The splitting between each is the B–F coupling constant, and the multiplet is centred at the shift of the fluorine.

^{11}B NMR: the ^{11}B nucleus is coupled to four equivalent ^{19}F nuclei, giving a multiplet with $2nI + 1$ lines; here $n = 4$ and $I = \frac{1}{2}$ so there are 5 lines. These lines have intensities in the ratio 1:4:6:4:1, each line is separated from the next by the B–F coupling constant, and the whole multiplet is centred at the shift of the boron.

E12B.8(b) In ^{14}NH$_4^+$ the four ^{1}H nuclei are equivalent, and are coupled to a single ^{14}N nucleus with $I = 1$. This splits the resonance into $2nI + 1 = 2 \times 1 \times 1 + 1 = 3$ lines with intensity ratio 1:1:1.

In ^{15}NH$_4^+$ coupling to a single ^{15}N nucleus with $I = \frac{1}{2}$ splits the resonance into $2nI + 1 = 2 \times 1 \times 1 + 1 = 2$ lines with intensity ratio 1:1.

E12B.9(b) Coupling to a nucleus with $I = 1$ splits the original resonance into $2I + 1 = 3$ lines of equal intensity: the lines appear at ν and $\nu \pm J$, where J is the coupling constant. Coupling to a second spin-1 nucleus splits each of these three lines into three in the same way. Because the two spins to which the coupling occurs are equivalent, the coupling is the same and some of the lines fall on top of one another, giving enhanced intensity. The result is a $\boxed{\text{1:2:3:2:1 multiplet}}$, as shown in Fig 12.3.

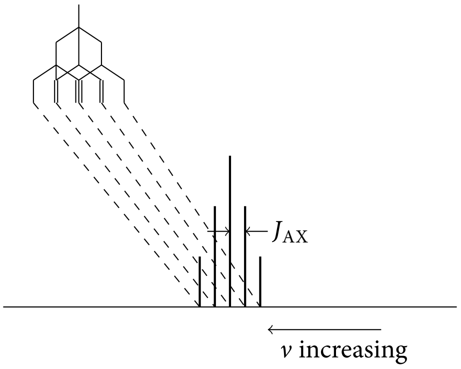


Figure 12.3

E12B.10(b) The multiplet resulting from coupling to two inequivalent $I = 1$ nuclei originates from the resonance of nucleus A being split into $(2I + 1) = 3$ lines by coupling with the X$_1$ nucleus, and then each of these lines being split into three by coupling to the X$_2$ nucleus.

Since the coupling between A and X$_1$ is not the same as that between A and X$_2$, no lines are necessarily coincident and so nine lines of equal intensity are observed, as shown in Fig. 12.4.

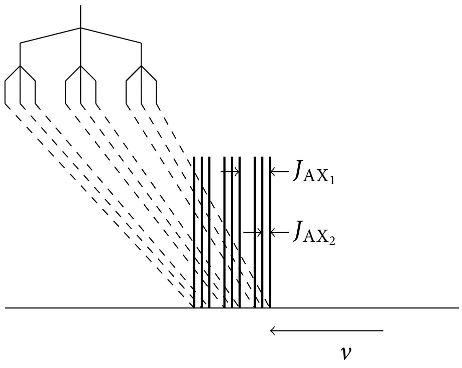


Figure 12.4

E12B.11(b) Coupling to one $I = \frac{5}{2}$ nucleus results in the original line being split into $(2I + 1) = 6$ lines. Each of these lines is then split into six in the same way by coupling to the second $I = \frac{5}{2}$ nucleus, and then split again by coupling to the third nucleus.

As a result of each nucleus being equivalent, the splittings are the same and thus some lines are coincident and give rise to absorption lines of increased intensity. The overall result is a $\boxed{\text{1:3:6:10:15:21:25:27:27:25:21:15:10:6:3:1 multiplet}}$, as is shown in Fig. 12.5.

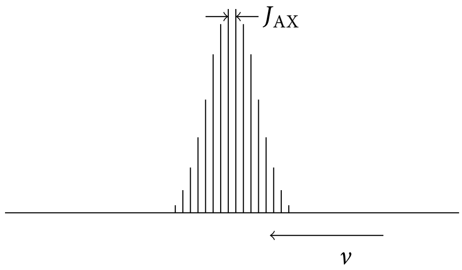
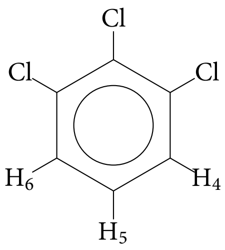


Figure 12.5

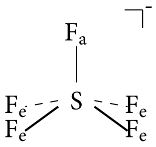
E12B.12(b) A group of nuclei are chemically equivalent if they are related by a symmetry operation of the molecule and therefore have the same chemical shift. Two chemically equivalent nuclei A and A′ are magnetically equivalent if the coupling between A and any other magnetic nucleus in the molecule, say Z, is the same as the coupling between A′ and Z. If Z itself is to be magnetically equivalent to Z′, then the couplings A–Z, A–Z′, A′–Z, and A′–Z′ must all be equal: that is, the couplings between any member of a group of equivalent spins with any member of another group of equivalent spins must be the same in order for the groups each to be magnetically equivalent.

In 1,2,3-trichlorobenzene, H_4 and H_6 are chemically equivalent because they are related by a 180° degree rotation about the C_2–C_5 axis; H_5 is unique. The coupling between H_4 and H_5 is the same as that between H_6 and H_5, therefore the test for magnetic equivalence is satisfied: H_4 and H_6 are magnetically equivalent.



E12B.13(b) The molecule SF_5^- is square pyramidal. The four equatorial fluorine atoms, F_e, are related by a 90° rotation about the F_a–S bond: these four atoms are therefore chemically equivalent. The axial fluorine atom, F_a, is unique.

Each F_e has the same coupling to F_a, thus satisfying the test for magnetic equivalence: the four equatorial fluorine atoms are magnetically equivalent.



E12B.14(b) Coalescence of two NMR lines due to rapid nuclei exchange occurs when the condition given in [12B.16–*505*], $\tau = 2^{1/2}/\pi\delta\nu$, is satisfied; in this expression τ is the lifetime of an environment, and $\delta\nu$ is the difference between the Larmor frequencies of the two environments. Using [12B.5–*494*],

$$\delta\nu = \nu_2 - \nu_1 = \left[\nu^\circ + \left(\frac{\nu_{\text{spec}}}{10^6}\right)\delta_2\right] - \left[\nu^\circ + \left(\frac{\nu_{\text{spec}}}{10^6}\right)\delta_1\right] = \left(\frac{\nu_{\text{spec}}}{10^6}\right)(\delta_2 - \delta_1)$$

For a proton jumping between two sites with first-order rate constant k, $k = 1/\tau$

$$\delta\nu = \left(\frac{\nu_{\text{spec}}}{10^6}\right)(\delta_2 - \delta_1) = \left(\frac{350 \times 10^6}{10^6}\right)(5.5 - 4.2) = 455\ \text{Hz}$$

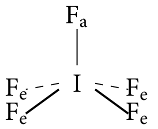
$$k = \frac{1}{\tau} = \frac{\pi\delta\nu}{2^{1/2}} = \frac{\pi \times (455\ \text{Hz})}{2^{1/2}} = \boxed{1.0 \times 10^3\ \text{s}^{-1}}$$

Solutions to problems

P12B.2 The ^{19}F NMR spectrum has two multiplets: a doublet and a quintet. The former indicates coupling to one spin-$\frac{1}{2}$ nucleus, the latter indicates coupling to four equivalent spin-$\frac{1}{2}$ nuclei.

VSEPR suggest that IF_5 is square pyramidal. The four equatorial fluorine atoms F_e are chemically equivalent as they are related by a 90° rotation about the I–F_a axis; the axial fluorine atom F_a is unique. Each F_e has the same coupling to F_a, therefore the four equatorial F atoms are magnetically equivalent.

The F_a atom will therefore appear as a 1:4:6:4:1 quintet, and the F_e atoms as a doublet. The splitting between the lines of the multiplets is the same in both cases.



P12B.4 The Karplus equation is given in [12B.14–*501*], ${}^3J_{HH} = A + B\cos\phi + C\cos 2\phi$. Figure 12.6 illustrates that increasing parameter C reduces the value of ${}^3J_{HH}$ in the range $45° < \phi < 135°$. In the ranges $\phi < 45°$ and $\phi > 135°$, increasing parameter C increases the value of ${}^3J_{HH}$, with the greatest influence when the X–H bonds are aligned parallel or anti-parallel ($\phi = 0$ or $\phi = 180°$).

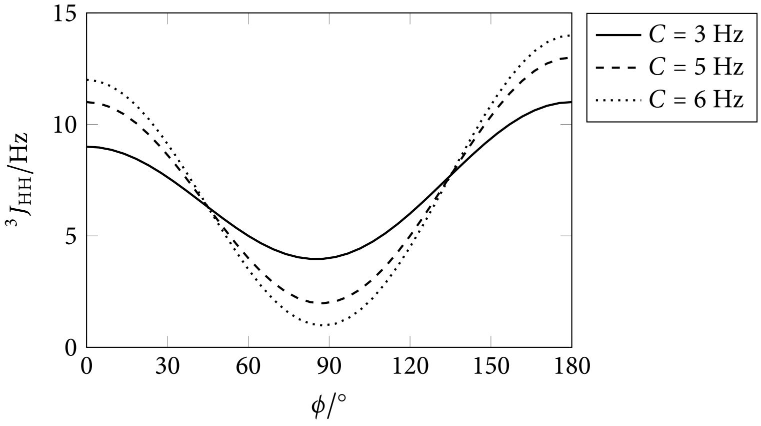


Figure 12.6

Figure 12.7 illustrates that making parameter B more positive increases the value of ${}^3J_{HH}$ in the range $0° < \phi < 90°$, with the greatest influence when the X–H bonds are aligned parallel ($\phi = 0$) and minimal influence near $\phi = 90°$. Changing the value of B has no affect on the size of the coupling at $\phi = 90°$. Increasing the value of B reduces the value of ${}^3J_{HH}$ in the range $90° < \phi < 180°$, with greatest influence when $\phi = 180°$. Increasing parameter A simply increases the value of ${}^3J_{HH}$ for all angles.

P12B.6 Note that there is an error in the problem as printed. The relationship between the Sn–Sn and H–H couplings should be expressed as

$$({}^3J_{SnSn}/\text{Hz}) = 78.86 \times ({}^3J_{HH}/\text{Hz}) + 27.84$$

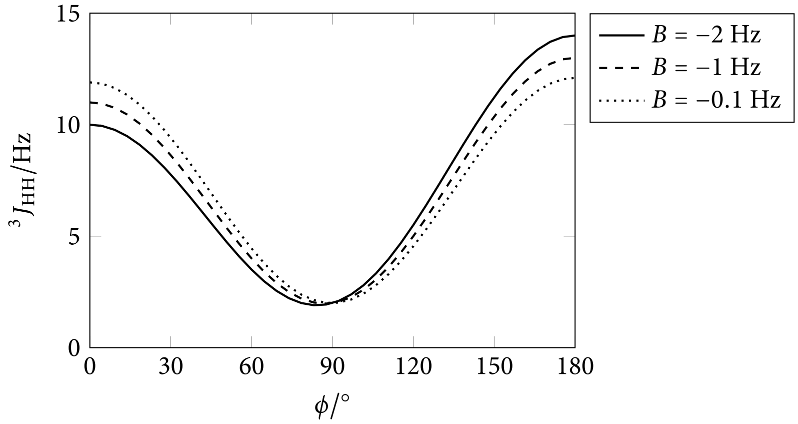


Figure 12.7

(a) The Karplus equation for $^3J_{\mathrm{HH}}$ is a linear equation in $\cos\phi$ and $\cos 2\phi$, and the experimentally determined equation for $^3J_{\mathrm{SnSn}}$ is linear in $^3J_{\mathrm{HH}}$. If $F(f)$ is linear in f, and $f(x)$ is linear in x, it follows that $F(x)$ is also linear in x. Therefore $^3J_{\mathrm{SnSn}}$ is a linear equation in $\cos\phi$ and $\cos 2\phi$.

(b) Substitution of the Karplus equation for $^3J_{\mathrm{HH}}$ into the expression for $^3J_{\mathrm{SnSn}}$ gives a Karplus-type expression for the latter.

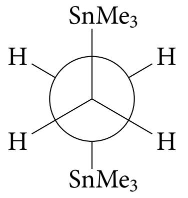
$$\begin{aligned}(^3J_{\mathrm{SnSn}}/\ \mathrm{Hz}) &= 78.86 \times (^3J_{\mathrm{HH}}/\ \mathrm{Hz}) + 27.84\\ &= 78.86 \times (A + B\cos\phi + C\cos 2\phi) + 27.84\\ &= (78.86A + 27.84) + 78.86B\cos\phi + 78.86C\cos 2\phi\\ &= A' + B'\cos\phi + C'\cos 2\phi\end{aligned}$$

Taking the values $A = 7$ Hz, $B = -1$ Hz, and $C = 5$ Hz from the text gives the parameters in this new Karplus-type equation as $(A'/\mathrm{Hz}) = 78.86\times(7)+27.84 = 580$, $(B'/\mathrm{Hz}) = 78.86\times(-1) = -78.9$, and $(C'/\mathrm{Hz}) = 78.86 \times (5) = 394$. Thus, the Karplus-type equation for the Sn–Sn couplings is

$$(^3J_{\mathrm{SnSn}}/\ \mathrm{Hz}) = \boxed{580 - 78.9\cos\phi + 394\cos 2\phi}$$

A plot of $^3J_{\mathrm{SnSn}}$ as a function of ϕ is shown in Fig. 12.8.

(c) A staggered conformation with the $\mathrm{SnMe_3}$ groups $\boxed{\text{trans}}$ to each other $(\phi = 180°)$ is the preferred arrangement as this minimised the steric repulsion between the bulky $\mathrm{SnMe_3}$ groups.



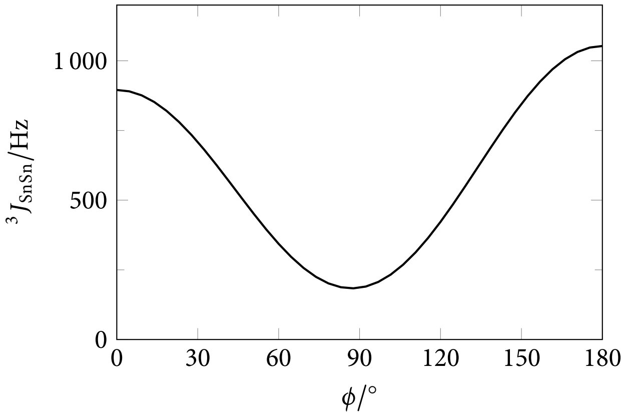


Figure 12.8

P12B.8 The average of $\mathcal{B}_{\mathrm{nuc}}$ over all orientations is found by integrating the expression for $\mathcal{B}_{\mathrm{nuc}}$ over the polar angles θ and ϕ, with θ in the range 0 to π, and ϕ in the range 0 to 2π; the volume element is $\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$. The constants which appear in the expression for $\mathcal{B}_{\mathrm{nuc}}$, $(\gamma_{\mathrm{N}}\hbar\mu_0 m_I)/(4\pi R^3)$, are written as A.

$$\begin{aligned}\langle\mathcal{B}_{\mathrm{nuc}}\rangle &= A\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}(1-3\cos^2\theta)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\\ &= A\int_{\theta=0}^{\pi}(\sin\theta-3\cos^2\theta\sin\theta)\,\mathrm{d}\theta\int_{\phi=0}^{2\pi}\mathrm{d}\phi\end{aligned}$$

The integral of the second term is found by recognising that $(\mathrm{d}/\mathrm{d}\theta)\cos^3\theta = -3\cos^2\theta\sin\theta$

$$\begin{aligned}\langle\mathcal{B}_{\mathrm{nuc}}\rangle &= A\left|-\cos\theta+\cos^3\theta\right|_{\theta=0}^{\pi}\times|\phi|_{\phi=0}^{2\pi}\\ &= A[(-\cos\pi+\cos^3\pi)-(-\cos 0+\cos^3 0)]\,[2\pi-0]\\ &= A[\underbrace{(-(-1)+(-1)^3)}_{=0}-\underbrace{(-(1)+(1)^3)}_{=0}]\,[2\pi]=0\end{aligned}$$

Hence $\boxed{\langle\mathcal{B}_{\mathrm{nuc}}\rangle = 0}$.

12C **Pulse techniques in NMR**

Answers to discussion questions

D12C.2 Relaxation results from the interaction between individual spins and local magnetic fields which arise in various ways. As is described in Topic 12A, the interaction between a spin and a magnetic field depends on the magnetogyric ratio of the spin: the greater the magnetogyric ratio, the stronger the interaction. Thus, a given local field has a greater interaction with a nucleus with a greater magnetogyric ratio and, all other things being equal, the relaxation caused by these fields will therefore be faster the greater the magnetogyric ratio.

The magnetogyric ratio for ^{1}H is about four times that of ^{13}C, hence the interactions between ^{1}H and local fields is stronger leading to faster relaxation and shorter relaxation times. A somewhat separate issue is that in typical molecules H atoms tend to be more accessible than C atoms, and so if the local field is from outside the molecule it may be felt more strongly by the more exposed H atoms.

D12C.4 This is discussed in Section 12C.4 on page 516.

Solutions to exercises

E12C.1(b) From the discussion in Section 12C.1(a) on page 510, the flip angle ϕ of a pulse of duration $\Delta\tau$ is given by $\phi = \gamma_N \mathcal{B}_1 \Delta\tau$, where $\mathcal{B}_1$ is the strength of the applied field. It follows that $\mathcal{B}_1 = \phi/\gamma_N\Delta\tau$. With the data given

$$\mathcal{B}_1 = \frac{\phi}{\gamma_N \Delta\tau} = \frac{\pi/2}{(26.752\times10^7\ \mathrm{T^{-1}\,s^{-1}})\times(5\times10^{-6}\ \mathrm{s})} = \boxed{1.2\ \mathrm{mT}}$$

The corresponding 180° pulse has twice the flip angle so, for the same $\mathcal{B}_1$, $\Delta\tau$ is doubled: $\Delta\tau = 2\times(5\ \mu\mathrm{s}) = \boxed{10\ \mu\mathrm{s}}$.

E12C.2(b) The effective transverse relaxation time, T_2^*, is given by [12C.6–*514*], $T_2^* = 1/\pi\Delta\nu_{1/2}$, where $\Delta\nu_{1/2}$ is the width of the (assumed) Lorentzian signal measured at half the peak height. Hence

$$T_2^* = \frac{1}{\pi\Delta\nu_{1/2}} = \frac{1}{\pi\times(12\ \mathrm{Hz})} = \boxed{0.027\ \mathrm{s}}$$

E12C.3(b) The amplitude of the free induction decay, $S(t)$, is proportional to e^{-t/T_2}, where t is time and T_2 is the transverse relaxation time. If $S(t_2) = \frac{1}{2}S(t_1)$ then

$$\frac{S(t_2)}{S(t_1)} = \frac{1}{2} = \frac{e^{-t_2/T_2}}{e^{-t_1/T_2}} = e^{-(t_2-t_1)/T_2} = e^{-\Delta t/T_2}$$

taking logarithms gives

$$\ln\tfrac{1}{2} = -\Delta t/T_2 \quad \text{therefore} \quad \Delta t = -T_2\ln\tfrac{1}{2} = T_2\ln 2$$

With the data given

$$\Delta t = (0.050\ \mathrm{s})\times\ln 2 = \boxed{0.035\ \mathrm{s}}$$

E12C.4(b) Monofluoroethanoic acid has two carbon environments: an sp^3 hybridised carbon and a carboxylic acid carbon. The ^{13}C NMR spectrum shows a signal at $\delta = 79$ which is due to the sp^3 carbon. This C atom is adjacent to two protons and one F atom. Coupling with the two protons splits the carbon signal into a triplet, which is further split by the coupling to the F atom into a doublet of triplets.

When the ^{13}C NMR spectrum is observed with proton decoupling, splittings due to C–H coupling are collapsed, leaving just the doublet due to coupling to F. The splitting is the one-bond C–F coupling, $^1J = 160$ Hz.

The signal at $\delta = 179$ is due to the carboxylic acid carbon. This is also split into a doublet of triplets by coupling to two protons and one F, but as these couplings are over two bonds they are much smaller than those seen for other carbon. When proton decoupling is used, this multiplet collapses to a doublet for the same reasons as above.

E12C.5(b) The maximal NOE enhancement is given by [12C.8–*517*], $\eta = \gamma_X/2\gamma_A$, where γ_X and γ_A are the magnetogyric ratios of nuclei X and A, respectively.

$$\eta = \frac{\gamma_{^1\mathrm{H}}}{2\gamma_{^{19}\mathrm{F}}} = \frac{(26.752\times10^7\ \mathrm{T^{-1}\,s^{-1}})}{2\times(25.177\times10^7\ \mathrm{T^{-1}\,s^{-1}})} = \boxed{0.5313}$$

Solutions to problems

P12C.2 The free-induction decay consists of signals of the form given by [12C.8–*517*]

$$S(t) = S_0\cos(2\pi\nu_L t)\mathrm{e}^{-t/T_2}$$

If there are several lines, the overall signal is the sum of several such signals, each in principle with a different intensity, frequency, and transverse relaxation time. As described in the problem, the frequencies measured by the spectrometer are the offset frequencies, given by $\delta\nu_L/10^6$, where δ is the chemical shift. In this case the peak at $\delta = 3.2$ in an 800 MHz spectrometer gives signal at $3.2\times(800\times10^6\ \mathrm{Hz})/(10^6) = 2560$ Hz; similarly, the other peaks give signals at 3280 Hz and 4000 Hz. The intensities are all assumed to be the same, S_0. Because the oscillations in the free-induction decay are rapid it is only possible to see them clearly by plotting a small section of signal, which is what is shown in Fig. 12.9.

If the signal at $\delta = 5.0$ is reduced in intensity to $S_0/10$, the free-induction decay, Fig. 12.10, shows a clear reduction in the highest-frequency component. The overall decay of the function is seen by plotting it out to longer times, as in Fig. 12.11 (note that, for practical reasons, in this plot the data points in insufficiently closely spaced to reproduce the waveform precisely, but the overall decay is correctly represented).

P12C.4 (a) The NMR lineshape is approximated using a Lorentzian function of the form

$$I_L(\omega) = \frac{S_0T_2}{1+T_2^2(\omega-\omega_0)^2}$$

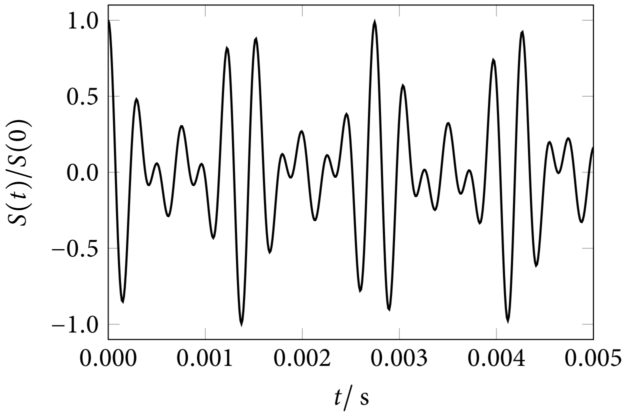


Figure 12.9

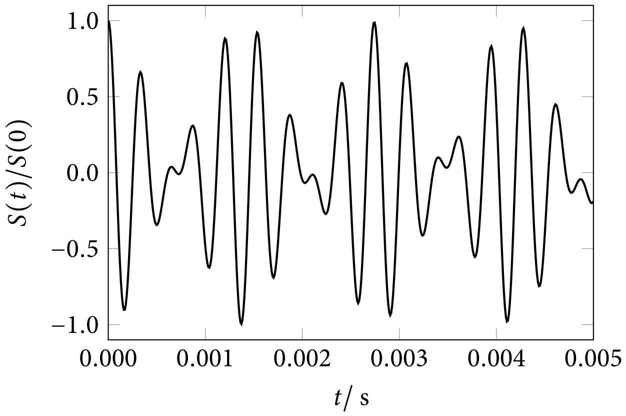


Figure 12.10

where $\omega = 2\pi\nu$ is the angular frequency, ω_0 is the resonance frequency, S_0 is a constant, and T_2 is the transverse relaxation time. Inspection of the function shows that it must be a maximum at $\omega = \omega_0$ as this minimises the denominator. At this point the function has the value $I_L(\omega_0) = S_0 T_2$. The peak reaches its half-height of $S_0 T_2/2$ when

$$S_0 T_2/2 = \frac{S_0 T_2}{1 + T_2^2(\omega_{1/2} - \omega_0)^2} \quad \text{hence} \quad (\omega_{1/2} - \omega_0)^2 = 1/T_2^2$$

It follows that $\omega_{1/2} = \omega_0 \pm 1/T_2$. Converting from angular frequency using $\omega = 2\pi\nu$ gives $\nu_{1/2} = \nu_0 \pm 1/2\pi T_2$. Hence the width at half-height is $2 \times (1/2\pi T_2) = \boxed{1/\pi T_2}$ in Hz, or $2/T_2$ when expressed as an angular frequency.

(b) The NMR lineshape can also be approximated using a Gaussian function of the form

$$I_G(\omega) = S_0 T_2 e^{-T_2^2(\omega-\omega_0)^2}$$

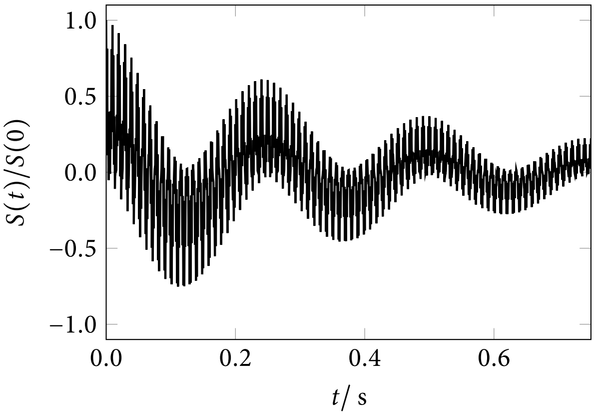


Figure 12.11

The exponential term is a maximum when $\omega = \omega_0$, so the maximum of the function is $I_G(\omega_0) = S_0T_2$. The peak reaches its half-height of $S_0T_2/2$ when

$$S_0T_2/2 = S_0T_2\mathrm{e}^{-T_2^2(\omega_{1/2}-\omega_0)^2} \quad \text{hence} \quad (\omega_{1/2}-\omega_0)^2 = (\ln 2)/T_2^2$$

It follows that $\omega_{1/2} = \omega_0 \pm (\ln 2)^{1/2}/T_2$. Converting from angular frequency using $\omega = 2\pi\nu$ gives $\nu_{1/2} = \nu_0 \pm (\ln 2)^{1/2}/2\pi T_2$. The width at half-height is $2 \times \nu_{1/2} = \boxed{(\ln 2)^{1/2}/\pi T_2}$ in Hz, or $2(\ln 2)^{1/2}/T_2$ when expressed as an angular frequency.

(c) Choosing $x = T_2(\omega - \omega_0)$ then both functions can be re-written.

$$I_L(\omega)/S_0T_2 = \frac{1}{1+x^2} \qquad I_G(\omega)/S_0T_2 = \mathrm{e}^{-x^2}$$

Figure 12.12 shows plots of both functions. The most noticeable feature is that the Gaussian is more compact and decays more quickly than does the Lorentzian. The functions as plotted are not normalised: if they were, such that the area under the curves is equal, the Lorentzian would have a lower peak height than the Gaussian.

P12C.6 The shape of a spectral line, $I(\omega)$, is given by the Fourier transform of the free-induction decay $G(t)$

$$I(\omega) = \mathrm{Re}\left[\int_0^\infty G(t)\mathrm{e}^{\mathrm{i}\omega t}\,\mathrm{d}t\right]$$

The form of this integral means that the Fourier transform is linear, in the sense that the Fourier transform of $G_1(t) + G_2(t)$ is equal to the Fourier transform of $G_1(t)$ + the Fourier transform of $G_2(t)$.

It is shown in the previous *Problem* that the Fourier transform of $a\cos\omega_0 t\,\mathrm{e}^{-t/\tau}$ consists of two Lorentzians at $\omega = \pm\omega_0$, with width $2/\tau$, and height scaled by a.

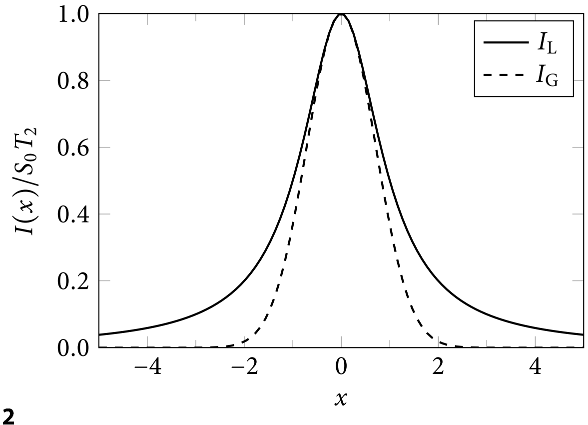


Figure 12.12

Therefore the Fourier transform of $a\cos\omega_1 t\,\mathrm{e}^{-t/\tau} + b\cos\omega_2 t\,\mathrm{e}^{-t/\tau}$ will consist of two Lorentzians at $\omega = \pm\omega_1$, with height scaled by a, and two Lorentzians at $\omega = \pm\omega_2$, with height scaled by b; all the peaks will have width $2/\tau$.

P12C.8 The differential equation which describes the time-dependence of the z-magnetization is given in *Problem* P12C.7

$$\frac{\mathrm{d}M_z(t)}{\mathrm{d}t} = -\frac{M_z(t) - M_0}{T_1}$$

Separate the differential equation and integrate between $t = 0$ and $t = \tau$, and the corresponding limits $M_z(0) = -M_0$ and $M_z(\tau)$.

$$\begin{aligned}
&\int_{-M_0}^{M_z(\tau)} \frac{1}{M_z(t) - M_0}\,\mathrm{d}M_z(t) = -\int_0^{\tau} \frac{1}{T_1}\,\mathrm{d}t\\
&|\ln\left(M_z(t) - M_0\right)|_{-M_0}^{M_z(\tau)} = \left|-\frac{t}{T_1}\right|_0^{\tau}\\
&\ln\left(\frac{M_z(\tau) - M_0}{-2M_0}\right) = -\frac{\tau}{T_1}\\
&\text{hence}\ \ M_z(\tau) = M_0(1 - 2\mathrm{e}^{-\tau/T_1})
\end{aligned}$$

The time τ_{null} at which $M_z(\tau_{\text{null}}) = 0$ is found by solving

$$M_0(1 - 2\mathrm{e}^{-\tau_{\text{null}}/T_1}) = 0 \quad \text{hence} \quad \tau_{\text{null}} = T_1 \ln 2$$

With the given data, $T_1 \ln 2 = 0.50$ s, hence $T_1 = (0.50\ \text{s})/\ln(2) = \boxed{0.72\ \text{s}}$.

P12C.10 Figure 12.13 shows the motion of magnetization vectors from typical 'fast' and 'slow' spin packets (relative to the rotating frame frequency) during the spin echo sequence. The 90° pulse rotates the magnetization onto $-y$, and then during the delay τ the vectors from the spin packets fan out. The 180° pulse applied about x rotates the vectors to mirror-image positions with respect to the xz-plane. In the subsequent period the vectors continue as before, but at the end of the delay τ they converge onto the $+y$ axis. Refocusing occurs, as it did in Fig. 12C.11 on page 515, but along the opposite axis.

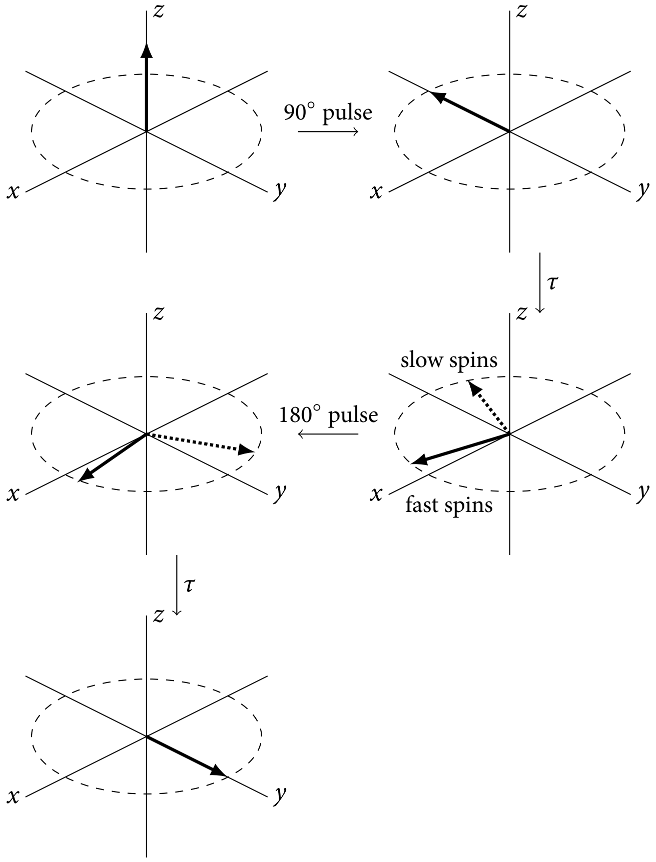


Figure 12.13

P12C.12 The magnitude of the local magnetic field is given by [12B.17a–*506*]

$$\mathcal{B}_{\text{loc}} = -\frac{\gamma_{\text{N}}\hbar\mu_0 m_I}{4\pi R^3}(1 - 3\cos^2\theta)$$

where $\mathcal{B}_{\text{loc}}$ is the local magnetic field, γ_{N} is the nuclear magnetogyric ratio, μ_0 is the vacuum permeability, $m_I\hbar$ is the z-component of the spin angular momentum, R is the internuclear separation, and θ is the angle between the direction of local field vector and the direction of the applied magnetic field. The average over angles $\theta = 0 \rightarrow \theta'$ is found by integrating $\mathcal{B}_{\text{loc}}$ over this range, with the appropriate volume element, which is $\sin\theta\,\mathrm{d}\theta$. The integral is divided by $\int_0^{\theta'} \sin\theta \, d\theta$ to ensure normalization

$$\langle \mathcal{B}_{\text{loc}} \rangle = \frac{\int_0^{\theta'} \mathcal{B}_{\text{loc}} \sin\theta \, d\theta}{\int_0^{\theta'} \sin\theta \, d\theta}$$
$$= \frac{\gamma_N \hbar \mu_0 m_I}{4\pi R^3} \times \frac{\int_0^{\theta'} (1 - 3\cos^2\theta) \sin\theta \, d\theta}{\int_0^{\theta'} \sin\theta \, d\theta}$$

The integral in the denominator evaluates to $1 - \cos\theta'$. The integral in the numerator separates into two: the first is $\int_0^{\theta'} \sin\theta \, d\theta$ which similarly evaluates to $1 - \cos\theta'$. The second is evaluated as follows

$$I = -3 \int_0^{\theta'} \cos^2\theta \sin\theta \, d\theta$$

Recognise that $(d/d\theta)\cos^3\theta = -3\cos^2\theta \sin\theta$

$$I = -3 \left| -\tfrac{1}{3}\cos^3\theta \right|_0^{\theta'} = \cos^3\theta' - 1$$

Putting this all together gives

$$\langle \mathcal{B}_{\text{loc}} \rangle = \frac{\gamma_N \hbar \mu_0 m_I}{4\pi R^3} \times \frac{(1 - \cos\theta') + (\cos^3\theta' - 1)}{1 - \cos\theta'}$$
$$= \frac{\gamma_N \hbar \mu_0 m_I}{4\pi R^3} \times \frac{\cos\theta'(\cos^2\theta' - 1)}{1 - \cos\theta'}$$
$$= \frac{\gamma_N \hbar \mu_0 m_I}{4\pi R^3} \times \frac{\cos\theta'(\cos\theta' + 1)'(\cos\theta' - 1)}{1 - \cos\theta'}$$
$$= -\frac{\gamma_N \hbar \mu_0 m_I}{4\pi R^3} \times \cos\theta'(\cos\theta' + 1)$$

When $\theta' = \pi$, $(\cos\theta' + 1) = (\cos\pi + 1) = 0$ and, as expected, the field averages to zero.

The separation R was found in *Problem* P12C.11 to be 158 pm. With $\theta' = 30°$ in the above expression, and taking $m_I = +\frac{1}{2}$, the average field is computed as

$$\langle \mathcal{B}_{\text{loc}} \rangle = -\frac{\gamma_N \hbar \mu_0 m_I}{4\pi R^3} \times \cos\theta'(\cos\theta' + 1)$$
$$= -\frac{(26.752 \times 10^7 \text{ T}^{-1}\text{ s}^{-1}) \times (1.0546 \times 10^{-34} \text{ J s}) \times (1.257 \times 10^{-6} \text{ T}^2 \text{ J}^{-1} \text{ m}^3)}{2 \times 4\pi \times (158 \times 10^{-12} \text{ m})^3}$$
$$\times \cos 30° \times (\cos 30° + 1)$$
$$= -(3.57... \times 10^{-4} \text{ T}) \times (3^{1/2}/2) \times (3^{1/2}/2 + 1)$$
$$= \boxed{-0.578 \text{ mT}}$$

12D Electron paramagnetic resonance

Answers to discussion questions

D12D.2 The hyperfine parameter a for the coupling between a nucleus and the electron in a radical is easily measured from the splittings of the lines in the EPR spectrum caused by the nucleus in question. If the quantitative relationship between a and ρ is know (for example, as it is for aromatic systems, the McConnell equation) it is possible to map out the spin density in the molecule, thus revealing the spatial distribution of the molecular orbital which is occupied by the unpaired electron.

Solutions to exercises

E12D.1(b) The EPR resonance condition is given by [12D.2–*519*], $h\nu = g\mu_B\mathcal{B}_0$, where ν is the spectrometer operating frequency, g is the g-value of the radical, μ_B is the Bohr magneton, and $\mathcal{B}_0$ is the magnetic field. Rearranging the expression gives

$$g = \frac{h\nu}{\mu_B\mathcal{B}_0} = \frac{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(9.2482\times10^{9}\,\mathrm{Hz})}{(9.2740\times10^{-24}\,\mathrm{J\,T^{-1}})\times(330.02\times10^{-3}\,\mathrm{T})} = \boxed{2.0022}$$

E12D.2(b) As described in Section 12D.2 on page 520, the splitting between the lines in the multiplet is the hyperfine coupling constant. In this case the splitting is $(338.0-335.8)$ mT = 2.2 mT, $(335.8-333.6)$ mT = 2.2 mT, and $(333.6-331.4)$ mT = 2.2 mT. Therefore $\boxed{a = 2.2\ \mathrm{mT}}$.

The g-value is computed from the centre of the multiplet, which is at $(333.6+\frac{1}{2}\times2.2)$ mT = 334.7 mT. Then, using [12D.2–*519*], $h\nu = g\mu_B\mathcal{B}_0$

$$g = \frac{h\nu}{\mu_B\mathcal{B}_0} = \frac{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(9.332\times10^{9}\,\mathrm{Hz})}{(9.2740\times10^{-24}\,\mathrm{J\,T^{-1}})\times(334.7\times10^{-3}\,\mathrm{T})} = \boxed{1.9921}$$

E12D.3(b) The total local magnetic field is given by [12D.3–*520*], $\mathcal{B}_{\mathrm{loc}} = \mathcal{B}_0 + am_{I_1}$, where $m_{I_1} = \pm\frac{1}{2}$ and a is the hyperfine coupling constant. Further interactions with a second and a third proton give the overall field as

$$\mathcal{B}_{\mathrm{loc}} = \mathcal{B}_0 + am_{I_1} + am_{I_2} + am_{I_3}$$

where each $m_{I_i} = \pm\frac{1}{2}$. There are 8 possible combinations of the m_{I_i} and hence 8 lines. The centre of the spectrum is at 332.8 mT.

For example, the line with all $m_{I_i} = +\frac{1}{2}$ is at

$$\mathcal{B}/\mathrm{mT} = 332.8 + \tfrac{1}{2}\times2.11 + \tfrac{1}{2}\times2.87 + \tfrac{1}{2}\times2.89 = 336.735$$

and that with $m_{I_1} = -\frac{1}{2}$, $m_{I_2} = +\frac{1}{2}$, and $m_{I_3} = +\frac{1}{2}$ is at

$$\mathcal{B}/\mathrm{mT} = 332.8 - \tfrac{1}{2}\times2.11 + \tfrac{1}{2}\times2.87 + \tfrac{1}{2}\times2.89 = 334.625$$

Repeating this process gives the 8 lines as (in order)

$\boxed{328.865, 330.975, 331.735, 331.755, 333.845, 333.865, 334.625 \text{ and } 336.735 \text{ mT}}$

All 8 lines have $\boxed{\text{equal intensity}}$. However, the third and fourth peak, and the fifth and sixth peak, are closely spaced and so, if the instrument does not have high enough resolution, may overlap with one another to give a peak of double height.

E12D.4(b) (i) The expectation is that the CH_2 protons will have a larger hyperfine constant than the CH_3 protons. Therefore the main splitting will be into a triplet (1:2:1), and each of the lines of the triplet may be further split by a smaller amount into a quartet (1:3:3:1). If all the lines are resolved the spectrum will be a triplet of quartets, a total of 12 lines with relative intensities 1:3:3:1; 2:6:6:2; 1:3:3:1.

(ii) The splittings due to couplings to equivalent spin 1 nuclei are illustrated in Fig. 12D.5 on page 521. Coupling to the CD_2 deuterons will give five lines with intensities (1:2:3:2:1). The smaller coupling to the CD_3 deuterons will split each of these lines into seven, with intensities (1:3:6:7:6:3:1), giving 35 lines in total.

E12D.5(b) The resonance frequency is related to the g-value by [12D.2–*519*], $h\nu = g\mu_B\mathcal{B}_0$. Rearranging this gives $\mathcal{B}_0 = h\nu/\mu_B$.

(i) For a spectrometer operating at 9.501 GHz,

$$\mathcal{B}_0 = \frac{h\nu}{g\mu_B} = \frac{(6.6261\times10^{-34}\,\text{J s})\times(9.501\times10^{9}\,\text{Hz})}{2.0024\times(9.2740\times10^{-24}\,\text{J T}^{-1})} = \boxed{339.0\text{ mT}}$$

(ii) For a spectrometer operating at 34.77 GHz,

$$\mathcal{B}_0 = \frac{h\nu}{g\mu_B} = \frac{(6.6261\times10^{-34}\,\text{J s})\times(34.77\times10^{9}\,\text{Hz})}{2.0024\times(9.2740\times10^{-24}\,\text{J T}^{-1})} = \boxed{1.241\text{ T}}$$

E12D.6(b) If a radical contains N equivalent nuclei with spin quantum number I, then there are $2NI+1$ hyperfine lines. The radical contains two magnetic nuclei, $N = 2$, and there are a total of five hyperfine lines. Therefore $2NI+1 = 2\times2\times I+1 = 5$ hence $\boxed{I = 1}$. The splitting pattern arising from coupling to equivalent nuclei with $I = 1$ is shown in Fig. 12D.5: coupling to two such nuclei gives five lines in the intensity ratio 1:2:3:2:1.

Solutions to problems

P12D.2 The EPR resonance condition is given by [12D.2–*519*], $h\nu = g\mu_B\mathcal{B}_0$, where ν is the spectrometer operating frequency, g is the g-value of the radical, μ_B is the Bohr magneton and $\mathcal{B}_0$ is the magnetic field. The expression is rearranged to make g the subject.

When the applied magnetic field is parallel to the OO direction,

$$g = \frac{h\nu}{\mu_B\mathcal{B}_0} = \frac{(6.6261\times10^{-34}\,\text{J s})\times(9.302\times10^{9}\,\text{Hz})}{(9.2740\times10^{-24}\,\text{J T}^{-1})\times(333.64\times10^{-3}\,\text{T})} = \boxed{1.992}$$

When the applied magnetic field lies along the bisector of the ONO angle,

$$g = \frac{h\nu}{\mu_B \mathcal{B}_0} = \frac{(6.6261 \times 10^{-34}\,\text{J s}) \times (9.302 \times 10^{9}\,\text{Hz})}{(9.2740 \times 10^{-24}\,\text{J T}^{-1}) \times (331.94 \times 10^{-3}\,\text{T})} = \boxed{2.002}$$

P12D.4 The splitting due to the two N atoms results in $2NI + 1 = 2 \times 2 \times 1 + 1 = 5$ lines with relative intensity ratio $\boxed{\text{1:2:3:2:1, a quintet}}$. Adjacent lines are separated by $a(\text{N}) = 0.148$ mT. Each of these lines is further split into a $\boxed{\text{1:4:6:4:1, a quintet}}$ by coupling to four H atoms results ($2NI + 1 = 2 \times 4 \times \frac{1}{2} + 1 = 5$). Adjacent lines in the quintet are separated by $a(\text{H}) = 0.112$ mT. Because the two hyperfine constant are similar the multiplets overlap extensively, giving a complex multiplet.

Figure 12.14 shows how the complete multiplet is formed from five overlapping 1:4:6:4:1 quintets, a–e, centred at the positions of the lines of the 1:2:3:2:1 quintet, and with intensities in proportion. For example, quintet a is centred at the field of the left-most line of the 1:2:3:2:1 a quintet, and has relative intensity 1. Quintet b is centred at the field of the next left-most line of the 1:2:3:2:1 a quintet, and has relative intensity 2. The dotted lines show the relationship of the multiplets a–e to the lines in the 1:2:3:2:1 a quintet.

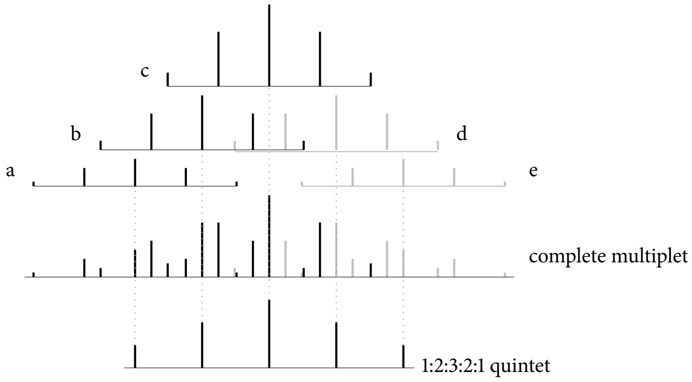


Figure 12.14

P12D.6 The McConnell equation is given in [12D.5–*521*], $a = Q\rho$, where a is the hyperfine coupling constant observed for a H atom in a given molecule, Q is a constant, and ρ is the spin density on the adjacent carbon atom. For the benzene radical anion, $Q = 2.25$ mT; the same value is used for each of the anions considered here. For example, at position 3 in **1**

$$\rho = \frac{a}{Q} = \frac{0.011\ \text{mT}}{2.25\ \text{mT}} = \boxed{4.89 \times 10^{-3}}$$

The spin densities for each carbon, computed in the same way, are shown in Fig. 12.15.

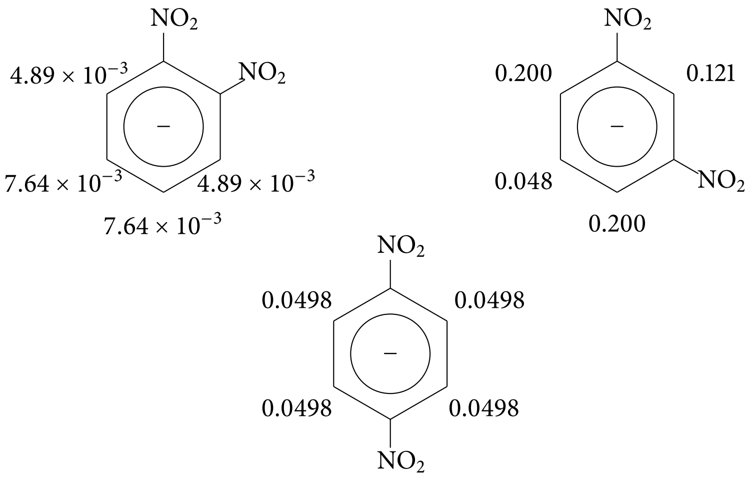
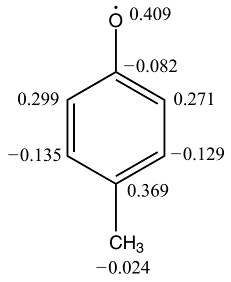


Figure 12.15

P12D.8 Simple considerations indicate that the EPR spectrum of **1** will be a 1:1:1 triplet on account of the coupling of the electron to a single ^{14}N, which has $I = 1$. Electron exchange, resulting from the physical interaction of two radicals, results in a scrambling of the spin state of the electron because the electron which is exchanged has an equal change of being in the α or β spin states. Such scrambling at first causes a broadening of the lines in the hyperfine multiplet, and if it is at a high enough rate the lines merge. For even faster rates, the merged line narrows. This is analogous to the effect that chemical exchange has on the coupling patterns seen in NMR, Section 12B.4 on page 505.

Answers to integrated activities

I12.2 (a) The spin densities, computed by molecular modelling software (ab initio, density functional theory, Gaussian 98), are shown below



The computed spin densities for the the two protons *ortho* to the oxygen, and to the two protons *meta* to the oxygen are different. This is undoubtedly a computational artefact, 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. Fast internal rotation is expected to make the two *meta* protons, and the two *ortho* protons, equivalent. The spin density at the *ortho* carbons is therefore taken as 0.285, and that at the *meta* carbons as −0.132.

(b) The hyperfine coupling constants resulting from coupling to the ring protons are computed using the McConnell equation, [12D.5–*521*]: $a = Q\rho$, with $Q = 2.25$ mT. Hence $a_{ortho} = 0.285 \times (2.25\ \text{mT}) = 0.641$ mT, and $a_{meta} = 0.132 \times (2.25\ \text{mT}) = 0.297$ mT. The hyperfine coupling for interaction with the methyl protons cannot be calcuated in the same way but is given by the software as 1.045 mT. The EPR spectrum will show a rather complex multiplet arising from splitting into a 1:2:1 triplet as a result of the coupling to the *ortho* protons, each line is then split into a 1:2:1 triplet as a result of the coupling to the *meta* protons, and each line is split once more into a 1:3:3:1 quartet as a result of the coupling to the methyl protons.

I12.4 Terms such as [I], [EI], [E], ν_I, ν_EI and ν need to be eliminated from the expressions. First, note that total I (free I plus bound I) is the same as initial I; similarly, total E (free E plus bound E) is the same as initial E.

$$[\text{I}]_\text{tot} = [\text{I}]_0 = [\text{I}] + [\text{EI}] \quad \text{and} \quad [\text{E}]_\text{tot} = [\text{E}]_0 = [\text{E}] + [\text{EI}]$$

Using this, the expression for K_I is rewritten

$$K_\text{I} = \frac{[\text{E}][\text{I}]}{[\text{EI}]} = \frac{([\text{E}]_0 - [\text{EI}])([\text{I}]_0 - [\text{EI}])}{[\text{EI}]}$$

Because $[\text{I}]_0 >> [\text{E}]_0$ it follows that $[\text{I}]_0$ must also be much greater than [EI], even if all of the E binds I. Hence $[\text{I}]_0 - [\text{EI}] \approx [\text{I}]_0$. This is substituted into the above expression which is then solved for [EI].

$$K_\text{I} = \frac{([\text{E}]_0 - [\text{EI}])[\text{I}]_0}{[\text{EI}]} \qquad \text{hence} \qquad [\text{EI}] = \frac{[\text{E}]_0[\text{I}]_0}{K_\text{I} + [\text{I}]_0} \tag{12.1}$$

The expression for ν is written using $[\text{I}] = [\text{I}]_0 - [\text{EI}]$ to give

$$\nu = f_\text{I}\nu_\text{I} + f_\text{EI}\nu_\text{EI} = \frac{[\text{I}]\nu_\text{I} + [\text{EI}]\nu_\text{EI}}{[\text{I}] + [\text{EI}]} = \frac{\nu_\text{I}([\text{I}]_0 - [\text{EI}]) + \nu_\text{EI}[\text{EI}]}{[\text{I}]_0}$$

This is rearranged to given an expression for [EI], and then [EI] is substituted using eqn 12.1

$$[\text{EI}] = \frac{(\nu - \nu_\text{I})[\text{I}]_0}{\nu_\text{EI} - \nu_\text{I}} = \frac{\delta\nu[\text{I}]_0}{\Delta\nu} \qquad \text{hence} \qquad \frac{[\text{E}]_0[\text{I}]_0}{K_\text{I} + [\text{I}]_0} = \frac{\delta\nu[\text{I}]_0}{\Delta\nu}$$

where $\delta\nu$ and $\Delta\nu$ as as defined in the text. Finally, $[\text{I}]_0$ is made the subject to give

$$\boxed{[\text{I}]_0 = \frac{\Delta\nu}{\delta\nu}[\text{E}]_0 - K_\text{I}}$$

It follows from this that a plot of $[\text{I}]_0$ against $1/(\delta\nu)$ is a straight line with slope $[\text{E}]_0\Delta\nu$ and y-intercept $-K_\text{I}$.

13 Statistical thermodynamics

13A The Boltzmann distribution

Answers to discussion questions

D13A.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 a certain amount of the energy of a molecule is in translational motion is just as likely as a state where this energy is in rotational motion, or in vibrational motion, or split between these different modes.

D13A.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. These include: the intensities of spectral transitions (Topic 11A); chemical equilibrium (Topic 13F), in which the distribution of reactant and product species is determined by a single Boltzmann distribution over the states of the system; the Maxwell–Boltzmann distribution of molecular speeds in the kinetic model of gases (Topic 1B); collision theory, in which the temperature dependence of the rate of reaction is understood through the Boltzmann distribution (Topic 18A).

Solutions to exercises

E13A.1(b) The weight of a configuration is given by [13A.1–*533*], $\mathcal{W} = N!/(N_0!N_1!N_2!...)$, thus

$$\mathcal{W} = \frac{21!}{6! \times 0! \times 5! \times 0! \times 4! \times 0! \times 3! \times 0! \times 2! \times 0! \times 0! \times 1!} = \boxed{2.05 \times 10^{12}}$$

E13A.2(b) (i) $10! = 10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1 = \boxed{3\,628\,800}$.

(ii) Stirling's approximation for $x \gg 1$ is given by [13A.2–*533*], $\ln(x!) \approx x\ln x - x$. This is rearranged for to $x! \approx e^{(x\ln x - x)}$, thus

$$10! \approx e^{(10\times\ln 10 - 10)} = \boxed{4.54 \times 10^5}.$$

(iii) Using the more accurate version of Stirling's approximation

$$10! \approx (2\pi)^{(1/2)} \times 10^{(10+1/2)} \times \mathrm{e}^{-10} = \boxed{3.60 \times 10^6}$$

E13A.3(b) The Boltzmann population ratio is given by [13A.13a–*536*], $N_i/N_j = \mathrm{e}^{-\beta(\varepsilon_i-\varepsilon_j)}$, where $\beta = 1/(kT)$. As temperature approaches zero, β approaches infinity. The relative populations of two levels, assuming $\varepsilon_0 < \varepsilon_1$, is therefore

$$N_1/N_0 = \lim_{\beta\to+\infty} \mathrm{e}^{-\beta(\varepsilon_1-\varepsilon_0)} = \boxed{0}$$

In this limit, only the lower state is occupied.

E13A.4(b) The Boltzmann population ratio is given by [13A.13a–*536*], $N_i/N_j = \mathrm{e}^{-\beta(\varepsilon_i-\varepsilon_j)}$. This is rearranged to $\beta = -\ln(N_i/N_j)/\Delta\varepsilon$, where $\Delta\varepsilon = (\varepsilon_i - \varepsilon_j)$. Substituting $\beta = 1/(kT)$ and rearranging for T gives

$$\begin{aligned} T &= -\frac{\Delta\varepsilon}{k\ln(N_1/N_0)} = -\frac{hc\tilde{\nu}}{k\ln(N_1/N_0)} \\ &= -\frac{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})\times(300\,\mathrm{cm^{-1}})}{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times\ln(1/2)} \\ &= \boxed{623\ \mathrm{K}} \end{aligned}$$

E13A.5(b) The Boltzmann population ratio for degenerate energy levels is given by [13A.13b–*536*], $N_i/N_j = (g_i/g_j)\mathrm{e}^{-\beta(\varepsilon_i-\varepsilon_j)}$. The rotational term of a spherical rotor is given by [11B.9–*432*], $\tilde{F}(J) = \tilde{B}J(J+1)$ and, as explained in Section 11B.1(c) on page 434, its degeneracy is given as $g_J = (2J+1)^2$. The rotational energy is related to the rotational term as $\varepsilon_J = hc\tilde{F}(J)$. Therefore

$$\frac{N_5}{N_0} = \frac{(2\times5+1)^2}{(2\times0+1)^2} \times \mathrm{e}^{-hc\tilde{B}[5\times(5+1)-0\times(0+1)]/kT} = 121\times\mathrm{e}^{-30\tilde{B}hc/kT}$$

using $kT/hc = 207.224\ \mathrm{cm^{-1}}$ at 298.15 K (from inside the front cover)

$$\frac{N_5}{N_0} = 121\times\mathrm{e}^{-30\times(2.71\ \mathrm{cm^{-1}})/(207.224\ \mathrm{cm^{-1}})} = \boxed{81.7}$$

E13A.6(b) The Boltzmann population ratio for degenerate energy levels is given by [13A.13b–*536*], $N_i/N_j = (g_i/g_j)\mathrm{e}^{-\beta(\varepsilon_i-\varepsilon_j)}$. This is rearranged to

$$\beta = -\ln[(N_i/N_j)(g_j/g_i)]/\Delta\varepsilon \quad \text{where} \quad \Delta\varepsilon = (\varepsilon_i - \varepsilon_j)$$

Substituting $\beta = 1/(kT)$ and rearranging for T gives

$$\begin{aligned} T &= -\frac{\Delta\varepsilon}{k\ln[(N_1/N_0)(g_0/g_1)]} = -\frac{hc\tilde{\nu}}{k\ln[(N_1/N_0)(g_0/g_1)]} \\ &= -\frac{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})\times(360\,\mathrm{cm^{-1}})}{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times\ln[(15\%/85\%)\times(1/2)]} \\ &= \boxed{213\ \mathrm{K}} \end{aligned}$$

Solutions to problems

P13A.2 The energy of a configuration is $E/\varepsilon = N_1 + 2N_2 + 3N_3 \ldots$, and the weight of a configuration is given by [13A.1–*533*], $\mathcal{W} = N!/(N_0!N_1!N_2!\ldots)$. The configurations satisfying the total energy constraint $E = 9\varepsilon$ are

N_0	N_1	N_2	N_3	N_4	N_5	N_6	N_7	N_8	N_9	$\mathcal{W}$
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
6	2	0	0	0	0	0	1	0	0	252
7	0	0	1	0	0	1	0	0	0	72
6	1	1	0	0	0	1	0	0	0	504
5	3	0	0	0	0	1	0	0	0	504
7	0	0	0	1	1	0	0	0	0	72
6	1	0	1	0	1	0	0	0	0	504
6	0	2	0	0	1	0	0	0	0	252
5	2	1	0	0	1	0	0	0	0	1512
4	4	0	0	0	1	0	0	0	0	630
6	1	0	0	2	0	0	0	0	0	252
6	0	1	1	1	0	0	0	0	0	504
5	1	2	0	1	0	0	0	0	0	1512
4	3	1	0	1	0	0	0	0	0	2520
3	5	0	0	1	0	0	0	0	0	504
6	0	0	3	0	0	0	0	0	0	84
5	1	1	2	0	0	0	0	0	0	1512
4	3	0	2	0	0	0	0	0	0	1260
5	0	3	1	0	0	0	0	0	0	504
4	2	2	1	0	0	0	0	0	0	3780
3	4	1	1	0	0	0	0	0	0	2520
2	6	0	1	0	0	0	0	0	0	252
4	1	4	0	0	0	0	0	0	0	630
3	3	3	0	0	0	0	0	0	0	1680
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

Hence the most probable configuration is $\boxed{\{4,2,2,1,0,0,0,0,0,0\}}$, which is the most reminiscent of an exponential distribution.

P13A.4 The Boltzmann distribution is given by [13A.10b–*535*], $N_i/N = \mathrm{e}^{-\beta\varepsilon_i}/q$, where q is the partition function defined in [13A.11–*535*], $q = \sum_i \mathrm{e}^{-\beta\varepsilon_i}$, and $\beta = 1/(kT)$.

Without loss of generality let the energy of A be 0, which implies that $\varepsilon_B = 5.0\ \text{kJ mol}^{-1}$ and $\varepsilon_C = \varepsilon_B + 0.5\ \text{kJ mol}^{-1} = 5.5\ \text{kJ mol}^{-1}$. The partition function is

$$q = e^{-\beta\varepsilon_A} + e^{-\beta\varepsilon_B} + e^{-\beta\varepsilon_C} = 1 + e^{-\beta\varepsilon_B} + e^{-\beta\varepsilon_C}$$

The proportion of molecules in conformation B is

$$\frac{N_B}{N} = \frac{e^{-\beta\varepsilon_B}}{q} = \frac{e^{-\beta\varepsilon_B}}{1 + e^{-\beta\varepsilon_B} + e^{-\beta\varepsilon_C}}$$

Because $\varepsilon_i = E_i/N_A$ and $k = R/N_A$, $\beta\varepsilon_i = E_i/RT$, it follows that

$$\begin{aligned}\frac{N_B}{N} &= \frac{e^{-E_B/RT}}{1 + e^{-E_B/RT} + e^{-E_C/RT}} \\ &= \frac{e^{-\frac{5.0\times10^3\ \text{J mol}^{-1}}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(273\ \text{K})}}}{1 + e^{-\frac{5.0\times10^3\ \text{J mol}^{-1}}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(273\ \text{K})}} + e^{-\frac{5.5\times10^3\ \text{J mol}^{-1}}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(273\ \text{K})}}} \\ &= \boxed{0.092}\end{aligned}$$

P13A.6 In Section 13A.1(a) on page 532 it is shown that $\ln \mathcal{W} = \ln N! - \sum_i \ln N_i!$. The full version of Stirling's approximation is used for the factorials to give

$$\begin{aligned}\ln \mathcal{W} &= \ln[(2\pi)^{1/2}N^{N+1/2}e^{-N}] - \sum_j \ln[(2\pi)^{1/2}N_j^{N_j+1/2}e^{-N_j}] \\ &= \tfrac{1}{2}\ln(2\pi) + (N+\tfrac{1}{2})\ln N - N - \sum_j\left[\tfrac{1}{2}\ln(2\pi) + (N_j+\tfrac{1}{2})\ln N_j - N_j\right]\end{aligned}$$

Because $\sum_j N_j = N$ it follows that

$$\ln \mathcal{W} = \tfrac{1}{2}\ln(2\pi) + \underbrace{(N+\tfrac{1}{2})\ln N}_{A} - \underbrace{\sum_j\left[(N_j+\tfrac{1}{2})\ln N_j\right.}_{B} \left.+ \tfrac{1}{2}\ln(2\pi)\right]$$

The next step is to compute $\partial \ln \mathcal{W}/\partial N_i$: only the non-constant terms A and B contribute to the derivative. First, consider the differential of term A

$$\begin{aligned}\frac{\partial[(N+\frac{1}{2})\ln N]}{\partial N_i} &= \left(\frac{\partial(N+\frac{1}{2})}{\partial N_i}\right)\ln N + (N+\tfrac{1}{2})\left(\frac{\partial \ln N}{\partial N_i}\right) \\ &= \left(\frac{\partial N}{\partial N_i}\right)\ln N + (N+\tfrac{1}{2})\frac{1}{N}\left(\frac{\partial N}{\partial N_i}\right)\end{aligned}$$

As explained in the text, $(\partial N/\partial N_i) = 1$. It therefore follows that

$$\frac{\partial[(N+\frac{1}{2})\ln N]}{\partial N_i} = \ln N + (N+\tfrac{1}{2})\frac{1}{N} = \ln N + \frac{N+\frac{1}{2}}{N}$$

Next, consider the differential of term B

$$\begin{aligned}\frac{\partial \sum_j \left[(N_j + \frac{1}{2})\ln N_j\right]}{\partial N_i} &= \sum_j \left[\left(\frac{\partial(N_j + \frac{1}{2})}{\partial N_i}\right)\ln N_j + (N_j + \tfrac{1}{2})\left(\frac{\partial \ln N_j}{\partial N_i}\right)\right] \\ &= \sum_j \left[\left(\frac{\partial(N_j + \frac{1}{2})}{\partial N_i}\right)\ln N_j + (N_j + \tfrac{1}{2})\frac{1}{N_j}\left(\frac{\partial N_j}{\partial N_i}\right)\right]\end{aligned}$$

Only the derivatives with $j = i$ are non-zero to give

$$= \ln N_i + \frac{N_i + \frac{1}{2}}{N_i}$$

Bringing the terms together gives the expression for the derivative

$$\frac{\partial \ln \mathcal{W}}{\partial N_i} = \ln N + \frac{N + \frac{1}{2}}{N} - \ln N_i - \frac{N_i + \frac{1}{2}}{N_i}$$

For a macroscopic sample $N \gg 1$ and $N_i \gg 1$, so $N + \frac{1}{2} \approx N$ and $N_i + \frac{1}{2} \approx N_i$; with these approximations

$$\frac{\partial \ln \mathcal{W}}{\partial N_i} = \ln N + 1 - (\ln N_i + 1)$$

This is identical to the expression found in *How is that done?* 13A.3 on page 534, and so it is concluded that for macroscopic samples the use of the full version of Stirling's approximation has no effect (with the possible exception of states with very low populations).

13B **Partition functions**

Answer to discussion questions

D13B.2 It is possible for there to be different wavefunctions which have the same energy: such wavefunctions are said to be degenerate. If this is the case, for a given 'energy level', that is a given value of the energy, there are several 'states' each of which is distinct but has the same energy.

The partition function is computed as a sum over the states. However, because degenerate states have the same energy, the sum may be computed as a sum over energy levels, as long as the degeneracy g_i of each level is taken into account.

$$q = \sum_{\text{states } i} e^{-\beta\varepsilon_i} = \sum_{\text{levels } i} g_i e^{-\beta\varepsilon_i}$$

Solutions to exercises

E13B.1(b) (i) The thermal wavelength is defined in [13B.7–*541*], $\Lambda = h/(2\pi mkT)^{1/2}$. Because the mass of a molecule m is $m = M/N_A$ and $k = R/N_A$ it follows that

$$\Lambda = \frac{h}{[2\pi(M/N_A)(R/N_A)T]^{1/2}} = \frac{hN_A}{(2\pi MRT)^{1/2}}$$

$$\begin{aligned}\Lambda(300\text{ K}) &= \frac{(6.6261\times10^{-34}\text{ J s})\times(6.0221\times10^{23}\text{ mol}^{-1})}{[2\pi\times(0.02018\text{ kg mol}^{-1})\times(8.3145\text{ J K}^{-1}\text{ mol}^{-1})\times(300\text{ K})]^{1/2}}\\ &= 2.24...\times10^{-11}\text{ m} = \boxed{2.244\times10^{-11}\text{ m}}\end{aligned}$$

Similarly, $\Lambda(3000\text{ K}) = \boxed{7.095\times10^{-12}\text{ m}}$

(ii) The translational partition function in three dimensions is given by [13B.10b–*541*], $q^{\mathrm{T}} = V/\Lambda^3$.

$$q^{\mathrm{T}}(300\text{ K}) = (1.00\times10^{-6}\text{ m}^3)/(2.24...\times10^{-11}\text{ m})^3 = \boxed{8.85\times10^{25}}$$

$$q^{\mathrm{T}}(3000\text{ K}) = \boxed{2.80\times10^{27}}$$

E13B.2(b) The translational partition function in three dimensions is given by [13B.10b–*541*], $q^{\mathrm{T}} = V/\Lambda^3$, where Λ is the thermal wavelength defined in [13B.7–*541*], $\Lambda = h/(2\pi mkT)^{1/2}$.

$$\frac{q^{\mathrm{T}}_{\mathrm{Ar}}}{q^{\mathrm{T}}_{\mathrm{Ne}}} = \frac{V/\Lambda^3_{\mathrm{Ar}}}{V/\Lambda^3_{\mathrm{Ne}}} = \left(\frac{\Lambda_{\mathrm{Ne}}}{\Lambda_{\mathrm{Ar}}}\right)^3 = \left(\frac{h/(2\pi m_{\mathrm{Ne}}kT)^{1/2}}{h/(2\pi m_{\mathrm{Ar}}kT)^{1/2}}\right)^3 = \left(\frac{m_{\mathrm{Ar}}}{m_{\mathrm{Ne}}}\right)^{3/2}$$

Because the mass of a molecule m is $m = M/N_A$ it follows that

$$\frac{q^{\mathrm{T}}_{\mathrm{Ar}}}{q^{\mathrm{T}}_{\mathrm{Ne}}} = \left(\frac{M_{\mathrm{Ar}}}{M_{\mathrm{Ne}}}\right)^{3/2} = \left(\frac{39.95\text{ g mol}^{-1}}{20.18\text{ g mol}^{-1}}\right)^{3/2} = \boxed{2.785}$$

E13B.3(b) The rotational partition function of a symmetric linear rotor is given by [13B.13a–*544*], $q^{\mathrm{R}} = kT/(2hc\tilde{B})$, where the rotational constant is defined in [11B.7–*432*], $\tilde{B} = \hbar/(4\pi cI)$. The moment of inertia of a diatomic is $I = \mu R^2$, where R is the bond length and $\mu = m_A m_B/(m_A+m_B)$. For a homonuclear diatomic $m_A = m_B$ so it follows that $\mu = m_B/2$. Using $m = M/N_A$, this becomes $\mu = M_B/2N_A$.

$$\begin{aligned}I = \mu R^2 &= \frac{M_B R^2}{2N_A} = \frac{(0.01401\text{ kg mol}^{-1})\times(109.75\times10^{-12}\text{ m})^2}{2\times(6.0221\times10^{23}\text{ mol}^{-1})}\\ &= 1.40...\times10^{-46}\text{ kg m}^2\end{aligned}$$

$$\begin{aligned}q^{\mathrm{R}} &= \frac{kT}{2hc\tilde{B}} = \left(\frac{kT}{2hc}\right)\left(\frac{4\pi cI}{\hbar}\right) = \left(\frac{kT}{4\pi c\hbar}\right)\left(\frac{4\pi cI}{\hbar}\right) = \frac{kT}{\hbar^2}I\\ &= \frac{(1.3806\times10^{-23}\text{ J K}^{-1})\times(300\text{ K})}{(1.0546\times10^{-34}\text{ J s})^2}\times(1.40...\times10^{-46}\text{ kg m}^2) = \boxed{52.2}\end{aligned}$$

E13B.4(b) The rotational partition function of a non-linear rotor is given by [13B.14–*545*], $q^{\mathrm{R}} = (1/\sigma)(kT/hc)^{3/2}(\pi/\tilde{A}\tilde{B}\tilde{C})^{1/2}$, where σ is the symmetry number. H_2O has a twofold axis so $\sigma = 2$.

(i) At 25 °C, which is 298.15 K

$$\begin{aligned}q^{\mathrm{R}} &= \frac{1}{2}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2}\\ &= \frac{1}{2}\times\left(\frac{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298.15\,\mathrm{K})}{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})}\right)^{3/2}\\ &\quad\times\left(\frac{\pi}{(27.877\,\mathrm{cm^{-1}})\times(14.512\,\mathrm{cm^{-1}})\times(9.285\,\mathrm{cm^{-1}})}\right)^{1/2}\\ &= \boxed{43.1}\end{aligned}$$

(ii) At 100 °C, which is 373.15 K

$$\begin{aligned}q^{\mathrm{R}} &= \frac{1}{2}\times\left(\frac{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(373.15\,\mathrm{K})}{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})}\right)^{3/2}\\ &\quad\times\left(\frac{\pi}{(27.877\,\mathrm{cm^{-1}})\times(14.512\,\mathrm{cm^{-1}})\times(9.285\,\mathrm{cm^{-1}})}\right)^{1/2}\\ &= \boxed{60.4}\end{aligned}$$

E13B.5(b) The rotational partition function of a heteronuclear diatomic is given by [13B.11–*542*], $q^{\mathrm{R}} = \sum_J(2J+1)\mathrm{e}^{-\beta hc\tilde{B}J(J+1)}$. This is evaluated explicitly by summing successive terms until they become too small to affect the result to a given level of precision. The partition function in the high-temperature limit is given by [13B.12a–*543*], $q^{\mathrm{R}} = kT/hc\tilde{B}$. For the data given it follows that

$$\begin{aligned}q^{\mathrm{R}} &= \frac{k\times T}{hc\tilde{B}} = \frac{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times T}{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})\times(6.511\,\mathrm{cm^{-1}})}\\ &= (0.106...\,\mathrm{K^{-1}})\times T\end{aligned}$$

The values of q^{R} computed in these two different ways are compared in Fig. 13.1. The high temperature limit becomes accurate to within 5 % of the exact solution at around $\boxed{61\ \mathrm{K}}$.

E13B.6(b) The partition function is given by [13B.1b–*538*], $q^{\mathrm{R}} = \sum_J g_J\mathrm{e}^{-\beta\varepsilon_J}$, where the degeneracy is given as $g_J = (2J+1)^2$, as explained in Section 11B.1(c) on page 434, and ε_J is given by [13B.1b–*538*], $\varepsilon_J = hc\tilde{B}J(J+1)$. This is evaluated explicitly by summing successive terms until they become too small to affect the result to a given level of precision.

The partition function in the high-temperature limit is given by [13B.12b–*544*], $q^{\mathrm{R}} = (kT/hc)^{3/2}(\pi/\tilde{A}\tilde{B}\tilde{C})^{1/2} = \pi^{1/2}(kT/hc\tilde{B})^{3/2}$, because for a spherical rotor

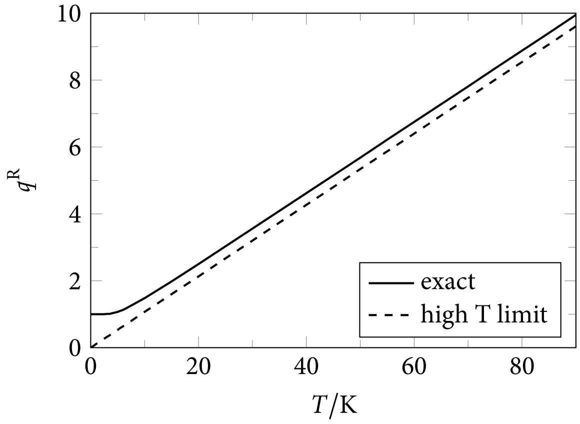


Figure 13.1

$\tilde{B} = \tilde{A} = \tilde{C}$. Ignoring the role of the nuclear spin means that all J states are accessible and have equal weight. For the data given it follows that

$$\begin{aligned}
q^R &= \pi^{1/2}\left(\frac{k \times T}{hc\tilde{B}}\right)^{3/2}\\
&= \pi^{1/2}\left(\frac{(1.3806 \times 10^{-23}\,\text{J K}^{-1})}{(6.6261 \times 10^{-34}\,\text{J s})\times(2.9979 \times 10^{10}\,\text{cm s}^{-1})\times(0.0572\,\text{cm}^{-1})}\right)^{3/2} \times T^{3/2}\\
&= (75.0...\,\text{K}^{-3/2}) \times T^{3/2}
\end{aligned}$$

The values of q^R computed in these two different ways are compared in Fig. 13.2. The high temperature limit becomes accurate to within 5 % of the exact solution at around $\boxed{0.4\ \text{K}}$.

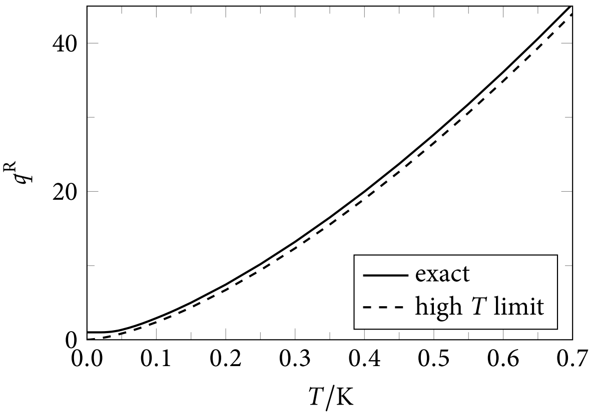


Figure 13.2

E13B.7(b) (i) CO_2 is a centrosymmetric linear molecule and so has $\boxed{\sigma = 2}$.

(ii) O_3 has a twofold rotational axis bisecting the O–O–O angle; rotation about this axis interchanges two identical oxygen atoms, therefore $\boxed{\sigma = 2}$.

(iii) SO_3 is trigonal planar. It has a threefold rotational axis perpendicular to the plane of the molecule and passing through the S atom, and three twofold axes, each located along an S–O bond. The symmetry number is therefore given by $\boxed{\sigma = 3 \times 2 = 6}$.

(iv) For a molecule with high symmetry, such as octahedral SF_6, the simplest was to determine the symmetry number is to count the total number of rotational symmetry operations, C_n, listed in the character table of the relevant point group, which in this case is O_h. The identity operation E is equivalent to a C_1 rotation axis, so is included in the count. For O_h the relevant operations are $(E, 8C_3, 6C_2, 6C_4, 3C_2)$, giving a total of 24. Hence $\boxed{\sigma = 24}$.

(v) The same procedure is used as in (iv). Al_2Cl_6 belongs to the point group D_{2h}, which has rotational operations (E, C_2^x, C_2^y, C_2^z). Therefore $\boxed{\sigma = 4}$.

E13B.8(b) The rotational partition function of an asymmetric rotor is given by [13B.14–*545*], $q^R = (1/\sigma)(kT/hc)^{3/2}(\pi/\tilde{A}\tilde{B}\tilde{C})^{1/2}$, where σ is the symmetry number. Pyridine has a twofold rotational axis along the C_4–N bond; rotation about this axis interchanges pairs of identical atoms, therefore $\sigma = 2$. An alternative way of deriving the value of the symmetry number is to note that both pyridine and H_2O belong to the point group C_{2v}, and so they have the same symmetry number, which in the text is shown to be 2 for H_2O.

$$\begin{aligned} q^R &= \frac{1}{2}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2} \\ &= \frac{1}{2} \times \left(\frac{(1.3806 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298.15\,\mathrm{K})}{(6.6261 \times 10^{-34}\,\mathrm{J\,s}) \times (2.9979 \times 10^{10}\,\mathrm{cm\,s^{-1}})}\right)^{3/2} \\ &\quad \times \left(\frac{\pi}{(0.2014\,\mathrm{cm^{-1}}) \times (0.1936\,\mathrm{cm^{-1}}) \times (0.0987\,\mathrm{cm^{-1}})}\right)^{1/2} \\ &= \boxed{4.26 \times 10^4} \end{aligned}$$

E13B.9(b) The vibrational partition function is given by [13B.15–*546*], $q^V = 1/(1-e^{-\beta hc\tilde{\nu}})$, where $\beta = 1/kT$. The high-temperature approximation is given by [13B.16–*547*], $q^V \approx kT/hc\tilde{\nu}$.

$$\begin{aligned} \frac{k \times T}{hc\tilde{\nu}} &= \frac{(1.3806 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times T}{(6.6261 \times 10^{-34}\,\mathrm{J\,s}) \times (2.9979 \times 10^{10}\,\mathrm{cm\,s^{-1}}) \times (214.5\,\mathrm{cm^{-1}})} \\ &= (3.24... \times 10^{-3}\,\mathrm{K^{-1}}) \times T \end{aligned}$$

The values of q^V computed using these two different expressions are compared in Fig. 13.3. The high temperature limit becomes accurate to within 5 % of the exact solution at $\boxed{3000\,\mathrm{K}}$.

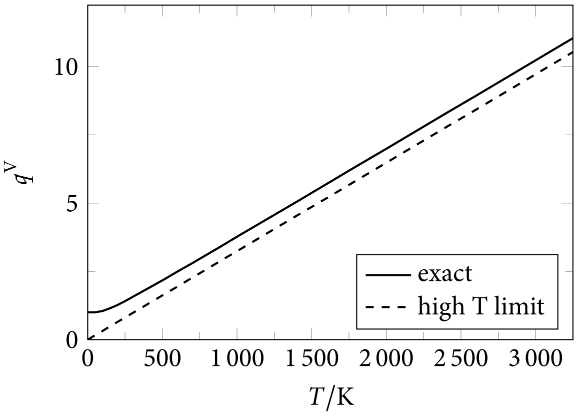


Figure 13.3

E13B.10(b) The vibrational partition function for each mode is given by [13B.15–*546*], $q^V = 1/(1-e^{-\beta hc\tilde{\nu}})$, where $\beta = 1/kT$. The overall vibrational partition function is the product of the partition functions of the individual modes; the bend is included twice as it is doubly degenerate.

$$hc\beta = \frac{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})}{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(900\,\mathrm{K})}$$
$$= 1.59...\times10^{-3}\,\mathrm{cm}$$

$$q_1^V = \left(1-e^{-hc\beta\tilde{\nu}_1}\right)^{-1}$$
$$= \left(1-e^{-(1.59...\times10^{-3}\,\mathrm{cm})\times(3311\,\mathrm{cm^{-1}})}\right)^{-1} = 1.00...$$

Similarly

$$q_2^V = \left(1-e^{-(1.59...\times10^{-3}\,\mathrm{cm})\times(712\,\mathrm{cm^{-1}})}\right)^{-1} = 1.47...$$
$$q_3^V = \left(1-e^{-(1.59...\times10^{-3}\,\mathrm{cm})\times(2097\,\mathrm{cm^{-1}})}\right)^{-1} = 1.03...$$

$$q^V = q_1^V \times (q_2^V)^2 \times q_3^V = (1.00...)\times(1.47...)^2\times(1.03...) = \boxed{2.25}$$

E13B.11(b) The vibrational partition function for each mode is given by [13B.15–*546*], $q^V = 1/(1-e^{-\beta hc\tilde{\nu}})$, where $\beta = 1/kT$. The overall vibrational partition function is the product of the partition functions of the individual modes, taking into account the stated degeneracies.

$$hc\beta = \frac{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})}{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(500\,\mathrm{K})}$$
$$= 2.87...\times10^{-3}\,\mathrm{cm}$$

$$\begin{aligned} q_1^{\mathrm{V}} &= \left(1 - \mathrm{e}^{-hc\beta\tilde{\nu}_1}\right)^{-1} \\ &= \left(1 - \mathrm{e}^{-(2.87...\times10^{-3}\ \mathrm{cm})\times(178\ \mathrm{cm}^{-1})}\right)^{-1} = 2.49... \end{aligned}$$

Similarly

$$\begin{aligned} q_2^{\mathrm{V}} &= \left(1 - \mathrm{e}^{-(2.87...\times10^{-3}\ \mathrm{cm})\times(90\ \mathrm{cm}^{-1})}\right)^{-1} = 4.38... \\ q_3^{\mathrm{V}} &= \left(1 - \mathrm{e}^{-(2.87...\times10^{-3}\ \mathrm{cm})\times(555\ \mathrm{cm}^{-1})}\right)^{-1} = 1.25... \\ q_4^{\mathrm{V}} &= \left(1 - \mathrm{e}^{-(2.87...\times10^{-3}\ \mathrm{cm})\times(125\ \mathrm{cm}^{-1})}\right)^{-1} = 3.30... \end{aligned}$$

$$\begin{aligned} q^{\mathrm{V}} &= q_1^{\mathrm{V}} \times (q_2^{\mathrm{V}})^2 \times (q_3^{\mathrm{V}})^3 \times (q_4^{\mathrm{V}})^3 \\ &= (2.49...) \times (4.38...)^2 \times (1.25...)^3 \times (3.30...)^3 = \boxed{3.43 \times 10^3} \end{aligned}$$

E13B.12(b) The partition function is given by [13B.1b–*538*], $q = \sum_i g_i \mathrm{e}^{-\beta\varepsilon_i}$, where g_i is degeneracy and the corresponding energy is given as $\varepsilon_i = hc\tilde{\nu}_i$. At $T = 2000$ K

$$\beta hc = \frac{(6.6261 \times 10^{-34}\ \mathrm{J\,s}) \times (2.9979 \times 10^{10}\ \mathrm{cm\,s^{-1}})}{(1.3806 \times 10^{-23}\ \mathrm{J\,K^{-1}}) \times (1900\ \mathrm{K})} = 7.19... \times 10^{-4}\ \mathrm{cm}$$

Therefore the electronic partition function is

$$\begin{aligned} q^{\mathrm{E}} &= g_0 + g_1 \times \mathrm{e}^{-\beta\varepsilon_1} + g_2 \times \mathrm{e}^{-\beta\varepsilon_2} \\ &= 3 + 1 \times \mathrm{e}^{-(7.19...\times10^{-4}\ \mathrm{cm})\times(850\ \mathrm{cm}^{-1})} \\ &+ 5 \times \mathrm{e}^{-(7.19...\times10^{-4}\ \mathrm{cm})\times(1100\ \mathrm{cm}^{-1})} \\ &= 3 + 0.542... + 2.26... = \boxed{5.809} \end{aligned} \tag{13.1}$$

The population of level i with degeneracy g_i is $N_i = (Ng_i/q)\mathrm{e}^{-\beta\varepsilon_i}$, therefore the relative populations of the levels are proportional to $g_i\mathrm{e}^{-\beta\varepsilon_i}$, which are the terms in eqn 13.1. Thus the populations, relative the ground state are

$$\begin{aligned} N_0/N_0 : N_1/N_0 : N_2/N_0 &= 3/3 : (0.542.../3) : (2.26.../3) \\ &= \boxed{1 : 0.181 : 0.755} \end{aligned}$$

Solutions to problems

P13B.2 The vibrational partition function is given by [13B.15–*546*], $q^{\mathrm{V}} = 1/(1-\mathrm{e}^{-\beta hc\tilde{\nu}})$, where $\beta = 1/kT$ and $\tilde{\nu}$ is the wavenumber of the vibration. The high-temperature approximation is given by [13B.16–*547*], $q_{\mathrm{HT}}^{\mathrm{V}} = kT/hc\tilde{\nu}$. If the characteristic vibrational temperature θ^{V} is defined as $\theta^{\mathrm{V}} = hc\tilde{\nu}/k$, the two forms of the partition function become

$$q^{\mathrm{V}} = \frac{1}{1 - \mathrm{e}^{-\theta^{\mathrm{V}}/T}} \qquad q_{\mathrm{HT}}^{\mathrm{V}} = \frac{T}{\theta^{\mathrm{V}}}$$

Plotting these as a function of T/θ^{V} gives a universal curve which applies to all vibrational wavenumbers; such a plot is shown in Fig 13.4. The high-temperature value is within 10% of the exact value when

$$(q^{\mathrm{V}} - q^{\mathrm{V}}_{\mathrm{HT}})/q^{\mathrm{V}} = 0.1$$

There is no analytical solution for the value of T/θ^{V} which solves this equation. However, by plotting the fraction on the left against T/θ^{V}, it is easy to see that this 10% deviation is reached when $T/\theta^{\mathrm{V}} \approx 4.7$

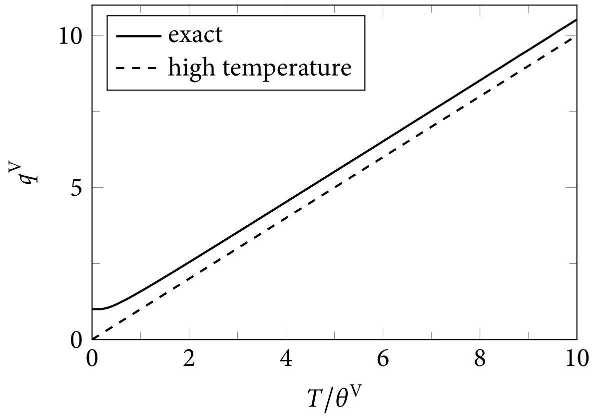


Figure 13.4

P13B.4 The translational partition function for a particle in a one-dimensional box of width X is given by [13B.7–*541*], $q^{\mathrm{T}}_X = X/\Lambda$ where $\Lambda = h/(2\pi mkT)^{1/2}$. This expression is rearranged to give the temperature in terms of Λ, and then in terms of q^{T}_X

$$T = \frac{h^2}{2\pi mk\Lambda^2} = \frac{h^2(q^{\mathrm{T}}_X)^2}{2\pi mkX^2}$$

The expression is further developed using $m = M/N_{\mathrm{A}}$ and $k = R/N_{\mathrm{A}}$, and then evaluated for the given data and $q^{\mathrm{T}}_X = 10$

$$\begin{aligned} T &= \frac{N_{\mathrm{A}}^2 h^2 (q^{\mathrm{T}}_X)^2}{2\pi MRX^2} \\ &= \frac{(6.0221\times10^{23}\,\mathrm{mol^{-1}})^2 \times (6.6261\times10^{-34}\,\mathrm{J\,s})^2 \times (10)^2}{2\pi \times (1.008\times10^{-3}\,\mathrm{kg\,mol^{-1}}) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})} \\ &\quad \times \frac{1}{(100\times10^{-9}\,\mathrm{m})^2} \\ &= 0.0302...\,\mathrm{K} = \boxed{0.030\,\mathrm{K}}. \end{aligned}$$

As explained in Section 13B.2(a) on page 540, the exact partition function is given as $q^{\mathrm{T}}_X = \sum_{n=1}^{\infty} \mathrm{e}^{-(n^2-1)\beta\varepsilon}$, where $\varepsilon = h^2/8mX^2$ and $\beta = 1/kT$. For the given data $\beta\varepsilon$ is evaluated at the above temperature as

$$\beta\varepsilon = \frac{h^2}{8mkTX^2} = \frac{h^2 N_A^2}{8MRTX^2}$$
$$= \frac{(6.0221\times10^{23}\,\mathrm{mol^{-1}})^2\times(6.6261\times10^{-34}\,\mathrm{J\,s})^2}{8\times(1.008\times10^{-3}\,\mathrm{kg\,mol^{-1}})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})}$$
$$\times\frac{1}{(0.0302...\,\mathrm{K})\times(100\times10^{-9}\,\mathrm{m})^2} = 0.00785...$$

With this value the partition function is then evaluated term by term to give

$$q_X^{\mathrm{T}} = \sum_{n=1}^{\infty} \mathrm{e}^{-(n^2-1)\beta\varepsilon} = 1 + \mathrm{e}^{-3\beta\varepsilon} + \mathrm{e}^{-8\beta\varepsilon} + \mathrm{e}^{-15\beta\varepsilon} + ...$$
$$= 1 + 0.977... + 0.939... + 0.889... + ... = \boxed{9.57}$$

Even under these conditions, the integral approximation deviates by less than 5% from the explicit sum.

P13B.6 The partition function is given by [13B.1b–*538*], $q = \sum_i g_i \mathrm{e}^{-\beta\varepsilon_i}$, where g_i is degeneracy and the corresponding energy is given as $\varepsilon_i = hc\tilde{\nu}_i$, and $\beta = 1/kT$. Here $g_i = 2J + 1$, where J is the right subscript in the term symbol. At 3287 °C, which is 3556 K

$$hc\beta = \frac{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})}{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(3556\,\mathrm{K})} = 4.04...\times10^{-4}\,\mathrm{cm}$$

Therefore the electronic partition function is

$$q^{\mathrm{E}} = 5 + 7\times\mathrm{e}^{-(4.04...\times10^{-4}\,\mathrm{cm})\times(170\,\mathrm{cm^{-1}})}$$
$$+ 9\times\mathrm{e}^{-(4.04...\times10^{-4}\,\mathrm{cm})\times(387\,\mathrm{cm^{-1}})} + 3\times\mathrm{e}^{-(4.04...\times10^{-4}\,\mathrm{cm})\times(6557\,\mathrm{cm^{-1}})}$$
$$= 5 + 6.53... + 7.69... + 0.211... = 19.4....$$

The population of level i is $N_i/N = (g_i \times \mathrm{e}^{-hc\beta\tilde{\nu}_i})/q^{\mathrm{E}}$. Thus

$$\frac{N(^3\mathrm{F}_2)}{N} = \frac{5}{19.4...} = \boxed{0.257} \qquad \frac{N(^3\mathrm{F}_3)}{N} = \frac{6.53...}{19.4...} = \boxed{0.336}$$
$$\frac{N(^3\mathrm{F}_4)}{N} = \frac{7.69...}{19.4...} = \boxed{0.396} \qquad \frac{N(^5\mathrm{F}_1)}{N} = \frac{0.211...}{19.4...} = \boxed{0.0109}$$

P13B.8 The wavenumbers of the lines in the pure rotational spectrum of a diatomic are given by [11B.20a–*436*], $\tilde{\nu}(J+1 \leftarrow J) = 2\tilde{B}(J+1)$. Therefore a plot of $\tilde{\nu}(J+1\leftarrow J)$ against $2(J+1)$ is expected to be a straight line with slope $\tilde{B}$. The separation of successive lines is $2\tilde{B}$, and from the first few lines a consistent value of $\tilde{B} \approx 10.6\,\mathrm{cm^{-1}}$ is found. Using this, the assignment of the lines is confirmed as $1 \leftarrow 0$ for that at $21.19\,\mathrm{cm^{-1}}$, and $2 \leftarrow 1$ for that at $42.37\,\mathrm{cm^{-1}}$. The given lines are therefore successive members of $\tilde{\nu}(J+1 \leftarrow J)$ starting from

$J = 0$. With the lines assigned the plot can be made and indeed it is a very good straight line whose slope gives $\tilde{B} = 10.593\ \text{cm}^{-1}$.

The rotational partition function of a heteronuclear diatomic is given by [13B.11–*542*], $q^{\text{R}} = \sum_J (2J+1)\text{e}^{-\beta hc\tilde{B}J(J+1)}$. At 25 °C, $kT/hc = 207.225\ \text{cm}^{-1}$.

$$\beta hc\tilde{B} = (10.593\ \text{cm}^{-1})/(207.225\ \text{cm}^{-1}) = 5.11... \times 10^{-2}$$

Evaluating the sum term by term gives $\boxed{q^{\text{R}}=19.90}$; the terms with $J > 14$ do not contribute significantly.

P13B.10 The partition function is given by [13B.1a–*538*], $q = \sum_i \text{e}^{-\beta\varepsilon_i}$, where the energy of state i is given as $\varepsilon_i = hc\tilde{\nu}_i$, and $\beta = 1/kT$.

$$q^{\text{V}} = 1 + \text{e}^{-hc\beta\tilde{\nu}_1} + \text{e}^{-hc\beta\tilde{\nu}_2} + \text{e}^{-hc\beta\tilde{\nu}_3} + \text{e}^{-hc\beta\tilde{\nu}_4}$$

The population of state i is $N_i/N = \text{e}^{-hc\tilde{\nu}_i/(kT)}/q^{\text{V}}$

(a) At $T = 100$ K

$$hc\beta = \frac{(6.6261\times10^{-34}\ \text{J s})\times(2.9979\times10^{10}\ \text{cm s}^{-1})}{(1.3806\times10^{-23}\ \text{J K}^{-1})\times(100\ \text{K})} = 1.43...\times10^{-2}\ \text{cm}$$

$$\begin{aligned} q^{\text{V}} &= 1 + \text{e}^{-(1.43...\times10^{-2}\ \text{cm})\times(215.30\ \text{cm}^{-1})} + \text{e}^{-(1.43...\times10^{-2}\ \text{cm})\times(425.39\ \text{cm}^{-1})} \\ &\quad + \text{e}^{-(1.43...\times10^{-2}\ \text{cm})\times(636.27\ \text{cm}^{-1})} + \text{e}^{-(1.43...\times10^{-2}\ \text{cm})\times(845.93\ \text{cm}^{-1})} \\ &= 1 + 0.0451... + 2.19...\times10^{-3} + 1.05...\times10^{-4} + 5.17...\times10^{-6} \\ &= 1.04... = \boxed{1.05} \end{aligned}$$

$$\begin{aligned} N_0/N &= 1/1.04... = \boxed{0.955} \\ N_1/N &= 0.0451.../1.04... = \boxed{4.31\times10^{-2}} \\ N_2/N &= (2.19...\times10^{-3})/1.04... = \boxed{2.10\times10^{-3}} \end{aligned}$$

(b) At $T = 298$ K

$$hc\beta = \frac{(6.6261\times10^{-34}\ \text{J s})\times(2.9979\times10^{10}\ \text{cm s}^{-1})}{(1.3806\times10^{-23}\ \text{J K}^{-1})\times(298\ \text{K})} = 4.82...\times10^{-3}\ \text{cm}$$

$$\begin{aligned} q^{\text{V}} &= 1 + \text{e}^{-(4.82...\times10^{-3}\ \text{cm})\times(215.30\ \text{cm}^{-1})} + \text{e}^{-(4.82...\times10^{-3}\ \text{cm})\times(425.39\ \text{cm}^{-1})} \\ &\quad + \text{e}^{-(4.82...\times10^{-3}\ \text{cm})\times(636.27\ \text{cm}^{-1})} + \text{e}^{-(4.82...\times10^{-3}\ \text{cm})\times(845.93\ \text{cm}^{-1})} \\ &= 1 + 0.353... + 0.128... + 4.63...\times10^{-2} + 1.68...\times10^{-2} \\ &= 1.54... = \boxed{1.54} \end{aligned}$$

$$\begin{aligned} N_0/N &= 1/1.54... = \boxed{0.647} \\ N_1/N &= 0.353.../1.54... = \boxed{0.229} \\ N_2/N &= 0.128.../1.54... = \boxed{8.30\times10^{-2}} \end{aligned}$$

13C Molecular energies

Answers to discussion questions

D13C.2 This is described in *Brief illustration* 13C.1 on page 550.

Solutions to exercises

E13C.1(b) The mean energy of a molecule is given by [13C.2–*549*], $\langle\varepsilon\rangle = (1/q)\sum_i \varepsilon_i \mathrm{e}^{-\beta\varepsilon_i}$, where $\varepsilon_i = hc\tilde{\nu}_i$, $\beta = 1/kT$, and q is the partition function given by [13A.11–*535*], $q = \sum_i \mathrm{e}^{-\beta\varepsilon_i}$. Therefore for the two-level system

$$\begin{aligned}\langle\varepsilon\rangle &= \frac{0+\varepsilon\mathrm{e}^{-\beta\varepsilon}}{1+\mathrm{e}^{-\beta\varepsilon}} = \frac{\varepsilon}{\mathrm{e}^{\beta\varepsilon}+1} = \frac{hc\tilde{\nu}}{\mathrm{e}^{hc\tilde{\nu}/kT}+1}\\ &= \frac{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})\times(600\,\mathrm{cm^{-1}})}{\mathrm{e}^{\frac{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})\times(600\,\mathrm{cm^{-1}})}{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(400\,\mathrm{K})}}+1}\\ &= \boxed{1.23\times10^{-21}\,\mathrm{J}}\end{aligned}$$

E13C.2(b) The mean molecular energy is given by [13C.4a–*549*], $\langle\varepsilon\rangle = -(1/q)(\partial q/\partial\beta)_V$, where $\beta = 1/kT$ and q is the partition function. The rotational partition function of a heteronuclear diatomic is given in terms of the rotational constant $\tilde{B}$ by [13B.11–*542*], $q^{\mathrm{R}} = \sum_J (2J+1)\mathrm{e}^{-\beta hc\tilde{B}J(J+1)}$.

$$\langle\varepsilon^{\mathrm{R}}\rangle = -\frac{1}{q^{\mathrm{R}}}\left(\frac{\partial q^{\mathrm{R}}}{\partial\beta}\right)_V = \frac{1}{q^{\mathrm{R}}}\sum_J hc\tilde{B}J(J+1)(2J+1)\mathrm{e}^{-\beta hc\tilde{B}J(J+1)}$$

The terms of the sum above and also of the sum needed to compute q^{R} are evaluated and summed until the result has converged to the required precision. The equipartition value is $\langle\varepsilon^{\mathrm{R}}\rangle = kT$. These two expressions for the energy are plotted as a function of T in Fig. 13.5. The value from the equipartition theorem comes within 5 % of the exact value at $\boxed{66.2\ \mathrm{K}}$.

E13C.3(b) The mean molecular energy is given by [13C.4a–*549*], $\langle\varepsilon\rangle = -(1/q)(\partial q/\partial\beta)_V$, where $\beta = 1/kT$, and q is the partition function given by [13B.1b–*538*], $q^{\mathrm{R}} = \sum_J g_J\mathrm{e}^{-\beta\varepsilon_J}$. The energy levels of a spherical rotor are given in [11B.8–*432*], $\varepsilon_J = hc\tilde{B}J(J+1)$ and, as is explained in Section 11B.1(c) on page 434, each has a degeneracy $g_J = (2J+1)^2$. It follows that

$$\begin{aligned}q^{\mathrm{R}} &= \sum_J (2J+1)^2\mathrm{e}^{-\beta hc\tilde{B}J(J+1)}\\ \langle\varepsilon^{\mathrm{R}}\rangle &= -\frac{1}{q^{\mathrm{R}}}\left(\frac{\partial q^{\mathrm{R}}}{\partial\beta}\right)_V = \frac{1}{q^{\mathrm{R}}}\sum_J hc\tilde{B}J(J+1)(2J+1)^2\mathrm{e}^{-\beta hc\tilde{B}J(J+1)}\end{aligned}$$

The terms in the sum needed to compute q^{R} and $\langle\varepsilon^{\mathrm{R}}\rangle$ are evaluated and summed until the result has converged to the required precision. The equipartition value

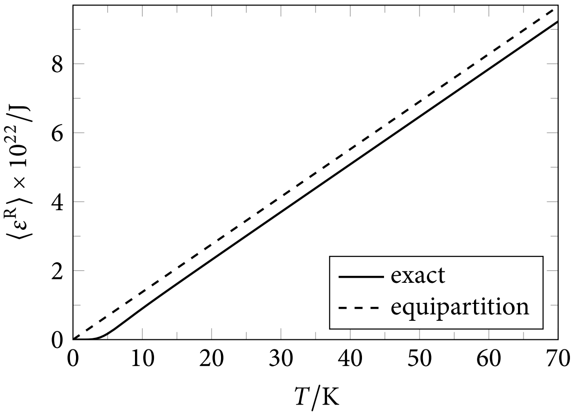


Figure 13.5

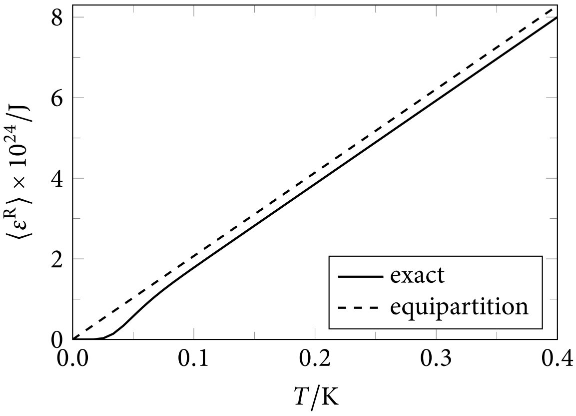


Figure 13.6

is $\langle\varepsilon^{\mathrm{R}}\rangle = \frac{3}{2}kT$, because for this non-linear molecule there are three rotational degrees of freedom. These two expressions for the energy are plotted as a function of T in Fig. 13.6. The value from the equipartition theorem comes within 5 % of the exact value at $\boxed{0.29\ \mathrm{K}}$.

E13C.4(b) The mean vibrational energy is given by [13C.8–*551*], $\langle\varepsilon^{\mathrm{V}}\rangle = hc\tilde{\nu}/(\mathrm{e}^{\beta hc\tilde{\nu}} - 1)$; this result is exact. The equipartition value is $\langle\varepsilon^{\mathrm{V}}\rangle = kT$, because there are two quadratic terms for a harmonic oscillator. These two expressions for the energy are plotted as a function of T in Fig. 13.7. The value from the equipartition theorem comes within 5 % of the exact value at $\boxed{3.19 \times 10^{3}\ \mathrm{K}}$.

E13C.5(b) The mean vibrational energy per vibrational mode is given by [13C.8–*551*], $\langle\varepsilon_i^{\mathrm{V}}\rangle = hc\tilde{\nu}_i/(\mathrm{e}^{\beta hc\tilde{\nu}_i}-1)$; this result is exact. The overall vibrational energy is the sum of the contributions from each normal mode, taking into account the degeneracy

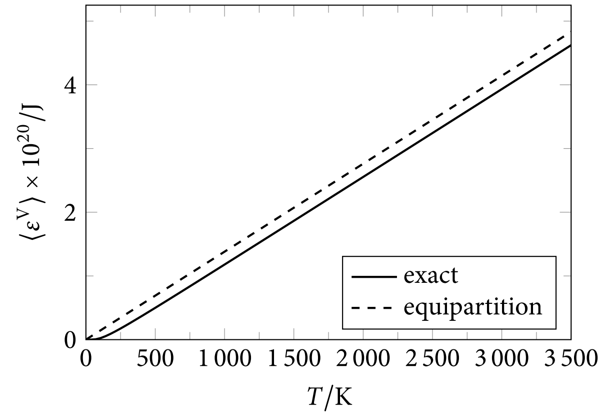


Figure 13.7

of each

$$\langle \varepsilon^{\mathrm{V}} \rangle = \langle \varepsilon_1^{\mathrm{V}} \rangle + 2 \times \langle \varepsilon_2^{\mathrm{V}} \rangle + \langle \varepsilon_3^{\mathrm{V}} \rangle$$

The equipartition value is $\langle \varepsilon^{\mathrm{V}} \rangle = 4kT$, because there are two quadratic terms for a harmonic oscillator, and four modes in total. These two expressions for the energy are plotted as a function of T in Fig. 13.8. The value from the equipartition theorem comes within 5% of the exact value at $\boxed{2.52 \times 10^4 \mathrm{~K}}$.

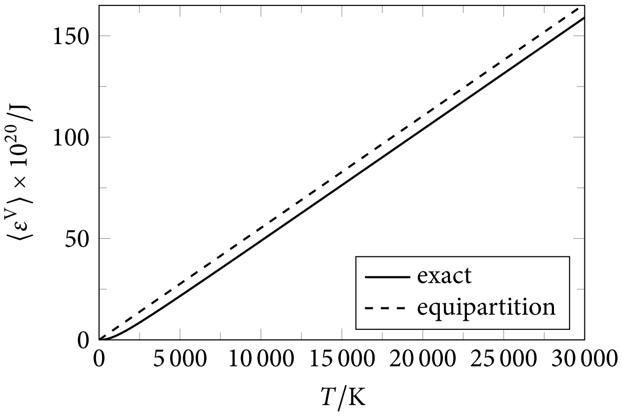


Figure 13.8

E13C.6(b) The mean vibrational energy per vibrational mode is given by [13C.8–*551*], $\langle \varepsilon_i^{\mathrm{V}} \rangle = hc\tilde{\nu}_i/(\mathrm{e}^{\beta hc\tilde{\nu}_i} - 1)$; this result is exact. The overall vibrational energy is the sum of the contributions from each normal mode, taking into account the degeneracy of each

$$\langle \varepsilon^{\mathrm{V}} \rangle = \langle \varepsilon_1^{\mathrm{V}} \rangle + 2 \times \langle \varepsilon_2^{\mathrm{V}} \rangle + 3 \times \langle \varepsilon_3^{\mathrm{V}} \rangle + 3 \times \langle \varepsilon_4^{\mathrm{V}} \rangle$$

The equipartition value is $\langle \varepsilon^{\mathrm{V}} \rangle = 9kT$, because there are two quadratic terms for a harmonic oscillator, and nine modes in total. These two expressions for the energy are plotted as a function of T in Fig. 13.9. The value from the equipartition theorem comes within 5% of the exact value at $\boxed{3.92 \times 10^3\ \mathrm{K}}$.

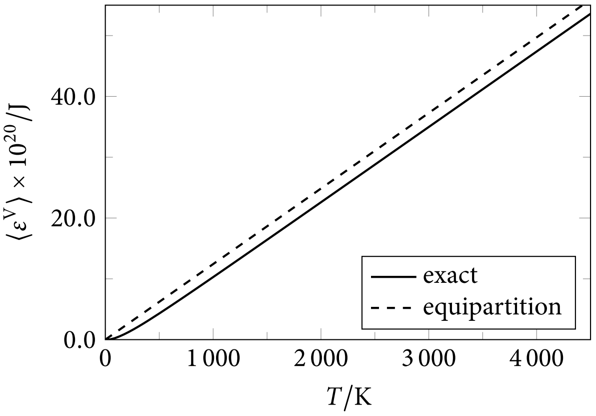


Figure 13.9

E13C.7(b) The mean molecular energy is given by [13C.4a–*549*], $\langle \varepsilon \rangle = -(1/q)(\partial q/\partial \beta)_V$, where $\beta = 1/kT$ and q is the partition function given by [13B.1b–*538*], $q = \sum_i g_i \mathrm{e}^{-\beta \varepsilon_i}$, where g_i is degeneracy and the corresponding energy is given as $\varepsilon_i = hc\tilde{\nu}_i$. At $T = 2000$ K

$$\beta hc = \frac{(6.6261 \times 10^{-34}\,\mathrm{J\,s}) \times (2.9979 \times 10^{10}\,\mathrm{cm\,s^{-1}})}{(1.3806 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (1900\,\mathrm{K})} = 7.19... \times 10^{-4}\ \mathrm{cm}$$

Therefore the electronic partition function is

$$q^{\mathrm{E}} = g_0 + g_1 \mathrm{e}^{-\beta hc\tilde{\nu}_1} + g_2 \mathrm{e}^{-\beta hc\tilde{\nu}_2} = 5.80...$$

Therefore the mean energy is

$$\begin{aligned}\langle \varepsilon^{\mathrm{E}} \rangle &= -\frac{1}{q^{\mathrm{E}}}\left(\frac{\partial q^{\mathrm{E}}}{\partial \beta}\right)_V = \frac{hc}{q^{\mathrm{E}}}\left(g_1\tilde{\nu}_1 \mathrm{e}^{-\beta hc\tilde{\nu}_1} + g_2\tilde{\nu}_2 \mathrm{e}^{-\beta hc\tilde{\nu}_2}\right)\\ &= \frac{(6.6261 \times 10^{-34}\,\mathrm{J\,s}) \times (2.9979 \times 10^{10}\,\mathrm{cm\,s^{-1}})}{5.80...}\\ &\qquad \times \Big[1 \times (850\ \mathrm{cm^{-1}}) \times \mathrm{e}^{-(7.19...\times 10^{-4}\ \mathrm{cm})\times(850\ \mathrm{cm^{-1}})}\\ &\qquad\qquad + 5 \times (1100\ \mathrm{cm^{-1}}) \times \mathrm{e}^{-(7.19...\times 10^{-4}\ \mathrm{cm})\times(1100\ \mathrm{cm^{-1}})}\Big]\\ &= \boxed{1.01 \times 10^{-20}\ \mathrm{J}}\end{aligned}$$

Solutions to problems

P13C.2 The mean molecular energy is given by [13C.2–*549*], $\langle \varepsilon \rangle = (1/q)\sum_i \varepsilon_i \mathrm{e}^{-\beta \varepsilon_i}$, where $\beta = 1/kT$, and q is the partition function given by [13A.11–*535*], $q =$

$\sum_i \mathrm{e}^{-\beta\varepsilon_i}$. Therefore

$$q = \mathrm{e}^{-\beta 0} + \mathrm{e}^{-\beta\varepsilon} + \mathrm{e}^{-\beta 2\varepsilon} = 1 + \mathrm{e}^{-\beta\varepsilon} + \mathrm{e}^{-\beta 2\varepsilon}$$

$$\begin{aligned}\langle\varepsilon\rangle &= \frac{1}{q}\left(0 + \varepsilon\mathrm{e}^{-\beta\varepsilon} + 2\varepsilon\mathrm{e}^{-\beta 2\varepsilon}\right) = \frac{\varepsilon\mathrm{e}^{-\beta\varepsilon} + 2\varepsilon\mathrm{e}^{-2\beta\varepsilon}}{1 + \mathrm{e}^{-\beta\varepsilon} + \mathrm{e}^{-2\beta\varepsilon}} \\ &= \boxed{\varepsilon\left(\frac{\mathrm{e}^{\beta\varepsilon} + 2}{\mathrm{e}^{2\beta\varepsilon} + \mathrm{e}^{\beta\varepsilon} + 1}\right)}\end{aligned}$$

To go to the last line the denominator and numerator of the fraction have both been multiplied by $\mathrm{e}^{2\beta\varepsilon}$.

P13C.4 The equipartition limit for the vibrational energy is kT. Consider

$$\frac{kT - \langle\varepsilon^{\mathrm{V}}\rangle}{\langle\varepsilon^{\mathrm{V}}\rangle} = 0.02$$

$$kT = 1.02 \times \langle\varepsilon^{\mathrm{V}}\rangle = 1.02 \times \frac{hc\tilde{\nu}}{\mathrm{e}^{\beta hc\tilde{\nu}} - 1}$$

Because $\beta = 1/kT$ it follows that

$$\mathrm{e}^{\beta hc\tilde{\nu}} - 1 = 1.02 \times \beta hc\tilde{\nu}$$

Using the Taylor expansion $\mathrm{e}^{x} = 1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3 + \ldots$ and $x = \beta hc\tilde{\nu}$

$$\left(1 + x + \tfrac{1}{2}x^2 + \tfrac{1}{6}x^3 + \ldots\right) - 1 = 1.02 \times x$$

$$x + \tfrac{1}{2}x^2 + \tfrac{1}{6}x^3 + \ldots = 1.02 \times x$$

For high temperature limit $x \ll 1$ is assumed, thus expansion terms after x^3 are ignored

$$x^3 + 3x^2 - 0.12x = 0$$

This equation has three solutions

$$x_1 = \frac{-3 + \sqrt{9 + 4 \times 0.12}}{2} = 0.0394\ldots$$

$$x_2 = \frac{-3 - \sqrt{9 + 4 \times 0.12}}{2} = -3.03\ldots \qquad x_3 = 0$$

Only the postive root is physically meaningful, thus

$$\begin{aligned}T &= \frac{hc\tilde{\nu}}{kx} = \frac{(6.6261 \times 10^{-34}\,\mathrm{J\,s}) \times (2.9979 \times 10^{10}\,\mathrm{cm\,s^{-1}})}{(1.3806 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (0.0394\ldots)} \times \tilde{\nu} \\ &= \boxed{(36.4\,\mathrm{K\,cm}) \times \tilde{\nu}}\end{aligned}$$

P13C.6 The partition function given by [13B.1b–*538*], $q = \sum_i g_i e^{-\beta\varepsilon_i}$, where g_i is degeneracy. The energy is given as $E_{nl} = k\theta X_{nl}^2$, where θ is the characteristic temperature, $\theta = \hbar^2/2m_e R^2 k$. Taking $E_{1,0}$ as the ground state

$$\begin{aligned} q &= \sum_{\text{levels}} g_l e^{-\beta\varepsilon_{nl}} = \sum_{\text{levels}} (2l+1)e^{-\beta(E_{nl}-E_{1,0})} \\ &= \sum_{\text{levels}} (2l+1)e^{-(\theta/T)\times(X_{nl}^2-X_{1,0}^2)} \end{aligned}$$

Relevant values are tabulated below and using these the sum is computed numerically to give the plot shown in Fig. 13.10.

n	1	1	1	2	1	2
l	0	1	2	0	3	1
X_{nl}	3.142	4.493	5.763	6.283	6.988	7.725
g_l	1	3	5	1	7	3
${X_{nl}}^2$	9.87	20.19	33.21	39.48	48.83	59.68
${X_{nl}}^2 - {X_{1,0}}^2$	0.00	10.31	23.34	29.60	38.96	49.80

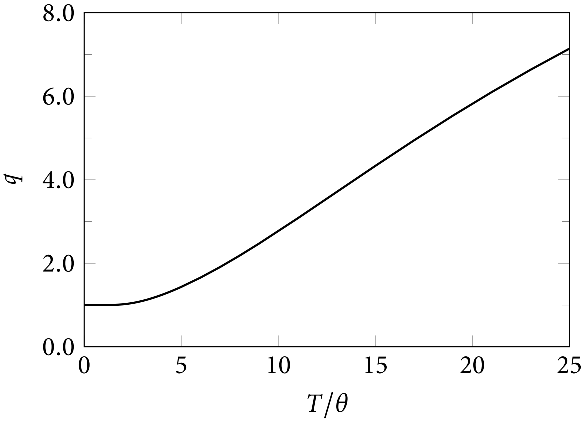


Figure 13.10

The mean energy is given by [13C.4a–*549*], $\langle\varepsilon\rangle = \varepsilon_{\text{gs}} - (1/q)\left(\partial q/\partial\beta\right)_V$. Therefore

$$\begin{aligned} \langle\varepsilon\rangle - E_{1,0} &= \frac{1}{q}\sum_{\text{levels}} (2l+1)e^{-\beta(E_{nl}-E_{1,0})} \times (E_{nl} - E_{1,0}) \\ &= \frac{k\theta}{q}\sum_{\text{levels}} (2l+1)e^{-(\theta/T)\times(X_{nl}^2-X_{1,0}^2)} \times (X_{nl}^2 - X_{1\,0}^2) \end{aligned}$$

This quantity is plotted in Fig. 13.11.

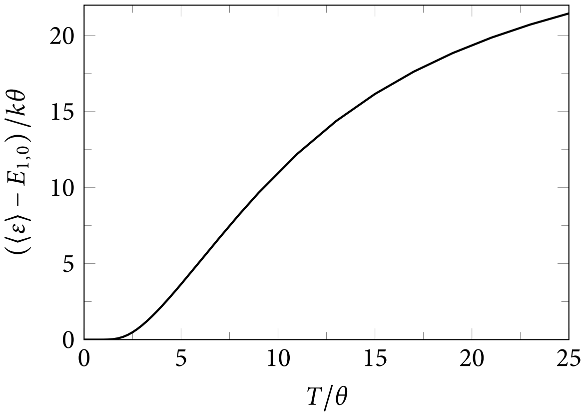


Figure 13.11

P13C.8 (a) The mean molecular energy is given by [13C.4a–*549*]

$$\langle\varepsilon\rangle = -(1/q)(\partial q/\partial\beta)_V$$

where $\beta = 1/kT$ and q is the partition function given by [13A.11–*535*], $q = \sum_i \mathrm{e}^{-\beta\varepsilon_i}$. For the uniformly spaced set of energy levels, $\varepsilon_j = j\varepsilon$, the partition function is given by [13B.2a–*539*], $q = \sum_j \mathrm{e}^{-\beta j\varepsilon} = 1/(1-\mathrm{e}^{-\beta\varepsilon})$. With these results the mean energy is calculated as

$$\langle\varepsilon\rangle = -\frac{1}{q}\frac{\mathrm{d}q}{\mathrm{d}\beta} = -(1-\mathrm{e}^{-\beta\varepsilon})\frac{-\varepsilon\mathrm{e}^{-\beta\varepsilon}}{(1-\mathrm{e}^{-\beta\varepsilon})^2}$$

$$= \frac{\varepsilon\mathrm{e}^{-\beta\varepsilon}}{(1-\mathrm{e}^{-\beta\varepsilon})} = \frac{\varepsilon}{(\mathrm{e}^{\beta\varepsilon}-1)}$$

Setting $\langle\varepsilon\rangle = a\varepsilon$

$$a\varepsilon = \varepsilon/(\mathrm{e}^{\beta\varepsilon}-1)$$

$$\mathrm{e}^{\beta\varepsilon} = 1 + 1/a$$

$$\text{thus } \beta = \frac{1}{\varepsilon}\ln\left(1+\frac{1}{a}\right)$$

Given $\langle\varepsilon\rangle = \varepsilon$, it follows that $a = 1$. Because $T = 1/k\beta$ and $\varepsilon = hc\tilde{\nu}$

$$T = \frac{\varepsilon}{k\ln(2)} = \frac{hc\tilde{\nu}}{k\ln(2)}$$

$$= \frac{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})\times(50\,\mathrm{cm^{-1}})}{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times\ln(2)}$$

$$= \boxed{1.0\times10^2\,\mathrm{K}}$$

(b) If $\langle\varepsilon\rangle = a\varepsilon$ it follows from the above discussion that $\beta\varepsilon = \ln(1+1/a)$, therefore

$$q = \frac{1}{1-\mathrm{e}^{-\beta\varepsilon}} = \frac{1}{1-\mathrm{e}^{-\ln(1+1/a)}} = \frac{1}{1-a/(a+1)} = \boxed{a+1}$$

13D The canonical ensemble

Answer to discussion questions

D13D.2 An ensemble is a set of a large number of imaginary replications of the actual system. These replications are identical in some, but not 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.

D13D.4 In the context of ensembles, the thermodynamic limit is achieved as the number of replications $\tilde{N}$ approaches infinity. In this limit, the dominating configuration is overwhelmingly the most probable configuration, and its properties are essentially the same as those of the system.

Solutions to exercises

E13D.1(b) It is essential to include the factor $1/N!$ when considering indistinguishable particles which are free to move. Thus, such a factor is always needed for gases. In the solid state, particles are distinguished by their positions in the lattice and therefore the particles are regarded as distinguishable on the basis that their locations are distinguishable. For the cases mentioned, the factor $1/N!$ is only needed for CO_2 gas: all the others materials are solids, for which the factor is not needed.

Solutions to problems

P13D.2 The mean energy of a system is given by [13D.5–*556*], $\langle E\rangle = -(\partial \ln Q/\partial\beta)_V$. Using this expression for $\langle E\rangle$ the required derivative is found by changing the order of the mixed partial derivatives

$$\left(\frac{\partial\langle E\rangle}{\partial V}\right)_T = -\left(\frac{\partial}{\partial V}\left(\frac{\partial \ln Q}{\partial\beta}\right)_V\right)_T = -\left(\frac{\partial}{\partial\beta}\left(\frac{\partial \ln Q}{\partial V}\right)_T\right)_V$$

A perfect gas is a collection of indistinguishable independent molecules, thus its canonical partition function is given by [13D.6b–*557*], $Q = q^N/N!$, where q is the molecular partition function. For a perfect gas q is just the translational partition function given by [13B.10b–*541*], $q^{\mathrm{T}} = V/\Lambda^3$, where Λ is the thermal wavelength, which is independent of volume. With these results the derivative of $\mathcal{Q}$ is developed as follows

$$\left(\frac{\partial \ln \mathcal{Q}}{\partial V}\right)_T = \left(\frac{\partial \ln(q^N/N!)}{\partial V}\right)_T = \left(\frac{\partial(N\ln q - \ln N!)}{\partial V}\right)_T$$
$$= N\left(\frac{\partial \ln q}{\partial V}\right)_T = N\left(\frac{\partial \ln(V/\Lambda^3)}{\partial V}\right)_T = N\left(\frac{\partial \ln V}{\partial V}\right)_T = \frac{N}{V}$$

At constant V, N/V does not depend on β thus

$$\left(\frac{\partial\langle E\rangle}{\partial V}\right)_T = -\left(\frac{\partial}{\partial\beta}\left(\frac{\partial \ln \mathcal{Q}}{\partial V}\right)_T\right)_V = -\left(\frac{\partial N/V}{\partial \beta}\right)_V = 0$$

13E The internal energy and entropy

Answer to discussion questions

D13E.2 The expressions for q, U, and S that have been derived are applicable to $T < 0$ as well as $T > 0$. However, if a plot of q or U against T is made (for example, for a two-level system), sharp discontinuities on passing through zero are found. It is seen that $T = +0$ (corresponding to only the lower state being populated) is quite distinct from $T = -0$, when only the upper state is populated. The entropy S is continuous at $T = 0$, but all these functions are continuous if $\beta = 1/kT$ is used as the independent variable. This indicates that $\beta \propto 1/T$ may be a more natural variable than T.

D13E.4 This is discussed in Section 13D.3 on page 556 and the consequences for the calculation of the entropy are further explored in Section 13E.2(a) on page 561.

D13E.6 This is discussed in Section 13E.2(e) on page 565.

Solutions to exercises

E13E.1(b) The equipartition value for $C_{V,\mathrm{m}}$ is expressed in [13E.6–*560*]: each translational or rotational mode contributes $\frac{1}{2}R$, and each active vibrational mode contributes R.

(i) O_3: three translational modes, three rotational modes (non-linear), and no active vibrational modes: $C_{V,\mathrm{m}}/R = 3 \times \frac{1}{2} + 3 \times \frac{1}{2} = \boxed{3}$.

(ii) C_2H_6: three translational modes, three rotational modes (non-linear), and no active vibrational modes: $C_{V,\mathrm{m}}/R = 3 \times \frac{1}{2} + 3 \times \frac{1}{2} = \boxed{3}$. There is one low-frequency normal mode which, if active, will contribute a further R.

(iii) CO_2: three translational modes, two rotational modes (linear), and no active vibrational modes: $C_{V,\mathrm{m}}/R = 3 \times \frac{1}{2} + 2 \times \frac{1}{2} = \boxed{\frac{5}{2}}$.

E13E.2(b) The equipartition value for $C_{V,\mathrm{m}}$ is expressed in [13E.6–*560*]: each translational or rotational mode contributes $\frac{1}{2}R$, and each active vibrational mode contributes R. The number of vibrational modes for a linear molecule is $(3N-5)$, which is 4 for $\mathrm{CO_2}$ This molecule has three translational modes, and two rotational modes (linear) giving $C_{V,\mathrm{m}} = \frac{5}{2}R$; if the 4 vibrations are included, $C_{V,\mathrm{m}} = \frac{13}{2}R$.

$$\gamma = C_{p,\mathrm{m}}/C_{V,\mathrm{m}} = (C_{V,\mathrm{m}} + R)/C_{V,\mathrm{m}} = 1 + R/C_{V,\mathrm{m}}$$

$$\gamma = 1 + R/(5R/2) = 1.40 \quad \text{no vibrational contribution}$$

$$\gamma = 1 + R/(13R/2) = 1.15 \quad \text{with vibrational contribution}$$

The experimental value for γ is 1.29; evidently the vibrational modes contribute to some small extent.

E13E.3(b) The partition function of this two-level system is

$$q = g_0 + g_1 \mathrm{e}^{-\beta hc\tilde{\nu}}$$

where g_0 and g_1 are the degeneracies of the ground and first excited state, respectively. The mean energy is given by [13C.4a–*549*], $\langle\varepsilon\rangle = -(1/q)(\partial q/\partial\beta)_V$

$$\langle\varepsilon\rangle = \frac{g_1 hc\tilde{\nu}\,\mathrm{e}^{-\beta hc\tilde{\nu}}}{g_0 + g_1\mathrm{e}^{-\beta hc\tilde{\nu}}} = \frac{g_1 hc\tilde{\nu}}{g_0\mathrm{e}^{\beta hc\tilde{\nu}} + g_1}$$

$$\text{hence } U_\mathrm{m} = N_\mathrm{A}\langle\varepsilon\rangle = \frac{N_\mathrm{A} g_1 hc\tilde{\nu}}{g_0\mathrm{e}^{\beta hc\tilde{\nu}} + g_1}$$

By definition $C_{V,\mathrm{m}} = (\partial U_\mathrm{m}/\partial T)_V$, therefore

$$\begin{aligned} C_{V,\mathrm{m}} &= \left(\frac{\partial U_\mathrm{m}}{\partial T}\right)_V = \left(\frac{\partial U_\mathrm{m}}{\partial \beta}\right)_V \frac{\mathrm{d}\beta}{\mathrm{d}T} = \left(\frac{\partial U_\mathrm{m}}{\partial \beta}\right)_V \times \frac{-1}{kT^2} \\ &= \frac{1}{kT^2} \times N_\mathrm{A} g_1 hc\tilde{\nu}\,\frac{g_0 hc\tilde{\nu}\mathrm{e}^{\beta hc\tilde{\nu}}}{(g_0\mathrm{e}^{\beta hc\tilde{\nu}} + g_1)^2} \\ &= \frac{N_\mathrm{A}(hc\tilde{\nu})^2}{kT^2}\,\frac{g_0 g_1 \mathrm{e}^{\beta hc\tilde{\nu}}}{(g_0\mathrm{e}^{\beta hc\tilde{\nu}} + g_1)^2} \end{aligned}$$

In this case $g_0 = 3$ and $g_1 = 2$. With the data given

$$\begin{aligned} hc\tilde{\nu} &= (6.6261\times10^{-34}\ \mathrm{J\,s}) \times (2.9979\times10^{10}\ \mathrm{cm\,s^{-1}}) \times (7918.1\ \mathrm{cm^{-1}}) \\ &= 1.57...\times10^{-19}\ \mathrm{J} \end{aligned}$$

$$\begin{aligned} \text{at 400 K } \beta hc\tilde{\nu} &= hc\tilde{\nu}/kT \\ &= (1.57...\times10^{-19}\ \mathrm{J})/[(1.3806\times10^{-23}\ \mathrm{J\,K^{-1}}) \times (400\ \mathrm{K})] = 28.4... \end{aligned}$$

$$\begin{aligned} C_{V,\mathrm{m}} &= \frac{N_\mathrm{A}(hc\tilde{\nu})^2}{kT^2}\,\frac{6\,\mathrm{e}^{\beta hc\tilde{\nu}}}{(3\,\mathrm{e}^{\beta hc\tilde{\nu}} + 2)^2} \\ &= \frac{(6.0221\times10^{23}\ \mathrm{mol^{-1}}) \times (1.57...\times10^{-19}\ \mathrm{J})^2}{(1.3806\times10^{-23}\ \mathrm{J\,K^{-1}}) \times (400\ \mathrm{K})^2}\,\frac{6\,\mathrm{e}^{28.4...}}{(3\,\mathrm{e}^{28.4...} + 2)^2} \\ &= \boxed{1.92\times10^{-9}\ \mathrm{J\,K^{-1}\,mol^{-1}}} \end{aligned}$$

Because $hc\tilde{\nu} \gg kT$ only the ground state is occupied and there is essentially no electronic contribution to the heat capacity.

E13E.4(b) The contribution of a collection of harmonic oscillators to the standard molar entropy is given by [13E.12b–*564*] (note that there is an error in the expression in the text: the argument of the exponential term in the ln should be negative)

$$S_m^V = R\left[\frac{\theta^V/T}{e^{\theta^V/T}-1} - \ln(1-e^{-\theta^V/T})\right] \qquad \theta^V = hc\tilde{\nu}/k$$

This function is plotted in Fig 13.12.

The following table shows the vibrational temperatures and the contribution to the molar entropy for each of the normal modes

		298 K		500 K	
$\tilde{\nu}/\text{cm}^{-1}$	θ^V/K	T/θ^V	S_m^V/R	T/θ^V	S_m^V/R
612	881	0.338	0.216	0.568	0.554
729	1049	0.284	0.137	0.477	0.424
1974	2840	0.1049	7.642×10^{-4}	0.1760	0.02287
3287	4729	0.06301	2.161×10^{-6}	0.1057	8.158×10^{-4}
3374	4855	0.06139	1.455×10^{-6}	0.1030	6.503×10^{-4}

The molar entropy is obtained by summing the contributions from each normal mode, taking into account the double degeneracy of the modes at 612 cm^{-1} and 729 cm^{-1} by counting each twice. Thus at 298 K $\boxed{S_m^V = 5.88\ \text{J K}^{-1}\,\text{mol}^{-1}}$ and at 500 K $\boxed{S_m^V = 16.5\ \text{J K}^{-1}\,\text{mol}^{-1}}$.

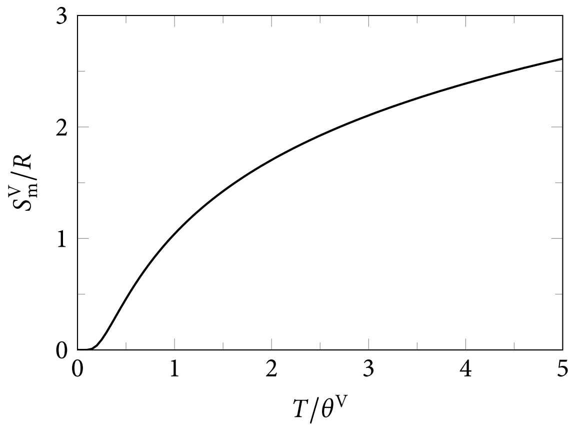


Figure 13.12

E13E.5(b) The translational contribution to the standard molar entropy is given by the Sackur–Tetrode equation [13E.9b–*563*]

$$S_m^\ominus = R\ln\left(\frac{kTe^{5/2}}{p^\ominus \Lambda^3}\right) \qquad \Lambda = h/(2\pi mkT)^{1/2}$$

(i) Taking the mass of H_2O as $18.016\, m_u$

$$\Lambda = \frac{6.6261\times 10^{-34}\,\text{J s}}{\left[2\pi(18.016\times 1.6605\times 10^{-27}\,\text{kg})\times(1.3806\times 10^{-23}\,\text{J K}^{-1})\times(298\,\text{K})\right]^{1/2}}$$
$$= 5.05\ldots\times 10^{-11}\,\text{m}$$
$$S_m^\ominus = (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times\ln\left[\frac{(1.3806\times 10^{-23}\,\text{J K}^{-1})\times(298\,\text{K})\times e^{5/2}}{(10^5\,\text{N m}^{-2})\times(5.05\ldots\times 10^{-11}\,\text{m})^3}\right]$$
$$= \boxed{144.9\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

(ii) Taking the mass of CO_2 as $44.01\, m_u$

$$\Lambda = \frac{6.6261\times 10^{-34}\,\text{J s}}{\left[2\pi(44.01\times 1.6605\times 10^{-27}\,\text{kg})\times(1.3806\times 10^{-23}\,\text{J K}^{-1})\times(298\,\text{K})\right]^{1/2}}$$
$$= 1.52\ldots\times 10^{-12}\,\text{m}$$
$$S_m^\ominus = (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times\ln\left[\frac{(1.3806\times 10^{-23}\,\text{J K}^{-1})\times(298\,\text{K})\times e^{5/2}}{(10^5\,\text{N m}^{-2})\times(1.52\ldots\times 10^{-12}\,\text{m})^3}\right]$$
$$= \boxed{156.0\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

E13E.6(b) The translational contribution to the standard molar entropy is given by the Sackur–Tetrode equation [13E.9b–*563*]

$$S_m^\ominus = R\ln\left(\frac{kTe^{5/2}}{p^\ominus \Lambda^3}\right) \qquad \Lambda = h/(2\pi mkT)^{1/2}$$

It follows that $S_m^\ominus = A\ln(T^{5/2}m^{3/2})$, where A is a constant. Therefore

$$S_m^\ominus(CO_2, T_1) - S_m^\ominus(H_2O, T_2) = A\ln(T_1^{5/2}m_{CO_2}^{3/2}) - A\ln(T_2^{5/2}m_{H_2O}^{3/2})$$

If $S_m^\ominus(CO_2, T_1) = S_m^\ominus(H_2O, 298)$

$$0 = A\ln[T_1^{5/2}m_{CO_2}^{3/2}] - A\ln[(298\,\text{K})^{5/2}m_{H_2O}^{3/2}]$$
$$\text{hence}\quad T_1^{5/2}m_{CO_2}^{3/2} = (298\,\text{K})^{5/2}m_{H_2O}^{3/2}$$
$$T_1 = \left[\frac{(298\,\text{K})^{5/2}\times(18.016)^{3/2}}{(44.01)^{3/2}}\right]^{2/5} = \boxed{174\,\text{K}}$$

E13E.7(b) The rotational partition function for a non-linear molecule is given by [13B.14–*545*]

$$q^{\mathrm{R}} = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2}$$

For SO_2 the symmetry factor $\sigma = 2$, the same value as for H_2O. At 298 K

$$\begin{aligned} kT/hc &= \frac{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})} \\ &= 207.1...\,\mathrm{cm^{-1}} \\ q^{\mathrm{R}} &= \tfrac{1}{2}(207.1...\,\mathrm{cm^{-1}})^{3/2}\times \\ &\quad\left(\frac{\pi}{(2.02736\,\mathrm{cm^{-1}})\times(0.34417\,\mathrm{cm^{-1}})\times(0.293535\,\mathrm{cm^{-1}})}\right)^{1/2} \\ &= \boxed{5837} \end{aligned}$$

The entropy is given in terms of the partition function by [13E.8a–*562*]

$$S_{\mathrm{m}} = [U_{\mathrm{m}}(T) - U_{\mathrm{m}}(0)]/T + R\ln q$$

This is the appropriate form for the rotational contribution; for the translational contribution the ln term is $\ln q\mathrm{e}/N$. At 298 K $kT/hc = 207\,\mathrm{cm^{-1}}$ which is significantly greater than any of the rotational constants, therefore the equipartition theorem can be used to find $U_{\mathrm{m}}(T)$: there are three rotational modes, therefore $U_{\mathrm{m}}(T) - U_{\mathrm{m}}(0) = \frac{3}{2}RT$.

$$\begin{aligned} S_{\mathrm{m}}^{\mathrm{R}} &= (\tfrac{3}{2}RT)/T + R\ln q^{\mathrm{R}} = R(\tfrac{3}{2} + \ln q^{\mathrm{R}}) \\ &= (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times[\tfrac{3}{2} + \ln(5837)] \\ &= \boxed{84.57\,\mathrm{J\,K^{-1}\,mol^{-1}}} \end{aligned}$$

E13E.8(b) Only the ground electronic state contributes to the electronic partition function, which is therefore simply the degeneracy of the ground state $q^{\mathrm{E}} = g_0$. The spin degeneracy is given by the value of S: $g_0 = (2S+1) = (2\times\frac{5}{2}+1) = 6$. The entropy is given in terms of the partition function by [13E.8a–*562*]

$$S_{\mathrm{m}} = [U_{\mathrm{m}}(T) - U_{\mathrm{m}}(0)]/T + R\ln q$$

This is the appropriate form for the electronic contribution; for the translational contribution the ln term is $\ln q\mathrm{e}/N$. In this case $U_{\mathrm{m}}(T) - U_{\mathrm{m}}(0) = 0$ as only the ground state is considered

$$S_{\mathrm{m}} = R\ln q = R\ln 6 = \boxed{14.89\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

E13E.9(b) The contribution of a collection of harmonic oscillators to the standard molar entropy is given by [13E.12b–*564*] (note that there is an error in the expression in the text: the argument of the exponential term in the ln should be negative)

$$S_{\mathrm{m}}^{\mathrm{V}} = R\left[\frac{\theta^{\mathrm{V}}/T}{\mathrm{e}^{\theta^{\mathrm{V}}/T}-1} - \ln(1-\mathrm{e}^{-\theta^{\mathrm{V}}/T})\right] \quad \theta^{\mathrm{V}} = hc\tilde{\nu}/k$$

The following table shows the vibrational temperatures and the contribution to the molar entropy for each of the normal modes

		298 K		500 K	
$\tilde{\nu}/\text{cm}^{-1}$	$\theta^{\text{V}}/\text{K}$	θ^{V}/T	$S_{\text{m}}^{\text{V}}/R$	θ^{V}/T	$S_{\text{m}}^{\text{V}}/R$
612	881	2.96	0.216	1.76	0.554
729	1049	3.52	0.137	2.10	0.424
1974	2840	9.531	7.643×10^{-4}	5.680	0.02287
3287	4729	15.87	2.161×10^{-6}	9.459	8.158×10^{-4}
3374	4855	16.29	1.455×10^{-6}	9.709	6.503×10^{-4}

The molar entropy is obtained by summing the contributions from each normal mode, taking into account the double degeneracy of the modes at 612 cm^{-1} and 729 cm^{-1} by counting each twice. Thus at 298 K $\boxed{S_{\text{m}}^{\text{V}} = 5.88\ \text{J K}^{-1}\ \text{mol}^{-1}}$ and at 500 K $\boxed{S_{\text{m}}^{\text{V}} = 16.5\ \text{J K}^{-1}\ \text{mol}^{-1}}$.

Solutions to problems

P13E.2 The unpaired electron in NO_2 will interact with the magnetic field and give rise to two energy levels, corresponding to the spin-up and spin-down states. Therefore, these electron spin levels form a two-level system, an expression for the heat capacity of which is derived in the solution to *Exercise* E13E.3(b).

$$C_{V,\text{m}} = \frac{N_{\text{A}}(hc\tilde{\nu})^2}{kT^2} \frac{g_0 g_1 \text{e}^{\beta hc\tilde{\nu}}}{(g_0 \text{e}^{\beta hc\tilde{\nu}} + g_1)^2}$$

where g_0 and g_1 are the degeneracies of the ground and first excited levels, respectively, and $(hc\tilde{\nu})$ is the energy separation of the two levels.

For a spin both levels are non-degenerate: $g_0 = 1$ and $g_1 = 1$. The energy levels of a electron spin in a magnetic field are given by [12A.11c–*492*], $E_m = g_{\text{e}}\mu_{\text{B}}\mathcal{B}_0 m$, where g_{e} is the g-value of the electron (taken as 2), μ_{B} is the Bohr magneton, $\mathcal{B}_0$ is the applied magnetic field, and $m = \pm\frac{1}{2}$ for the two states. The energy separation of the states is therefore $E_{+1/2} - E_{-1/2} = g_{\text{e}}\mu_{\text{B}}\mathcal{B}_0$; this it the equivalent of the term $(hc\tilde{\nu})$ in the above expression, hence

$$C_{V,\text{m}} = \frac{N_{\text{A}}(g_{\text{e}}\mu_{\text{B}}\mathcal{B}_0)^2}{kT^2} \frac{\text{e}^{\beta g_{\text{e}}\mu_{\text{B}}\mathcal{B}_0}}{(\text{e}^{\beta g_{\text{e}}\mu_{\text{B}}\mathcal{B}_0} + 1)^2} = N_{\text{A}}k(\beta g_{\text{e}}\mu_{\text{B}}\mathcal{B}_0)^2 \frac{\text{e}^{\beta g_{\text{e}}\mu_{\text{B}}\mathcal{B}_0}}{(\text{e}^{\beta g_{\text{e}}\mu_{\text{B}}\mathcal{B}_0} + 1)^2}$$

With the data given, and at 50 K

$$\begin{aligned}\beta g_{\text{e}}\mu_{\text{B}}\mathcal{B}_0 &= g_{\text{e}}\mu_{\text{B}}\mathcal{B}_0/kT \\ &= \frac{2 \times (9.2740 \times 10^{-24}\ \text{J T}^{-1}) \times (5.0\ \text{T})}{(1.3806 \times 10^{-23}\ \text{J K}^{-1}) \times (50\ \text{K})} = 0.134... \\ C_{V,\text{m}}/R &= (0.134...)^2 \frac{\text{e}^{0.134...}}{(\text{e}^{0.134...} + 1)^2} = \boxed{4.49 \times 10^{-3}}\end{aligned}$$

A similar calculation at 298 K gives $(\beta g_e \mu_B \mathcal{B}_0) = 0.0225...$ and a resulting heat capacity $\boxed{C_{V,m}/R = 1.27 \times 10^{-4}}$.

Assuming that vibrations do not contribute, the equipartition value for the heat capacity of NO_2 arises from three translational and three rotational modes, hence $C_{V,m}/R = 3$. At 50 K the electron spin contribution expressed as a fraction of the overall heat capacity is $4.49 \times 10^{-3}/3 = 1.50 \times 10^{-3}$ or $\boxed{0.15\,\%}$. At 298 K the electron spin contribution is $\boxed{4.2 \times 10^{-3}\,\%}$ of the overall heat capacity.

P13E.4 An expression for the heat capacity of a two-level system is derived in the solution to *Exercise* E13E.3(b).

$$C_{V,m} = \frac{N_A(hc\tilde{\nu})^2}{kT^2}\frac{g_0 g_1 e^{\beta hc\tilde{\nu}}}{(g_0 e^{\beta hc\tilde{\nu}} + g_1)^2}$$

where g_0 and g_1 are the degeneracies of the ground and first excited levels, respectively, and $(hc\tilde{\nu})$ is the energy separation of the two levels.

For a linear rotor the terms are given by [11B.14–*434*], $\tilde{F}(J) = \tilde{B}J(J+1)$, so the separation of the $J=0$ and $J=2$ terms is $6\tilde{B}$: this is the equivalent of the term $\tilde{\nu}$. The degeneracy of each level is $(2J+1)$, so $g_0 = 1$ and $g_2 = 5$.

The heat capacity is therefore

$$C_{V,m} = \frac{N_A(6hc\tilde{B})^2}{kT^2}\frac{5\,e^{6\beta hc\tilde{B}}}{(e^{6\beta hc\tilde{B}}+5)^2} = N_A k(6\beta hc\tilde{B})^2\frac{5\,e^{6\beta hc\tilde{B}}}{(e^{6\beta hc\tilde{B}}+5)^2}$$

With the data given

$$\begin{aligned}6\beta hc\tilde{B} &= 6hc\tilde{B}/k \times T^{-1}\\ &= \frac{6\times(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})\times(60.684\,\mathrm{cm^{-1}})}{1.3806\times10^{-23}\,\mathrm{J\,K^{-1}}}\times T^{-1}\\ &= (525.4...\,\mathrm{K})\times T^{-1}\end{aligned}$$

A plot of $C_{V,m}$ as a function of T is shown in Fig. 13.13.

P13E.6 The partition function of this two-level system is

$$q = 1 + e^{-\beta\delta}$$

where δ is the energy spacing between the two levels and where it is assumed that both are non-degenerate. The mean energy is given by [13C.4a–*549*], $\langle\varepsilon\rangle = -(1/q)(\partial q/\partial\beta)_V$

$$\langle\varepsilon\rangle = \frac{\delta\,e^{-\beta\delta}}{1+e^{-\beta\delta}} = \frac{\delta}{e^{\beta\delta}+1}$$

$$\text{hence } U_m = N_A\langle\varepsilon\rangle = \frac{N_A\delta}{e^{\beta\delta}+1}$$

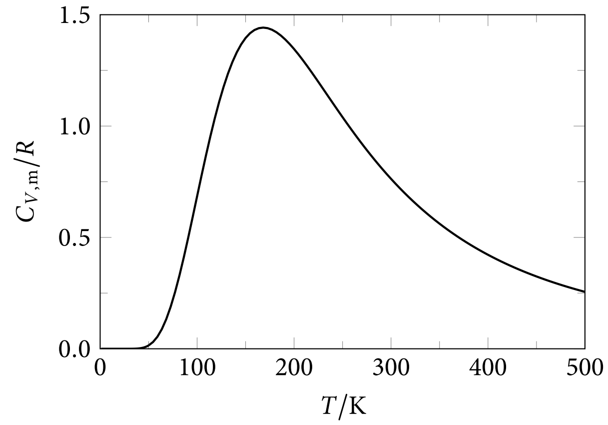


Figure 13.13

The entropy is given in terms of the partition function by [13E.8a–*562*]

$$\begin{aligned}S_\mathrm{m} &= [U_\mathrm{m}(T) - U_\mathrm{m}(0)]/T + R\ln q = \frac{N_\mathrm{A}\delta}{T(\mathrm{e}^{\beta\delta}+1)} + R\ln(1+\mathrm{e}^{-\beta\delta})\\ &= R\left[\frac{\delta\beta}{(\mathrm{e}^{\beta\delta}+1)} + \ln(1+\mathrm{e}^{-\beta\delta})\right]\end{aligned}$$

where $N_\mathrm{A}/T = N_\mathrm{A}\beta k = R\beta$ is used. The required temperature coefficient is found from

$$\begin{aligned}\frac{\mathrm{d}S_\mathrm{m}}{\mathrm{d}T} &= \frac{\mathrm{d}S_\mathrm{m}}{\mathrm{d}\beta}\frac{\mathrm{d}\beta}{\mathrm{d}T} = \frac{\mathrm{d}S_\mathrm{m}}{\mathrm{d}\beta}\times\frac{-1}{kT^2}\\ &= \frac{-R}{kT^2}\frac{\mathrm{d}}{\mathrm{d}\beta}\left(\frac{\delta\beta}{(\mathrm{e}^{\beta\delta}+1)} + \ln(1+\mathrm{e}^{-\beta\delta})\right)\\ &= \frac{-R}{kT^2}\left(\frac{-\delta^2\beta\mathrm{e}^{\beta\delta}}{(\mathrm{e}^{\beta\delta}+1)^2} + \frac{\delta}{(\mathrm{e}^{\beta\delta}+1)} - \frac{\delta\mathrm{e}^{-\beta\delta}}{1+\mathrm{e}^{-\beta\delta}}\right)\\ &= \frac{R}{T}\left(\frac{(\delta\beta)^2\mathrm{e}^{\beta\delta}}{(\mathrm{e}^{\beta\delta}+1)^2} - \frac{\delta\beta}{(\mathrm{e}^{\beta\delta}+1)} + \frac{\delta\beta\mathrm{e}^{-\beta\delta}}{1+\mathrm{e}^{-\beta\delta}}\right)\\ &= \frac{Rk}{\delta}(\delta\beta)\left(\frac{(\delta\beta)^2\mathrm{e}^{\beta\delta}}{(\mathrm{e}^{\beta\delta}+1)^2} - \frac{\delta\beta}{(\mathrm{e}^{\beta\delta}+1)} + \frac{\delta\beta\mathrm{e}^{-\beta\delta}}{1+\mathrm{e}^{-\beta\delta}}\right)\end{aligned}$$

The final line shows that the size of the derivative is scaled by $1/\delta$, but that the temperature dependence is a function of the dimensionless parameter $\beta\delta$. It is not possible to find the maximum value of the derivative analytically, but by plotting a graph this maximum is easily located at $\beta\delta \approx 3.243$, which is alternatively expressed as $kT \approx \delta/3.243$.

When $kT \ll \delta$ all of the particles are in the lower level, which can only be achieved in one way so the contribution to the entropy is zero. When $kT \gg \delta$ the entropy reaches a limiting value because the populations of the two levels are equal and no longer changing. In between these two extremes the entropy rises, and it makes sense that the rate of change of the entropy is greatest when $kT \approx \delta$ because this is the temperature at which the population of the upper level starts to become significant.

P13E.8 It will be useful first to consider $\partial q/\partial\beta$

$$\begin{aligned}\frac{\partial}{\partial\beta}\sum_j \mathrm{e}^{-\beta\varepsilon_j} &= -\sum_j \varepsilon_j \mathrm{e}^{-\beta\varepsilon_j}\\ &= -(1/\beta)\sum_j \beta\varepsilon_j \mathrm{e}^{-\beta\varepsilon_j} = -\dot{q}/\beta\end{aligned}$$

Likewise $\partial\dot{q}/\partial\beta$

$$\begin{aligned}\frac{\partial}{\partial\beta}\sum_j \beta\varepsilon_j\mathrm{e}^{-\beta\varepsilon_j} &= \sum_j \varepsilon_j \mathrm{e}^{-\beta\varepsilon_j} - \sum_j \beta\varepsilon_j^2\mathrm{e}^{-\beta\varepsilon_j}\\ &= \dot{q}/\beta - (1/\beta)\sum_j(\beta\varepsilon_j)^2\mathrm{e}^{-\beta\varepsilon_j} = \dot{q}/\beta - \ddot{q}/\beta\end{aligned}$$

In summary

$$\frac{\partial q}{\partial\beta} = -\frac{\dot{q}}{\beta} \qquad \frac{\partial\dot{q}}{\partial\beta} = \frac{\dot{q}}{\beta} - \frac{\ddot{q}}{\beta} \tag{13.2}$$

The mean energy is given by [13C.4a–*549*], $\langle\varepsilon\rangle = -(1/q)(\partial q/\partial\beta)_V$

$$\langle\varepsilon\rangle = -\frac{1}{q}\frac{\partial q}{\partial\beta} = \frac{1}{q}\frac{\dot{q}}{\beta}$$

where the first relationship from eqn 13.2 is used. The molar internal energy is therefore

$$U_\mathrm{m} = N_\mathrm{A}\langle\varepsilon\rangle = N_\mathrm{A}\frac{1}{q}\frac{\dot{q}}{\beta} = \boxed{RT\frac{\dot{q}}{q}}$$

where $N_\mathrm{A}/\beta = N_\mathrm{A}kT = RT$ is used.

By definition $C_{V,\mathrm{m}} = (\partial U_\mathrm{m}/\partial T)_V$. It is convenient to compute the derivative with respect to β and to use $U_\mathrm{m} = N_\mathrm{A}\dot{q}/q\beta$.

$$\begin{aligned}C_{V,\mathrm{m}} &= \left(\frac{\partial U_\mathrm{m}}{\partial T}\right)_V = \left(\frac{\partial U_\mathrm{m}}{\partial\beta}\right)_V\frac{\partial\beta}{\partial T} = \left(\frac{\partial U_\mathrm{m}}{\partial\beta}\right)_V \times \frac{-1}{kT^2} = \frac{-N_\mathrm{A}}{kT^2}\frac{\partial}{\partial\beta}\frac{\dot{q}}{q\beta}\\ &= \frac{-N_\mathrm{A}}{kT^2}\left[\frac{-\dot{q}}{(q\beta)^2}\left(q+\beta\frac{\partial q}{\partial\beta}\right)+\frac{\partial\dot{q}}{\partial\beta}\frac{1}{q\beta}\right]\\ &= \frac{-N_\mathrm{A}}{kT^2}\left[\frac{-\dot{q}}{(q\beta)^2}\left(q-\beta\frac{\dot{q}}{\beta}\right)+\left(\frac{\dot{q}}{\beta}-\frac{\ddot{q}}{\beta}\right)\frac{1}{q\beta}\right]\\ &= \frac{-N_\mathrm{A}}{kT^2}\left[\frac{-\dot{q}}{q\beta^2}+\frac{\dot{q}^2}{(q\beta)^2}+\frac{\dot{q}}{q\beta^2}-\frac{\ddot{q}}{q\beta^2}\right]\\ &= -R\beta^2\left[\frac{\dot{q}^2}{(q\beta)^2}-\frac{\ddot{q}}{q\beta^2}\right]\\ &= \boxed{R\left[\frac{\ddot{q}}{q}-\left(\frac{\dot{q}}{q}\right)^2\right]}\end{aligned}$$

On the penultimate line $N_A/kT^2 = N_A k\beta^2 = R\beta^2$ is used.

The molar entropy is given by [13E.8a–*562*]

$$S_m = [U_m(T) - U_m(0)]/T + R\ln q$$
$$= \boxed{R\left(\frac{\dot{q}}{q} + \ln q\right)}$$

To use the data given, account needs to be taken of the degeneracies and it is convenient to write the energies in terms of wavenumbers to give

$$q = \sum_j g_j e^{-hc\beta\tilde{\nu}_j} \qquad \dot{q} = \beta hc\sum_j g_j\tilde{\nu}_j e^{-hc\beta\tilde{\nu}_j} \qquad \ddot{q} = \beta^2 h^2 c^2\sum_j g_j\tilde{\nu}_j^2 e^{-hc\beta\tilde{\nu}_j}$$

At 5000 K

$$hc/kT = \frac{(6.6261\times10^{-34}\,\text{J s})\times(2.9979\times10^{10}\,\text{cm s}^{-1})}{(1.3806\times10^{-23}\,\text{J K}^{-1})\times(5000\,\text{K})} = 2.87...\times10^{-4}\,\text{cm}$$

term	g	$\tilde{\nu}/\text{cm}^{-1}$	$hc\beta\tilde{\nu}$	$ge^{-hc\beta\tilde{\nu}}$	$hc\beta\tilde{\nu}ge^{-hc\beta\tilde{\nu}}$	$(hc\beta\tilde{\nu})^2 ge^{-hc\beta\tilde{\nu}}$
$^1S_0$	1	0	1	0	0	0
$^3P_0$	1	21850	6.2877	1.8591×10^{-3}	0.01169	0.07350
$^3P_1$	3	21870	6.2934	5.5453×10^{-3}	0.03490	0.21963
$^3P_2$	5	21911	6.3052	9.1337×10^{-3}	0.05759	0.36312
$^1P_1$	3	35051	10.086	1.2492×10^{-4}	1.260×10^{-3}	0.01271
$^3S_1$	3	41197	11.855	2.1308×10^{-5}	2.526×10^{-4}	2.9946×10^{-3}

The sum of the terms in the fifth column is q, the sixth is $\dot{q}$, and the seventh is $\ddot{q}$

$$q = 1.016\,684 \qquad \dot{q} = 0.105\,691 \qquad \ddot{q} = 0.671\,954$$

$$C_{V,m} = R\left[\frac{\ddot{q}}{q} - \left(\frac{\dot{q}}{q}\right)^2\right]$$
$$= (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times\left[\frac{0.671954}{1.016684} - \left(\frac{0.105690}{1.016684}\right)^2\right]$$
$$= \boxed{5.41\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

P13E.10 Contributions to the entropy from translation and rotation are expected, along with a smaller contribution from vibration. N_2 has a $^1\Sigma$ ground electronic state which is non-degenerate and so makes no contribution to the entropy.

The translational contribution to the standard molar entropy is given by the Sackur–Tetrode equation [13E.9b–*563*]

$$S_{\mathrm{m}}^{\mathrm{T}} = R\ln\left(\frac{kT\mathrm{e}^{5/2}}{p^{\ominus}\Lambda^3}\right) \qquad \Lambda = h/(2\pi mkT)^{1/2}$$

Taking the mass of N_2 as 28.02 m_{u}

$$\begin{aligned}\Lambda &= \frac{6.6261\times10^{-34}\,\mathrm{J\,s}}{\left[2\pi(28.02\times1.6605\times10^{-27}\,\mathrm{kg})\times(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})\right]^{1/2}}\\ &= 1.91...\times10^{-11}\,\mathrm{m}\\ S_{\mathrm{m}}^{\mathrm{T}} &= (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times\ln\left[\frac{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})\times\mathrm{e}^{5/2}}{(10^5\,\mathrm{N\,m^{-2}})\times(1.91...\times10^{-11}\,\mathrm{m})^3}\right]\\ &= 1.50...\times10^{2}\,\mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

The rotational contribution to the entropy is given by [13E.11a–*564*]; this high-temperature form is applicable at 298 K because this temperature is much higher than the characteristic rotational temperature, $\theta^{\mathrm{R}} = hc\tilde{B}/k = 2.88$ K.

$$\begin{aligned}S_{\mathrm{m}}^{\mathrm{R}} &= R\left(1+\ln\frac{kT}{\sigma hc\tilde{B}}\right)\\ &= (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times\left(1+\right.\\ &\qquad\left.\ln\frac{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}{2(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})\times(1.9987\,\mathrm{cm^{-1}})}\right)\\ &= 41.1...\,\mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

The characteristic vibrational temperature is $\theta^{\mathrm{V}} = hc\tilde{\nu}/k = 3392$ K. This is so much greater than 298 K that it may safely be assumed that the vibrational contribution is negligible at this temperature (a calculation using [13E.12b–*564*] gives $S_{\mathrm{m}}^{\mathrm{V}} \approx 0.001\,\mathrm{J\,K^{-1}\,mol^{-1}}$, confirming that validity of this assumption). The molar entropy is therefore

$$S_{\mathrm{m}}^{\ominus} = S_{\mathrm{m}}^{\mathrm{T}} + S_{\mathrm{m}}^{\mathrm{R}} = 1.50...\times10^{2} + 41.1... = \boxed{191.5\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

The calculated and experimental values agree to within 0.3%, so it can be concluded that there is no residual entropy in the solid at 0 K.

P13E.12 (a) The probability distribution over the rotational states is given by

$$P(J) = \frac{n_J}{N} = \frac{1}{q^{\mathrm{R}}}(2J+1)\mathrm{e}^{-hc\tilde{B}J(J+1)/kT} \qquad q^{\mathrm{R}} = kT/hc\tilde{B}$$

The high-temperature form of q^{R} is appropriate because $\theta^{\mathrm{R}} = 2.78$ K, which is much less than the lowest temperature to be explored. Figure 13.14 shows plots of $P(J)$ for 100 K and 1000 K. In both cases it is seen that the

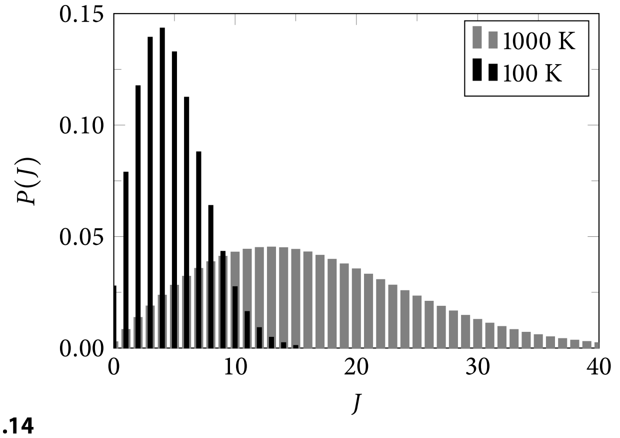


Figure 13.14

distribution peaks before tailing off: at the lower temperature the peak comes at a lower value of J and the distribution is narrower. Even at the lowest temperature, many states have significant probabilities of being occupied.

The probability distribution over the vibrational states is given by

$$P(v) = \frac{n_v}{N} = \frac{1}{q^{\mathrm{V}}} e^{-hc\tilde{\nu}v/kT} \qquad q^{\mathrm{V}} = (1 - e^{-hc\tilde{\nu}/kT})^{-1}$$

Figure 13.15 shows plots of $P(v)$ for 100 K and 1000 K. Because the vibrational temperature is so high ($\theta^{\mathrm{V}} = 3122$ K) at 100 K only the ground state is occupied, and even at 1000 K there is only a small probability of the first excited state being occupied.

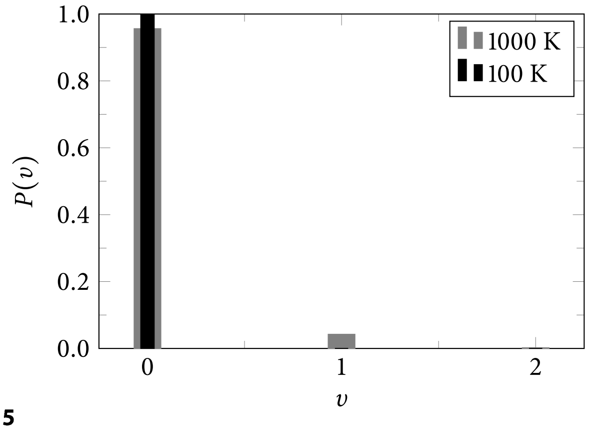


Figure 13.15

(b) The rotational partition function of a heteronuclear diatomic is given by [13B.11–*542*], $q^{\mathrm{R}} = \sum_J (2J+1) e^{-\beta hc\tilde{B}J(J+1)}$. This expression can be written in terms of the vibrational temperature $\theta^{\mathrm{R}} = hc\tilde{B}/k$ as

$$q^{\mathrm{R}} = \sum_{J}(2J+1)\mathrm{e}^{-J(J+1)\theta^{\mathrm{R}}/T}$$

In the high-temperature limit this sum is well-approximated by [13B.12a–*543*], $q^{\mathrm{R}} = kT/(hc\tilde{B}) = T/\theta^{\mathrm{R}}$. For the data given

$$\begin{aligned}\theta^{\mathrm{R}} &= \frac{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})\times(1.931\,\mathrm{cm^{-1}})}{1.3806\times10^{-23}\,\mathrm{J\,K^{-1}}}\\ &= 2.77...\,\mathrm{K}\end{aligned}$$

This is much less than even the lowest temperature (100 K) to be considered, so the high-temperature form of the partition function will give a precise result. For example, explicit summation at 100 K gives $q^{\mathrm{R}} = 36.3$, whereas using the high-temperature approximation gives 36.0, an error of just 0.8%. The error will reduce as the temperature increases.

(c) The translational contribution to U_{m} will be given by the equipartition theorem as $U_{\mathrm{m}}^{\mathrm{T}} = \frac{3}{2}RT$, and likewise the rotational contribution (two rotational modes) is $U_{\mathrm{m}}^{\mathrm{R}} = RT$. The vibrational contribution must be calculated explicitly using [13C.8–*551*]

$$U_{\mathrm{m}}^{\mathrm{V}} = \frac{N_{\mathrm{A}}hc\tilde{\nu}}{\mathrm{e}^{hc\tilde{\nu}/kT}-1} = \frac{R\theta^{\mathrm{V}}}{\mathrm{e}^{\theta^{\mathrm{V}}/T}-1}$$

These three contributions are compared in Fig. 13.16.

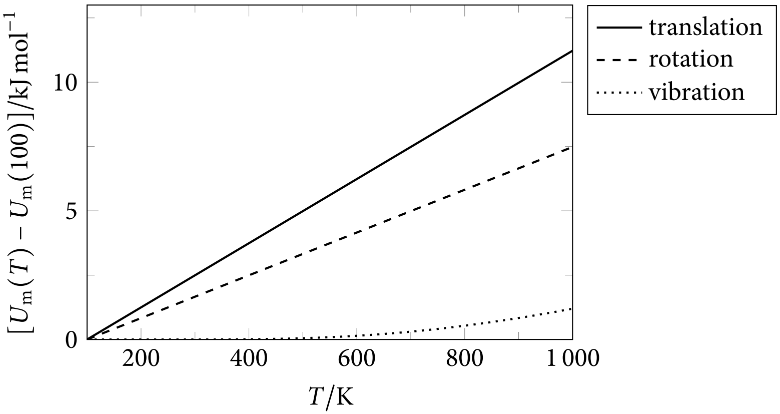


Figure 13.16

The translational and rotational contributions to the heat capacity are temperature independent because the internal energy is linear in the temperature: $C_{V,\mathrm{m}}^{\mathrm{T}} = \frac{3}{2}R$ and $C_{V,\mathrm{m}}^{\mathrm{R}} = R$. The vibrational contribution to the heat capacity is given by [13E.3–*560*]

$$C_{V,\mathrm{m}}^{\mathrm{V}} = R\left(\frac{\theta^{\mathrm{V}}}{T}\right)^2\left(\frac{\mathrm{e}^{-\theta^{\mathrm{V}}/2T}}{1-\mathrm{e}^{-\theta^{\mathrm{V}}/T}}\right)^2$$

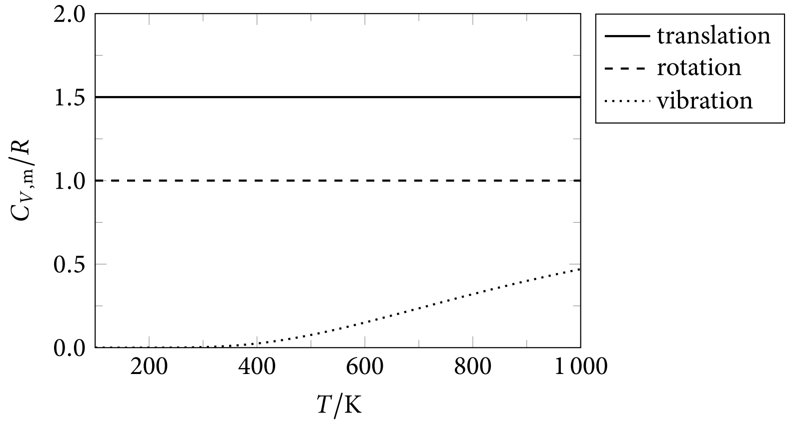


Figure 13.17

These three contributions are compared in Fig. 13.17.

The translational contribution to the standard molar entropy is given by the Sackur–Tetrode equation [13E.9b–*563*]

$$S_\mathrm{m}^\mathrm{T} = R\ln\left(\frac{kT\mathrm{e}^{5/2}}{p^\ominus\Lambda^3}\right) \qquad \Lambda = h/(2\pi mkT)^{1/2}$$

Taking the mass of CO as 28.01 m_u and inserting the values of the other constants gives

$$S_\mathrm{m}^\mathrm{T}/R = \ln[(46.8\ldots\ \mathrm{K}^{-5/2})T^{5/2}]$$

The rotational contribution to the entropy is given by [13E.11a–*564*] with $\sigma = 1$

$$S_\mathrm{m}^\mathrm{R}/R = 1 + \ln\frac{kT}{hc\tilde{B}} = 1 + \ln\frac{T}{\theta^\mathrm{R}}$$

The vibrational contribution to the standard molar entropy is given by [13E.12b–*564*] (note that there is an error in the expression in the text: the argument of the exponential term in the ln should be negative)

$$S_\mathrm{m}^\mathrm{V}/R = \frac{\theta^\mathrm{V}/T}{\mathrm{e}^{\theta^\mathrm{V}/T} - 1} - \ln(1 - \mathrm{e}^{-\theta^\mathrm{V}/T})$$

These three contributions are compared in Fig. 13.18.

P13E.14 The partition function for a two-level system with energy spacing ε is

$$q = 1 + \mathrm{e}^{-\beta\varepsilon}$$

An expression for the internal energy is given in *Brief illustration* 13C.1 on page 550

$$U_\mathrm{m} = \frac{N_\mathrm{A}\varepsilon}{\mathrm{e}^{\beta\varepsilon} + 1}$$

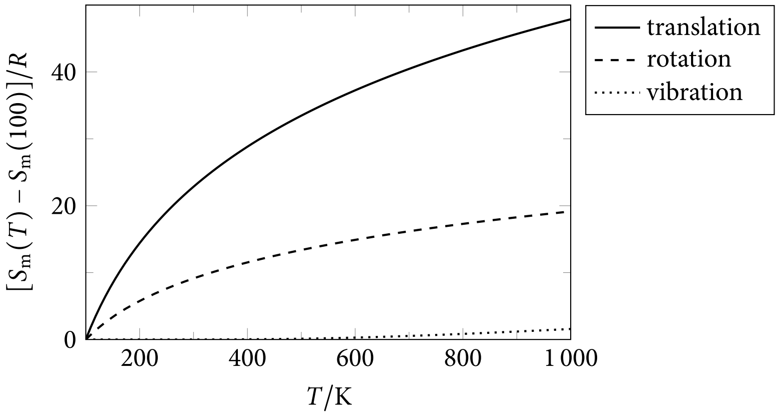


Figure 13.18

and hence the molar entropy is give by [13E.8a–*562*]

$$\begin{aligned} S_m &= U_m/T + R\ln q \\ &= \frac{N_A\varepsilon}{T(e^{\beta\varepsilon}+1)} + R\ln(1+e^{-\beta\varepsilon}) \\ &= R\left[\frac{\beta\varepsilon}{e^{\beta\varepsilon}+1} + \ln(1+e^{-\beta\varepsilon})\right] \end{aligned}$$

where to go to the last line $N_A/T = N_A k\beta = R\beta$ is used.

Figure 13.19 shows a plot of the molar entropy as a function of $\beta\varepsilon$. In the limit $|\beta\varepsilon| \to 0$, which corresponds to large positive temperatures or large negative temperatures, the entropy reaches a maximum, corresponding to equal populations of the two levels. As $\beta\varepsilon$ becomes more positive, corresponding to a decreasing (but always positive) temperature, the entropy decreases as the populations of the levels become more unequal. In the limit $\beta\varepsilon \gg 0$, corresponding to a very low positive temperature, only the ground state is populated: this can only be achieved in one way, therefore the entropy is zero.

As $\beta\varepsilon$ becomes more negative, corresponding to a negative temperature which is increasing towards zero, the entropy decreases as the populations of the levels become more unequal. In the limit $\beta\varepsilon \ll 0$, corresponding to a negative temperature with very small magnitude, only the *upper* state is populated: this can only be achieved in one way, therefore the entropy is zero.

P13E.16 The equipartition value for the $C_{V,m}$ is expressed in [13E.6–*560*]: each translational or rotational mode contributes $\frac{1}{2}R$, and each active vibrational mode contributes R. Because $C_{p,m} - C_{V,m} = R$ it follows that

$$\gamma = C_{p,m}/C_{V,m} = (C_{V,m}+R)/C_{V,m} = 1 + R/C_{V,m}$$

(a) A diatomic has three translational modes, and two rotational modes giving $C_{V,m} = \frac{5}{2}R$. Hence $\gamma = 1 + R/(5R/2) = 1.40$ and $\boxed{c_s = (1.40RT/M)^{1/2}}$.

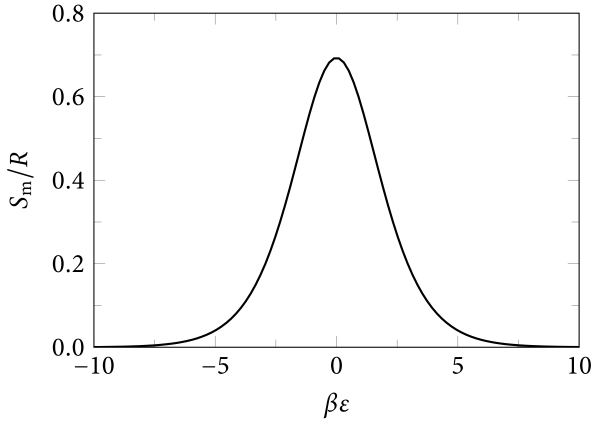


Figure 13.19

(b) The same calculation applies to a linear triatomic.

(c) For a non-linear triatomic there is one additional rotational mode giving $C_{V,\mathrm{m}} = 3R$. Hence $\gamma = 1 + R/(3R) = 4/3$ and $\boxed{c_\mathrm{s} = (3RT/4M)^{1/2}}$.

Taking the molar mass of air as 29.0 g mol^{-1} and using the value of γ for a diatomic gives at 298 K

$$\begin{aligned} c_\mathrm{s} &= \left(\frac{1.40RT}{M}\right)^{1/2} \\ &= \left(\frac{1.40 \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})}{29.0 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}}\right)^{1/2} = \boxed{346\ \mathrm{m\,s^{-1}}} \end{aligned}$$

P13E.18 It is convenient to rewrite the given expression for the energy by multiplying the numerator and denominator by $e^{\varepsilon/kT}$ to give

$$E = \frac{N\varepsilon}{e^{\varepsilon/kT} + 1}$$

(a) By definition $C_{V,\mathrm{m}} = (\partial U_\mathrm{m}/\partial T)_V$. Here U_m is E with $N = N_\mathrm{A}$ therefore

$$\begin{aligned} C_{V,\mathrm{m}} &= \left(\frac{\partial}{\partial T}\right)_V \frac{N_\mathrm{A}\varepsilon}{e^{\varepsilon/kT} + 1} = \frac{\varepsilon\, e^{\varepsilon/kT}}{kT^2}\frac{N_\mathrm{A}\varepsilon}{(e^{\varepsilon/kT} + 1)^2} \\ &= N_\mathrm{A}k\left(\frac{\varepsilon}{kT}\right)^2 \frac{e^{\varepsilon/kT}}{(e^{\varepsilon/kT} + 1)^2} = R\left(\frac{\varepsilon}{kT}\right)^2 \frac{e^{\varepsilon/kT}}{(e^{\varepsilon/kT} + 1)^2} \end{aligned}$$

Multiplying the numerator and denominator of this expression by $e^{-2\varepsilon/kT}$ gives the required expression.

(b) Figure 13.20 shows a plot of $C_{V,\mathrm{m}}$ as a function of the dimensionless parameter kT/ε.

(c) There is a maximum in the plot but it is not possible to find an analytic expression for its position. Graphical work indicates that the maximum is at $\boxed{kT/\varepsilon = 0.417}$.

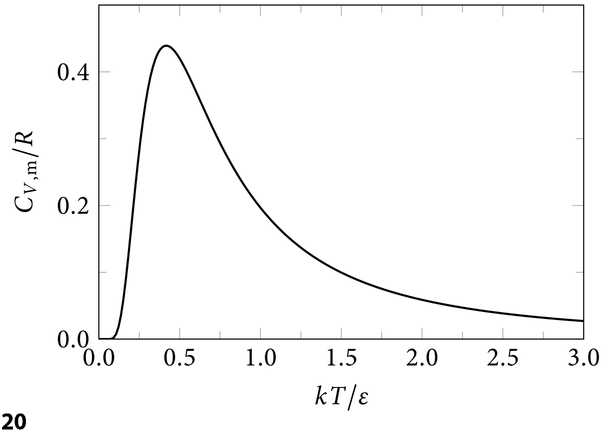


Figure 13.20

13F **Derived functions**

Answers to discussion questions

D13F.2 This is discussed in Section 13F.2(c) on page 571.

Solutions to exercises

E13F.1(b) The Gibbs energy is computed from the partition function using [13F.8–*568*], $G(T) = G(0) - nRT \ln q/N$. As usual, the partition function is factored into separate contributions from translation, rotation and so on. The factor of $1/N$ is usually taken with the translational contribution, so that, for example, the rotational contribution to the Gibbs energy is $-nRT \ln q^{\mathrm{R}}$, or $-RT \ln q^{\mathrm{R}}$ for the molar quantity.

The rotational partition function of a non-linear rotor is given by [13B.14–*545*], $q^{\mathrm{R}} = (1/\sigma)(kT/hc)^{3/2}(\pi/\tilde{A}\tilde{B}\tilde{C})^{1/2}$, where σ is the symmetry number. O_3 has a twofold axis so $\sigma = 2$.

$$\begin{aligned} q^{\mathrm{R}} &= \frac{1}{2}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2} \\ &= \frac{1}{2} \times \left(\frac{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}}) \times (298.\,\mathrm{K})}{(6.6261\times10^{-34}\,\mathrm{J\,s}) \times (2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})}\right)^{3/2} \\ &\quad \times \left(\frac{\pi}{(3.553\,\mathrm{cm^{-1}}) \times (0.4452\,\mathrm{cm^{-1}}) \times (0.3938\,\mathrm{cm^{-1}})}\right)^{1/2} \\ &= 3.34... \times 10^{3} \\ G_{\mathrm{m}}^{\mathrm{R}} &= -RT \ln q^{\mathrm{R}} \\ &= -(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K}) \times \ln(3.34... \times 10^{3}) = \boxed{-20.11\,\mathrm{kJ\,mol^{-1}}} \end{aligned}$$

The vibrational partition function for each mode is given by [13B.15–*546*], $q^{\mathrm{V}} =$

$1/(1-e^{-\beta hc\tilde{\nu}})$, where $\beta = 1/kT$.

$$hc\beta = \frac{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})}{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}$$
$$= 4.82...\times10^{-3}\,\mathrm{cm}$$

$$q_1^{\mathrm{V}} = \left(1-e^{-hc\beta\tilde{\nu}_1}\right)^{-1}$$
$$= \left(1-e^{-(4.82...\times10^{-3}\,\mathrm{cm})\times(1110\,\mathrm{cm^{-1}})}\right)^{-1} = 1.00...$$
$$q_2^{\mathrm{V}} = \left(1-e^{-(4.82...\times10^{-3}\,\mathrm{cm})\times(705\,\mathrm{cm^{-1}})}\right)^{-1} = 1.03...$$
$$q_3^{\mathrm{V}} = \left(1-e^{-(4.82...\times10^{-3}\,\mathrm{cm})\times(1042\,\mathrm{cm^{-1}})}\right)^{-1} = 1.00...$$
$$q^{\mathrm{V}} = q_1^{\mathrm{V}}\times q_2^{\mathrm{V}}\times q_3^{\mathrm{V}} = (1.00...)\times(1.03...)\times(1.00...) = 1.04...$$

Hence

$$G_{\mathrm{m}}^{\mathrm{V}} = -RT\ln q^{\mathrm{V}}$$
$$= -(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})\times\ln(1.04...) = \boxed{-0.112\,\mathrm{kJ\,mol^{-1}}}$$

E13F.2(b) The Gibbs energy is computed from the partition function using [13F.8–*568*], $G(T) = G(0) - nRT\ln q/N$. As usual, the partition function is factored into separate contributions from translation, rotation and so on. The factor of $1/N$ is usually taken with the translational contribution, therefore the electronic contribution to the Gibbs energy is $-nRT\ln q^{\mathrm{E}}$, or $-RT\ln q^{\mathrm{E}}$ for the molar quantity.

The electronic partition function of this two-level system is

$$q^{\mathrm{E}} = g_0 + g_1 e^{-\beta hc\tilde{\nu}}$$

where g_0 and g_1 are the degeneracies of the ground and first excited state, respectively. In this case $g_0 = 3$ and $g_1 = 2$. With the data given

$$\beta hc\tilde{\nu} = hc\tilde{\nu}/kT$$
$$= \frac{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})\times(7918.1\,\mathrm{cm^{-1}})}{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(400\,\mathrm{K})}$$
$$= 28.4...$$
$$q^{\mathrm{E}} = 3 + 2e^{-28.4...} = 3.00...$$
$$G_{\mathrm{m}}^{\mathrm{E}} = -(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(400\,\mathrm{K})\times\ln(3.00...) = \boxed{-3.65\,\mathrm{kJ\,mol^{-1}}}$$

Because $hc\tilde{\nu} \gg kT$ only the ground state is occupied and essentially only this state contributes to the Gibbs energy.

E13F.3(b) The equilibrium constant for $2\,\mathrm{AB} \rightleftharpoons \mathrm{A_2} + \mathrm{B_2}$ is given by [13F.10b–*570*]

$$K = \frac{q^{\ominus}_{\mathrm{A_2,m}} q^{\ominus}_{\mathrm{B_2,m}}}{(q^{\ominus}_{\mathrm{AB,m}})^2} \mathrm{e}^{-\Delta_r E_0/RT}$$

where A is ^{79}Br and B is ^{81}Br. It is convenient to consider the contribution of each mode to the fraction in the above expression separately.

The standard molar translational partition function is $q^{\ominus}_{\mathrm{m}} = V^{\ominus}_{\mathrm{m}}/\Lambda^3$, with $\Lambda = h/(2\pi mkT)^{1/2}$, therefore $q^{\ominus}_{\mathrm{m}}$ goes as $m^{3/2}$. In the fraction all of the other constants cancel to leave

$$\left(\frac{q^{\ominus}_{\mathrm{A_2,m}} q^{\ominus}_{\mathrm{B_2,m}}}{(q^{\ominus}_{\mathrm{AB,m}})^2}\right)_{\mathrm{trans}} = \left(\frac{m_{\mathrm{A_2}} m_{\mathrm{B_2}}}{m^2_{\mathrm{AB}}}\right)^{3/2}$$

$$= \left(\frac{(2 \times 78.92) \times (2 \times 80.92)}{(78.92 + 80.92)^2}\right)^{3/2} = 0.999...$$

For a diatomic the rotational partition function in the high-temperature limit is given by [13B.13b–*544*] $q^{\mathrm{R}} = kT/\sigma hc\tilde{B}$ where $\sigma = 1$ for heteronuclear and $\sigma = 2$ for homonuclear diatomics. The rotational constant is given by [11B.7–*432*], $\tilde{B} = \hbar/4\pi cI$, with $I = \mu R^2$ and $\mu = m_{\mathrm{A}} m_{\mathrm{B}}/(m_{\mathrm{A}} + m_{\mathrm{B}})$. To a good approximation it can be assumed that the bond length does not vary with isotopic substitution, so it follows that q^{R} goes as $1/\sigma\tilde{B}$ which is as μ/σ. For a homonuclear diatomic, $\mu = m/2$. In the fraction all of the other constants cancel to leave

$$\left(\frac{q_{\mathrm{A_2}} q_{\mathrm{B_2}}}{(q_{\mathrm{AB}})^2}\right)_{\mathrm{rot}} = \frac{(\mu_{\mathrm{A_2}}/2)(\mu_{\mathrm{B_2}}/2)}{[(\mu_{\mathrm{AB}}/1)]^2} = \frac{\mu_{\mathrm{A_2}} \mu_{\mathrm{B_2}}}{4\mu^2_{\mathrm{AB}}}$$

$$= \frac{\frac{1}{2} \times 78.92 \times \frac{1}{2} \times 80.92}{4[(78.92 \times 80.92)/(78.92 + 80.92)]^2} = 0.250...$$

The vibrational partition function is given by [13B.15–*546*] $q^{\mathrm{V}} = (1-\mathrm{e}^{-hc\tilde{\nu}/kT})^{-1}$. The vibrational frequency goes as $(k_{\mathrm{f}}/m_{\mathrm{eff}})^{1/2}$ where k_{f} is the force constant and $m_{\mathrm{eff}} = m_{\mathrm{A}} m_{\mathrm{B}}/(m_{\mathrm{A}} + m_{\mathrm{B}})$. To a good approximation it can be assumed that the force constant does not vary with isotopic substitution, so it follows that for isotopic species $\tilde{\nu}_{\mathrm{A_2}}/\tilde{\nu}_{\mathrm{AB}} = (m_{\mathrm{eff,AB}}/m_{\mathrm{eff,A_2}})^{1/2}$. Applying this expression gives

$$\tilde{\nu}_{\mathrm{A_2}} = (323.22\ \mathrm{cm^{-1}}) \left(\frac{(78.92 \times 80.92)/(78.92 + 80.92)}{\frac{1}{2} \times 78.92}\right)^{1/2}$$

$$= 325.3...\ \mathrm{cm^{-1}}$$

$$\tilde{\nu}_{\mathrm{B_2}} = (323.22\ \mathrm{cm^{-1}}) \left(\frac{(78.92 \times 80.92)/(78.92 + 80.92)}{\frac{1}{2} \times 80.92}\right)^{1/2}$$

$$= 321.3...\ \mathrm{cm^{-1}}$$

Using these frequencies the vibrational partition functions are evaluated as

$$
\begin{aligned}
hc\tilde{\nu}/kT &= \frac{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})\times(323.22\,\mathrm{cm^{-1}})}{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}\\
&= 1.56...\\
q^{\mathrm{V}}_{\mathrm{AB}} &= (1-\mathrm{e}^{-1.56...})^{-1} = 1.26...
\end{aligned}
$$

and likewise

$$
q^{\mathrm{V}}_{\mathrm{A_2}} = 1.26... \qquad q^{\mathrm{V}}_{\mathrm{B_2}} = 1.26...
$$

The fraction for vibration is therefore

$$
\left(\frac{q_{\mathrm{A_2}}q_{\mathrm{B_2}}}{(q_{\mathrm{AB}})^2}\right)_{\mathrm{vib}} = \frac{(1.26...)\times(1.26...)}{(1.26...)^2} = 0.999...
$$

The term $\Delta_\mathrm{r}E_0$ is computed as

$$
\Delta_\mathrm{r}E_0 = N_\mathrm{A}hc(-\tilde{D}_{0,\mathrm{A_2}} - \tilde{D}_{0,\mathrm{B_2}} + 2\tilde{D}_{0,\mathrm{AB}})
$$

The dissociation energy is related to the well depth $\tilde{D}_\mathrm{e}$ by $\tilde{D}_0 = \tilde{D}_\mathrm{e} - \frac{1}{2}\tilde{\nu}$, where $\frac{1}{2}\tilde{\nu}$ is the energy of the vibrational ground state. To a good approximation it can be assumed that $\tilde{D}_\mathrm{e}$ is unaffected by isotopic substitution, hence

$$
\begin{aligned}
\Delta_\mathrm{r}E_0 &= \tfrac{1}{2}N_\mathrm{A}hc(\tilde{\nu}_{0,\mathrm{A_2}} + \tilde{\nu}_{0,\mathrm{B_2}} - 2\tilde{\nu}_{0,\mathrm{AB}})\\
&= \tfrac{1}{2}(6.0221\times10^{23}\,\mathrm{mol^{-1}})\times(6.6261\times10^{-34}\,\mathrm{J\,s})\\
&\quad\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})\times([325.3... + 321.3... - 2\times323.33]\,\mathrm{cm^{-1}})\\
&= +1.24...\,\mathrm{J\,mol^{-1}}
\end{aligned}
$$

Hence

$$
\mathrm{e}^{-\Delta_\mathrm{r}E_0/RT} = \mathrm{e}^{-(+1.24...\,\mathrm{J\,mol^{-1}})/[(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})]} = 0.999...
$$

Putting together all of the parts gives the equilibrium constant as

$$
K = \underbrace{(0.999...)}_{\text{trans}}\times\underbrace{(0.250...)}_{\text{rot}}\times\underbrace{(0.999...)}_{\text{vib}}\times\underbrace{(0.999...)}_{\Delta_\mathrm{r}E_0\ \text{term}} = \boxed{0.250}
$$

What is evident from this calculation is that difference in mass between the two isotopes is a small fraction of their actual mass, and therefore to an excellent approximation it can be assumed that the partition functions for the isotopologues are all the same with the exception of the symmetry factor which is different for the homo- and heteronuclear diatomics. In essence the value of the equilibrium constant is simply determined by the factor of $\sigma^2 = 4$ appearing in the denominator, hence $K = \frac{1}{4}$.

Solutions to problems

P13F.2 The equilibrium constant for this reaction is given by [13F.10b–*570*]

$$K = \frac{q^{\ominus}_{\mathrm{HDO,m}} q^{\ominus}_{\mathrm{HCl,m}}}{q^{\ominus}_{\mathrm{H_2O,m}} q^{\ominus}_{\mathrm{DCl,m}}} \mathrm{e}^{-\Delta_r E_0/RT}$$

It is convenient to consider the contribution of each mode to the fraction in the above expression separately.

The standard molar translational partition function is $q^{\ominus}_{\mathrm{m}} = V^{\ominus}_{\mathrm{m}}/\Lambda^3$, with $\Lambda = h/(2\pi mkT)^{1/2}$, therefore $q^{\ominus}_{\mathrm{m}}$ goes as $m^{3/2}$. In the fraction all of the other constants cancel to leave

$$\left(\frac{q^{\ominus}_{\mathrm{HDO,m}} q^{\ominus}_{\mathrm{HCl,m}}}{q^{\ominus}_{\mathrm{H_2O,m}} q^{\ominus}_{\mathrm{DCl,m}}}\right)_{\mathrm{trans}} = \left(\frac{m_{\mathrm{HDO}} m_{\mathrm{HCl}}}{m_{\mathrm{H_2O}} m_{\mathrm{DCl}}}\right)^{3/2}$$
$$= \left(\frac{19.02 \times 36.46}{18.02 \times 37.46}\right)^{3/2} = 1.04...$$

Assuming the high-temperature limit, the rotational partition function for a heteronuclear diatomic is given by [13B.13b–*544*], $q^{\mathrm{R}} = kT/hc\tilde{B}$, and for a nonlinear molecule by [13B.14–*545*], $q^{\mathrm{R}} = (1/\sigma)(kT/hc)^{3/2}(\pi/\tilde{A}\tilde{B}\tilde{C})^{1/2}$; the symmetry number is 2 for H_2O and 1 for HDO. In the fraction the terms in kT/hc cancel to leave

$$\left(\frac{q_{\mathrm{HDO}} q_{\mathrm{HCl}}}{q_{\mathrm{H_2O}} q_{\mathrm{DCl}}}\right)_{\mathrm{rot}} = \frac{2}{1}\left(\frac{\tilde{A}_{\mathrm{H_2O}}\tilde{B}_{\mathrm{H_2O}}\tilde{C}_{\mathrm{H_2O}}}{\tilde{A}_{\mathrm{HDO}}\tilde{B}_{\mathrm{HDO}}\tilde{C}_{\mathrm{HDO}}}\right)^{1/2} \frac{\tilde{B}_{\mathrm{DCl}}}{\tilde{B}_{\mathrm{HCl}}}$$
$$= \frac{2}{1}\left(\frac{(27.88) \times (14.51) \times (9.29)}{(23.38) \times (9.102) \times (6.417)}\right)^{1/2} \frac{5.449}{10.59} = 1.70...$$

The vibrational partition function is given by [13B.15–*546*] $q^{\mathrm{V}} = (1-\mathrm{e}^{-hc\tilde{\nu}/kT})^{-1}$, which is conveniently expressed as $q^{\mathrm{V}} = (1-\mathrm{e}^{-(1.4388\ \mathrm{cm\ K})\tilde{\nu}/T})^{-1}$. This term is temperature dependent and so needs to be re-evaluated at each temperature. The vibrational partition function for HDO and H_2O is the product of the partition function for each normal mode, for example

$$q^{\mathrm{V}}_{\mathrm{H_2O}} = q^{\mathrm{V}}_{(3656.7\ \mathrm{cm^{-1}})} \times q^{\mathrm{V}}_{(1594.8\ \mathrm{cm^{-1}})} \times q^{\mathrm{V}}_{(3755.8\ \mathrm{cm^{-1}})}$$

The term $\Delta_r E_0$ is computed as

$$\Delta_r E_0 = E_0(\mathrm{HDO}) + E_0(\mathrm{HCl}) - E_0(\mathrm{H_2O}) - E_0(\mathrm{DCl})$$

To a good approximation it can be assumed that the pure electronic energy of a species is unaffected by isotopic substitution, however the vibrational zero point energy will be affected. For a harmonic oscillator the energy of the ground state is $\frac{1}{2}hc\tilde{\nu}$, therefore to compute the total vibrational zero point energy of HDO and H_2O the contribution from each normal mode has to be taken into account.

$$\begin{aligned}E_0(\mathrm{H_2O})_{\mathrm{vib}} &= \tfrac{1}{2}N_{\mathrm{A}}hc(3656.7 + 1594.8 + 3755.8) = N_{\mathrm{A}}hc(4503.65\ \mathrm{cm^{-1}})\\ E_0(\mathrm{HDO})_{\mathrm{vib}} &= \tfrac{1}{2}N_{\mathrm{A}}hc(2726.7 + 1402.2 + 3707.5) = N_{\mathrm{A}}hc(3918.2\ \mathrm{cm^{-1}})\\ E_0(\mathrm{HCl})_{\mathrm{vib}} &= N_{\mathrm{A}}hc(1495.5\ \mathrm{cm^{-1}}) \quad E_0(\mathrm{DCl})_{\mathrm{vib}} = N_{\mathrm{A}}hc(1072.5\ \mathrm{cm^{-1}})\\ \Delta_{\mathrm{r}}E_0 &= N_{\mathrm{A}}hc(3918.2 + 1495.5 - 4503.65 - 1072.5)\\ &= N_{\mathrm{A}}hc(-162.5\ \mathrm{cm^{-1}})\end{aligned}$$

Thus the term $-\Delta_{\mathrm{r}}E_0/RT$ evaluates as

$$\begin{aligned}\frac{-\Delta_{\mathrm{r}}E_0}{RT} &= \frac{-N_{\mathrm{A}}hc(-162.5\ \mathrm{cm^{-1}})}{RT}\\ &= -(6.0221\times10^{23}\ \mathrm{mol^{-1}})\times(6.6261\times10^{-34}\ \mathrm{J\,s})\times(2.9979\times10^{10}\ \mathrm{cm\,s^{-1}})\\ &\quad\times\frac{(-162.5\ \mathrm{cm^{-1}})}{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times T} = (233.7\ \mathrm{K})/T\end{aligned}$$

With these expressions the equilibrium constant is evaluated using mathematical software to give $\boxed{K = 3.90}$ at 298 K and $\boxed{K = 2.42}$ at 800 K. The value of the equilibrium constant is dominated by the symmetry factors and the $\mathrm{e}^{-\Delta_{\mathrm{r}}E_0/RT}$ term.

P13F.4 The standard molar Gibbs energy is computed from the partition function using [13F.9b–*569*], $G^{\ominus}_{\mathrm{m}}(T) = G^{\ominus}_{\mathrm{m}}(0) - RT\ln q^{\ominus}_{\mathrm{m}}/N_{\mathrm{A}}$. As usual, the partition function is factored into separate contributions from translation, rotation and so on. The factor of $1/N_{\mathrm{A}}$ is usually taken with the translational contribution.

The standard molar translational partition function is given by $q^{\ominus}_{\mathrm{m}} = V^{\ominus}_{\mathrm{m}}/\Lambda^3 = RT/p^{\ominus}\Lambda^3$. Taking the mass of BSi as $10.81 + 28.09 = 38.90\ m_{\mathrm{u}}$, Λ is given by [13B.7–*541*]

$$\begin{aligned}\Lambda &= h/(2\pi mkT)^{1/2}\\ &= \frac{6.6261\times10^{-34}\ \mathrm{J\,s}}{[2\pi(38.90\times1.6605\times10^{-27}\ \mathrm{kg})\times(1.3806\times10^{-23}\ \mathrm{J\,K^{-1}})\times(2000\ \mathrm{K})]^{1/2}}\\ &= 6.25...\times10^{-12}\ \mathrm{m}\\ q^{\ominus}_{\mathrm{m}}/N_{\mathrm{A}} &= \frac{RT}{p^{\ominus}\Lambda^3N_{\mathrm{A}}}\\ &= \frac{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(2000\ \mathrm{K})}{(10^5\ \mathrm{N\,m^{-2}})\times(6.25...\times10^{-12}\ \mathrm{m})^3\times(6.0221\times10^{23}\ \mathrm{mol^{-1}})}\\ &= 1.12...\times10^{9}\end{aligned}$$

For a heteronuclear diatomic the rotational partition function in the high temperature limit is given by [13B.13b–*544*] $q^{\mathrm{R}} = kT/hc\tilde{B}$. The rotational constant is given by [11B.7–*432*], $\tilde{B} = \hbar/4\pi c I$, with $I = \mu R^2$ and $\mu = m_A m_B/(m_A + m_B)$.

$$\begin{aligned}\tilde{B} &= \frac{\hbar}{4\pi c R^2}\frac{(m_A + m_B)}{m_A m_B}\\ &= \frac{1.0546\times10^{-34}\,\mathrm{J\,s}}{4\pi\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})\times(190.5\times10^{-12}\,\mathrm{m})^2}\\ &\quad\times\frac{(10.81+28.09)}{10.81\times28.09}\times\frac{1}{1.6605\times10^{-27}\,\mathrm{kg}} = 0.595...\,\mathrm{cm^{-1}}\\ q^R &= \frac{kT}{hc\tilde{B}}\\ &= \frac{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(2000\,\mathrm{K})}{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})\times(0.595...\,\mathrm{cm^{-1}})}\\ &= 2.33...\times10^3\end{aligned}$$

The vibrational partition function is given by [13B.15–*546*], $q^V = 1/(1-e^{-\beta hc\tilde{\nu}})$, where $\beta = 1/kT$.

$$\begin{aligned}hc\beta &= \frac{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})}{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(2000\,\mathrm{K})}\\ &= 7.19...\times10^{-4}\,\mathrm{cm}\\ q^V &= \left(1-e^{-(7.19...\times10^{-4}\,\mathrm{cm})\times(772\,\mathrm{cm^{-1}})}\right)^{-1} = 2.34...\end{aligned}$$

The electronic ground state has a degeneracy of 4 (the spin multiplicity); the excited state has spin degeneracy of 2 and an orbital degeneracy of 2, giving a total degeneracy of 4.

$$\begin{aligned}q^E &= g_0 + g_1 e^{-hc\beta\tilde{\nu}}\\ &= 4 + 4e^{-(7.19...\times10^{-4}\,\mathrm{cm})\times(8000\,\mathrm{cm^{-1}})} = 4.01...\end{aligned}$$

The overall partition function is the product of these individual contributions, therefore

$$\begin{aligned}G_m^{\ominus}(2000)-G_m^{\ominus}(0) &= -RT\ln q_m^{\ominus}/N_A\\ &= -(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(2000\,\mathrm{K})\\ &\quad\times\ln\left[(1.12...\times10^9)\times(2.33...\times10^3)\times(2.34...)\times(4.01...)\right]\\ &= \boxed{-512\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

P13F.6 The standard molar Gibbs energy is computed from the partition function using [13F.9b–*569*], $G_m^{\ominus}(T) = G_m^{\ominus}(0) - RT\ln q_m^{\ominus}/N_A$. As usual, the partition function is factored into separate contributions from translation, rotation and so on; the factor of $1/N_A$ is usually taken with the translational contribution.

The standard molar translational partition function is given by $q_{\mathrm{m}}^{\ominus} = V_{\mathrm{m}}^{\ominus}/\Lambda^3 = RT/p^{\ominus}\Lambda^3$. Taking the mass of C_3 as $3(12.01) = 36.03\,m_{\mathrm{u}}$, Λ is given by [13B.7–*541*]. At 10.00 K

$$\begin{aligned}\Lambda &= h/(2\pi mkT)^{1/2}\\ &= \frac{6.6261\times10^{-34}\,\mathrm{J\,s}}{[2\pi(102.9\times1.6605\times10^{-27}\,\mathrm{kg})\times(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(10.00\,\mathrm{K})]^{1/2}}\\ &= 9.19...\times10^{-11}\,\mathrm{m}\\ q_{\mathrm{m}}^{\ominus}/N_{\mathrm{A}} &= \frac{RT}{p^{\ominus}\Lambda^3N_{\mathrm{A}}}\\ &= \frac{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(10.00\,\mathrm{K})}{(10^5\,\mathrm{N\,m^{-2}})\times(9.19...\times10^{-11}\,\mathrm{m})^3\times(6.0221\times10^{23}\,\mathrm{mol^{-1}})}\\ &= 1.77...\times10^3\end{aligned}$$

A similar calculation at 100.0 K gives $q_{\mathrm{m}}^{\ominus}/N_{\mathrm{A}} = 5.61...\times10^5$

For a nonlinear molecule the rotational partition function is given by [13B.14–*545*], $q^{\mathrm{R}} = (1/\sigma)(kT/hc)^{3/2}(\pi/\tilde{A}\tilde{B}\tilde{C})^{1/2}$; assuming that the molecule is 'bent' (angular), $\sigma = 2$. The rotational constant, in the high-temperature limit, is given by [11B.7–*432*], $\tilde{B} = \hbar/4\pi cI$. The first step is to compute the rotational constants.

$$\begin{aligned}\tilde{B} &= \frac{\hbar}{4\pi cI}\\ &= \frac{6.6261\times10^{-34}\,\mathrm{J\,s}}{4\pi(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})\times(1.6605\times10^{-27}\,\mathrm{kg})\times(39.340\times10^{-20}\,\mathrm{m^2})}\\ &= 0.428...\,\mathrm{cm^{-1}}\end{aligned}$$

Similar calculations gives the other two rotational constants as $0.431...\,\mathrm{cm^{-1}}$ and $54.7...\,\mathrm{cm^{-1}}$. Expressed as characteristic rotational temperatures these give $\theta^{\mathrm{R}} = hc\tilde{B}/k = 0.616\,\mathrm{K}, 0.621\,\mathrm{K}$, and 78.7 K. At 10 K, and possibly even at 100 K, the condition $T > \theta^{\mathrm{R}}$ is not satisfied for all the rotational constants, therefore the high-temperature expression for the partition function cannot be used.

As described, the C_3 molecule is an asymmetric rotor, for which there is no explicit expression for the energy levels. However, given that two of the rotational constants are quite similar, it is reasonable to approximate the molecule as a symmetric rotor with $\tilde{A} = 54.7...\,\mathrm{cm^{-1}}$ and $\tilde{B} = 0.430...\,\mathrm{cm^{-1}}$ (the latter being the average of the two similar rotational constants). The partition function is then evaluated term by term using the approach described in *How is that done?* 13B.2 on page 543; this is best done using mathematical software. At 10 K the result is $q^{\mathrm{R}} = 16.5...$ and at 100 K $q^{\mathrm{R}} = 323.4...$

At 100 K the high temperature form of the partition function gives

$$\begin{aligned} q^{\mathrm{R}} &= (1/\sigma)(kT/hc)^{3/2}(\pi/\tilde{A}\tilde{B}\tilde{C})^{1/2} \\ &= \tfrac{1}{2}\left(\frac{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(100.0\,\mathrm{K})}{6.6261\times10^{-34}\,\mathrm{J\,s}}\right)^{3/2} \\ &\quad\times\left(\frac{\pi}{(0.428...\,\mathrm{cm^{-1}})\times(0.431...\,\mathrm{cm^{-1}})\times(54.7...\,\mathrm{cm^{-1}})}\right)^{1/2} \\ &= 161.3... \end{aligned}$$

Taking into account the symmetry factor, this is very close to the value obtained by explicit summation. At 10.00 K the high-temperature form gives (excluding the symmetry factor) $q^{\mathrm{R}} = 10.2...$ which, as expected, does not agree with the result obtained by explicit summation. The nuclear spin effects are more complex to account for in the term-by-term summation, and in the absence of a detailed analysis of this it is simply assumed that a symmetry factor of 2 is appropriate, giving the final value of the rotational partition function at 10.00 K of $q^{\mathrm{R}} = \frac{1}{2}\times 16.5... = 8.25....$

The vibrational partition function for each mode is given by [13B.15–*546*], $q^{\mathrm{V}} = 1/(1-\mathrm{e}^{-\beta hc\tilde{\nu}})$, where $\beta = 1/kT$. At 10.00 K

$$\begin{aligned} hc\beta &= \frac{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{10}\,\mathrm{cm\,s^{-1}})}{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(10.00\,\mathrm{K})} \\ &= 0.143...\,\mathrm{cm} \\ q_1^{\mathrm{V}} &= \left(1-\mathrm{e}^{-hc\beta\tilde{\nu}_1}\right)^{-1} \\ &= \left(1-\mathrm{e}^{-(0.143...\,\mathrm{cm})\times(63.4\,\mathrm{cm^{-1}})}\right)^{-1} = 1.00... \end{aligned}$$

The partition functions for the other normal modes also evaluate to 1.00...; given the low temperature, it is is to be expected that q^{V} will be essentially 1 as only the ground state contributes. The overall vibrational partition function is the product of these individual contributions: $q^{\mathrm{V}} = 1.00....$ A similar calculation at 100.0 K gives $q^{\mathrm{V}} = 1.67....$

The overall partition function is the product of these contributions from the different modes, therefore

$$\begin{aligned} G_{\mathrm{m}}^{\ominus}(10.00)-G_{\mathrm{m}}^{\ominus}(0) &= -RT\ln q_{\mathrm{m}}^{\ominus}/N_{\mathrm{A}} \\ &= -(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(10.00\,\mathrm{K}) \\ &\quad\times\ln\left[(1.77...\times10^{3})\times(8.25...)\times(1.00...)\right] \\ &= \boxed{-798\,\mathrm{J\,mol^{-1}}} \end{aligned}$$

A similar calculation at 100.0 K gives $G_{\mathrm{m}}^{\ominus}(100.0)-G_{\mathrm{m}}^{\ominus}(0) = \boxed{-15.7\,\mathrm{kJ\,mol^{-1}}}$.

Answers to integrated activities

I13.2 Note that there is an error in the question: the expression for $\xi(\beta)$ should include an additional factor of $g(J)$. To make the notation more compact the energy levels will be written ε_J and the degeneracies g_J; derivatives with respect to β will be assumed to be at constant V.

First, an expression for C_V is developed.

$$\begin{aligned} U &= -N\frac{1}{q}\frac{\mathrm{d}q}{\mathrm{d}\beta} = -N\frac{1}{q}\frac{\mathrm{d}}{\mathrm{d}\beta}\sum_J g_J \mathrm{e}^{-\beta\varepsilon_J} \\ &= N\frac{1}{q}\sum_J g_J\varepsilon_J \mathrm{e}^{-\beta\varepsilon_J} \end{aligned}$$

Noting that $\mathrm{d}/\mathrm{d}T = -k\beta^2(\mathrm{d}/\mathrm{d}\beta)$

$$\begin{aligned} C_V &= \frac{\mathrm{d}U}{\mathrm{d}T} = -k\beta^2\frac{\mathrm{d}U}{\mathrm{d}\beta} \\ &= -Nk\beta^2\frac{\mathrm{d}}{\mathrm{d}\beta}\left[\frac{1}{q}\sum_J g_J\varepsilon_J\mathrm{e}^{-\beta\varepsilon_J}\right] \\ &= -Nk\beta^2\left[\frac{-1}{q^2}\frac{\mathrm{d}q}{\mathrm{d}\beta}\sum_J g_J\varepsilon_J\mathrm{e}^{-\beta\varepsilon_J} - \frac{1}{q}\sum_J g_J\varepsilon_J^2\mathrm{e}^{-\beta\varepsilon_J}\right] \\ &= -Nk\beta^2\left[\frac{1}{q^2}\left(\sum_{J'} g_{J'}\varepsilon_{J'}\mathrm{e}^{-\beta\varepsilon_{J'}}\right)\left(\sum_J g_J\varepsilon_J\mathrm{e}^{-\beta\varepsilon_J}\right) - \frac{1}{q}\sum_J g_J\varepsilon_J^2\mathrm{e}^{-\beta\varepsilon_J}\right] \end{aligned}$$

The numerator and denominator of the final term in the bracket are both multiplied by q, and then a factor of $1/q^2$ is taken outside the bracket to give

$$\begin{aligned} C_V &= \frac{-Nk\beta^2}{q^2}\left[\left(\sum_{J'} g_{J'}\varepsilon_{J'}\mathrm{e}^{-\beta\varepsilon_{J'}}\right)\left(\sum_J g_J\varepsilon_J\mathrm{e}^{-\beta\varepsilon_J}\right) - q\sum_J g_J\varepsilon_J^2\mathrm{e}^{-\beta\varepsilon_J}\right] \\ &= \frac{-Nk\beta^2}{q^2}\left[\left(\sum_{J'} g_{J'}\varepsilon_{J'}\mathrm{e}^{-\beta\varepsilon_{J'}}\right)\left(\sum_J g_J\varepsilon_J\mathrm{e}^{-\beta\varepsilon_J}\right)\right. \\ &\qquad\left. - \left(\sum_{J'} g_{J'}\mathrm{e}^{-\beta\varepsilon_{J'}}\right)\left(\sum_J g_J\varepsilon_J^2\mathrm{e}^{-\beta\varepsilon_J}\right)\right] \end{aligned}$$

The product of the sums are next rewritten as double sums

$$C_V = \frac{-Nk\beta^2}{q^2}\left[\sum_{J,J'} g_J g_{J'}\varepsilon_J\varepsilon_{J'}\mathrm{e}^{-\beta(\varepsilon_J+\varepsilon_{J'})} - \sum_{J,J'} g_J g_{J'}\varepsilon_J^2\mathrm{e}^{-\beta(\varepsilon_J+\varepsilon_{J'})}\right]$$

Taking a hint from the final result, consider the double sum

$$\begin{aligned} &\sum_{J,J'}(\varepsilon_J - \varepsilon_{J'})^2 g_J g_{J'}\mathrm{e}^{-\beta(\varepsilon_J+\varepsilon_{J'})} \\ &= \sum_{J,J'}\varepsilon_J^2 g_J g_{J'}\mathrm{e}^{-\beta(\varepsilon_J+\varepsilon_{J'})} + \sum_{J,J'}\varepsilon_{J'}^2 g_J g_{J'}\mathrm{e}^{-\beta(\varepsilon_J+\varepsilon_{J'})} - 2\sum_{J,J'}\varepsilon_J\varepsilon_{J'} g_J g_{J'}\mathrm{e}^{-\beta(\varepsilon_J+\varepsilon_{J'})} \end{aligned}$$

The first two sums only differ by swapping the indices J and J', so they are in fact identical. Hence the last line may be written

$$= 2\sum_{J,J'} \varepsilon_J^2 g_J g_{J'} \mathrm{e}^{-\beta(\varepsilon_J+\varepsilon_{J'})} - 2\sum_{J,J'} \varepsilon_J \varepsilon_{J'} g_J g_{J'} \mathrm{e}^{-\beta(\varepsilon_J+\varepsilon_{J'})}$$

Apart from an overall sign and a factor of $\frac{1}{2}$, these two terms are the same as those in the bracket in the expression for C_V above, hence

$$\begin{aligned} C_V &= \frac{-Nk\beta^2}{q^2}\left[\sum_{J,J'} g_J g_{J'} \varepsilon_J \varepsilon_{J'} \mathrm{e}^{-\beta(\varepsilon_J+\varepsilon_{J'})} - \sum_{J,J'} g_J g_{J'} \varepsilon_J^2 \mathrm{e}^{-\beta(\varepsilon_J+\varepsilon_{J'})}\right] \\ &= \frac{Nk\beta^2}{2q^2}\sum_{J,J'} (\varepsilon_J - \varepsilon_{J'})^2 g_J g_{J'} \mathrm{e}^{-\beta(\varepsilon_J+\varepsilon_{J'})} \end{aligned}$$

which is the required expression.

For a diatomic $\beta\varepsilon_J = \beta hc\tilde{B}J(J+1) = hc\tilde{B}J(J+1)/kT = \theta^{\mathrm{R}}J(J+1)/T$, where $\theta^{\mathrm{R}} = hc\tilde{B}/k$; the degeneracy is $g_J = (2J+1)$. For the molar quantity $N_{\mathrm{A}}k\beta^2 = N_{\mathrm{A}}k/k^2T^2 = R/k^2T^2$. The molar hear capacity is therefore given by

$$\begin{aligned} C_{V,\mathrm{m}}/R &= \frac{1}{k^2T^2}\frac{1}{2q^2}(hc\tilde{B})^2 \\ &\quad \times \sum_{J,J'}[J(J+1) - J'(J'+1)]^2(2J+1)(2J'+1)\,\mathrm{e}^{-\theta^{\mathrm{R}}[J(J+1)+J'(J'+1)]/T} \\ &= \left(\frac{\theta^{\mathrm{R}}}{T}\right)^2 \frac{1}{2q^2} \\ &\quad \times \sum_{J,J'}[J(J+1) - J'(J'+1)]^2(2J+1)(2J'+1)\,\mathrm{e}^{-\theta^{\mathrm{R}}[J(J+1)+J'(J'+1)]/T} \end{aligned}$$

This expression is used to generate the curves in Fig. 13.21 for particular pairs of values of J and J', that is just one term from the double sum. However, the term for $J = 0, J' = 1$ is identical to that for $J = 1, J' = 0$, so the curves plotted in the figure are *twice* the value for the particular combination of J and J' indicated.

This double sum is not a particularly efficient method for computing the heat capacity, but it can be evaluated using mathematical software to give the curve also shown in Fig. 13.21. For a plot up to $T/\theta^{\mathrm{R}} = 5$ if is sufficient to consider contributions from levels with $J \leq 10$; this makes the calculation more tractable.

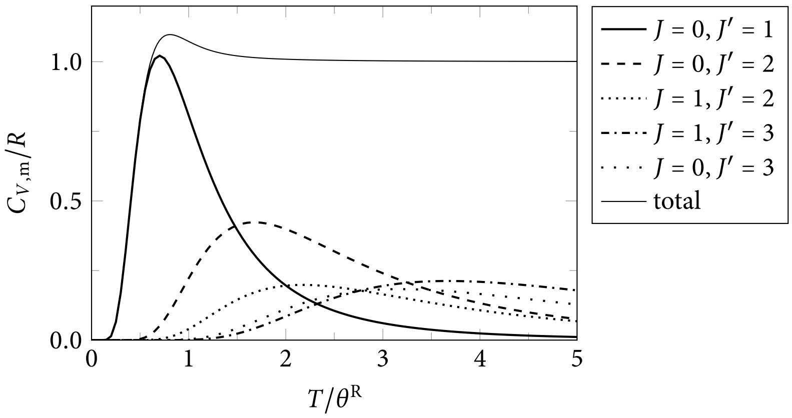

$C_{V,\mathrm{m}}/R$
1.0
0.5
0.0
0
1
2
3
4
5
T/θ^{R}
$J = 0, J' = 1$
$J = 0, J' = 2$
$J = 1, J' = 2$
$J = 1, J' = 3$
$J = 0, J' = 3$
total

Figure 13.21

14

Molecular Interactions

14A Electric properties of molecules

Answers to discussion questions

D14A.2 When the applied field changes direction slowly, the permanent dipole moment has time to reorientate and so follows the field: the whole molecule rotates into a new direction in response to a change in 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). It is said that *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 distorted 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.

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

E14A.1(b) The molecules are shown in Fig. 14.1: SO_3 is trigonal planar, XeF_4 is square planar, and SF_4 is based on a trigonal bipyramid with one equatorial position not occupied by a ligand.

SO_3 and XeF_4 are $\boxed{\text{nonpolar}}$ because, although there are partial charges on each of the atoms, the dipole moments associated with each bond cancel to give no resultant dipole. However, SF_4 is $\boxed{\text{polar}}$ because the dipole moments do not cancel.

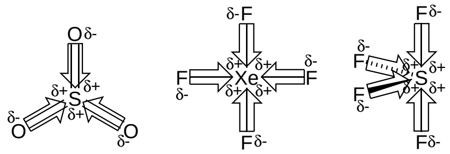


Figure 14.1

An alternative approach is use a symmetry argument. As explained in Section 10A.3(a) on page 394, only molecules belonging to point groups C_n, C_{nv} or C_s may have a permanent electric dipole moment. SO_3 and XeF_4 belong to point groups D_{3h} and D_{4h} respectively, so they are not polar, while SF_4 belongs to point group C_{2v} so is polar.

E14A.2(b) The magnitude of the resultant dipole moment, μ_{res}, is given by [14A.3a–*586*], $\mu_{res} = (\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta)^{1/2}$.

$$\mu_{res} = \left((2.5\text{ D})^2 + (0.5\text{ D})^2 + 2 \times (2.5\text{ D}) \times (0.5\text{ D}) \times \cos 120°\right)^{1/2} = \boxed{2.3\text{ D}}$$

E14A.3(b) The arrangement of charges is shown on the left of Fig. 14.2

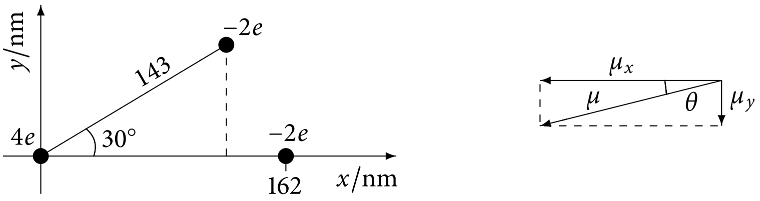


Figure 14.2

The x component of the dipole are given by [14A.4a–*586*], $\mu_x = \sum_J Q_J x_J$, and similarly for the y and z components; note that in this case $\mu_z = 0$ because all of the point charges have a z coordinate of zero. The components are then combined using [14A.4b–*586*], $\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$, which is represented graphically on the right of Fig. 14.2.

$$\begin{aligned}\mu_x = \sum_J Q_J x_J = \Big[&-2 \times (1.6022 \times 10^{-19}\text{ C}) \times (162 \times 10^{-12}\text{ m}) \\ &-2 \times (1.6022 \times 10^{-19}\text{ C}) \times (143 \times 10^{-12}\text{ m}) \times \cos 30°\Big] \\ &\times \frac{1\text{ D}}{3.3356 \times 10^{-30}\text{ C m}} = -27.4...\text{ D}\end{aligned}$$

where 1 D = 3.3356×10^{-30} C m is used from inside the front cover.

$$\begin{aligned}\mu_y &= \sum_J Q_J y_J \\ &= -2 \times (1.6022 \times 10^{-19}\,\mathrm{C}) \times (143 \times 10^{-12}\,\mathrm{m}) \times \sin 30° \\ &\quad \times \frac{1\,\mathrm{D}}{3.3356 \times 10^{-30}\,\mathrm{C\,m}} = -6.86...\,\mathrm{D}\end{aligned}$$

The magnitude of the resultant is

$$\mu = \left(\mu_x^2 + \mu_y^2\right)^{1/2} = \left[(-27.4...\,\mathrm{D})^2 + (-6.86...\,\mathrm{D})^2\right] = \boxed{28\,\mathrm{D}}$$

and, from the diagram on the right of Fig. 14.2, the direction is given by

$$\theta = \tan^{-1}\left(\frac{6.86...\,\mathrm{D}}{27.4...\,\mathrm{D}}\right) = \boxed{14°}$$

E14A.4(b) The relationship between the induced dipole moment μ^* and the electric field strength $\mathcal{E}$ is given by [14A.5a–*587*], $\mu^* = \alpha\mathcal{E}$, where α is the polarizability. The polarizability volume α' is related to the polarizability α by [14A.6–*587*], $\alpha' = \alpha/4\pi\varepsilon_0$. Combining these equations, rearranging for $\mathcal{E}$, and using 1 V = 1 J C^{-1} gives

$$\begin{aligned}\mathcal{E} &= \frac{\mu^*}{4\pi\varepsilon_0\alpha'} = \frac{(2.5 \times 10^{-6}\,\mathrm{D}) \times [(3.3356 \times 10^{-30}\,\mathrm{C\,m})/(1\,\mathrm{D})]}{4\pi \times (8.8542 \times 10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}}) \times (1.05 \times 10^{-29}\,\mathrm{m^3})} \\ &= \boxed{7.1 \times 10^3\,\mathrm{V\,m^{-1}}}\end{aligned}$$

E14A.5(b) The molar polarization P_m is defined by [14A.11–*590*], $P_m = (N_A/3\varepsilon_0)(\alpha + \mu^2/3kT)$, where α is the polarizability of the molecule and μ is its dipole moment. This equation is written as

$$P_m = \frac{N_A\alpha}{3\varepsilon_0} + \frac{N_A\mu^2}{9\varepsilon_0 k}\frac{1}{T}$$

which implies that a graph of P_m against $1/T$ should be a straight line with slope $N_A\mu^2/9\varepsilon_0 k$ and intercept $N_A\alpha/3\varepsilon_0$. However, as there are only two data points it is convenient to calculate the required quantities directly from the data. Writing the molar polarization at the two temperatures as $P_m(T_1)$ and $P_m(T_2)$ and considering $P_m(T_2) - P_m(T_1)$ gives

$$P_m(T_2) - P_m(T_1) = \frac{N_A\mu^2}{9\varepsilon_0 k}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

which is rearranged to give

$$\begin{aligned}\mu &= \left(\frac{9\varepsilon_0 k}{N_A}\times\frac{P_m(T_2)-P_m(T_1)}{1/T_2-1/T_1}\right)^{1/2}\\ &= \left(\frac{9\times(8.8542\times10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}})\times(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})}{6.0221\times10^{23}\,\mathrm{mol^{-1}}}\right.\\ &\qquad\left.\times\frac{(71.43\times10^{-6}\,\mathrm{m^3\,mol^{-1}})-(75.74\times10^{-6}\,\mathrm{m^3\,mol^{-1}})}{1/(421.7\,\mathrm{K})-1/(320.0\,\mathrm{K})}\right)^{1/2}\\ &= 3.23...\times10^{-30}\,\mathrm{C\,m} = \boxed{0.9690\,\mathrm{D}}\end{aligned}$$

The value of α is found using this value of μ together with one of the data points; both give the same answer. Rearranging [14A.11–*590*], $P_m = (N_A/3\varepsilon_0)(\alpha + \mu^2/3kT)$, for α and using the data for 320.0 K gives

$$\begin{aligned}\alpha &= \frac{3\varepsilon_0 P_m}{N_A}-\frac{\mu^2}{3kT}\\ &= \frac{3\times(8.8542\times10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}})\times(75.74\times10^{-6}\,\mathrm{m^3\,mol^{-1}})}{6.0221\times10^{23}\,\mathrm{mol^{-1}}}\\ &\qquad-\frac{(3.23...\times10^{-30}\,\mathrm{C\,m})^2}{3\times(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(320.0\,\mathrm{K})} = \boxed{2.552\times10^{-39}\,\mathrm{C^2\,m^2\,J^{-1}}}\end{aligned}$$

E14A.6(b) The relationship between relative permittivity and molar polarization is given by the Debye equation, [14A.10–*590*], $(\varepsilon_r-1)/(\varepsilon_r+2) = \rho P_m/M$. Rearranging gives

$$\varepsilon_r - 1 = \frac{\rho P_m}{M}(\varepsilon_r+2) \quad\text{hence}\quad \varepsilon_r - 1 = \varepsilon_r\left(\frac{\rho P_m}{M}\right)+\frac{2\rho P_m}{M}$$

$$\text{hence}\quad \varepsilon_r\left(1-\frac{\rho P_m}{M}\right) = 1+\frac{2\rho P_m}{M} \quad\text{hence}\quad \varepsilon_r = \frac{1+2\rho P_m/M}{1-\rho P_m/M}$$

Taking the molar mass as $M = 85.0\,\mathrm{g\,mol^{-1}}$ gives

$$\begin{aligned}\varepsilon_r &= \frac{1+2\rho P_m/M}{1-\rho P_m/M}\\ &= \frac{1+2\times(1.92\,\mathrm{g\,cm^{-3}})\times(32.16\,\mathrm{cm^3\,mol^{-1}})/(85.0\,\mathrm{g\,mol^{-1}})}{1-(1.92\,\mathrm{g\,cm^{-3}})\times(32.16\,\mathrm{cm^3\,mol^{-1}})/(85.0\,\mathrm{g\,mol^{-1}})} = \boxed{8.97}\end{aligned}$$

E14A.7(b) The relationship between the refractive index n_r at a specified wavelength and the relative permittivity ε_r at the same wavelength is given by [14A.13–*592*], $n_r = \varepsilon_r^{1/2}$, hence $\varepsilon_r = n_r^2$. In addition the relationship between relative permittivity and the polarizability α is given by the Clausius–Mossotti equation, [14A.12–*590*], $(\varepsilon_r - 1)/(\varepsilon_r + 2) = \rho N_A\alpha/3M\varepsilon_0$. In using this equation it is assumed that there are no contributions from permanent electric dipole moments to the polarization, either because the molecules are nonpolar 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. Replacing ε_r by n_r^2 in the Clausius–Mossotti equation gives

$$\frac{n_r^2-1}{n_r^2+2}=\frac{\rho N_A\alpha}{3M\varepsilon_0} \quad \text{hence} \quad \alpha=\frac{3M\varepsilon_0}{\rho N_A}\times\frac{n_r^2-1}{n_r^2+2}$$

Taking $M = 65.5\ \text{g mol}^{-1}$ gives

$$\begin{aligned}\alpha &= \frac{3\times(65.5\ \text{g mol}^{-1})\times(8.8542\times10^{-12}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^{-1})}{(2.99\times10^6\ \text{g m}^{-3})\times(6.0221\times10^{23}\ \text{mol}^{-1})}\times\frac{1.622^2-1}{1.622^2+2}\\ &= \boxed{3.40\times10^{-40}\ \text{C}^2\ \text{m}^2\ \text{J}^{-1}}\end{aligned}$$

E14A.8(b) The relationship between the refractive index n_r at a specified wavelength and the relative permittivity ε_r at the same wavelength is given by [14A.13–*592*], $n_r = \varepsilon_r^{1/2}$. In order to find ε_r the Clausius–Mossotti equation, [14A.12–*590*], $(\varepsilon_r - 1)/(\varepsilon_r + 2) = \rho N_A\alpha/3M\varepsilon_0$, is used, with the value of the polarizability α being determined from the polarizability volume α' using [14A.6–*587*], $\alpha' = \alpha/4\pi\varepsilon_0$.

In using the Clausius–Mossotti equation it is assumed that there are no contributions from permanent electric dipole moments to the polarization, either because the molecules are nonpolar 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.

The first step is to rearrange the Clausius–Mossotti equation for ε_r

$$\frac{\varepsilon_r-1}{\varepsilon_r+2}=\frac{\rho N_A\alpha}{3M\varepsilon_0} \quad \text{hence} \quad \varepsilon_r-1=\frac{\rho N_A\alpha}{3M\varepsilon_0}(\varepsilon_r+2)$$

$$\text{hence} \quad \varepsilon_r\left(1-\frac{\rho N_A\alpha}{3M\varepsilon_0}\right)=1+\frac{2\rho N_A\alpha}{3M\varepsilon_0} \quad \text{hence} \quad \varepsilon_r=\frac{1+2\rho N_A\alpha/3M\varepsilon_0}{1-\rho N_A\alpha/3M\varepsilon_0}$$

Replacing α by $4\pi\varepsilon_0\alpha'$ and ε_r by n_r^2 gives

$$n_r^2=\frac{1+2\rho N_A(4\pi\varepsilon_0\alpha')/3M\varepsilon_0}{1-\rho N_A(4\pi\varepsilon_0\alpha')/3M\varepsilon_0}=\frac{1+8\pi\rho N_A\alpha'/3M}{1-4\pi\rho N_A\alpha'/3M}=\frac{1+2C}{1-C}$$

where $C = 4\pi\rho N_A\alpha'/3M$. Using $M = 72.3\ \text{g mol}^{-1} = 0.0723\ \text{kg mol}^{-1}$ gives

$$\begin{aligned}C &= 4\pi\rho N_A\alpha'/3M\\ &= \frac{4\pi\times(865\ \text{kg m}^{-3})\times(6.0221\times10^{23}\ \text{mol}^{-1})\times(2.2\times10^{-30}\ \text{m}^3)}{3\times(0.0723\ \text{kg mol}^{-1})}\\ &= 0.0663...\end{aligned}$$

$$n_r=\left(\frac{1+2C}{1-C}\right)^{1/2}=\left(\frac{1+2\times0.0663...}{1-0.0663...}\right)^{1/2}=\boxed{1.1}$$

E14A.9(b) The Debye equation, [14A.10–*590*], is $(\varepsilon_r-1)/(\varepsilon_r+2) = \rho P_m/M$, where P_m is the molar polarizability. The latter is defined by [14A.11–*590*], $P_m = (N_A/3\varepsilon_0)(\alpha + \mu^2/3kT)$, where μ is the dipole moment and α is the polarizability, which is related to the polarizability volume α' according to [14A.6–*587*], $\alpha' = \alpha/4\pi\varepsilon_0$.

Replacing α in the expression for P_m by $4\pi\varepsilon_0\alpha'$ gives

$$\begin{aligned} P_m &= \frac{N_A}{3\varepsilon_0}\left(4\pi\varepsilon_0\alpha' + \frac{\mu^2}{3kT}\right) \\ &= \frac{6.0221\times10^{23}\ \text{mol}^{-1}}{3\times(8.8542\times10^{-12}\ \text{J}^{-1}\,\text{C}^2\,\text{m}^{-1})}\times\Bigg(4\pi\times(8.8542\times10^{-12}\ \text{J}^{-1}\,\text{C}^2\,\text{m}^{-1}) \\ &\quad \times(1.5\times10^{-29}\ \text{m}^3) + \frac{(5.17\times10^{-30}\ \text{C m})^2}{3\times(1.3806\times10^{-23}\ \text{J K}^{-1})\times([25+273.15]\ \text{K})}\Bigg) \\ &= 8.69...\times10^{-5}\ \text{m}^3\,\text{mol}^{-1} \end{aligned}$$

The Debye equation is then rearranged for ε_r

$$\frac{\varepsilon_r-1}{\varepsilon_r+2} = \frac{\rho P_m}{M} \quad \text{hence} \quad \varepsilon_r = \frac{1+2\rho P_m/M}{1-\rho P_m/M}$$

The molar mass of bromobenzene, C_6H_5Br is 156.9995 g mol^{-1} or 0.156995 kg mol^{-1}. Hence the relative permittivity is

$$\begin{aligned} \varepsilon_r &= \frac{1+2\rho P_m/M}{1-\rho P_m/M} \\ &= \frac{1+2\times(1491\ \text{kg m}^{-3})\times(8.69...\times10^{-5}\ \text{m}^3\,\text{mol}^{-1})/(0.156995\ \text{kg mol}^{-1})}{1-(1491\ \text{kg m}^{-3})\times(8.69...\times10^{-5}\ \text{m}^3\,\text{mol}^{-1})/(0.156995\ \text{kg mol}^{-1})} \\ &= \boxed{15} \end{aligned}$$

Solutions to problems

P14A.2 The hydrogen peroxide molecule is shown in Fig. 14.3. For convenience the bond lengths are denoted r_{OH} and r_{OO}.

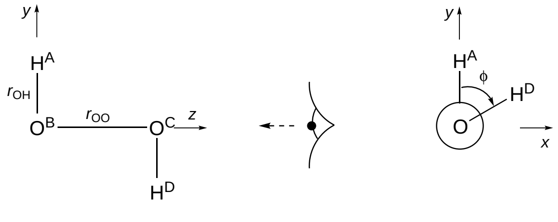


Figure 14.3

Because the molecule is neutral overall, the choice of origin is arbitrary, and is chosen for convenience to be the O^B oxygen, with the z axis along the O–O bond and the y axis along the O^B–H^A bond. With this coordinate system, the coordinates of the atoms are

$$H^A\,(0, r_{OH}, 0) \quad O^B\,(0,0,0) \quad O^C\,(0,0,r_{OO}) \quad H^D\,(r_{OH}\sin\phi, r_{OH}\cos\phi, r_{OO})$$

The x component of the dipole μ_x is given by [14A.4a–*586*], $\mu_x = \sum_J Q_J x_J$, and similarly for the y and z components. The magnitude of the dipole is given by [14A.4b–*586*], $\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$.

$$\mu_x = \sum_J Q_J x_J = +q r_{OH}\sin\phi \quad \mu_y = \sum_J Q_J y_J = +q r_{OH} + q r_{OH}\cos\phi \quad \mu_z = 0$$

$$\begin{aligned}\mu^2 &= \mu_x^2 + \mu_y^2 + \mu_z^2 = (q r_{OH}\sin\phi)^2 + (q r_{OH} + q r_{OH}\sin\phi)^2 \\ &= q^2 r_{OH}^2(\sin^2\phi + 1 + 2\cos\phi + \cos^2\phi) = q^2 r_{OH}^2(2\cos\phi + 2)\end{aligned}$$

where $\cos^2\phi + \sin^2\phi = 1$ is used. Hence $\mu = q r_{OH}\sqrt{2\cos\phi + 2}$. The quantity $\mu/q r_{OH}$ is plotted as a function of ϕ in Fig. 14.4.

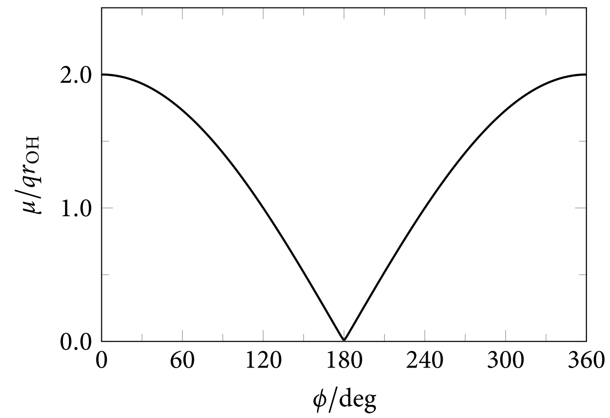


Figure 14.4

P14A.4 The complex is shown in Fig. 14.5, in which the charges on the nitrogen and carbon are denoted $-q$ and $+q$ and the C–N distance by r_{CN}.

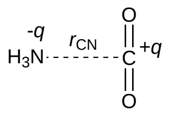


Figure 14.5

The dipole is directed along the N–C bond, taken to be the x-axis, and its magnitude is given by [14A.4a–*586*], $\mu_x = \sum_J Q_J x_J$. Note that $\mu = \mu_x$ in this case as μ_y and μ_z are both zero. The complex overall is neutral so the origin of the coordinate system is arbitrary and is chosen for convenience to be at the nitrogen atom; the carbon atom then has x-coordinate r_{CN}. The dipole is therefore $\mu = qr_{\mathrm{CN}}$ and hence

$$\mu = \sum_{\mathrm{J}} Q_{\mathrm{J}} x_{\mathrm{J}} = qr_{\mathrm{CN}} \quad \text{hence} \quad q = \frac{\mu}{r_{\mathrm{CN}}}$$

Dividing through by e gives the charge as a multiple of e as

$$q/e = \frac{\mu}{r_{\mathrm{CN}}e} = \frac{1.77\ \mathrm{D} \times [(3.3356 \times 10^{-30}\ \mathrm{C\,m})/(1\ \mathrm{D})]}{(299 \times 10^{-12}\ \mathrm{m}) \times (1.6022 \times 10^{-19}\ \mathrm{C})} = \boxed{0.123}$$

The nitrogen atom therefore has a charge of $-0.123e$ and the carbon atom a charge of $+0.123e$.

P14A.6 The relationship between induced dipole moment μ^* and electric field strength $\mathcal{E}$ is given by [14A.5a–*587*], $\mu^* = \alpha\mathcal{E}$ where α is the polarizability. The polarizability volume α' is related to α by [14A.6–*587*], $\alpha' = \alpha/4\pi\varepsilon_0$, so the induced dipole is $\mu^* = \alpha\mathcal{E} = 4\pi\varepsilon_0\alpha'\mathcal{E}$. Replacing $\mathcal{E}$ by the given expression $Q/4\pi\varepsilon_0 r^2$ gives

$$\mu^* = 4\pi\varepsilon_0\alpha' \times \frac{Q}{4\pi\varepsilon_0 r^2} = \frac{\alpha' Q}{r^2} \quad \text{hence} \quad r = \left(\frac{\alpha' Q}{\mu^*}\right)^{1/2}$$

The charge on a proton is equal to e, so

$$r = \left(\frac{\alpha' e}{\mu^*}\right)^{1/2} = \left(\frac{(1.48 \times 10^{-30}\ \mathrm{m}^3) \times (1.6022 \times 10^{-19}\ \mathrm{C})}{(1.85\ \mathrm{D}) \times [(3.3356 \times 10^{-30}\ \mathrm{C\,m})/(1\ \mathrm{D})]}\right)^{1/2}$$
$$= 1.96... \times 10^{-10}\ \mathrm{m} = \boxed{196\ \mathrm{pm}}$$

P14A.8 The temperature-dependence of molar polarization is given by [14A.11–*590*],

$$P_{\mathrm{m}} = \frac{N_{\mathrm{A}}\alpha}{3\varepsilon_0} + \frac{N_{\mathrm{A}}\mu^2}{9\varepsilon_0 k} \times \frac{1}{T} \quad \text{or} \quad P_{\mathrm{m}} = \tfrac{4}{3}\pi N_{\mathrm{A}}\alpha' + \frac{N_{\mathrm{A}}\mu^2}{9\varepsilon_0 k}$$

where in the second form the definition of polarizability volume, which is given by [14A.6–*587*], $\alpha' = \alpha/4\pi\varepsilon_0$, is used to replace α by $4\pi\varepsilon_0\alpha'$. This equation implies that a graph of P_{m} against $1/T$ should be a straight line of slope $N_{\mathrm{A}}\mu^2/9\varepsilon_0 k$ and intercept $\frac{4}{3}\pi N_{\mathrm{A}}\alpha'$.

The molar polarization is calculated from the data using the Debye equation [14A.10–*590*], $(\varepsilon_{\mathrm{r}}-1)/(\varepsilon_{\mathrm{r}}+2) = \rho P_{\mathrm{m}}/M$, which is rearranged to $P_{\mathrm{m}} = (M/\rho)(\varepsilon_{\mathrm{r}}-1)/(\varepsilon_{\mathrm{r}}+2)$. Taking the molar mass of methanol as $M = 32.0416\ \mathrm{g\,mol^{-1}}$ and the density as $\rho = 0.791\ \mathrm{g\,cm^{-3}}$ at all temperatures, values of P_{m} are as shown in the table below and are plotted in Fig. 14.6. The plot shows that P_{m} is neither linear in $1/T$ for the liquid state, nor constant for the solid.

$\theta/°\mathrm{C}$	ε_r	$1/(T/K)$	$P_\mathrm{m}/\mathrm{cm^3\,mol^{-1}}$
−185	3.2	0.011 34	17.14
−170	3.6	0.009 69	18.81
−150	4.0	0.008 12	20.25
−140	5.1	0.007 51	23.39
−110	67.0	0.006 13	38.75
−80	57.0	0.005 18	38.45
−50	49.0	0.004 48	38.12
−20	43.0	0.003 95	37.81
0	38.0	0.003 66	37.47
20	34.0	0.003 41	37.13

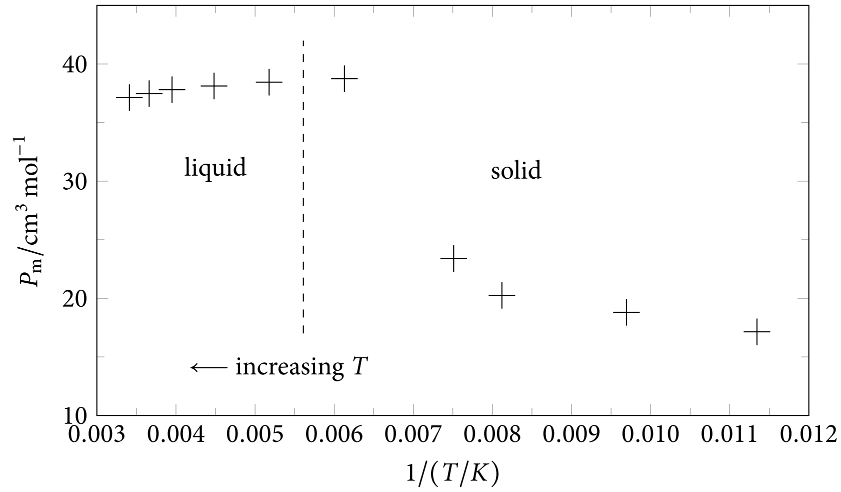


Figure 14.6

To interpret these data, note that the temperature-dependent term $N_\mathrm{A}\mu^2/9\varepsilon_0 kT$ in the expression for P_m stems from the orientation contribution to the polarization, that is, the tendency of polar molecules to align themselves in response to the electric field. If the molecules are not able to rotate then there is no contribution from this term and therefore P_m is expected to be lower and also independent of temperature.

The plot shows that as liquid methanol is cooled, P_m begins to increase less rapidly than expected, that is, the points begin to level off. This indicates that hydrogen-bonding between methanol molecules is hindering molecular rotation and reducing the orientation polarization. The effect extends below the melting point with the −110 °C data point exhibiting liquid-like, hindered rotation. The large decline of P_m below −110 °C is interpreted as corresponding to a stronger hindrance of the dipole moment rotation but the non-constancy of P_m seems to indicate that rotational excitation is never completely eliminated.

Because the points do not give a straight line, it is not possible to determine reliable values of μ or α' from these data.

P14A.10 The temperature-dependence of molar polarization is given by [14A.11–*590*],

$$P_m = \frac{N_A\alpha}{3\varepsilon_0} + \frac{N_A\mu^2}{9\varepsilon_0 k} \times \frac{1}{T} \quad \text{or} \quad P_m = \tfrac{4}{3}\pi N_A\alpha' + \frac{N_A\mu^2}{9\varepsilon_0 k} \times \frac{1}{T}$$

where in the second form the definition of polarizability volume, which is given by [14A.6–*587*], $\alpha' = \alpha/4\pi\varepsilon_0$, is used to replace α by $4\pi\varepsilon_0\alpha'$. This equation implies that a graph of P_m against $1/T$ should be a straight line of slope $N_A\mu^2/9\varepsilon_0 k$ and intercept $\frac{4}{3}\pi N_A\alpha'$. The data are plotted in Fig. 14.7.

T/K	$1/(T/K)$	P_m/cm^3 mol^{-1}
384.3	0.002 60	57.40
420.1	0.002 38	53.50
444.7	0.002 25	50.10
484.1	0.002 07	46.80
521.0	0.001 92	43.10

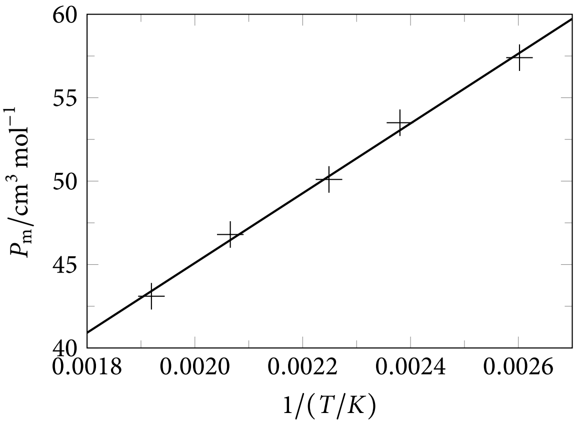


Figure 14.7

The data fall on a good straight line, the equation for which is

$$(P_m/\text{cm}^3\,\text{mol}^{-1}) = (2.091 \times 10^4) \times 1/(T/\text{K}) + 3.27$$

Identifying the slope with $N_A\mu^2/9\varepsilon_0 k$ gives

$$N_A\mu^2/9\varepsilon_0 k = (2.091 \times 10^4\ \text{cm}^3\,\text{mol}^{-1}\,\text{K}) = (2.091 \times 10^{-2}\text{m}^3\,\text{mol}^{-1}\,\text{K})$$

and hence

$$\mu = \left(\frac{9\varepsilon_0 k}{N_A} \times (2.091 \times 10^{-2}\ \mathrm{m^3\,mol^{-1}\,K})\right)^{1/2}$$
$$= \left(\frac{9 \times (8.8542 \times 10^{-12}\ \mathrm{J^{-1}\,C^2\,m^{-1}}) \times (1.3806 \times 10^{-23}\ \mathrm{J\,K^{-1}})}{6.0221 \times 10^{23}\ \mathrm{mol^{-1}}}\right.$$
$$\left.\times (2.09 \times 10^{-2}\ \mathrm{m^3\,mol^{-1}\,K})\right)^{1/2} = 6.17... \times 10^{-30}\ \mathrm{C\,m} = \boxed{1.85\ \mathrm{D}}$$

Similarly, identifying $\frac{4}{3}\pi N_A \alpha'$ with the intercept gives

$$\alpha' = \frac{3}{4\pi N_A} \times (3.27\ \mathrm{cm^3\,mol^{-1}})$$
$$= \frac{3}{4\pi \times (6.0221 \times 10^{23}\ \mathrm{mol^{-1}})} \times (3.27\ \mathrm{cm^3\,mol^{-1}}) = \boxed{1.30 \times 10^{-24}\ \mathrm{cm^3}}$$

P14A.12 The relationship between refractive index and relative permittivity is given by [14A.13–*592*], $n_r = \varepsilon_r^{1/2}$. In addition the relationship between relative permittivity and the molar polarization is given by the Debye equation [14A.10–*590*], $(\varepsilon_r - 1)/(\varepsilon_r + 2) = \rho P_m/M$ where ρ is the mass density and M is the molar mass.

The mass density ρ is given by M/V_m, where V_m is the molar volume. Assuming perfect gas behaviour, $V_m = RT/p$, so $\rho = pM/RT$ and hence the Debye equation becomes

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{pP_m}{RT} \quad \text{hence} \quad \varepsilon_r - 1 = \frac{pP_m}{RT}(\varepsilon_r + 2)$$

If $\varepsilon_r \approx 1$ then $(\varepsilon_r + 2) \approx 3$ so the equation becomes

$$\varepsilon_r - 1 = \frac{pP_m}{RT} \times 3 \quad \text{hence} \quad \varepsilon_r = 1 + \frac{3pP_m}{RT}$$

Introducing $n_r = \varepsilon_r^{1/2}$ and using the series expansion $(1 + x)^{1/2} \approx 1 + \frac{1}{2}x$ for small x gives

$$n_r = \left(1 + \frac{3pP_m}{RT}\right)^{1/2} \approx 1 + \tfrac{1}{2} \times \frac{3pP_m}{RT} = 1 + \frac{3pP_m}{2RT}$$

This expression implies that a plot of n_r against p should be a straight line of slope $3P_m/2RT$. Hence, by measuring n_r as a function of pressure, the molar polarization P_m can be determined.

The molar polarization is given by [14A.11–*590*], $P_m = (N_A/3\varepsilon_0)(\alpha + \mu^2/3kT)$. However, assuming that the frequency of oscillation of the electric field is high, as it will be for visible light, there will be no contribution from orientation polarization because the molecules cannot reorientate themselves quickly enough to follow the field. Therefore the term $\mu^2/3kT$ in the expression for P_m does not contribute, and the equation reduces to $P_m = N_A\alpha/3\varepsilon_0$. This expression is used in that for the slope

$$\text{slope} = \frac{3P_m}{2RT} = \frac{3}{2RT}\frac{N_A\alpha}{3\varepsilon_0} = \frac{\alpha}{2kT\varepsilon_0}$$

It is therefore possible to determine α from the slope of the graph, and hence α'.

14B Interactions between molecules

Answer to discussion questions

D14B.2 The arrangement of charges corresponding to the various multipoles are shown in Fig. 14A.2 on page 587. According to [14B.4–*596*], the potential energy of interaction between an n-pole and an m-pole goes as $1/r^{n+m+1}$. Two examples of this relationship are derived in the text for the interaction between: (i) a point charge ($n = 0$) and a dipole ($m = 1$), giving a $1/r^{0+1+1} = 1/r^2$ dependence; and (ii) a dipole ($n = 1$) and a dipole ($m = 1$) giving a $1/r^{1+1+1} = 1/r^3$ dependence. In both cases this form of the interaction arises by assuming that the distance r is much greater than the separation between charges which form the dipole.

Consider the interaction between a point charge and a dipole, with the point charge along the line of the dipole. The point charge interacts with the two charges which form the dipole: these interactions are opposite in sign but different in magnitude because the distances between the point charge and the two charges which form the dipole are not the same. As the point charge moves further away, these interactions both decrease in magnitude. However, because the distance between these charges is becoming less significant compared to the distance of the point charge, the magnitude of the interaction with each becomes more similar. As a result, the terms with opposite sign come closer to cancelling one another out and the overall interaction therefore goes to zero faster than does the simple interaction between point charges.

Effectively, as r increases the two charges which form the dipole merge and begin to cancel one another. This is why the potential energy of interaction falls off more quickly than it does for the interaction between two point charges. For quadrupoles and high n-poles the effect is greater, leading to an even faster fall off of the interaction, presumably because the effective cancellation of the charges happens more quickly when there are more charges forming the n-pole.

D14B.4 This is discussed in Section 14B.2 on page 598.

Solutions to exercises

E14B.1(b) The interaction between a point charge and a point dipole orientated directly away the charge is given by [14B.1–*593*], $V = -\mu_1 Q_2/4\pi\varepsilon_0 r^2$. In this case the magnesium ion has a charge of $+2e = +2 \times (1.6022 \times 10^{-19}\,\text{C})$.

$$\begin{aligned} V &= -\frac{\mu_1 Q_2}{4\pi\varepsilon_0 r^2} \\ &= -\frac{(1.08\,\text{D}) \times \left[(3.3356 \times 10^{-30}\,\text{C m})/(1\,\text{D})\right] \times 2 \times (1.6022 \times 10^{-19}\,\text{C})}{4\pi \times (8.8542 \times 10^{-12}\,\text{J}^{-1}\,\text{C}^2\,\text{m}^{-1}) \times (300 \times 10^{-12}\,\text{m})^2} \\ &= -1.15... \times 10^{-19}\,\text{J} \end{aligned}$$

The potential energy if the dipole has the reverse orientation is $+1.15... \times 10^{-19}$ J so the energy required to reverse the direction is

$$\Delta V = (1.15... \times 10^{-19}\,\text{J}) \times 2 = 2.30... \times 10^{-19}\,\text{J} = \boxed{2.31 \times 10^{-19}\,\text{J}}$$

The energy per mole is found by multiplying by N_A

$$\Delta V_m = (2.30... \times 10^{-22}\,\text{kJ}) \times (6.0221 \times 10^{23}\,\text{mol}^{-1}) = \boxed{139\,\text{kJ mol}^{-1}}$$

E14B.2(b) The potential energy interaction between two parallel point dipoles separated by distance r at angle Θ is given by [14B.3b–*595*], $V = \mu_1\mu_2(1-3\cos^2\Theta)/4\pi\varepsilon_0 r^3$. However, because in this case the interaction is not in a vacuum, it is necessary to replace ε_0 by $\varepsilon_0\varepsilon_r$ where ε_r is the relative permittivity of the medium.

$$\begin{aligned} V &= \frac{\mu_1\mu_2(1-3\cos^2\Theta)}{4\pi\varepsilon_0\varepsilon_r r^3} \\ &= \frac{(2.7\,\text{D}) \times (1.85\,\text{D}) \times \left[(3.3356 \times 10^{-30}\,\text{C m})/(1\,\text{D})\right]^2 \times (1-3\cos^2 45^\circ)}{4\pi \times (8.8542 \times 10^{-12}\,\text{J}^{-1}\,\text{C}^2\,\text{m}^{-1}) \times 3.5 \times (3.0 \times 10^{-9}\,\text{m})^3} \\ &= \boxed{-2.6 \times 10^{-24}\,\text{J}} \quad \text{which corresponds to} \quad \boxed{-1.6\,\text{J mol}^{-1}} \end{aligned}$$

E14B.3(b) The shape of a linear quadrupole is given in Fig. 14A.2 on page 587; an example of such an arrangement is a CO_2 molecule which has negative charges on the oxygen atoms and a balancing positive charge on the central carbon. Two such quadrupoles are shown in Fig. 14.8, arranged so that they are parallel and separated by a distance r The distances between atoms that are not directly opposite each other are found using Pythagoras' theorem, so that the distances A–E, B–D, B–F and C–E are all $\sqrt{r^2+l^2}$, while the distances A–F and C–D are both $\sqrt{r^2+(2l)^2} = \sqrt{r^2+4l^2}$.

The interaction energy is derived in a similar way to that used in Section 14B.1(b) on page 594 for dipole–dipole interactions. The total interaction energy is the sum of nine pairwise terms, one for each combination of a point charge in one quadrupole with a point charge in the other quadrupole. Each term has the form $Q_1Q_2/4\pi\varepsilon_0 r_{12}$ where Q_1 and Q_2 are the charges being considered in that

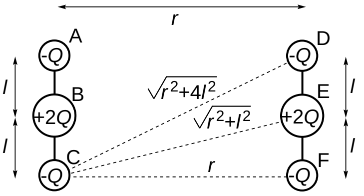


Figure 14.8

term and r_{12} is the distance between them.

$$\begin{aligned}
V = -\frac{1}{4\pi\varepsilon_0}\Bigg(&\overbrace{\frac{(-Q)(-Q)}{r}}^{\text{A–D}} + \overbrace{\frac{(-Q)(2Q)}{\sqrt{r^2+l^2}}}^{\text{A–E}} + \overbrace{\frac{(-Q)(-Q)}{\sqrt{r^2+4l^2}}}^{\text{A–F}} + \overbrace{\frac{(2Q)(-Q)}{\sqrt{r^2+l^2}}}^{\text{B–D}} \\
&+ \underbrace{\frac{(2Q)(2Q)}{r}}_{\text{B–E}} + \underbrace{\frac{(2Q)(-Q)}{\sqrt{r^2+l^2}}}_{\text{B–F}} + \underbrace{\frac{(-Q)(-Q)}{\sqrt{r^2+4l^2}}}_{\text{C–D}} + \underbrace{\frac{(-Q)(2Q)}{\sqrt{r^2+l^2}}}_{\text{C–E}} + \underbrace{\frac{(-Q)(-Q)}{r}}_{\text{C–F}}\Bigg) \\
&= \frac{1}{4\pi\varepsilon_0}\left(\frac{6Q^2}{r} - \frac{8Q^2}{\sqrt{r^2+l^2}} + \frac{2Q^2}{\sqrt{r^2+4l^2}}\right) \\
&= \frac{Q^2}{4\pi\varepsilon_0 r}\left(6 - \frac{8}{\sqrt{1+(l/r)^2}} + \frac{2}{\sqrt{1+4(l/r)^2}}\right) \\
&= \frac{Q^2}{4\pi\varepsilon_0 r}\left(6 - 8(1+x^2)^{-1/2} + 2(1+4x^2)^{-1/2}\right)
\end{aligned}$$

where $x = l/r$. Assuming that $r \gg l$, so that $x \ll 1$, the series expansion $(1+y)^n = 1 + ny + \frac{1}{2}n(n-1)y^2 + \ldots$ can be used: it is sufficient to retain the first three terms, $(1+y)^{-1/2} \approx 1 - \frac{1}{2}y + \frac{3}{8}y^2$. The required expansions are therefore $(1+x^2)^{-1/2} \approx 1 - \frac{1}{2}x^2 + \frac{3}{8}x^4$ and $(1+4x^2)^{-1/2} \approx 1 - 2x^2 + 6x^4$

$$\begin{aligned}
V &= \frac{Q^2}{4\pi\varepsilon_0 r}\left(6 - 8\left[1 - \tfrac{1}{2}x^2 + \tfrac{3}{8}x^4 + \ldots\right] + 2\left[1 - 2x^2 + 6x^4 + \ldots\right]\right) \\
&= \frac{Q^2}{4\pi\varepsilon_0 r}\left(6 - 8 + 4x^2 - 3x^4 + 2 - 4x^2 + 12x^4\right) = \frac{Q^2}{4\pi\varepsilon_0 r} \times 9x^4 \\
&= \frac{Q^2}{4\pi\varepsilon_0 r} \times 9\left(\frac{l}{r}\right)^4 = \boxed{\frac{9Q^2 l^4}{4\pi\varepsilon_0 r^5}}
\end{aligned}$$

E14B.4(b) The average energy of interaction between rotating polar molecules is given by the Keesom interaction [14B.4–*596*].

$$\langle V \rangle = -\frac{C}{r^6} \qquad C = \frac{2\mu_1^2\mu_2^2}{3(4\pi\varepsilon_0)^2 kT}$$

In this case $\mu_1 = \mu_2$, so

$$\begin{aligned}C &= \frac{2\mu_1^4}{3(4\pi\varepsilon_0)^2 kT}\\ &= \frac{2\times\left[(2.5\,\mathrm{D})\times(3.3356\times10^{-30}\,\mathrm{C\,m})/(2.5\,\mathrm{D})\right]^4}{3\times(4\pi\times(8.8542\times10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}}))^2\times(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(273\,\mathrm{K})}\\ &= 6.90...\times10^{-77}\,\mathrm{J\,m^6}\end{aligned}$$

Hence $\langle V\rangle = -\dfrac{C}{r^6} = -\dfrac{6.90...\times10^{-77}\,\mathrm{J\,m^6}}{(1.0\times10^{-9}\,\mathrm{m})^6} = \boxed{-6.9\times10^{-23}\,\mathrm{J}}$. This energy corresponds, after multiplication by N_A, to $\boxed{-41\,\mathrm{J\,mol^{-1}}}$. This is very much smaller than the average molar kinetic energy of the molecules which, as explained in Section 2A.2(a) on page 37, is given by

$$\tfrac{3}{2}RT = \tfrac{3}{2}\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(273\,\mathrm{K}) = 3.4\,\mathrm{kJ\,mol^{-1}}$$

E14B.5(b) The energy of the dipole–induced dipole interaction between a polar molecule such as water and a polarizable molecule such as CCl_4 is given by [14B.6–*597*], $V = -\mu_1^2\alpha_2'/4\pi\varepsilon_0 r^6$. From the data in the *Resource section* the dipole moment of water is 1.85 D and the polarizability volume of CCl_4 is $10.3\times10^{-30}\,\mathrm{m^3}$.

$$\begin{aligned}V &= -\frac{\mu_1^2\alpha_2'}{4\pi\varepsilon_0 r^6}\\ &= -\frac{\left[(1.85\,\mathrm{D})\times(3.3356\times10^{-30}\,\mathrm{C\,m})/(1\,\mathrm{D})\right]^2\times(10.3\times10^{-30}\,\mathrm{m^3})}{4\pi\times(8.8542\times10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}})\times(1.0\times10^{-9}\,\mathrm{m})^6}\\ &= -3.52...\times10^{-24}\,\mathrm{J}\end{aligned}$$

This interaction energy corresponds, after multiplication by Avogadro's constant, to $\boxed{-2.1\,\mathrm{J\,mol^{-1}}}$.

E14B.6(b) The London formula for the energy of the dispersion interaction is given by [14B.7–*598*]

$$V = -\frac{C}{r^6} \qquad C = \tfrac{3}{2}\alpha_1'\alpha_2'\frac{I_1I_2}{I_1+I_2}$$

In the case that the two interacting species are the same, with polarizability volume α' and ionisation energy I, this expression becomes

$$C = -\tfrac{3}{2}\alpha'^2\frac{I^2}{2I} = \tfrac{3}{4}\alpha'^2 I \quad \text{hence} \quad V = -\frac{3\alpha'^2 I}{4r^6}$$

Table 14A.1 on page 585 in the *Resource section* gives the polarizability volume of argon as $\alpha' = 1.66\times10^{-30}\,\mathrm{m^3}$ and Table 8B.4 on page 325 gives the first ionisation energy as $I = 1520.4\,\mathrm{kJ\,mol^{-1}}$, so

$$V = -\frac{3\alpha'^2 I}{4r^6} = -\frac{3\times(1.66\times10^{-30}\,\mathrm{m^3})^2\times(1520.4\times10^3\,\mathrm{J\,mol^{-1}})}{4\times(1.0\times10^{-9}\,\mathrm{m})^6} = \boxed{3.1\,\mathrm{J\,mol^{-1}}}$$

Solutions to problems

P14B.2 The electrostatic interaction between two charges is given by Coulomb's law, given in *The chemist's toolkit* 6 in Topic 2A on page 35 as $V = Q_1Q_2/4\pi\varepsilon r$. According to the electrostatic model, the energy of interaction of a hydrogen bond in a vacuum is

$$\begin{aligned} V &= \frac{Q_1Q_2}{4\pi\varepsilon_0 r} = \frac{(+0.42\times 1.6022\times 10^{-19}\,\mathrm{C})\times(-0.84\times 1.6022\times 10^{-19}\,\mathrm{C})}{4\pi\times(8.8542\times 10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}})\times(170\times 10^{-12}\,\mathrm{m})} \\ &= -4.78...\times 10^{-19}\,\mathrm{J} \end{aligned}$$

The energy required to break the hydrogen bond is therefore $\boxed{4.8\times 10^{-19}\,\mathrm{J}}$, which corresponds to $\boxed{2.9\times 10^{2}\,\mathrm{kJ\,mol^{-1}}}$.

The energy of interaction in water, where $\varepsilon = \varepsilon_0\varepsilon_r \approx \varepsilon_0\times 80$, is

$$\begin{aligned} V &= \frac{Q_1Q_2}{4\pi\varepsilon r} = \frac{(+0.42\times 1.6022\times 10^{-19}\,\mathrm{C})\times(-0.84\times 1.6022\times 10^{-19}\,\mathrm{C})}{4\pi\times(8.8542\times 10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}})\times 80\times(170\times 10^{-12}\,\mathrm{m})} \\ &= -5.98...\times 10^{-21}\,\mathrm{J} \end{aligned}$$

The energy required to break the hydrogen bond is therefore $\boxed{6.0\times 10^{-21}\,\mathrm{J}}$, which corresponds after multiplying by Avogadro's constant to $\boxed{3.6\,\mathrm{kJ\,mol^{-1}}}$. This is much less than the energy required to break the bond in a vacuum.

P14B.4 The most favourable orientation is that in which the positive end of the dipole, that is, the side of the molecule with the δ+ hydrogen atoms, lies closer to the anion (Fig. 14.9).

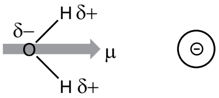


Figure 14.9

The interaction potential energy between a dipole μ and a charge Q is given by [14B.1–593], $V = -\mu Q/4\pi\varepsilon_0 r^2$; the field experienced by a charge Q is $\mathcal{E} = -(1/Q)(\mathrm{d}V/\mathrm{d}r)$. The field experienced by the anion is therefore

$$\mathcal{E} = -\frac{1}{Q}\frac{\mathrm{d}V}{\mathrm{d}r} = -\frac{1}{Q}\frac{\mathrm{d}}{\mathrm{d}r}\left(-\frac{\mu Q}{4\pi\varepsilon_0 r^2}\right) = \frac{\mu}{4\pi\varepsilon_0}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^{-2}\right) = -\frac{\mu}{2\pi\varepsilon_0 r^3}$$

Noting that $1\,\mathrm{J\,C^{-1}} = 1\,\mathrm{V}$, the field experienced at each of the distances is

(a) At 1.0 nm

$$\begin{aligned} \mathcal{E} &= -\frac{\mu}{2\pi\varepsilon_0 r^3} = -\frac{(1.85\,\mathrm{D})\times(3.3356\times 10^{-30}\,\mathrm{C\,m})/(1\,\mathrm{D})}{2\pi\times(8.8542\times 10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}})\times(1.0\times 10^{-9}\,\mathrm{m})^3} \\ &= \boxed{-1.1\times 10^{8}\,\mathrm{V\,m^{-1}}} \end{aligned}$$

(b) At 0.3 nm

$$\begin{aligned}\mathcal{E} &= -\frac{\mu}{2\pi\varepsilon_0 r^3} = -\frac{(1.85\ \mathrm{D})\times(3.3356\times10^{-30}\ \mathrm{C\,m})/(1\ \mathrm{D})}{2\pi\times(8.8542\times10^{-12}\ \mathrm{J^{-1}\,C^2\,m^{-1}})\times(0.3\times10^{-9}\ \mathrm{m})^3}\\ &= \boxed{-4.1\times10^{9}\ \mathrm{V\,m^{-1}}}\end{aligned}$$

(c) At 30 nm

$$\begin{aligned}\mathcal{E} &= -\frac{\mu}{2\pi\varepsilon_0 r^3} = -\frac{(1.85\ \mathrm{D})\times(3.3356\times10^{-30}\ \mathrm{C\,m})/(1\ \mathrm{D})}{2\pi\times(8.8542\times10^{-12}\ \mathrm{J^{-1}\,C^2\,m^{-1}})\times(30\times10^{-9}\ \mathrm{m})^3}\\ &= \boxed{-4.1\times10^{3}\ \mathrm{V\,m^{-1}}}\end{aligned}$$

P14B.6 (a) The London formula for the energy of the dispersion interaction is given by [14B.7–*598*]

$$V = -\frac{C}{r^6} \qquad C = \tfrac{3}{2}\alpha_1'\alpha_2'\frac{I_1I_2}{I_1+I_2}$$

In the case that the two interacting species are the same, with polarizability volume α' and ionisation energy I, this expression becomes

$$C = -\tfrac{3}{2}\alpha'^2\frac{I^2}{2I} = \tfrac{3}{4}\alpha'^2 I \quad \text{hence} \quad V = -\frac{3\alpha'^2 I}{4r^6}$$

In this case, using the given data and the polarizability volume of benzene from the previous problem, the energy of interaction is

$$\begin{aligned}V &= -\frac{3\alpha'^2 I}{4r^6}\\ &= -\frac{3\times(1.04\times10^{-29}\ \mathrm{m^3})^2\times(5.0\ \mathrm{eV})\times(1.6022\times10^{-19}\ \mathrm{C})/(1\ \mathrm{eV})}{4\times(0.4\times10^{-9}\ \mathrm{m})^6}\\ &= -1.58...\times10^{-20}\ \mathrm{J}\end{aligned}$$

This interaction energy corresponds to $\boxed{-9.6\ \mathrm{kJ\,mol^{-1}}}$.

(b) Because the force is the negative slope of the potential energy, an expression for the force is obtained by differentiating the expression for V

$$F = -\frac{\mathrm{d}V}{\mathrm{d}r} = -\frac{\mathrm{d}}{\mathrm{d}r}\left(-\frac{3\alpha'^2 I}{4r^6}\right) = \boxed{-\frac{9\alpha'^2 I}{2r^7}}$$

The negative sign indicates that the force is attractive; the force goes to zero as the distance goes to infinity.

P14B.8 The arrangement is shown in Fig. 14.10. For convenience the distances are denoted by R and r. The task is to calculate the potential energy of interaction between the O–H group and the oxygen atom $\mathrm{O^B}$ as a function of the angle θ, assuming the distances r and R to be fixed. Because the electrostatic interaction

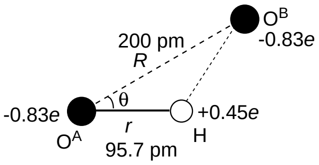


Figure 14.10

of O^B with the O–H group is of interest, the interaction between O^A and the H atom is not included in this calculation.

The sum of the potential energies of O^B interacting with O^A and with H is given by

$$V = \frac{Q_A Q_B}{4\pi\varepsilon_0 r_{AB}} + \frac{Q_H Q_B}{4\pi\varepsilon_0 r_{HB}}$$

where Q_A, Q_B and Q_H are the partial charges on the atoms. The O^A–O^B distance is fixed as R, and from Fig. 14.10 the H–OB distance is found using the cosine rule as $r_{HB}^2 = R^2 + r^2 - 2Rr\cos\theta$. Hence, using the partial charges and distances given in the question, the interaction energy is

$$\begin{aligned}
V &= \frac{(-0.83e)(-0.83e)}{4\pi\varepsilon_0 R} + \frac{(+0.45e)(-0.83e)}{4\pi\varepsilon_0\sqrt{R^2 + r^2 - 2Rr\cos\theta}} \\
&= \frac{e^2}{4\pi\varepsilon_0 R}\left(0.83^2 - \frac{0.45 \times 0.83}{\sqrt{(1 + (r/R)^2 - 2(r/R)\cos\theta}}\right) \\
&= \frac{(1.6022 \times 10^{-19}\,\mathrm{C})^2}{4\pi \times (8.8542 \times 10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}}) \times (200 \times 10^{-12}\,\mathrm{m})} \times \left(0.6889\right. \\
&\quad \left. - \frac{0.3755}{\sqrt{1 + [(95.7\,\mathrm{pm})/(200\,\mathrm{pm})]^2 - 2 \times [(95.7\,\mathrm{pm})/(200\,\mathrm{pm})] \times \cos\theta}}\right) \\
&= (1.15... \times 10^{-18}\,\mathrm{J}) \times \left(0.6889 - \frac{0.3755}{\sqrt{1.22... - 0.957\cos\theta}}\right)
\end{aligned}$$

This energy corresponds, after multiplying by Avogadro's constant, to

$$V = (6.94... \times 10^2\,\mathrm{kJ\,mol^{-1}}) \times \left(0.6889 - \frac{0.3755}{\sqrt{1.22... - 0.957\cos\theta}}\right)$$

This function is plotted in Fig. 14.11. As expected the minimum energy occurs for $\theta = 0°$, when the δ+ hydrogen lies between the δ− oxygen atoms. Note that the energy is only negative (that is, favourable) over a small range of angles about this minimum.

P14B.10 Figure 14.12 shows a molecule A interacting with the molecules in a volume $d\tau$ located at distance R. The number of molecules in the volume $d\tau$ is $\mathcal{N}\,d\tau$ where $\mathcal{N}$ is the number density, the number of molecules per unit volume. If the potential energy of interaction of A with a single molecule at distance R is

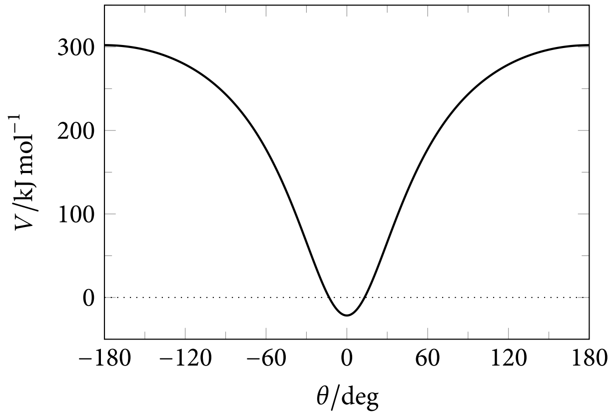


Figure 14.11

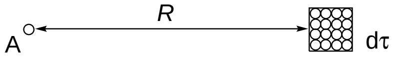


Figure 14.12

$V(R)$ then the energy of interaction of A with the volume $\mathrm{d}\tau$, which contains $\mathcal{N}\,\mathrm{d}\tau$ molecules, is $V(R)\mathcal{N}\,\mathrm{d}\tau$.

The total interaction of A with all the N molecules in the sample, as opposed to just those in the volume element $\mathrm{d}\tau$, is found by integrating over all relevant space, giving $\int V(R)\mathcal{N}\,\mathrm{d}\tau$. Multiplication by $\frac{1}{2}N$ then gives the total interaction for all the N molecules of the sample as $U = \frac{1}{2}N\int V(R)\mathcal{N}\,\mathrm{d}\tau$. The factor of $\frac{1}{2}$ is necessary to avoid double-counting, for example to avoid counting the interaction of molecule B with A as a distinct and additional contribution to that of A interacting with B.

The cohesive energy density is then given by

$$\mathcal{U} = \frac{U}{V} = \frac{\frac{1}{2}N}{V}\int V(R)\mathcal{N}\,\mathrm{d}\tau = \tfrac{1}{2}\left(\frac{N}{V}\right)\mathcal{N}\int V(R)\,\mathrm{d}\tau = \boxed{\tfrac{1}{2}\mathcal{N}^2\int V(R)\,\mathrm{d}\tau}$$

where V is the total volume of the sample and N/V is equal to the number density $\mathcal{N}$.

To perform the integration, note from *The chemist's toolkit* 21 in Topic 7F on page 286 that in spherical polar coordinates the volume element $\mathrm{d}\tau$ is given by $R^2\sin\theta\,\mathrm{d}R\,\mathrm{d}\theta\,\mathrm{d}\phi$, and that the limits of the integrals are $\phi = 0$ to $\phi = 2\pi$, $\theta = 0$ to $\theta = \pi$, and, in this case, $R = d$ to $R = \infty$. Replacing $V(R)$ by a van der Waals attraction of the form $-C_6/R^6$ and performing the integration gives

$$\begin{aligned}
\mathcal{U} &= \tfrac{1}{2}\mathcal{N}^2\int_{R=d}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} -\frac{C_6}{R^6}\,R^2\sin\theta\,\mathrm{d}R\,\mathrm{d}\theta\,\mathrm{d}\phi \\
&= \tfrac{1}{2}\mathcal{N}^2\int_{d}^{\infty} -\frac{C_6}{R^4}\,\mathrm{d}R \times \int_0^{\pi}\sin\theta\,\mathrm{d}\theta \times \int_0^{2\pi}\mathrm{d}\phi \\
&= \tfrac{1}{2}\mathcal{N}^2 \times \left[\frac{C_6}{3R^3}\right]_d^{\infty} \times [-\cos\theta]_0^{\pi} \times [\phi]_0^{2\pi} = \tfrac{1}{2}\mathcal{N}^2 \times \left(-\frac{C_6}{3d^3}\right) \times 2 \times 2\pi \\
&= -\tfrac{2}{3}\pi\mathcal{N}^2\,\frac{C_6}{d^3}
\end{aligned}$$

The number density $\mathcal{N}$ is related to the mass density ρ by noting that in volume V there are $\mathcal{N}V$ molecules and hence $\mathcal{N}V/N_A$ moles. The mass of this amount is $M \times \mathcal{N}V/N_A$, where M is the molar mass. Therefore the mass density ρ is $\rho = M \times \mathcal{N}V/N_A V = M\mathcal{N}/N_A$; rearranging this gives $\mathcal{N} = N_A\rho/M$. Using this expression for $\mathcal{N}$ in the expression for $\mathcal{U}$ gives

$$\mathcal{U} = -\tfrac{2}{3}\pi\left(\frac{N_A\rho}{M}\right)^2\frac{C_6}{d^3} = \boxed{-\tfrac{2}{3}\pi\frac{N_A^2}{d^3M^2}\rho^2 C_6}$$

14C Liquids

Answers to discussion questions

D14C.2 This is discussed in Section 14C.4 on page 611.

Solutions to exercises

E14C.1(b) The vapour pressure of a liquid when it is dispersed as spherical droplets of radius r is given by the Kelvin equation [14C.15–*611*], $p = p^* \mathrm{e}^{2\gamma V_m(\mathrm{l})/rRT}$, where p^* is the vapour pressure of bulk liquid to which no additional pressure has been applied. Because the mass density of a substance with molar volume V_m and molar mass M is given by $\rho = M/V_m$, it follows that $V_m = M/\rho$. Substituting this into the Kelvin equation gives $p = p^* \mathrm{e}^{2\gamma(M/\rho)/rRT}$.

The surface tension γ of water at 35 °C is not given in Table 14C.1 on page 605, so the value at this temperature is estimated from the graph in Fig. 14C.7 on page 607 as being approximately 71 mN m^{-1}, which is equal to 71×10^{-3} J m^{-2}. Hence, taking p^* as 5.623 kPa and M as 18.0158 g mol^{-1} (18.0158×10^{-3} kg mol^{-1}),

$$\begin{aligned}
p &= p^* \exp\left(\frac{2\gamma M/\rho}{rRT}\right) = (5.623\ \text{kPa}) \\
&\quad \times \exp\left(\frac{2\times(71\times10^{-3}\ \text{J m}^{-2})\times(18.0158\times10^{-3}\ \text{kg mol}^{-1})/(994.0\ \text{kg m}^{-3})}{(20\times10^{-9}\ \text{m})\times(8.3145\ \text{J K}^{-1}\,\text{mol}^{-1})\times([35+273.15]\ \text{K})}\right) \\
&= \boxed{5.9\ \text{kPa}}
\end{aligned}$$

E14C.2(b) The height climbed by a liquid in a capillary tube of radius r is given by [14C.8–*607*], $h = 2\gamma/\rho g_{\text{acc}} r$, assuming that the contact angle is zero. Rearranging for γ, replacing r by $\frac{1}{2}d$ where d is the diameter of the tube, and noting that 1 N = 1 kg m s^{-2} gives

$$\begin{aligned}\gamma &= \tfrac{1}{2}\rho g_{\text{acc}} rh = \tfrac{1}{4}\rho g_{\text{acc}} dh\\ &= \tfrac{1}{4}(0.9956\times10^{3}\ \text{kg m}^{-3})\times(9.807\ \text{m s}^{-2})\times(0.320\times10^{-3}\ \text{m})\\ &\qquad\times(9.11\times10^{-2}\ \text{m}) = 0.0711...\ \text{kg s}^{-2} = \boxed{71.2\ \text{mN m}^{-1}}\end{aligned}$$

E14C.3(b) The pressure difference between the inside and outside of a spherical droplet is given by the Laplace equation [14C.7–*606*], $p_{\text{in}} = p_{\text{out}} + 2\gamma/r$. Hence, noting that 1 Pa = 1 N m^{-2},

$$\Delta p = p_{\text{in}} - p_{\text{out}} = \frac{2\gamma}{r} = \frac{2\times(22.39\times10^{-3}\ \text{N m}^{-1})}{(220\times10^{-9}\ \text{m})} = \boxed{204\ \text{kPa}}$$

E14C.4(b) The height climbed by a liquid in a capillary tube of radius r is given by [14C.8–*607*], $h = 2\gamma/\rho g_{\text{acc}} r$, assuming that the contact angle is zero. Rearranging for γ and noting that 1 N = 1 kg m s^{-2} gives

$$\begin{aligned}\gamma &= \tfrac{1}{2}\rho g_{\text{acc}} rh\\ &= \tfrac{1}{2}\times(0.9500\times10^{3}\ \text{kg m}^{-3})\times(9.807\ \text{m s}^{-2})\times(0.300\times10^{-3}\ \text{m})\\ &\qquad\times(10.00\times10^{-2}\ \text{m}) = 0.139...\ \text{kg s}^{-2} = \boxed{139.7\ \text{mN m}^{-1}}\end{aligned}$$

Solutions to problems

P14C.2 The dependence of the surface tension on surfactant concentration is given by [14C.14–*610*], $(\partial\gamma/\partial\ln[c/c^{\ominus}])_T = -RT\Gamma_{\text{S}}$. This equation implies that a plot of γ against $\ln(c/c^{\ominus})$ has a slope equal to $-RT\Gamma_{\text{S}}$. The data are plotted in Fig. 14.13.

$[\text{A}]/\text{mol dm}^{-3}$	$\ln([\text{A}]/c^{\ominus})$	$\gamma/\text{N m}^{-1}$
0.10	−2.303	0.070 2
0.20	−1.609	0.067 7
0.30	−1.204	0.065 1
0.40	−0.916	0.062 8
0.50	−0.693	0.059 8

The points appear to lie on a curve rather than a straight line, indicating that Γ_{S} is not constant over this range of concentration. The data are a good fit to the quadratic

$$(\gamma/\text{N m}^{-1}) = -0.003288\times[\ln([\text{A}]/c^{\ominus})]^{2} - 0.01614\times\ln([\text{A}]/c^{\ominus}) + 0.05042$$

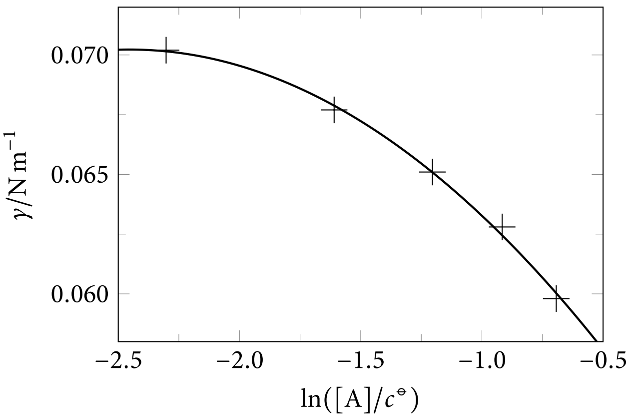


Figure 14.13

This equation has been used to draw the line on Fig. 14.13. Differentiation gives

$$\left(\frac{\partial \gamma}{\partial \ln([\mathrm{A}]/c^{\ominus})}\right)_T = [-0.006576 \times \ln([\mathrm{A}]/c^{\ominus}) - 0.01614] \times (\mathrm{N\,m^{-1}})$$

Equating this expression for the slope to $-RT\Gamma_\mathrm{S}$ and rearranging gives

$$\Gamma_\mathrm{S} = \frac{[0.006576 \times \ln([\mathrm{A}]/c^{\ominus}) + 0.01614] \times (\mathrm{N\,m^{-1}})}{RT}$$

This result is used to calculate Γ_S at any concentration of interest. For example, at $[\mathrm{A}] = 0.1\ \mathrm{mol\,dm^{-3}}$, using $c^{\ominus} = 1\ \mathrm{mol\,dm^{-3}}$ and $1\ \mathrm{J} = 1\ \mathrm{N\,m}$, the surface excess concentration is

$$\begin{aligned}\Gamma_\mathrm{S} &= \frac{\left[0.006576 \times \ln\left([0.1\ \mathrm{mol\,dm^{-3}}]/[1\ \mathrm{mol\,dm^{-3}}]\right) + 0.01614\right] \times (\mathrm{N\,m^{-1}})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times ([20 + 273.15]\ \mathrm{K})} \\ &= \boxed{4.1 \times 10^{-7}\ \mathrm{mol\,m^{-2}}}\end{aligned}$$

14D Macromolecules

Answers to discussion questions

D14D.2 The primary structure of a macromolecule is the sequence of small molecular residues making up the polymer, whereas the secondary structure is the (often local) spatial arrangement of a chain. The tertiary structure is the overall three-dimensional structure of a single macromolecule. Two or more macromolecules may form an aggregation that yields an overall quaternary structure.

D14D.4 In these expressions N is the number of monomer units and l is the length of each unit. The conditions for the validity of these expressions are the same as those used in the derivation of the probability distribution for a random coil, in particular the model does not take into account the impossibility of two or more monomer units occupying the same space.

(a) Contour length: the length of the macromolecule measured along its backbone, that is the length of all its monomer units placed end to end. This is the stretched-out length of the macromolecule with bond angles maintained within the monomer units and 180° angles at unit links.

(b) Root mean square separation: a measure of the average separation of the ends of a random coil.

(c) Root mean square separation: a measure of the average separation of the ends of a tetrahedrally ($\theta = 109.5°$) constrained jointed chain.

(d) Root mean square separation: a measure of the average separation of the ends of a constrained jointed chain in which each successive individual bond is constrained to a single cone of angle θ relative to its neighbour. The factor F is given by $F = [(1-\cos\theta)/(1+\cos\theta)]^{1/2}$.

(e) Radius of gyration of a one-dimensional random coil.

(f) Radius of gyration of a three-dimensional random coil.

(g) Radius of gyration of a tetrahedrally ($\theta = 109.5°$) constrained jointed chain.

Solutions to exercises

E14D.1(b) The number-average molar mass is given by [14D.1a–*613*], $\overline{M}_\mathrm{n} = (1/N_\mathrm{total})\sum_i N_iM_i$. Denoting the polymers as 1 and 2 gives

$$\overline{M}_\mathrm{n} = \frac{\sum_i N_iM_i}{N_\mathrm{total}} = \frac{N_1M_1 + N_2M_2}{N_\mathrm{total}}$$

Because the two polymers are present in a 3 : 2 ratio of amounts in moles, and hence also a 3 : 2 ratio of numbers of molecules, the numbers of each polymer are $N_1 = \frac{3}{5}N_\mathrm{total}$ and $N_2 = \frac{2}{5}N_\mathrm{total}$. Hence

$$\begin{aligned}\overline{M}_\mathrm{n} &= \frac{N_1M_1 + N_2M_2}{N_\mathrm{total}} = \frac{\frac{3}{5}N_\mathrm{total}M_1 + \frac{2}{5}N_\mathrm{total}M_2}{N_\mathrm{total}} = \tfrac{3}{5}M_1 + \tfrac{2}{5}M_2 \\ &= \tfrac{3}{5}\times(62\ \mathrm{kg\,mol^{-1}}) + \tfrac{2}{5}\times(78\ \mathrm{kg\,mol^{-1}}) = \boxed{68\ \mathrm{kg\,mol^{-1}}}\end{aligned}$$

The weight-average molar mass is given by [14D.1b–*613*], $\overline{M}_\mathrm{W} = (1/m_\mathrm{total})\sum_i m_iM_i$, where m_i is the mass of polymer i present. Using $m_i = n_iM_i$ and $m_\mathrm{total} = \sum_i m_i$ gives

$$\overline{M}_\mathrm{W} = \frac{\sum_i m_iM_i}{\sum_i m_i} = \frac{\sum_i (n_iM_i)M_i}{\sum_i n_iM_i} = \frac{\sum_i n_iM_i^2}{\sum_i n_iM_i}$$

From above the amounts in moles of each polymer are $\frac{3}{5}n_{\text{total}}$ and $\frac{2}{5}n_{\text{total}}$ so

$$\overline{M}_{\text{W}} = \frac{n_1M_1^2 + n_2M_2^2}{n_1M_1 + n_2M_2} = \frac{\frac{3}{5}n_{\text{total}}M_1^2 + \frac{2}{5}n_{\text{total}}M_2^2}{\frac{3}{5}n_{\text{total}}M_1 + \frac{2}{5}n_{\text{total}}M_2} = \frac{3M_1^2 + 2M_2^2}{3M_1 + 2M_2}$$

$$= \frac{3 \times (62\ \text{kg mol}^{-1})^2 + 2 \times (78\ \text{kg mol}^{-1})^2}{3 \times (62\ \text{kg mol}^{-1}) + 2 \times (78\ \text{kg mol}^{-1})} = \boxed{69\ \text{kg mol}^{-1}}$$

E14D.2(b) The root mean square separation of the ends of a freely jointed one-dimensional chain is given by [14D.6–*617*], $R_{\text{rms}} = N^{1/2}l$, where N is the number of monomer units and l is the length of each unit. In this case

$$R_{\text{rms}} = N^{1/2}l = 1200^{1/2} \times (1.125\ \text{nm}) = \boxed{38.97\ \text{nm}}$$

E14D.3(b) The contour length R_{c} of a polymer is given by [14D.5–*617*], $R_{\text{c}} = Nl$, and the root mean square separation of the ends of a freely jointed one-dimensional chain is given by [14D.6–*617*], $R_{\text{rms}} = N^{1/2}l$. In both cases N is the number of monomer units and l is the length of each unit.

The monomer of polypropene $-[\text{CH}_2\text{CH}(\text{CH}_3)]_n-$ is taken to be $\text{CH}_2\text{CH}(\text{CH}_3)$. The number of monomers in the chain is given by

$$N = \frac{M_{\text{polymer}}}{M_{\text{CH}_2\text{CH}(\text{CH}_3)}} = \frac{174 \times 10^3\ \text{g mol}^{-1}}{42.0774\ \text{g mol}^{-1}} = 4.13... \times 10^3$$

The length of each $\text{CH}_2\text{CH}(\text{CH}_3)$ unit is estimated as the length of a two C–C bonds: one C–C bond in the centre and half a bond length either side where the unit connects to carbons in adjacent units. From Table 9C.2 on page 362 in the *Resource section* a C–C bond length is approximately 154 pm, so the monomer length l is taken as $2 \times (154\ \text{pm}) = 308\ \text{pm}$. The contour length and root mean square separation are then given by

$$R_{\text{c}} = Nl = (4.13... \times 10^3) \times (308\ \text{pm}) = 1.27... \times 10^6\ \text{pm} = \boxed{1.27\ \mu\text{m}}$$

$$R_{\text{rms}} = N^{1/2}l = (4.13... \times 10^3)^{1/2} \times (308\ \text{pm}) = 1.98... \times 10^4\ \text{pm} = \boxed{19.8\ \text{nm}}$$

E14D.4(b) The radius of gyration R_{g} of a one-dimensional random coil is given by [14D.7a–*618*], $R_{\text{g}} = N^{1/2}l$. Rearranging gives

$$N = \left(\frac{R_{\text{g}}}{l}\right)^2 = \left(\frac{18.9 \times 10^{-9}\ \text{m}}{450 \times 10^{-12}\ \text{m}}\right)^2 = \boxed{1.8 \times 10^3}$$

E14D.5(b) The probability that the ends of a one-dimensional random coil are a distance nl apart is given by [14D.3–*616*], $P = (2/\pi N)^{1/2}\text{e}^{-n^2/2N}$ where N is the total number of monomers in the chain and l is the length of each monomer unit.

The monomer of polyethene $-[\mathrm{CH_2CH_2}]_n-$ is taken to be $\mathrm{CH_2CH_2}$, so the number of monomers in the chain is given by

$$N = \frac{M_{\text{polymer}}}{M_{\mathrm{CH_2CH_2}}} = \frac{85\times10^3\ \mathrm{g\,mol^{-1}}}{28.0516\ \mathrm{g\,mol^{-1}}} = 3.03...\times10^3$$

The length of each $\mathrm{CH_2CH_2}$ unit is estimated as the length of a two C–C bonds: one C–C bond in the centre and half a bond length either side where the unit connects to carbons in adjacent units. From Table 9C.2 on page 362 a C–C bond length is approximately 154 pm, so the monomer length l is taken as $2\times(154\ \mathrm{pm}) = 308\ \mathrm{pm}$.

If the end-to-end distance is d, then $d = nl$ and hence $n = d/l$. In this case $d = 15$ nm and $l = 308$ pm hence

$$n = \frac{d}{l} = \frac{15\times10^{-9}\ \mathrm{m}}{308\times10^{-12}\ \mathrm{m}} = 48.7...$$

The probability of the ends being this distance apart is therefore

$$\begin{aligned}P &= \left(\frac{2}{\pi N}\right)^{1/2} \mathrm{e}^{-n^2/2N}\\ &= \left(\frac{2}{\pi\times(3.03...\times10^3)}\right)^{1/2}\times \mathrm{e}^{-(48.7...)^2/2\times(3.03...\times10^3)} = \boxed{9.8\times10^{-3}}\end{aligned}$$

E14D.6(b) The probability distribution function for a three-dimensional freely jointed chain is given by [14D.4–*616*]

$$f(r) = 4\pi\left(\frac{a}{\pi^{1/2}}\right)^3 r^2\mathrm{e}^{-a^2r^2}\qquad a = \left(\frac{3}{2Nl^2}\right)^{1/2}$$

where N is the number of monomers in the chain, l is the length of each monomer, and $f(r)\,\mathrm{d}r$ is the probability that the ends of the chain are a distance between r and $r+\mathrm{d}r$ apart.

The monomer of polyethene $-[\mathrm{CH_2CH_2}]_n-$ is taken to be $\mathrm{CH_2CH_2}$, so the number of monomers in the chain is given by

$$N = \frac{M_{\text{polymer}}}{M_{\mathrm{CH_2CH_2}}} = \frac{75\times10^3\ \mathrm{g\,mol^{-1}}}{28.0516\ \mathrm{g\,mol^{-1}}} = 2.67...\times10^3$$

The length of each $\mathrm{CH_2CH_2}$ unit is estimated as the length of a two C–C bonds: one C–C bond in the centre and half a bond length either side where the unit connects to carbons in adjacent units. From Table 9C.2 on page 362 a C–C bond length is approximately 154 pm, so the monomer length l is taken as $2\times(154\ \mathrm{pm}) = 308\ \mathrm{pm} = 0.308\ \mathrm{nm}$. Therefore

$$a = \left(\frac{3}{2Nl^2}\right)^{1/2} = \left(\frac{3}{2\times(2.67...\times10^3)\times(0.308\ \mathrm{nm})^2}\right)^{1/2} = 0.0769...\ \mathrm{nm^{-1}}$$

$$\begin{aligned} f(14.0\text{ nm}) &= 4\pi\left(\frac{a}{\pi^{1/2}}\right)^3 r^2 e^{-a^2r^2} \\ &= 4\pi\left(\frac{0.0769...\text{ nm}^{-1}}{\pi^{1/2}}\right)^3 \times (14.0\text{ nm})^2 \times e^{-(0.0769\text{ nm}^{-1})^2\times(14.0\text{ nm})^2} \\ &= 0.0631...\text{ nm}^{-1} \end{aligned}$$

The probability that the ends will be found in a narrow range of width $\delta r = 0.1$ nm at 14.0 nm is therefore

$$f(14.0\text{ nm})\delta r = (0.0631...\text{ nm}^{-1}) \times (0.1\text{ nm}) = \boxed{6.3 \times 10^{-3}}$$

E14D.7(b) As explained in Section 14D.3(b) on page 618, the radius of gyration of a constrained chain is given by the value for a free chain multiplied by a factor F, where F is given by [14D.8–*618*], $F = [(1 - \cos\theta)/(1 + \cos\theta)]^{1/2}$. For $\theta = 120°$,

$$F = \left(\frac{1 - \cos\theta}{1 + \cos\theta}\right)^{1/2} = \left(\frac{1 - \cos 120°}{1 + \cos 120°}\right)^{1/2} = 1.73...$$

This corresponds to a percentage increase of $[(1.73...) - 1] \times 100\% = \boxed{+73.2\%}$. The volume is proportional to the cube of the radius, so the volume of the constrained chain is related to that of a free chain by a factor of $F^3 = (1.73...)^3 = 5.19....$ This corresponds to a percentage increase of $[(5.19...) - 1] \times 100\% = \boxed{+420\%}$.

E14D.8(b) As explained in Section 14D.3(c) on page 618, the root mean square separation of the ends of a partially rigid chain with persistence length l_p is given by the value for a free chain multiplied by a factor F, where F is given by [14D.10–*619*], $F = (2l_p/l - 1)^{1/2}$. The contour length is given by [14D.5–*617*], $R_c = Nl$, so a persistence length of 2.5% of the contour length corresponds to $l_p = 0.025R_c = 0.025Nl$. Hence, for $N = 1000$,

$$\begin{aligned} F &= \left(\frac{2l_p}{l} - 1\right)^{1/2} = \left(\frac{2 \times (0.025Nl)}{l} - 1\right)^{1/2} = (0.050N - 1)^{1/2} \\ &= (0.050 \times 1000 - 1)^{1/2} = 7.00\ldots \end{aligned}$$

This corresponds to a percentage increase of $[(7.00...) - 1] \times 100\% = \boxed{+600\%}$. The volume is proportional to the cube of the radius, so the volume of the partially rigid chain is related to that of a free chain by a factor of $F^3 = (7.00...)^3 = 3.43... \times 10^2$. This corresponds to a percentage increase of $[(3.43... \times 10^2) - 1] \times 100\% = \boxed{(3.42 \times 10^4)\%}$.

E14D.9(b) By analogy with [14D.10–*619*], the radius of gyration R_g of a partially rigid coil is related to that of a freely jointed chain according to $R_g = F \times R_{g,\text{free}}$ where

$F = (2l_p/l - 1)^{1/2}$. The radius of gyration for a three-dimensional freely jointed chain is given by [14D.7b–*618*], $R_{g,\text{free}} = (N/6)^{1/2}l$, so

$$R_g = F \times R_{g,\text{free}} = \left(\frac{2l_p}{l} - 1\right)^{1/2} \times \left(\frac{N}{6}\right)^{1/2} l$$

Rearranging gives

$$R_g^2 = \left(\frac{2l_p}{l} - 1\right)\left(\frac{N}{6}\right) l^2 \quad \text{hence} \quad \frac{6R_g^2}{Nl^2} = \frac{2l_p}{l} - 1 \quad \text{hence} \quad l_p = \frac{l}{2}\left(\frac{6R_g^2}{Nl^2} + 1\right)$$

Therefore for the polymer in question, taking $l = 0.164$ nm,

$$l_p = \frac{l}{2}\left(\frac{6R_g^2}{Nl^2} + 1\right) = \frac{0.164\ \text{nm}}{2}\left(\frac{6 \times (3.0\ \text{nm})^2}{1500 \times (0.164\ \text{nm})^2} + 1\right) = \boxed{0.19\ \text{nm}}$$

E14D.10(b) Modelling the polyethene as a 1D random coil perfect elastomer, the restoring force is given by [14D.12a–*620*], $F = (kT/2l)\ln[(1+\lambda)/(1-\lambda)]$ where $\lambda = x/Nl$.

The monomer of polyethene $-[\text{CH}_2\text{CH}_2]_n-$ is taken to be CH_2CH_2, so the number of monomers in the chain is given by

$$N = \frac{M_{\text{polymer}}}{M_{\text{CH}_2\text{CH}_2}} = \frac{85 \times 10^3\ \text{g mol}^{-1}}{28.0516\ \text{g mol}^{-1}} = 3.03... \times 10^3$$

The length of each CH_2CH_2 unit is estimated as the length of a two C–C bonds: one C–C bond in the centre and half a bond length either side where the unit connects to carbons in adjacent units. From Table 9C.2 on page 362 a C–C bond length is approximately 154 pm, so the monomer length l is taken as $2 \times (154\ \text{pm}) = 308\ \text{pm} = 0.308\ \text{nm}$. The value of λ corresponding to a 2.0 nm extension is therefore

$$\lambda = \frac{x}{Nl} = \frac{2.0\ \text{nm}}{(3.03... \times 10^3) \times (0.308\ \text{nm})} = 2.14... \times 10^{-3}$$

Because $\lambda \ll 1$ the simplified equation for the restoring force, [14D.12b–*621*], $F = (kT/Nl^2)x$ is used. Noting that $1\ \text{J m}^{-1} = 1\ \text{N}$ gives

$$F = \frac{kT}{Nl^2}x = \frac{(1.3806 \times 10^{-23}\ \text{J K}^{-1}) \times ([25 + 273.15]\ \text{K})}{(3.03... \times 10^3) \times (0.308 \times 10^{-9}\ \text{m})^2} \times (2.0 \times 10^{-9}\ \text{nm})$$
$$= \boxed{2.9 \times 10^{-14}\ \text{N}}$$

E14D.11(b) The entropy change when a 1D random coil is stretched or compressed by a distance x is given by [14D.11–*620*], $\Delta S = -\frac{1}{2}kN\ln[(1+\lambda)^{(1+\lambda)}(1-\lambda)^{(1-\lambda)}]$ where $\lambda = x/R_c$. The contour length R_c is given by [14D.5–*617*], $R_c = Nl$, so it follows that $\lambda = x/Nl$.

The monomer of polyethene $-[\mathrm{CH_2CH_2}]_n-$ is taken to be $\mathrm{CH_2CH_2}$, so the number of monomers in the chain is given by

$$N = \frac{M_{\text{polymer}}}{M_{\mathrm{CH_2CH_2}}} = \frac{85 \times 10^3\ \mathrm{g\,mol^{-1}}}{28.0516\ \mathrm{g\,mol^{-1}}} = 3.03... \times 10^3$$

The length of each $\mathrm{CH_2CH_2}$ unit is estimated as the length of a two C–C bonds: one C–C bond in the centre and half a bond length either side where the unit connects to carbons in adjacent units. From Table 9C.2 on page 362 a C–C bond length is approximately 154 pm, so the monomer length l is taken as $2 \times (154\ \mathrm{pm}) = 308\ \mathrm{pm} = 0.308\ \mathrm{nm}$. The value of λ corresponding to a 2.0 nm extension is therefore

$$\lambda = \frac{x}{Nl} = \frac{2.0\ \mathrm{nm}}{(3.03... \times 10^3) \times (0.308\ \mathrm{nm})} = 0.00214...$$

The entropy change is therefore

$$\begin{aligned}\Delta S &= \tfrac{1}{2}kN\ln\left[(1+\lambda)^{(1+\lambda)}(1-\lambda)^{(1-\lambda)}\right] \\ &= \tfrac{1}{2} \times (1.3806 \times 10^{-23}\ \mathrm{J\,K^{-1}}) \times (3.03... \times 10^3) \\ &\quad \times \ln\left[(1+0.00214...)^{(1+0.00214...)} \times (1-0.00214...)^{(1-0.00214...)}\right] \\ &= -9.60... \times 10^{-26}\ \mathrm{J\,K^{-1}}\end{aligned}$$

The molar entropy change is obtained by multiplying by Avogadro's constant

$$\Delta S_\mathrm{m} = (-9.60... \times 10^{-26}\ \mathrm{J\,K^{-1}}) \times (6.0221 \times 10^{23}\ \mathrm{mol^{-1}}) = \boxed{-0.058\ \mathrm{J\,K^{-1}\,mol^{-1}}}$$

Solutions to problems

P14D.2 The probability distribution for the separation of the ends in a 3D random coil is given by [14D.4–*616*]

$$f(r) = 4\pi\left(\frac{a}{\pi^{1/2}}\right)^3 r^2 \mathrm{e}^{-a^2r^2} \quad \text{where} \quad a = \left(\frac{3}{2Nl^2}\right)^{1/2}$$

(a) The root-mean-square separation is given by $R_\text{rms} = \langle r^2 \rangle^{1/2}$ where the mean value of r^2 is calculated as

$$\begin{aligned}\langle r^2 \rangle &= \int r^2 f(r)\,\mathrm{d}r = \int_0^\infty r^2 \times 4\pi\left(\frac{a}{\pi^{1/2}}\right)^3 r^2\mathrm{e}^{-a^2r^2}\,\mathrm{d}r \\ &= 4\pi\left(\frac{a}{\pi^{1/2}}\right)^3 \underbrace{\int_0^\infty r^4\mathrm{e}^{-a^2r^2}\,\mathrm{d}r}_{\text{Integral G.5 with } k = a^2} = 4\pi\left(\frac{a}{\pi^{1/2}}\right)^3 \times \frac{3}{8(a^2)^2}\left(\frac{\pi}{a^2}\right)^{1/2} \\ &= \frac{3}{2a^2} = \frac{3}{2}\left(\frac{2Nl^2}{3}\right) = Nl^2\end{aligned}$$

Hence $R_\text{rms} = \langle r^2 \rangle^{1/2} = (Nl^2)^{1/2} = \boxed{N^{1/2}l}$, in agreement with [14D.6–*617*].

(b) The mean separation is

$$\begin{aligned}\langle r\rangle &= \int rf(r)\,\mathrm{d}r = \int_0^{\infty} r\times 4\pi\left(\frac{a}{\pi^{1/2}}\right)^3 r^2\mathrm{e}^{-a^2r^2}\\ &= 4\pi\left(\frac{a}{\pi^{1/2}}\right)^3 \underbrace{\int_0^{\infty} r^3\mathrm{e}^{-a^2r^2}}_{\text{Integral G.4 with } k\,=\,a^2} = 4\pi\left(\frac{a}{\pi^{1/2}}\right)^3\times\frac{1}{2(a^2)^2} = \frac{2}{\pi^{1/2}}\left(\frac{1}{a}\right)\\ &= \frac{2}{\pi^{1/2}}\left(\frac{2Nl^2}{3}\right) = \boxed{\left(\frac{8N}{3\pi}\right)l}\end{aligned}$$

(c) The most probable separation is the value of r for which $f(r)$ is a maximum. Differentiating $f(r)$ using the product rule gives

$$\begin{aligned}\frac{\mathrm{d}f(r)}{\mathrm{d}r} &= 4\pi\left(\frac{a}{\pi^{1/2}}\right)^3\times\left[(2r)(\mathrm{e}^{-a^2r^2}) + (r^2)(-2a^2r\mathrm{e}^{-a^2r^2})\right]\\ &= \pi\left(\frac{a}{\pi^{1/2}}\right)^3\times 2r\mathrm{e}^{-a^2r^2}\left[1-a^2r^2\right]\end{aligned}$$

At the maximum $\mathrm{d}f(r)/\mathrm{d}r = 0$, which implies that

$$r(1-a^2r^2) = 0 \quad \text{hence} \quad r_{\mathrm{mp}} = \frac{1}{a} = \left(\frac{2Nl^2}{3}\right) = \boxed{\left(\frac{2N}{3}\right)^{1/2} l}$$

The solution $r = 0$ is rejected because this does not correspond to a maximum, as implied by the fact that $f(0) = 0$.

For the case that $N = 4000$ and $l = 154$ pm these expressions give

$$\begin{aligned}R_{\mathrm{rms}} &= N^{1/2}l = 4000^{1/2}\times(154\text{ pm}) = 9.73...\times 10^3\text{ pm} = \boxed{9.74\text{ nm}}\\ \langle r\rangle &= \left(\frac{8N}{3\pi}\right)^{1/2} l = \left(\frac{8\times 4000}{3\pi}\right)^{1/2}\times(154\text{ pm}) = 8.97...\times 10^3\text{ pm} = \boxed{8.97\text{ nm}}\\ r_{\mathrm{mp}} &= \left(\frac{2N}{3}\right)^{1/2} l = \left(\frac{2\times 4000}{3}\right)^{1/2}\times(154\text{ pm}) = 7.95...\times 10^3\text{ pm} = \boxed{7.95\text{ nm}}\end{aligned}$$

P14D.4 There is some lack of clarity in the text over the definition of the radius of gyration, R_{g}. For a polymer consisting of N identical monomer units, R_{g} is defined as

$$R_{\mathrm{g}}^2 = (1/N)\sum_{i=1}^{N} r_i^2 \tag{14.1}$$

where r_i is the distance of monomer unit i from the centre of mass. In other words, the radius of gyration is the root-mean-square of the distance of the monomer units from the centre of mass.

A related quantity is the moment of inertia I about an axis, which is defined in the following way

$$I = \sum_{i=1}^{N} md_i^2 \tag{14.2}$$

where m is the mass of the monomer unit and d_i is the *perpendicular distance* from the monomer to the axis. In general, the distance d_i is *not* the same as r_i: the first is the perpendicular distance to the axis, the second is the distance to the centre of mass.

A radius of gyration can be related to a moment of inertia by imagining a rigid rotor consisting of a mass m_{tot} equal to the total mass of the polymer held at a distance R_{g} from the origin; the moment of inertia of this rotor is $I = m_{\text{tot}}R_{\text{g}}^2$, and hence $R_{\text{g}}^2 = I/m_{\text{tot}}$. However, note that this radius of gyration is associated by the rotation about a particular axis.

(a) For the purposes of this discussion there is no distinction between a 'thin disc' and a 'long rod': both are cylinders with circular cross sections of radius a and length either h or l. The case of a solid rod is considered in (b).

(b) For a solid rod it is convenient to use eqn 14.2 for rotation about (i) the long axis of the rod, and (ii) an axis perpendicular to this and which passes through the centre of mass. The long axis of the rod defines the z-axis and the centre of mass is at $z = 0$; the rod therefore extends from $-l/2$ to $+l/2$ along z. It is convenient to use cylindrical polar coordinates described in *The chemist's toolkit* 19 in Topic 7F on page 281. In such a coordinate system the volume element is $r\,\text{d}r\,\text{d}\phi\,\text{d}z$, and ϕ ranges from 0 to 2π.

Equation 14.2 is adapted for a solid object by replacing the mass by a volume element $\text{d}V$ which has mass $\rho\,\text{d}V$, where ρ is the mass density; the summation becomes an integration over the relevant coordinates which describe the rod: $z = -l/2$ to $+l/2$, $\phi = 0$ to 2π, and $r = 0$ to a. To compute the moment of inertia about the long axis note that the perpendicular distance to the axis is r so the integral is

$$\begin{aligned}
I_{||} &= \int_{z=-l/2}^{z=+l/2}\int_{r=0}^{r=a}\int_{\phi=0}^{\phi=2\pi} r^2 \times \rho\,\text{d}V \\
&=\rho \int_{z=-l/2}^{z=+l/2}\int_{r=0}^{r=a}\int_{\phi=0}^{\phi=2\pi} r^2 \times r\,\text{d}z\,\text{d}r\,\text{d}\phi \\
&=\rho \int_{z=-l/2}^{z=+l/2}\text{d}z \int_{r=0}^{r=a} r^3\,\text{d}r \int_{\phi=0}^{\phi=2\pi}\text{d}\phi \\
&=\rho \times l \times \frac{a^4}{4} \times 2\pi = \rho l a^4 \pi/2
\end{aligned}$$

The total mass of the rod is $m_{\text{tot}} = \rho V = \rho\pi a^2 l$, hence the moment of inertia is $\boxed{I_{||} = \tfrac{1}{2}m_{\text{tot}}a^2}$. A rigid rotor with the same mass as the rod has moment of inertia $I = m_{\text{tot}}R_{\text{g},||}^2$. Equating the moments of inertia gives an expression for the radius of gyration as $\boxed{R_{\text{g},||} = (1/2)^{1/2}a}$.

To compute the moment of inertia perpendicular to the long axis, say about the x-axis, it is necessary to know the perpendicular distance d between an arbitrary point (x, y, z) and that axis. This distance is that between the points (x, y, z) and $(x, 0, 0)$; by Pythagoras' theorem $d^2 =$

$y^2 + z^2 = r^2 \sin^2\phi + z^2$. The moment is inertia is therefore found from the integral

$$I = \int_{\text{cyl.}} (r^2 \sin^2\phi + z^2) \times \rho\, \mathrm{d}V = \underbrace{\rho \int_{\text{cyl.}} r^2 \sin^2\phi\, \mathrm{d}V}_{A} + \underbrace{\rho \int_{\text{cyl.}} z^2\, \mathrm{d}V}_{B}$$

where the integration is over the complete cylinder. The integrals A and B are conveniently evaluated separately.

$$\begin{aligned} A =& \rho \int_{z=-l/2}^{z=+l/2} \int_{r=0}^{r=a} \int_{\phi=0}^{\phi=2\pi} r^2 \sin^2\phi \times r\, \mathrm{d}z\, \mathrm{d}r\, \mathrm{d}\phi \\ =& \rho \int_{z=-l/2}^{z=+l/2} \mathrm{d}z \int_{r=0}^{r=a} r^3\, \mathrm{d}r \int_{\phi=0}^{\phi=2\pi} \sin^2\phi\, \mathrm{d}\phi \\ =& \rho \times l \times \frac{a^4}{4} \times \pi = \rho l a^4 \pi/4 = m_{\text{tot}} a^2/4 \end{aligned}$$

where the integral over ϕ is found using Integral T.2 with $k = 1$ and $a = 2\pi$.

$$\begin{aligned} B =& \rho \int_{z=-l/2}^{z=+l/2} \int_{r=0}^{r=a} \int_{\phi=0}^{\phi=2\pi} z^2 \times r\, \mathrm{d}z\, \mathrm{d}r\, \mathrm{d}\phi \\ =& \rho \int_{z=-l/2}^{z=+l/2} z^2\, \mathrm{d}z \int_{r=0}^{r=a} r\, \mathrm{d}r \int_{\phi=0}^{\phi=2\pi} \mathrm{d}\phi \\ =& \rho \times \frac{l^3}{12} \times \frac{a^2}{2} \times 2\pi = \rho l^3 a^2 \pi/12 = m_{\text{tot}} l^2/12 \end{aligned}$$

The moment of inertia about the perpendicular axis is therefore

$$I_\perp = A + B = m_{\text{tot}} a^2/4 + m_{\text{tot}} l^2/12 = \boxed{m_{\text{tot}}(a^2/4 + l^2/12)}$$

A rigid rotor with the same total mass has moment of inertia $I = m_{\text{tot}} R_{\text{g},\perp}^2$, hence $\boxed{R_{\text{g},\perp} = (a^2/4 + l^2/12)^{1/2}}$.

(c) Consider the moment of inertia about the z-axis passing through the centre of a solid sphere. The square of the perpendicular distance of a point to this axis is $x^2 + y^2$, hence $I = \int_{\text{sphere}} (x^2 + y^2)\rho\, \mathrm{d}V$. In spherical polar coordinates

$$x^2 + y^2 = r^2 \sin^2\theta \cos^2\phi + r^2 \sin^2\theta \sin^2\phi = r^2 \sin^2\theta$$

The integral is therefore evaluated as

$$\begin{aligned} I =& \rho \int_{r=0}^{r=a} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} (r^2 \sin^2\theta) \times r^2 \sin\theta\, \mathrm{d}r\, \mathrm{d}\theta\, \mathrm{d}\phi \\ =& \rho \int_{r=0}^{r=a} r^4\, \mathrm{d}r \int_{\theta=0}^{\theta=\pi} \sin^3\theta\, \mathrm{d}\theta \int_{\phi=0}^{\phi=2\pi} \mathrm{d}\phi \\ =& \rho \times \frac{a^5}{5} \times \frac{4}{3} \times 2\pi \end{aligned}$$

where the integral over θ is of the form of Integral T.3 with $k = 1$ and $a = \pi$. The total mass of the sphere is $m_{\text{tot}} = \rho V = (4/3)\rho\pi a^3$, hence the moment of inertia can be expressed as

$$I = m_{\text{tot}} \times \frac{3}{4\rho\pi a^3} \times \rho \times \frac{a^5}{5} \times \frac{4}{3} \times 2\pi = \boxed{\tfrac{2}{5} m_{\text{tot}} a^2}$$

A rigid rotor with the same mass as the sphere has moment of inertia $I = m_{\text{tot}} R_g^2$, hence $\boxed{R_g = (2/5)^{1/2} a}$. Note that this is the radius of gyration associated with rotation about this axis.

P14D.6 The radius of gyration R_g is found by equating $m_{\text{total}} R_g^2$ to the moment of inertia I, hence $R_g^2 = I/m_{\text{total}}$. The moment of inertia is given by $I = \sum_j^N m_j R_j^2$, where m_j is the mass of unit j and R_j is its distance from the centre of mass. If all N units have the same mass m then $I = m \sum_j R_j^2$ and $m_{\text{total}} = Nm$. Hence

$$R_g = \frac{1}{m_{\text{total}}} \sum_j m_j R_j^2 = \frac{1}{Nm} \times m \sum_j R_j^2 = \frac{1}{N} \sum_j R_j^2$$

P14D.8 As explained in *The chemist's toolkit* 18 in Topic 7E on page 273, the frequency of a harmonic oscillator with mass m and force constant k_f is $\nu = (1/2\pi)(k_f/m)^{1/2}$. The force constant is given by [14D.12c–*621*], $k_f = kT/Nl^2$. The mass is taken as the mass of one monomer, which is given by $m = M/NN_A$ where M is the molar mass of the macromolecule and N is the number of monomers in the chain. Combining these expressions gives

$$\nu = \frac{1}{2\pi}\left(\frac{k_f}{m}\right)^{1/2} = \frac{1}{2\pi}\left(\frac{kT/Nl^2}{M/NN_A}\right)^{1/2} = \boxed{\frac{1}{2\pi l}\left(\frac{RT}{M}\right)^{1/2}}$$

where $R = kN_A$ is used.

The monomer of polyethene $-[\mathrm{CH_2CH_2}]_n-$ is taken to be $\mathrm{CH_2CH_2}$. The length of each $\mathrm{CH_2CH_2}$ unit is estimated as the length of a two C–C bonds: one C–C bond in the centre and half a bond length either side where the unit connects to carbons in adjacent units. From Table 9C.2 on page 362 a C–C bond length is approximately 154 pm, so the monomer length l is taken as $2 \times (154\ \text{pm}) = 308\ \text{pm}$. Noting that $1\ \text{J} = 1\ \text{kg m}^2\ \text{s}^{-2}$ and $1\ \text{Hz} = 1\ \text{s}^{-1}$, the vibration frequency is therefore

$$\begin{aligned}\nu &= \frac{1}{2\pi l}\left(\frac{RT}{M}\right)^{1/2} \\ &= \frac{1}{2\pi \times (308 \times 10^{-12}\ \text{m})}\left(\frac{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times ([20 + 273.15]\ \text{K})}{65\ \text{kg mol}^{-1}}\right)^{1/2} \\ &= 3.16... \times 10^9\ \text{Hz} = \boxed{3.2\ \text{GHz}}\end{aligned}$$

The expression shows that the frequency increases with temperature and decreases with increasing molar mass. The $T^{1/2}$ dependence reflects the thermal energy needed to establish a displacement from equilibrium. The $M^{-1/2}$ dependence indicates that a larger chain mass requires more thermal energy to establish the same displacement.

P14D.10 As explained in Section 14D.5 on page 621 the glass transition temperature corresponds to a transition from a state of high to low chain mobility as the temperature decreases. This corresponds to the freezing of the internal bond rotations. In effect, the easier such rotations are, the lower T_g. Internal rotations are more difficult for polymers that have bulky side chains than for polymers without such chains because the side chains of neighbouring molecules can impede each other's motion. Of the four polymers in this problem, polystyrene has the largest side chain (phenyl) and the largest T_g. The chlorine atoms in poly(vinyl chloride) interfere with each other's motion more than the smaller hydrogen atoms that hang from the carbon backbone of polyethylene. Poly(oxymethylene), like polyethylene, has only hydrogen atoms protruding from its backbone; however, poly(oxymethylene) has fewer hydrogen protrusions and a still lower T_g than polyethylene.

14E Self-assembly

Answers to discussion questions

D14E.2 This is discussed in Section 14E.2(a) on page 626.

D14E.4 Sterols, like cholesterol, prevent the hydrophobic chains of lipids bilayers from 'freezing' into a gel and, by disrupting the packing of the chains, spread the melting point of the membrane over a range of temperatures.

Solutions to exercises

E14E.1(b) The isoelectric point of a protein is the pH at which the protein has no net charge and therefore is unaffected by an electric field. This is the pH at which the velocity is zero; solving for this gives

$$0 = 0.80 - (4.0 \times 10^{-3})(\text{pH}) - (5.0 \times 10^{-2})(\text{pH})^2$$

Solving this equation for pH gives

$$\begin{aligned}\text{pH} &= \frac{-(-4.0 \times 10^{-3}) \pm \sqrt{(-4.0 \times 10^{-3})^2 - 4 \times (-5.0 \times 10^{-2}) \times (0.8)}}{2 \times (-5.0 \times 10^{-2})} \\ &= +3.96... \text{ or } -4.04...\end{aligned}$$

The negative solution is rejected as it is outside the pH range 3.0–5.0 over which the expression is valid. Therefore the isoelectric point is $\boxed{4.0}$.

Solutions to problems

P14E.2 The equilibrium constant for the formation of micelles containing N monomers, M_N, is given by [14E.6b–*627*] (the factors of $1/c^{\ominus}$ are omitted for clarity)

$$K = \frac{[M_N]}{([M]_{\text{total}} - N[M_N])^N}$$

In the text the fraction of surfactant molecules present as micelles is defined as $f = [M_N]/[M]_{\text{total}}$; it could be argued that a better definition would be $f = N \times [M_N]/[M]_{\text{total}}$ on the grounds that each micelle contains N monomers. Using the first definition for f the equilibrium constant is rewritten

$$K = \frac{f}{[M]_{\text{total}}^{N-1}(1 - Nf)^N}$$

This equation is solved numerically to find f as a function of $[M]_{\text{total}}$ for given values of K and N. The results for three such situations are shown in Fig. 14.14. For $N = 30$ there is a sudden increase in f once $[M]_{\text{total}}/c^{\ominus}$ exceeds a certain value; this corresponds to the critical micelle concentration. This concentration depends on both N and K.

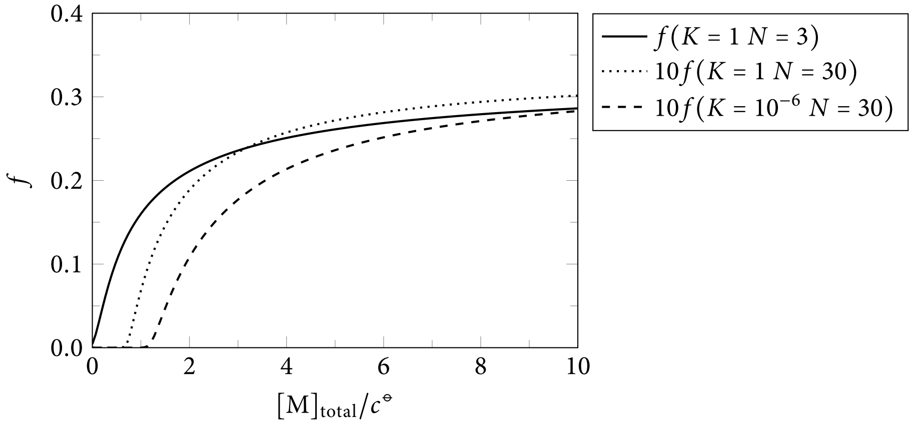


Figure 14.14

Solutions to integrated activities

I14.2 (a) The Lennard-Jones potential is given by [14B.12–*600*], $V_{\text{LJ}}(r) = 4\varepsilon\{(r_0/r)^{12} - (r_0/r)^6\}$. As shown in Fig. 14B.8 on page 600, the depth of the potential well is given by ε and the position of the minimum is given by $r_e = 2^{1/6}r_0$. The results for He_2 give the depth of the well as $hc\widetilde{D}_e = 1.51 \times 10^{-23}$ J and the position of the minimum as $R = 297$ pm so it follows that

$$\varepsilon = \boxed{1.51 \times 10^{-23}\ \text{J}} \quad \text{and} \quad r_0 = \frac{r_e}{2^{1/6}} = \frac{297\ \text{pm}}{2^{1/6}} = \boxed{265\ \text{pm}}$$

A plot of the potential with these values is shown in Fig. 14.15.

(b) The Morse potential is given by [11C.7–*444*], $V_\mathrm{M}(x) = hc\widetilde{D}_\mathrm{e}(1 - \mathrm{e}^{-ax})^2$, where $x = r - r_\mathrm{e}$ and $hc\widetilde{D}_\mathrm{e}$ is the depth of the well. With this potential $V_\mathrm{M}(0) = 0$, in contrast to the Lennard-Jones potential for which $V_\mathrm{LJ}(\infty) = 0$. To compare the two, the Morse potential is replotted as $V_\mathrm{M}(x) = hc\widetilde{D}_\mathrm{e}\left(1 - \mathrm{e}^{-a(r-r_\mathrm{e})}\right)^2 - hc\widetilde{D}_\mathrm{e}$; this is shown plotted in Fig. 14.15 using the given values of $hc\widetilde{D}_\mathrm{e} = 1.51 \times 10^{-23}$ J and $a = 5.79 \times 10^{10}$ m^{-1}.

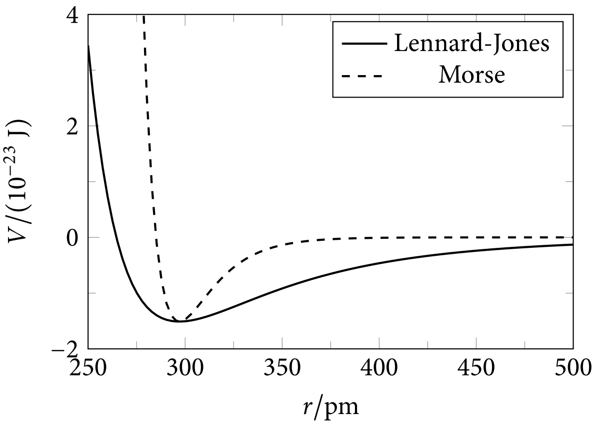
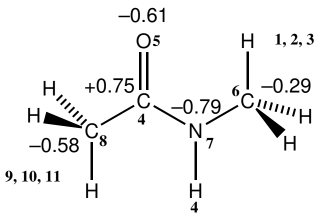


Figure 14.15

I14.4 (a) The charges on the atoms as calculated using a 6-31G* basis are shown in the table below, and the diagram shows the numbering of the atoms and the charges on the heteroatoms.



atom type	number	q/e	$x/\text{Å}$	$y/\text{Å}$	$z/\text{Å}$
C	4	0.746	0.469	−0.168	−0.583
O	5	−0.611	1.228	−0.554	−1.430
C	6	−0.288	0.674	−2.216	0.767
N	7	−0.790	0.143	−0.896	0.509
C	8	−0.577	−0.186	1.194	−0.685
H	3	0.231	1.339	−2.475	−0.041
H	1	0.168	1.227	−2.235	1.700
H	2	0.168	−0.122	−2.951	0.819
H	9	0.161	−0.848	1.425	0.141
H	10	0.207	0.591	1.946	−0.738
H	11	0.207	−0.746	1.236	−1.611
H	12	0.380	−0.492	−0.509	1.167

The dipole moment along x is computed as $\mu_x = \sum_i q_i x_i$, where i is the index for the atom, q_i is its charge, and x_i its coordinate. Using the data in the table the components of the dipole moment are easily computed in units of the elementary charge times Å, and then these values are converted to Debye in the usual way. The total dipole moment is $\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$.

$$\begin{aligned}\mu_x &= -0.461\,e\,\text{Å}\\ &= (-0.461\times 10^{-10}\,\text{m})\times(1.6022\times 10^{-19}\,\text{C})/(3.3356\times 10^{-30}\,\text{C m})\\ &= -2.212\,\text{D}\end{aligned}$$

Similarly $\mu_y = 0.607$ D and $\mu_z = 2.897$ D, giving $\boxed{\mu = 3.695\,\text{D}}$.

The energy of interaction of two dipoles is given by [14B.3b–*595*]

$$V = \frac{\mu_1\mu_2}{4\pi\varepsilon_0 r^3}\times(1-3\cos^2\Theta)$$

With the data given, and converting to molar units

$$\begin{aligned}V &= \frac{[(3.695\,\text{D})\times(3.3356\times 10^{-30}\,\text{C m})/(1\,\text{D})]^2)}{4\pi\times(8.8542\times 10^{-12}\,\text{J}^{-1}\,\text{C}^2\,\text{m}^{-1})\times(3.0\times 10^{-9}\,\text{nm})^3}\\ &\qquad\times(1-3\cos^2\Theta)\times(6.0221\times 10^{23}\,\text{mol}^{-1})\\ &= (30.4...\,\text{J mol}^{-1})\times(1-3\cos^2\Theta)\end{aligned}$$

A plot of this function is shown in Fig. 14.16.

(b) The maximum of the dipole–dipole interaction is $-61\,\text{J mol}^{-1}$ which is only 0.3% of the energy of the hydrogen bond.

I14.6 Starting from $G = U - TS - tl$, the differential is formed and the basic equation $\mathrm{d}U = T\mathrm{d}S + t\mathrm{d}l$ is introduced to give

$$\begin{aligned}\mathrm{d}G &= \mathrm{d}U - \mathrm{d}(TS) - \mathrm{d}(tl) = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T - t\mathrm{d}l - l\mathrm{d}t\\ &= T\mathrm{d}S + t\mathrm{d}l - T\mathrm{d}S - S\mathrm{d}T - t\mathrm{d}l - l\mathrm{d}t = \boxed{-S\mathrm{d}T - l\mathrm{d}t}\end{aligned}$$

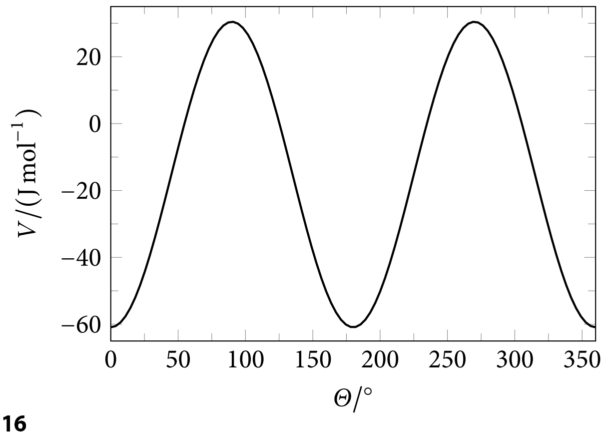


Figure 14.16

The Helmholtz energy A is given by [3D.4a–*97*], $A = U - TS$. Forming the differential gives

$$\mathrm{d}A = \mathrm{d}U - \mathrm{d}(TS) = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T = T\mathrm{d}S + t\mathrm{d}l - T\mathrm{d}S - S\mathrm{d}T = \boxed{-S\mathrm{d}T + t\mathrm{d}l}$$

The Maxwell relations are derived using the method described in Section 3E.1(a) on page 104. Because G is a state function, $\mathrm{d}G = -S\mathrm{d}T - l\mathrm{d}t$ is an exact differential. Therefore according to the criterion in [3E.4–*104*], $(\mathrm{d}g/\mathrm{d}y)_x = (\mathrm{d}h/\mathrm{d}x)_y$ if $\mathrm{d}f = g\mathrm{d}x + h\mathrm{d}y$ is an exact differential, it follows that

$$-\left(\frac{\partial S}{\partial t}\right)_T = -\left(\frac{\partial l}{\partial T}\right)_t \quad \text{hence} \quad \boxed{\left(\frac{\partial S}{\partial t}\right)_T = \left(\frac{\partial l}{\partial T}\right)_t}$$

Applying the same approach to $\mathrm{d}A = -S\mathrm{d}T + t\mathrm{d}l$ gives

$$-\left(\frac{\partial S}{\partial l}\right)_T = \left(\frac{\partial t}{\partial T}\right)_l \quad \text{hence} \quad \boxed{\left(\frac{\partial S}{\partial l}\right)_T = -\left(\frac{\partial t}{\partial T}\right)_l}$$

To deduce the equation of state, the basic equation $\mathrm{d}U = T\mathrm{d}S + t\mathrm{d}l$ is divided by $\mathrm{d}l$ and the condition of constant T is imposed

$$\left(\frac{\partial U}{\partial l}\right)_T = T\left(\frac{\partial S}{\partial l}\right)_T + t = -T\left(\frac{\partial t}{\partial T}\right)_l + t = \boxed{t - T\left(\frac{\partial t}{\partial T}\right)_l}$$

In the second step the Maxwell relation $(\partial S/\partial l)_T = -(\partial T/\partial t)_l$, derived above, is used.

I14.8 The osmotic pressure Π is expressed in terms of the concentration [J] by the virial-like expression of [5B.18–*163*], $\Pi = RT\left([\mathrm{J}] + B[\mathrm{J}]^2\right)$. In this equation the units of B are the inverse of the units of [J].

The osmotic virial coefficient arises largely from the effect of excluded volume. If a solution of a macromolecule is imagined as being built by the successive addition of macromolecules of effective radius a to the solvent, each one being excluded by the ones that preceded it, then B is the excluded volume per mole of molecules. The volume of a molecule is $v_{\mathrm{mol}} = (4/3)\pi a^3$, but the excluded volume is determined by the smallest distance possible between centres of two molecules, which is $2a$. Therefore the excluded volume is $(4/3)\pi(2a)^3 = 8v_{\mathrm{mol}}$ for a pair of molecules. The volume excluded per molecule is one-half this volume or $4v_{\mathrm{mol}}$. Thus, for an effective radius of $a = \gamma R_{\mathrm{g}} = 0.85R_{\mathrm{g}}$ the osmotic virial coefficient is

$$B = 4N_{\mathrm{A}}v_{\mathrm{mol}} = \frac{16\pi}{3}N_{\mathrm{A}}a^3 = \frac{16\pi}{3}N_{\mathrm{A}}\gamma^3R_{\mathrm{g}}^3$$

(a) For a freely jointed chain $R_{\mathrm{g}} = (N/6)^{1/2}l$ hence

$$\begin{aligned} B &= \frac{16\pi}{3}N_{\mathrm{A}}\gamma^3\left(\frac{N}{6}\right)^{3/2} \\ &= \frac{16\pi}{3}(6.0221\times10^{23}\ \mathrm{mol^{-1}})\times[0.85\times(154\times10^{-12}\ \mathrm{m})]^3\left(\frac{4000}{6}\right)^{3/2} \\ &= \boxed{0.39\ \mathrm{m^3\ mol^{-1}}}. \end{aligned}$$

(b) For a chain with tetrahedral bond angles $R_{\mathrm{g}} = (N/3)^{1/2}l$ hence

$$\begin{aligned} B &= \frac{16\pi}{3}N_{\mathrm{A}}\gamma^3\left(\frac{N}{3}\right)^{3/2} \\ &= \frac{16\pi}{3}(6.0221\times10^{23}\ \mathrm{mol^{-1}})\times[0.85\times(154\times10^{-12}\ \mathrm{m})]^3\left(\frac{4000}{3}\right)^{3/2} \\ &= \boxed{1.1\ \mathrm{m^3\ mol^{-1}}}. \end{aligned}$$

15 Solids

15A Crystal structure

Answers to discussion questions

D15A.2 Lattice planes are labelled 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. These axes may be non-orthogonal.

Solutions to exercises

E15A.1(b) The volume of an orthorhombic unit cell is given by $V = abc$, and the mass of the unit cell m is given by $m = \rho V$, where ρ is the mass density. Using the estimate of mass density $\rho = 2.9\ \text{g cm}^{-3}$

$$\begin{aligned} m = abc\rho &= [(589 \times 822 \times 798) \times 10^{-36}\ \text{m}^3] \times (2.9 \times 10^6\ \text{g m}^{-3}) \\ &= 1.12... \times 10^{-21}\ \text{g} \end{aligned}$$

The mass of the unit cell is also related to the molar mass by $m = nM = NM/N_\text{A}M$ where n is the amount in moles in the unit cell, M is the molar mass, and N is the number molecules per unit cell.

$$N = \frac{mN_\text{A}}{M} = \frac{(1.12... \times 10^{-21}\ \text{g}) \times (6.0221 \times 10^{23}\ \text{mol}^{-1})}{135.01\ \text{g mol}^{-1}} = 4.99...$$

If it is assumed that there are no defects in the crystal lattice then N is expected to be an integer and hence $\boxed{N = 5}$. With this value a more precise value of the mass density is calculated as

$$\begin{aligned} \rho &= \frac{m}{V} = \frac{NM}{N_\text{A}V} \\ &= \frac{5 \times (135.01\ \text{g mol}^{-1})}{(6.0221 \times 10^{23}\ \text{mol}^{-1}) \times [(589 \times 822 \times 798) \times 10^{-36}\ \text{m}^3]} = \boxed{2.90\ \text{g cm}^{-3}} \end{aligned}$$

E15A.2(b) Miller indices are of the form (hkl) where h, k, and l are the reciprocals of the intersection distances along the a, b and c axes, respectively. If the reciprocal intersection distances are fractions then the Miller indices are achieved by multiplying through by the lowest common denominator.

intersect axes at	$(-a, 2b, -c)$	$(a, 4b, -4c)$
remove cell dimensions	$(-1, 2, -1)$	$(1, 4, -4)$
take reciprocals	$(-1, \frac{1}{2}, -1)$	$(-1, \frac{1}{4}, -\frac{1}{4})$
Miller indices	$(\bar{2}1\bar{2})$	$(\bar{4}1\bar{1})$

E15A.3(b) The separation of (hkl) planes d_{hkl} of a cubic lattice is given by [15A.1a–*645*], $d_{hkl} = a/(h^2 + k^2 + l^2)^{1/2}$.

$$d_{123} = \frac{(712\ \text{pm})}{(1^2 + 2^2 + 3^2)^{1/2}} = \boxed{190\ \text{pm}} \qquad d_{222} = \frac{(712\ \text{pm})}{(2^2 + 2^2 + 2^2)^{1/2}} = \boxed{206\ \text{pm}}$$

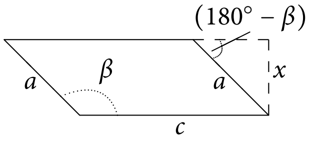
$$d_{246} = \frac{(712\ \text{pm})}{(2^2 + 4^2 + 6^2)^{1/2}} = \boxed{95.1\ \text{pm}}$$

E15A.4(b) The separation of (hkl) planes d_{hkl} of an orthorhombic lattice is given by [15A.1b–*645*], $1/d_{hkl}^2 = h^2/a^2 + k^2/b^2 + l^2/c^2$. Therefore, $d_{hkl} = (h^2/a^2 + k^2/b^2 + l^2/c^2)^{-1/2}$.

$$\begin{aligned} d_{312} &= \left[\frac{3^2}{(769\ \text{pm})^2} + \frac{1^2}{(891\ \text{pm})^2} + \frac{2^2}{(690\ \text{pm})^2}\right]^{-1/2} \\ &= (2.48... \times 10^{19})^{-1/2}\ \text{m} = \boxed{200\ \text{pm}} \end{aligned}$$

Solutions to problems

P15A.2 From Fig. 15A.8 on page 643 it is seen that the unit cell can be envisaged as a prism of height b whose base is a parallelogram with sides a and c and interior angle β. The volume V of the unit cell is b times the area of the parallelogram, which is depicted below.



The area of the parallelogram is cx, and $x = a\sin(180° - \beta)$. It follows that $V = bcx = bc \times [a\sin(180° - \beta)]$. This is further developed using the identity $\sin(A - B) = \sin(A)\cos(B) - \cos(A)\sin(B)$ to give

$$\begin{aligned} V &= bca[\sin(180°)\cos(\beta) - \cos(180°)\sin(\beta)] \\ &= -bca(-1)\sin(\beta) = \boxed{abc\sin\beta} \end{aligned}$$

P15A.4 Refer to Fig. 15A.4 on page 642 to see how the angles are defined in relation to $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$. The volume of the unit cell, V, is $V = \boldsymbol{a}\cdot\boldsymbol{b}\times\boldsymbol{c}$ where $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$ are vectors defining the sides of the unit cell. Writing vector $\boldsymbol{a}$ in terms of its components along the orthogonal set of unit vectors $\boldsymbol{i}$, $\boldsymbol{j}$ and $\boldsymbol{k}$ gives $\boldsymbol{a} = a_i\boldsymbol{i} + a_j\boldsymbol{j} + a_k\boldsymbol{k}$. It is convenient to first find V^2, given by

$$V^2 = (\boldsymbol{a}\cdot\boldsymbol{b}\times\boldsymbol{c})(\boldsymbol{a}\cdot\boldsymbol{b}\times\boldsymbol{c})$$

$$= \begin{vmatrix} a_i & a_j & a_k \\ b_i & b_j & b_k \\ c_i & c_j & c_k \end{vmatrix}\begin{vmatrix} a_i & a_j & a_k \\ b_i & b_j & b_k \\ c_i & c_j & c_k \end{vmatrix}$$

$$= \begin{vmatrix} a_i & a_j & a_k \\ b_i & b_j & b_k \\ c_i & c_j & c_k \end{vmatrix}\begin{vmatrix} a_i & b_i & c_i \\ a_j & b_j & c_j \\ a_k & b_k & c_k \end{vmatrix}$$

Note that transposing a matrix does not alter the value of the determinant.

$$= \begin{vmatrix} a_ia_i + a_ja_j + a_ka_k & a_ib_i + a_jb_j + a_kb_k & a_ic_i + a_jc_j + a_kc_k \\ b_ia_i + b_ja_j + b_ka_k & b_ib_i + b_jb_j + b_kb_k & b_ic_i + b_jc_j + b_kc_k \\ c_ia_i + c_ja_j + c_ka_k & c_ib_i + c_jb_j + c_kb_k & c_ic_i + c_jc_j + c_kc_k \end{vmatrix}$$

$$= \begin{vmatrix} \boldsymbol{a}\cdot\boldsymbol{a} & \boldsymbol{a}\cdot\boldsymbol{b} & \boldsymbol{a}\cdot\boldsymbol{c} \\ \boldsymbol{a}\cdot\boldsymbol{b} & \boldsymbol{b}\cdot\boldsymbol{b} & \boldsymbol{b}\cdot\boldsymbol{c} \\ \boldsymbol{a}\cdot\boldsymbol{c} & \boldsymbol{b}\cdot\boldsymbol{c} & \boldsymbol{c}\cdot\boldsymbol{c} \end{vmatrix}$$

$$= \begin{vmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ac\cos\beta & bc\cos\alpha & c^2 \end{vmatrix}$$

$$= a^2b^2c^2(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)$$

For the penultimate line the fact that γ is the angle between $\boldsymbol{a}$ and $\boldsymbol{b}$ is used so that the dot product is $\boldsymbol{a}\cdot\boldsymbol{b} = ab\cos\gamma$, and likewise for the other pairs of vectors; the final line simply involves evaluating the determinant. Thus for a triclinic unit cell

$$V = \boxed{abc(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)^{1/2}}$$

For a monoclinic unit cell $\alpha = \gamma = 90°$ so $\cos\alpha = \cos\gamma = 0$ and

$$V = abc(1 - \cos^2\beta)^{1/2} = \boxed{abc\sin\beta}$$

where the identity $\cos^2\theta + \sin^2\theta = 1$ has been used. For a orthorhombic unit cell $\alpha = \beta = \gamma = 90°$ so $\cos\alpha = \cos\beta = \cos\gamma = 0$ and

$$V = \boxed{abc}$$

A tetragonal unit cell, as shown in Fig. 15A.8 on page 643, has $a = b \neq c$ so

$$V = (651\text{ pm})^2 \times (934\text{ pm}) = \boxed{3.96\times10^{-28}\text{ m}^3}$$

P15A.6 For an orthorhombic unit cell, $V = abc$. Given that $m = M/N_A$, where m is the mass per repeating unit CH_2CH_2 and M is its molar mass ($M = 28.0...\ \mathrm{g\,mol^{-1}}$), it follows that for two repeating units per cell the mass density ρ is

$$\begin{aligned}\rho &= \frac{2m}{V} = \frac{2M}{N_A abc}\\ &= \frac{2\times(28.0...\ \mathrm{g\,mol^{-1}})}{(6.0221\times10^{23}\ \mathrm{mol^{-1}})\times(740\ \mathrm{pm})\times(493\ \mathrm{pm})\times(253\ \mathrm{pm})}\\ &= \boxed{1.01\ \mathrm{g\,cm^{-3}}}\end{aligned}$$

P15A.8 For an orthorhombic unit cell, $V = abc$. Because there are 8 molecules per unit cell, the mass density ρ is $\rho = 8m/V = 8M/N_A V$ where m is the mass per molecule, V is the volume of the unit cell and M is the molar mass.

$$\begin{aligned}M &= M([\mathrm{N(C_4H_9)_4}][\mathrm{Ru(N)(S_2C_6H_4)_2}]) + 2M(\mathrm{C_6H_4S_2}^{2-})\\ &= [(637.9...) + 2\times(140.2...)]\ \mathrm{g\,mol^{-1}} = 918.3...\ \mathrm{g\,mol^{-1}}\end{aligned}$$

$$\begin{aligned}\rho &= \frac{8M}{N_A abc}\\ &= \frac{8\times(918.3...\ \mathrm{g\,mol^{-1}})}{(6.0221\times10^{23}\ \mathrm{mol^{-1}})\times(3.6881\ \mathrm{nm})\times(0.9402\ \mathrm{nm})\times(1.7652\ \mathrm{nm})}\\ &= \boxed{1.99\ \mathrm{g\,cm^{-3}}}\end{aligned}$$

For the osmium analogue, $M = 1007.5...\ \mathrm{g\,mol^{-1}}$. The osmium mass density is estimated, assuming that the unit cell volume remains constant, using

$$\rho_{\mathrm{Os}} = \frac{M(\mathrm{Os})\rho_{\mathrm{Ru}}}{M(\mathrm{Ru})} = \frac{(1007.5...\ \mathrm{g\,mol^{-1}})\times(1.99\ \mathrm{g\,cm^{-3}})}{918.3...\ \mathrm{g\,mol^{-1}}} = \boxed{2.19\ \mathrm{g\,cm^{-3}}}$$

15B **Diffraction techniques**

Answers to discussion questions

D15B.2 The scattering factor determines how strongly an atom scatters the X-rays, and hence how strong the contribution from a particular atom is to a reflection. It is defined and described in Section 15B.1(c) on page 649. For forward scattering, the scattering factor is equal to the number of electrons in the atom.

Solutions to exercises

E15B.1(b) Bragg's law [15B.1b–*648*], $\lambda = 2d\sin\theta$, describes the relationship between wavelength of the X-rays λ, the Bragg angle θ, and the plane separation d. Thus

$$\lambda = 2d\sin\theta = 2\times(99.3\ \mathrm{pm})\times\sin(19.76^\circ) = \boxed{67.1\ \mathrm{pm}}$$

E15B.2(b) As shown in Fig. 15B.10 on page 652, for the cubic F lattice reflections from planes where h, k and l are all even or all odd are present in the diffraction pattern. Hence the first three possible reflections occur for planes (111), (200) and (220). Using the Bragg law [15B.1b–*648*], $\lambda = 2d_{hkl}\sin\theta$, and the expression for the spacing of the planes [15A.1a–*645*], $d_{hkl} = a/(h^2+k^2+l^2)^{1/2}$, the following table is drawn up

Miller indices	(111)	(200)	(220)
d_{hkl}	$a/(1^2+1^2+1^2)^{1/2}$	$a/(2^2)^{1/2}$	$a/(2^2+2^2)^{1/2}$
d_{hkl}/pm	234.9...	203.5	143.8...
$\sin\theta$	0.274...	0.316...	0.448...
$\theta/°$	15.9	18.5	26.6

E15B.3(b) The separation of the (hkl) planes of an orthorhombic lattice is given by [15A.1b–*645*], $1/d_{hkl}^2 = h^2/a^2 + k^2/b^2 + l^2/c^2$. This distance is used with [15B.1b–*648*] to compute the angle of reflection as $\theta = \sin^{-1}(\lambda/2d_{hkl})$.

Miller indices	(100)	(010)	(111)
$(1/d_{hkl}^2)/\text{pm}^{-2}$	$1^2/574.1^2$	$1^2/796.8^2$	$1^2/574.1^2 + 1^2/796.8^2 + 1^2/495.9^2$
d_{hkl}/pm	574.1	796.8	339.5...
$\theta/°$	4.166°	3.001°	7.057°

E15B.4(b) The Bragg law [15B.1b–*648*], $\lambda = 2d\sin(\theta)$, is rearranged to give the glancing angle as $2\theta = 2\sin^{-1}(\lambda/2d)$, where d is the plane separation and λ is the wavelength of the X-rays. For the case where $\lambda = 93.222$ pm,

$$2\theta = 2\times\sin^{-1}\left[(93.222\text{ pm})/2\times(82.3\text{ pm})\right] = 68.9...°$$

For the case where $\lambda = 95.123$ pm,

$$2\theta = 2\times\sin^{-1}\left[(95.123\text{ pm})/2\times(82.3\text{ pm})\right] = 70.6...°$$

The difference in the glancing angles is 70.6...° − 68.9...° = $\boxed{1.61°}$.

E15B.5(b) In Section 15B.1(c) on page 649 it is shown that the scattering factor in the forward direction, $f(0)$, is equal to the total number of electrons in the species, N_e. Thus for Mg^{2+} $\boxed{f(0) = 10}$.

E15B.6(b) The structure factor is given by [15B.3–*650*]

$$F_{hkl} = \sum_j f_j\,e^{i\phi_{hkl}(j)}$$

where f_j is the scattering factor of species j and $\phi_{hkl}(j) = 2\pi(hx_j + ky_j + lz_j)$ is the phase of the scattering from that species.

It is assumed that all the atoms are the same and have the same scattering factor f. Species at the corners of the unit cell are shared between eight adjacent unit cells so they have weight $\frac{1}{8}$ and so the contribution from each is $\frac{1}{8}f$. The atom at position $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ has weight 1 with scattering factor f.

$$\begin{aligned}F_{hkl} &= \sum_j f_j \mathrm{e}^{\mathrm{i}\phi_{hkl}(j)}\\ &= \tfrac{1}{8}f\left[1 + \mathrm{e}^{2\mathrm{i}\pi k} + \mathrm{e}^{2\mathrm{i}\pi l} + \mathrm{e}^{2\mathrm{i}\pi(k+l)} + \mathrm{e}^{2\mathrm{i}\pi h} + \mathrm{e}^{2\mathrm{i}\pi(h+k)} + \mathrm{e}^{2\mathrm{i}\pi(h+l)} + \mathrm{e}^{2\mathrm{i}\pi(h+k+l)}\right]\\ &\qquad + f\mathrm{e}^{2\mathrm{i}\pi(\frac{1}{2}h+\frac{1}{2}k+\frac{1}{2}l)}\end{aligned}$$

The indices h, k and l are all integers, and $\mathrm{e}^{\mathrm{i}n\pi} = (-1)^n$ for integer n. For the terms in the bracket all the exponents are even multiples of $\mathrm{i}\pi$, so all the terms are equal to $+1$ and together they contribute $+f$ to the structure factor. The term due to the central atom evaluates to $f(-1)^{h+k+l}$. For $(h+k+l)$ even this term is f so the structure factor is $\boxed{F_{hkl} = f + f = 2f}$, for $(h+k+l)$ odd this term is $-f$ so the structure factor is $\boxed{F_{hkl} = f - f = 0}$.

E15B.7(b) The cubic I unit cell is shown in Fig. 15A.8 on page 643. The structure factor is given by [15B.3–*650*]

$$F_{hkl} = \sum_j f_j\, \mathrm{e}^{\mathrm{i}\phi_{hkl}(j)}$$

where f_j is the scattering factor of species j and $\phi_{hkl}(j) = 2\pi(hx_j + ky_j + lz_j)$ is the phase of the scattering from that species.

The ions at the corners of the unit cell are shared between eight adjacent unit cells so they have weight $\frac{1}{8}$ and therefore, if they all have the same scattering factor f, the contribution from each is $\frac{1}{8}f$. As is shown in *Exercise* E15B.6(b), these ions together contribute $+f$ to the structure factor.

The body centre atom at position $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ has weight 1 with a scattering factor given as twice that of the other ions, hence its contribution is $2f$. The contribution of this ion to the structure factor is

$$2f\mathrm{e}^{2\mathrm{i}\pi(\frac{1}{2}h+\frac{1}{2}k+\frac{1}{2}l)} = 2f(-1)^{(h+k+l)}$$

The structure factor is therefore $F_{hkl} = f + 2f(-1)^{(h+k+l)}$. For $(h+k+l)$ odd, $\boxed{F_{hkl} = f - 2f = -f}$, and for $(h+k+l)$ even, $\boxed{F_{hkl} = f + 2f = 3f}$.

E15B.8(b) The electron density distribution $\rho(\boldsymbol{r})$ in the unit cell is given by [15B.4–*651*], $\rho(\boldsymbol{r}) = (1/V)\sum_{hkl} F_{hkl}\mathrm{e}^{-2\pi\mathrm{i}(hx+ky+lz)}$, where V is the volume of the unit cell. In this case the structure factors are only given for the x direction so the sum is just over the index h. Furthermore, because $F_h = F_{-h}$ the summation can be taken from $h = 0$ to $h = +\infty$

$$\begin{aligned}V\rho(x) &= \sum_{h=-\infty}^{\infty} F_h \mathrm{e}^{-2\pi\mathrm{i}hx} = F_0 + \sum_{h=1}^{\infty}\left(F_h\mathrm{e}^{-2\pi\mathrm{i}hx} + F_{-h}\mathrm{e}^{2\pi\mathrm{i}hx}\right)\\ &= F_0 + \sum_{h=1}^{\infty} F_h\left(\mathrm{e}^{-2\pi\mathrm{i}hx} + \mathrm{e}^{2\pi\mathrm{i}hx}\right) = F_0 + 2\sum_{h=1}^{\infty} F_h\cos(2\pi hx)\end{aligned}$$

In this case there are a total of ten terms to include, $h = 0$ to 9. Figure 15.1 shows a plot of $V\rho(x)$ against x; the electron density is at a maximum of $142/V$ at $x = 0$ or $x = 1$, the boundaries of the unit cell.

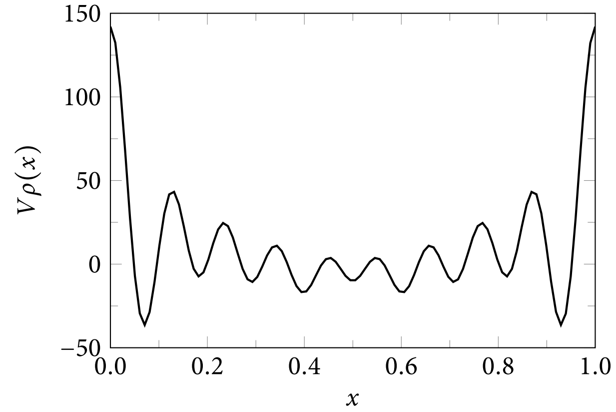


Figure 15.1

E15B.9(b) The Patterson synthesis is given by [15B.5–*653*],

$$P(\boldsymbol{r}) = \frac{1}{V}\sum_{hkl}|F_{hkl}|^2\,\mathrm{e}^{-2\pi\mathrm{i}(hx+ky+lz)}$$

In this case the structure factors are only given for the x direction so the sum is just over the index h. Furthermore, because $F_h = F_{-h}$ the summation can be taken from from $h = 0$ to $h = +\infty$. Using a similar line of argument to that in *Exercise* E15B.7(b), the Patterson synthesis is

$$VP(x) = F_0^2 + 2\sum_{h=1}^{\infty} F_h^2 \cos(2\pi hx)$$

In this case there are a total of ten terms to include, $h = 0$ to 9. Figure 15.2 shows a plot of $VP(x)$ against x. As expected, there strong feature at the origin; this arises from the separation between each atom and itself. There is also a strong feature at $x = 1$ which indicate that atoms are separated by $1 \times a$ unit along the x-axis.

E15B.10(b) To constructor the Patterson map, choose the position of one atom to be the origin. Then add peaks to the map corresponding to vectors joining each pair of atoms (Fig. 15.3). The vector between atom A and atom B has the same magnitude as that between B and A, but points in the opposite direction; the map therefore includes two symmetry related peaks on either side of the origin. The vectors between each atom and itself give a peak at the centre point of the Patterson map, and the many contributions at this position create an intense peak.

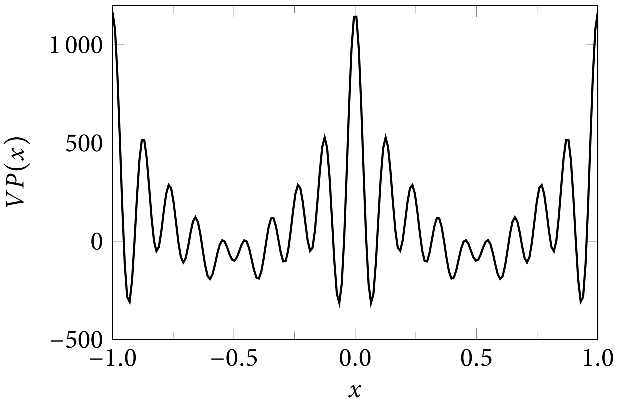
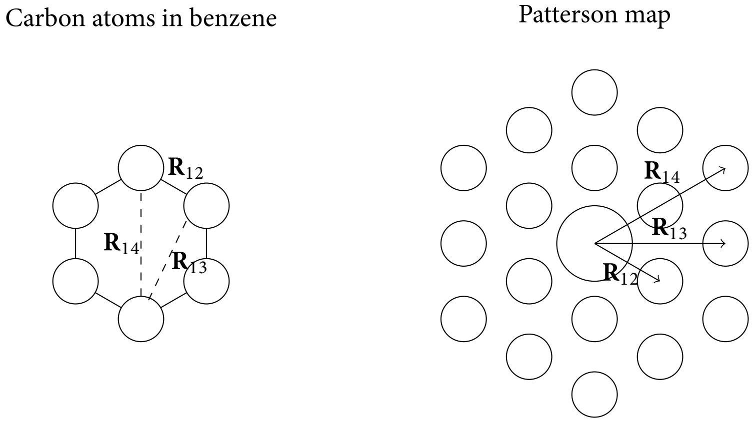


Figure 15.2


Carbon atoms in benzene

Patterson map

Figure 15.3

E15B.11(b) Using the de Broglie relation [7A.11–*244*], $\lambda = h/p = h/(m_e v)$, where p is the momentum, m_e is the mass of a electron and v its speed, it follows that

$$v = \frac{h}{\lambda m_e} = \frac{6.6261\times10^{-34}\,\mathrm{J\,s}}{(105\times10^{-12}\,\mathrm{m})\times(9.1094\times10^{-31}\,\mathrm{kg})} = \boxed{6.93\times10^{3}\,\mathrm{km\,s^{-1}}}$$

E15B.12(b) From the equipartition principle the kinetic energy is $E_k = \frac{1}{2}kT$. This energy can be written in terms of the momentum as $p^2/(2m)$ and hence $p = (mkT)^{1/2}$. The de Broglie relation [7A.11–*244*], $\lambda = h/p$, is then used to find the wavelength

$$\lambda = \frac{h}{(mkT)^{1/2}} = \frac{6.6261\times10^{-34}\,\mathrm{J\,s}}{[(9.1094\times10^{-31}\,\mathrm{kg})\times(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(380\,\mathrm{K})]^{1/2}}$$
$$= \boxed{9.58\,\mathrm{nm}}$$

Solutions to problems

P15B.2 Combining Bragg's law [15B.1b–*648*], $\lambda = 2d\sin\theta$, with the expression for the the separation of planes for a cubic lattice [15A.1a–*645*], $d_{hkl} = a/(h^2+k^2+l^2)^{1/2}$, gives $\sin\theta = (\lambda/2a)(h^2+k^2+l^2)^{1/2}$.

The diffraction patterns for cubic cells of different types is illustrated in Fig. 15B.10 on page 652. Diffraction is possible for all (hkl) planes for a cubic P lattice, but reflections corresponding to $(h+k+l)$ odd are absent for a cubic I lattice. For a cubic F lattice, reflections are absent where two out of h, k and l are odd. These systematic absences in a diffraction pattern allow the lattice type to be assigned.

The observation of a (100) reflection, for which $(h+k+l)$ is odd, rules out cubic I. The observation of a (110) reflection, for which h and k are odd, but l is even, rules out cubic F. Therefore polonium must be cubic P, for which all reflections are present.

The sequence of reflections expected for cubic P is shown in Fig. 15B.10 on page 652: the fifth, sixth and seventh reflections are (210), (211) and (220), respectively. The sine of the reflection angle is proportional to $(h^2+k^2+l^2)^{1/2}$, which for these three reflections is $5^{1/2}$, $6^{1/2}$, and $8^{1/2}$: the separation between the sixth and seventh is indeed larger than that between the fifth and sixth, as described.

The cell dimension is calculated from $a = \lambda(h^2+k^2+l^2)^{1/2}/(2\sin\theta)$; each reflection allows a separate determination of a. For the (100) reflection

$$\begin{aligned} a &= \frac{\lambda(h^2+k^2+l^2)^{1/2}}{2\sin\theta} = \frac{\lambda(1^2+0^2+0^2)^{1/2}}{2\sin\theta} = \frac{\lambda(1)^{1/2}}{2\sin\theta} \\ &= \frac{(154\ \text{pm})\times(1)^{1/2}}{2\times 0.225} = 3.42...\times 10^2\ \text{pm} \end{aligned}$$

Similar calculations for the other reflections given $a = 3.44... \times 10^2$ pm and $a = 3.43... \times 10^2$ pm. The average is $\boxed{a = 344\ \text{pm}}$.

P15B.4 Combining Bragg's law [15B.1b–*648*], $\lambda = 2d\sin\theta$, with the expression for the the separation of planes for a cubic lattice [15A.1a–*645*], $d_{hkl} = a/(h^2+k^2+l^2)^{1/2}$, gives $\sin\theta = (\lambda/2a)(h^2+k^2+l^2)^{1/2}$. For the same reflection, a is proportional to $1/\sin\theta$, therefore

$$a_{\text{KCl}} = a_{\text{NaCl}}\frac{\sin\theta_{\text{NaCl}}}{\sin\theta_{\text{KCl}}} = \frac{(564\ \text{pm})\times(\sin 6.00°)}{\sin 5.38°} = 628.7...\ \text{pm} = \boxed{629\ \text{pm}}$$

The mass density ρ is $\rho = m/V$, where m is the mass of the unit cell. If there are N formula units per cell then $\rho = NM/N_\text{A}V$, where M is the molar mass of a formula unit. Based on the cell parameter a, the ratio of densities of KCl and NaCl is therefore

$$\frac{\rho_{\text{KCl}}}{\rho_{\text{NaCl}}} = \frac{M_{\text{KCl}}a^3_{\text{NaCl}}}{M_{\text{NaCl}}a^3_{\text{KCl}}} = \frac{(74.55\ \text{g mol}^{-1})\times(564\ \text{pm})^3}{(58.44\ \text{g mol}^{-1})\times(628.7...\ \text{pm})^3} = \boxed{0.921}$$

The experimentally determined ratio of mass densities is $1.99\ \text{g cm}^{-3}/2.17\ \text{g cm}^{-3} = 0.917$, which is close to the value determined from the diffraction data. The data therefore support the X-ray analysis.

P15B.6 The intensity of a reflection is proportional to the square modulus of the structure factor given by [15B.3–*650*], $F_{hkl} = \sum_j f_j e^{i\phi_{hkl}(j)}$, where the phase is $\phi_{hkl}(j) = 2\pi(hx_j + ky_j + lz_j)$.

For atoms at positions (0,0,0), $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and $(\frac{1}{2}, 0, \frac{3}{4})$ with the same scattering factor f

$$F_{hkl} = f\left(e^{0i} + e^{i\pi(k+l)} + e^{i\pi(h+k+l)} + e^{i\pi(h+3l/2)}\right)$$

For the (114) reflection, $F_{114} = f\left(1 + e^{5\pi i} + e^{6\pi i} + e^{7\pi i}\right)$. Using the result $e^{i\pi n} = (-1)^n$ it follows that $F_{114} = f(1-1+1-1) = \boxed{0}$. The I atoms therefore contribute no net intensity to the (114) reflection.

P15B.8 The scattering intensity is given by the Wierl equation [15B.8–*654*],

$$I(\theta) = \sum_{i,j} f_i f_j \sin(sR_{ij})/(sR_{ij})$$

where $s = 4\pi \sin(\theta/2)/\lambda$ and the sum is over all pairs of atoms in the species.

(a) For the Br_2 molecule, $f_1 = f_2 = f$ with $R_{12} = R$. Thus $I(\theta) = f^2 \sin(sR)/(sR)$. To find the positions of the first maximum and minimum, differentiate I with respect to θ and set equal to zero.

$$\frac{dI}{d\theta} = \frac{dI}{ds}\frac{ds}{d\theta} = \frac{2\pi f^2}{s^2 R\lambda}\left[sR\cos(sR) - \sin(sR)\right]\cos(\theta/2) = 0$$

Rearranging $sR\cos(sR) - \sin(sR) = 0$ gives $\tan(sR) = sR$ which is solved numerically to give solutions at $sR = 0,\ 4.493,\ 7.725, \ldots$. Inspection of the form of the function $I(\theta)$ shows that the solution $sR = 0$ corresponds to the first maximum, therefore $sR = 4.493$ corresponds to the first minimum. The angle θ is computed from sR using $\theta = 2\sin^{-1}(s\lambda/4\pi) = 2\sin^{-1}(sR\lambda/4\pi R)$. Taking the Br_2 bond length as 228.3 pm gives for neutron scattering

$$\theta_{\max} = \boxed{0} \quad \theta_{\min} = 2 \times \sin^{-1}\frac{(4.493) \times (78\ \text{pm})}{4\pi(228.3\ \text{pm})} = \boxed{14.0°}$$

and for electron scattering

$$\theta_{\max} = \boxed{0} \quad \theta_{\min} = 2 \times \sin^{-1}\frac{(4.493) \times (4.0\ \text{pm})}{4\pi(228.3\ \text{pm})} = \boxed{0.72°}$$

(b) For CCl_4 there are four carbon-chlorine pairs and six chlorine-chlorine pairs

$$I = 4f_C f_{Cl}\frac{\sin sR_{CCl}}{sR_{CCl}} + 6f_{Cl}^2\frac{\sin sR_{ClCl}}{sR_{ClCl}}$$

$$= 4 \times 6 \times 17 \times f^2\frac{\sin sR_{CCl}}{sR_{CCl}} + 6 \times (17)^2 \times f^2\frac{\sin\left[(8/3)^{1/2} sR_{CCl}\right]}{(8/3)^{1/2} sR_{CCl}}$$

$$\frac{I}{f^2} = 408\frac{\sin sR_{CCl}}{sR_{CCl}} + 1061.8\ldots \times \frac{\sin\left[(8/3)^{1/2} sR_{CCl}\right]}{sR_{CCl}}$$

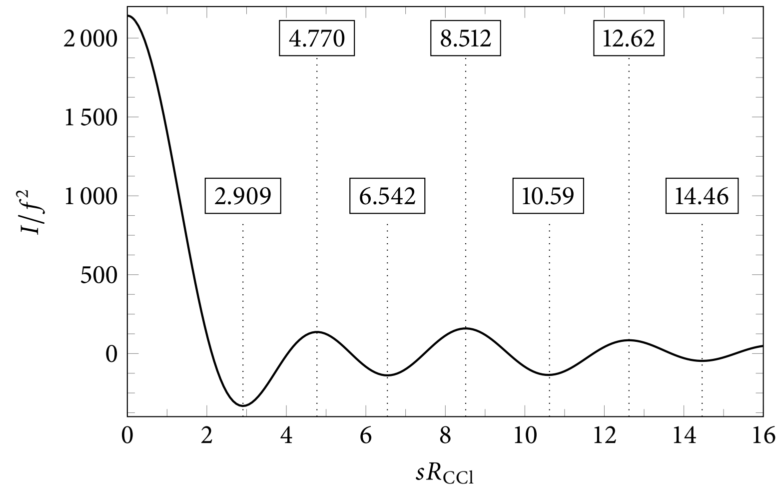


Figure 15.4

A plot of I/f^2 against sR_{CCl} is shown in Fig. 15.4. The values of sR_{CCl} at which the maxima and minima occur are found using mathematical software or, alternatively, the values can be estimated from the graph. These values are indicted on the plot.

From the experimental data on the angles at which extrema occur, θ_{ex}, it is possible to calculate an experimental value s_{ex} using $s_{\text{ex}} = 4\pi \sin(\theta_{\text{ex}}/2)/\lambda$. From the graph the values of $(sR)_{\text{theo}}$ at which extrema occur are known, so from each item of data a value of R is found by computing $R_{\text{ex}} = (sR)_{\text{theo}}/s_{\text{ex}}$. The data and computed values are shown in the table.

To complete these calculations it is necessary to know the de Broglie wavelength associated with 10 keV electrons. The kinetic energy is $E = p^2/(2m_e) = eV$ where p is momentum, m_e is the electron mass, e is its charge and V is the potential difference applied. Using the de Broglie relation,

$$\begin{aligned}\lambda &= \frac{h}{p} = \frac{h}{(2m_e eV)^{1/2}}\\ &= \frac{6.6261\times10^{-34}\,\text{J s}}{[2\times(9.1094\times10^{-31}\,\text{kg})\times(1.6022\times10^{-19}\,\text{C})\times(1.00\times10^{4}\,\text{V})]^{1/2}}\\ &= 12.2...\,\text{pm}\end{aligned}$$

	maxima			minima			
θ_{ex}	3.17°	5.37°	7.90°	1.77°	4.10°	6.67°	9.17°
$s_{\text{ex}}/\text{pm}^{-1}$	0.0283	0.0480	0.0706	0.0158	0.0367	0.0596	0.0819
$(sR)_{\text{theo}}$	4.770	8.512	12.62	2.909	6.542	10.59	14.46
R_{ex}/pm	168.3	177.3	178.8	183.8	178.5	177.7	176.5

The outlying values 168.3 pm and 183.8 pm are rejected, to give an average value of $\boxed{R_{\text{CCl}} = 178\ \text{pm}}$.

15C Bonding in solids

Answers to discussion questions

D15C.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 Cl^- ions in which Na^+ ions have filled the octahedral holes.

The caesium-chloride structure can be considered to be derived from the ccp structure by having Cl^- ions occupy all the primitive lattice points and octahedral sites, with all tetrahedral sites occupied by Cs^+ ions. This is rather 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

E15C.1(b) The distance x, indicated in Fig. 15.5, is half of the width of the triangular face of a rod. The area A of this face is $\frac{1}{2}$ × base × height which is $A = \frac{1}{2} \times 2x \times 2x \times \sin 60° = \sqrt{3}x^2$. The small equilateral triangles which are formed by the spaces between the rods have edges of length x and thus area $A_{\text{space}} = \sqrt{3}x^2/4$. Each rod is adjacent to 6 of these small triangular spaces, but in turn each of these spaces is in contact with 3 rods. Overall, therefore, there are two small triangular spaces per rod. The length of the rods is irrelent to the packing fraction, and so

$$f = \frac{A}{A + 2A_{\text{space}}} = \frac{\sqrt{3}x^2}{\sqrt{3}x^2 + 2 \times \sqrt{3}x^2/4} = \boxed{\frac{2}{3}}$$

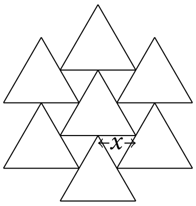


Figure 15.5

E15C.2(b) The packing fraction is $f = NV_a/V_c$ where N is the number of spheres per unit cell, $V_a = 4\pi R^3/3$ is the volume of each sphere of radius R, and V_c is the volume of the unit cell.

An orthorhombic C cell is shown in Fig. 15A.8 on page 643. The spheres touch along a face diagonal which therefore has length $4R$. If the edge of the cube has length a it follows, by considering a face, that $(4R)^2 = a^2 + a^2$ and hence $a = \sqrt{8}R$. For this cell $N = 2$ and hence

$$f = \frac{2 \times 4\pi R^3/3}{(\sqrt{8}R)^3} = \frac{\pi}{6\sqrt{2}} = \boxed{0.3702}$$

E15C.3(b) The coordination number N of an ionic lattice depends on the radius ratio of the cation and anion of the lattice. The radius-ratio rule, which considers the maximum possible packing density of hard spheres of a given radius around a hard sphere of a different radius, provides a method to determine the structure type. The radius ratio is $\gamma = r_s/r_l$ where r_s is the radius of the smallest ion and r_l is the radius of the largest ion. If $\gamma \le (2^{1/2} - 1)$ then $N < 6$; for $(2^{1/2} - 1) < \gamma < (3^{1/2} - 1)$ then $N = 6$; for $\gamma \ge (3^{1/2} - 1)$ then $N = 8$.

The range for sixfold coordination is therefore $0.414 < \gamma < 0.732$, and hence $r_l \times 0.414 < r_s < r_l \times 0.732$. For the case of the Rb^+ anion $(149\ \text{pm}) \times 0.414 = 61.7\ \text{pm}$ and $(149\ \text{pm}) \times 0.732 = 109\ \text{pm}$. Therefore for sixfold coordination the smallest radius for the anion is $\boxed{61.7\ \text{pm}}$, whilst for eightfold coordination the smallest radius is $\boxed{109\ \text{pm}}$.

E15C.4(b) The unit cell volume V is related to the packing density f and the atomic volume v by $fV = v$. Assuming the atoms can be approximated as spheres then $v = 4\pi R^3/3$ where R is the atomic radius. The packing densities for bcc and hcp are 0.6802 and 0.7405, respectively (*Exercise* E15C.2(a)). With the given data

$$\frac{V_{\text{bcc}}}{V_{\text{hcp}}} = \frac{v_{\text{bcc}}}{v_{\text{hcp}}} \times \frac{f_{\text{hcp}}}{f_{\text{bcc}}} = \frac{(R_{\text{bcc}})^3 f_{\text{hcp}}}{(R_{\text{hcp}})^3 f_{\text{bcc}}} = \frac{122^3 \times 0.7405...}{126^3 \times 0.6802...} = 0.988...$$

Thus transformation from hcp to bcc causes cell volume to $\boxed{\text{contract by } 1.2\%}$

E15C.5(b) The lattice enthalpy ΔH_L is the change in standard molar enthalpy for the process $MX(s) \rightarrow M^+(g) + X^-(g)$ and its equivalent. The value of the lattice enthalpy is determined indirectly using a Born–Haber cycle, as shown in Fig. 15.6 (all quantities are given in kJ mol^{-1}). From the cycle it follows that

$$-524\ \text{kJ mol}^{-1} + \Delta H_L = (148 + 2187 + 31 + 193 - 2 \times 331)\ \text{kJ mol}^{-1}$$

Thus $\Delta H_L = \boxed{2421\ \text{kJ mol}^{-1}}$

Solutions to problems

P15C.2 Figure 15.7 shows the packing of the ellipses; the area of an ellipse is πab where a and b are the semi-major and -minor axes, respectively. The unit cell, indicated by the dashed lines, is a parallelogram and contains one rod cross-section. A pair of stacked ellipses have relative coordinates (x, y) and $(x, y + 2b)$. The adjacent column of ellipses is centred b higher and so the contact point has y-coordinate $b/2$ higher. The equation for an ellipse is $(x/a)^2 + (y/b)^2 = 1$,

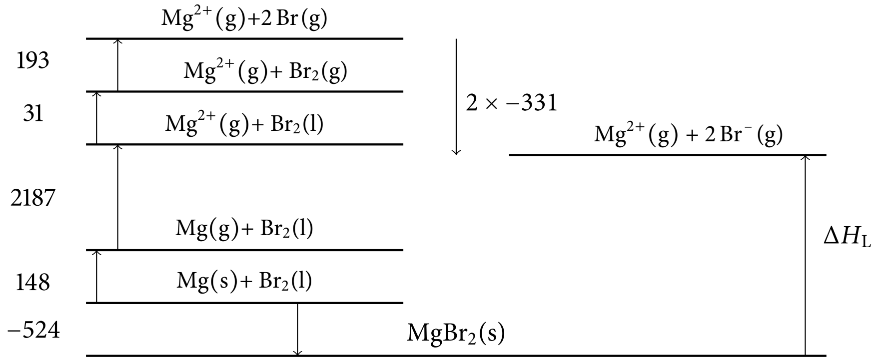


Figure 15.6

and with this the x coordinate corresponding to $y = b/2$ is found as $x = \sqrt{3}a/2$. If follows that the distance h is given by $h = 2x = a\sqrt{3}$, and thus the area of the unit cell is $2bh = 2\sqrt{3}ab$. It follows that the packing density is

$$f = \frac{1 \times \pi ab}{2\sqrt{3}ab} = \frac{\pi}{2\sqrt{3}} = \boxed{0.907}$$

The eccentricity of an ellipse is defined as $\varepsilon = [1 - (b^2/a^2)]^{1/2}$. The packing fraction is independent of a and b and thus is independent of eccentricity.

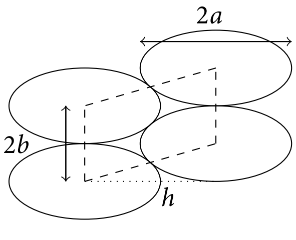


Figure 15.7

P15C.4 (a) The general expression for the energy levels in a one-dimensional metallic conductor is given by [15C.1–*658*], $E(k) = \alpha + 2\beta\cos(k\pi/[N+1])$ where $k = 1, 2, ..., N$. It is convenient to first compute $\mathrm{d}E/\mathrm{d}k$

$$\frac{\mathrm{d}E}{\mathrm{d}k} = \frac{\mathrm{d}}{\mathrm{d}k}\left[\alpha + 2\beta\cos\left(\frac{k\pi}{N+1}\right)\right] = -\frac{2\beta\pi}{N+1}\sin\left(\frac{k\pi}{N+1}\right)$$

The identity $\cos^2 x + \sin^2 x = 1$ is used to write $\sin x = \left(1 - \cos^2 x\right)^{1/2}$, and in turn this is used to rewrite $\sin[k\pi/(N+1)]$ as $\left[1 - \cos^2(k\pi/[N+1])\right]^{1/2}$. The expression for the energy levels, $E(k) = \alpha + 2\beta\cos[k\pi/(N+1)]$, is rearranged to give $\cos(k\pi/[N+1]) = (E-\alpha)/(2\beta)$. These two substitutions are used in the expression for the derivative

$$\begin{aligned}\frac{\mathrm{d}E}{\mathrm{d}k} &= -\frac{2\beta\pi}{N+1}\sin\left(\frac{k\pi}{N+1}\right) = -\frac{2\beta\pi}{N+1}\left[1-\cos^2\left(\frac{k\pi}{N+1}\right)\right]^{1/2}\\ &= -\frac{2\beta\pi}{N+1}\left[1-\left(\frac{E-\alpha}{2\beta}\right)^2\right]^{1/2}\end{aligned}$$

Density of states $\rho(E)$ is defined as $\rho(E) = \mathrm{d}k/\mathrm{d}E$, thus

$$\rho(E) = \frac{\mathrm{d}k}{\mathrm{d}E} = \frac{1}{\mathrm{d}E/\mathrm{d}k} = -\frac{(N+1)/2\beta\pi}{\left[1-\left(\frac{E-\alpha}{2\beta}\right)^2\right]^{1/2}}$$

(b) As $E \to \alpha \pm 2\beta$, $E-\alpha \to \pm 2\beta$, and thus $(E-\alpha)/2\beta \to \pm 1$. It follows that

$$\rho(E) \to -\frac{(N+1)/2\beta\pi}{[1-(\pm 1)^2]^{1/2}} = \infty$$

Thus the density of states increases towards the edges of the bands in a one-dimensional metallic conductor.

P15C.6 The wavefunction for a ring of N atoms must be such that it has the same value at the (hypothetical) atom with index $(N+1)$ as it does for the atom with index 1 because, in a ring these two atoms are the same. This can only be achieved if the wavefunction varies in such a way that it goes through a whole number of cycles around the ring.

The wavefunction for a line of atoms is not constrained in this way, so if a linear chain were to have its ends 'connected' to form a ring, some wavefunctions of the linear chain would not satisfy requirements necessary to be a wavefunction for a ring of atoms.

The energy levels of a line of atoms are non-degenerate, but for a ring all of the levels, apart from the one with $k = 0$, are doubly degenerate. This degeneracy can be associated with the possibility that the electron can travel clockwise or anti-clockwise around the ring. For a chain, no such net motion is possible.

P15C.8 (a) Assuming that the ionic radius of Ca^+ is close to that of K^+, the radius-ratio rule can be used to predict the lattice structure of CaCl. The radius ratio is $\gamma = 138\ \text{pm}/181\ \text{pm} = 0.762$; this is > 0.732, therefore eightfold coordination, as in CsCl, is predicted and the appropriate value of the Madelung constant (Table 15C.3 on page 662) is $A = 1.763$.

The Born–Mayer equation, [15C.5–*662*], is used to estimate the lattice enthalpy since when zero-point contributions to potential energy are neglected then lattice enthalpy is equal to the negative of $E_{\mathrm{p,min}}$. In this expression, z_i is the charge number of ion i, d is the distance between neighbouring centres, A is the Madelung constant, ε_0 is the vacuum permittivity and d^* is taken to be 34.5 pm.

Taking the ionic radii from Table 15C.2 on page 661 as $r_{\mathrm{Ca}^+} \approx r_{\mathrm{K}^+} = 138\ \mathrm{pm}$ and $r_{\mathrm{Cl}^-} = 181\ \mathrm{pm}$, $d = (138 + 181)\ \mathrm{pm} = 319\ \mathrm{pm}$.

$$\begin{aligned}E_{\mathrm{p,min}} &= -\frac{N_{\mathrm{A}}|z_{\mathrm{A}}z_{\mathrm{B}}|e^2}{4\pi\varepsilon_0 d}\left(1-\frac{d^*}{d}\right)A\\ &= \frac{(6.0221\times10^{23}\ \mathrm{mol^{-1}})\times(1.6022\times10^{-19}\ \mathrm{C})^2}{4\pi\times(8.8542\times10^{-12}\ \mathrm{J^{-1}\,C^2\,m^{-1}})\times(319\ \mathrm{pm})}\\ &\quad\times\left(1-\frac{34.5\ \mathrm{pm}}{319\ \mathrm{pm}}\right)\times1.763 = -685\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

Thus the lattice enthalpy of CaCl(s) is $\Delta H_{\mathrm{L}} = \boxed{685\ \mathrm{kJ\,mol^{-1}}}$.

The relevant Born–Haber cycle is shown in Fig. 15.8; all of the enthalpy changes quoted in the diagram are in $\mathrm{kJ\,mol^{-1}}$. The first ionisation energy of Ca, $+589.7\ \mathrm{kJ\,mol^{-1}}$, is taken from Table 8B.4 in the *Resource section*. It follows from the cycle that $\Delta_{\mathrm{f}}H^{\ominus} = 176 + 589.7 + 122 - 349 - 685 = \boxed{-146\ \mathrm{kJ\,mol^{-1}}}$

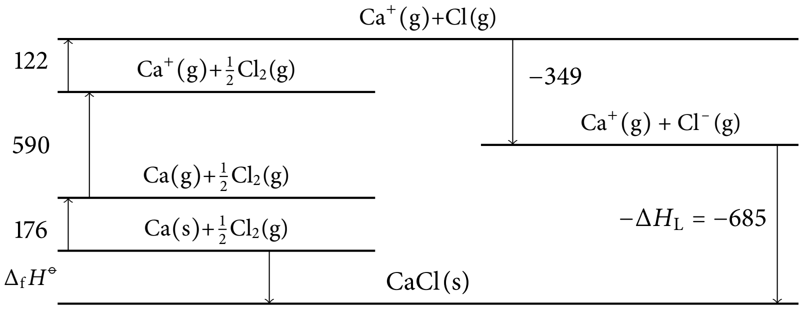


Figure 15.8

(b) The disproportionation reaction for CaCl(s) is $2\,\mathrm{CaCl(s)} \rightarrow \mathrm{Ca(s)} + \mathrm{CaCl_2(s)}$. Using data from Table 2C.5 in the *Resource section* and using the enthalpy of formation of CaCl(s) calculated in part (a),

$$\begin{aligned}\Delta_{\mathrm{r}}H^{\ominus} &= \Delta_{\mathrm{f}}H^{\ominus}(\mathrm{Ca(s)}) + \Delta_{\mathrm{f}}H^{\ominus}(\mathrm{CaCl_2(s)}) - 2\Delta_{\mathrm{f}}H^{\ominus}(\mathrm{CaCl(s)})\\ &= [0 - 795.8 - 2(-146)]\ \mathrm{kJ\,mol^{-1}} = -504\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

Hence the disproportionation reaction is strongly exothermic. The entropy change for this reaction is expected to be close to zero since there is no change in the number of species or their physical state, so it can reasonably by concluded that $\Delta_{\mathrm{r}}G^{\ominus}$ will also be negative, thus favouring the products of the reaction. Thus, it is plausible that CaCl is thermodynamically unstable with respect to disproportionation.

P15C.10 The Madelung constant is found by considering the contributions to the potential energy of an ion that arise from interactions with the surrounding ions, taking into account their number and distance from the ion in question. Consider the central cation, and assume that the successive circles of anions and cations are at distances $r,\ 2r\ldots$. The first circle contains four anions, so the interaction with these will result in a negative contribution to the potential energy of $-4\times e^2/(4\pi\varepsilon_0 r)$. The next closest are four cations, and these will make a positive contribution to the potential energy of $+4\times e^2/(4\pi\varepsilon_0 2r)$. Similar considerations apply to further circles of ions giving a series

$$\begin{aligned}V &= -\frac{4e^2}{4\pi\varepsilon_0 r}+\frac{4e^2}{4\pi\varepsilon_0(2r)}-\frac{4e^2}{4\pi\varepsilon_0(3r)}+\frac{4e^2}{4\pi\varepsilon_0(4r)}+\ldots\\ &= -\frac{e^2}{4\pi\varepsilon_0 r}\times 4\times\left(1-\frac{1}{2}+\frac{1}{3}-\frac{1}{4}+\ldots\right)\end{aligned}$$

The series in parenthesis is the series expansion of ln 2, so the potential energy is

$$V=-\frac{e^2}{4\pi\varepsilon_0 r}\times 4\times\ln 2$$

The Madelung constant in therefore $\boxed{A=4\ln 2=2.773}$.

For the periodic lattices described in the text the same result is obtained regardless of which ion it chosen as the 'central' ion in the calculation. This is certainly not the case for the arrangement considered in this *Problem* simply because the arrangement of ions is not periodic and no unit cell can be defined.

15D The mechanical properties of solids

Answer to discussion question

Solutions to exercises

E15D.1(b) The relationship between the applied pressure p, the bulk modulus K, and the fractional change in volume $\Delta V/V$ is given by [15D.1b–666], $K=p/(\Delta V/V)$. From *Exercise* E15D.1(a) the bulk modulus of polystyrene is 3.43 GPa. The fractional change in the volume is therefore

$$\frac{\Delta V}{V}=\frac{p}{K}=\frac{1000\times 10^5\ \text{Pa}}{3.43\times 10^9\ \text{Pa}}=0.029...$$

The change in volume is expressed in terms of the initial and final volumes, V_i and V_f

$$\Delta V/V=(V_\text{f}-V_\text{i})/V_\text{i}\qquad\text{hence}\qquad V_\text{f}=(\Delta V/V)V_\text{i}+V_\text{i}$$

where it is assumed that the change in volume is small enough that V is well-approximated by V_i. Thus $V_\text{f}=-(0.029...\times 1.0\ \text{cm}^3)+1.0\ \text{cm}^3=\boxed{0.97\ \text{cm}^3}$. Note that ΔV must be negative because the sample is compressed by the additional pressure.

E15D.2(b) The Young's modulus E is related to the stress σ and the strain ε by [15D.1a–*666*], $E = \sigma/\varepsilon$. Stress is given by $\sigma = F/A$ where F is the force applied and A is the cross-sectional area. Strain is given by $\varepsilon = \Delta L/L$ where L is the initial length of the rod. It follows that $E = FL/A\Delta L$ and hence $F = EA\Delta L/L$. The Young's modulus of polystyrene is 4.42 GPa.

$$F = \frac{EA\Delta L}{L}$$
$$= \frac{(4.42\times10^{9}\ \text{Pa})\times[\pi\times(0.5\times10^{-3}\ \text{m})^{2}]\times(10.05\ \text{cm}-10.00\ \text{cm})}{10.00\ \text{cm}} = \boxed{17\ \text{N}}$$

E15D.3(b) Poisson's ratio, ν_P, is defined in [15D.2–*667*], $\nu_\text{P} = \varepsilon_\text{trans}/\varepsilon_\text{norm}$, where ε_trans is the transverse strain and ε_norm is the normal (uniaxial) strain. If the normal strain is 2.0%, it follows that the change in length ΔL_norm is

$$\Delta L_\text{norm} = \varepsilon_\text{norm}L_\text{norm} = 0.02\times(0.1\ \text{m}) = 2.0\times10^{-3}\ \text{m}$$

The transverse strain is $\varepsilon_\text{trans} = \nu_\text{P}\varepsilon_\text{norm}$, so the change in dimension in the transverse direction ΔL_trans is

$$\Delta L_\text{trans} = \varepsilon_\text{trans}L_\text{trans} = \nu_\text{P}\varepsilon_\text{norm}L_\text{trans} = 0.41\times0.02\times(0.1\ \text{m}) = 8.2\times10^{-4}\ \text{m}$$

It is expected that the result of applying the stress will be to decrease the size of the cube in the transverse dimension (that is ΔL_trans is negative), and that the decrease will be the same in each transverse direction. The volume after the stress has been applied is therefore

$$(0.1\ \text{m}+2.0\times10^{-3}\ \text{m})\times(0.1\ \text{m}-8.2\times10^{-4}\ \text{m})^{2} = 1.00334...\times10^{-3}\ \text{m}^{3}$$

The change in volume is $1.00334...\times10^{-3}\ \text{m}^{3} - 1.0\times10^{-3}\ \text{m}^{3} = \boxed{3.3\times10^{-3}\ \text{dm}^{3}}$

Solutions to problems

P15D.2 If neighbouring molecules interact by a Lennard-Jones potential energy then the bulk modulus K is related to the Lennard-Jones parameter ε (the depth of the potential well) by $K = 8N_\text{A}\varepsilon/V_\text{m}$, where V_m is the molar volume. The molar volume is expressed in terms of the molar mass M and the mass density ρ as $V_\text{m} = M/\rho$. From the *Resource* section the mass density for water at 298 K is $1.0\ \text{g cm}^{-3}$, and the molar mass is $18.01...\ \text{g mol}^{-1}$.

$$\varepsilon = \frac{KV_\text{m}}{8N_\text{A}} = \frac{KM}{8N_\text{A}\rho} = \frac{(3.4\times10^{9}\ \text{Pa})\times(18.01...\ \text{g mol}^{-1})}{8\times(6.0221\times10^{23}\ \text{mol}^{-1})\times(1.0\times10^{6}\ \text{g m}^{-3})}$$
$$= 1.27...\times10^{-20}\ \text{J}$$

Hence $\varepsilon = (1.27...\times10^{-20}\ \text{J})\times(6.0221\times10^{23}\ \text{mol}^{-1}) = \boxed{7.7\ \text{kJ mol}^{-1}}$

15E The electrical properties of solids

Answer to discussion question

Solutions to exercises

E15E.1(b) Assuming that the temperature, T, is not so high that many electrons are excited to states above the Fermi energy, E_F, the Fermi–Dirac distribution can be written as [15E.2b–*671*], $f(E) = 1/[e^{(E-E_F)/kT} + 1]$, where $f(E)$ is the probability of occupation of a state with energy E.

For $E = E_F - kT$, $f(E_F - kT) = 1/[e^{(E_F-kT-E_F)/kT} + 1] = 1/[e^{-1} + 1] = \boxed{0.731}$

Compared to the state with energy $E = E_F + kT$, for $E = E_F - kT$ the probability of the state being occupied is much greater, and this is simply a reflection of the fact that the probability of a state being occupied decreases as the energy increases.

E15E.2(b) The Fermi–Dirac distribution is given by [15E.2b–*671*], $f(E) = 1/[e^{(E-E_F)/kT} + 1]$, where $f(E)$ is the probability of occupation of a state with energy E, and E_F is the Fermi energy. In this case $E_F = 2.00\text{ eV} = 3.20... \times 10^{-19}$ J, using the conversion factor from inside of the front cover. With some rearrangement of the expression for $f(E)$ it follows that

$$\begin{aligned} E &= kT\ln[1/f(E) - 1] + E_F \\ &= (1.3806 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K}) \times \ln(1/0.10 - 1) + (3.20... \times 10^{-19}\,\mathrm{J}) \\ &= 3.29... \times 10^{-19}\,\mathrm{J} = \boxed{2.06\,\mathrm{eV}} \end{aligned}$$

E15E.3(b) Gallium is a Group 13 element and germanium is a Group 14 element. Thus, an electron can be transferred from a germanium atom to a neighbouring gallium atom, thereby creating a hole in the valence band and increasing the conductivity of the material relative to pure germanium. This type of doping results in an $\boxed{\text{p-type}}$ semi-conductor.

Solutions to problems

P15E.2 The Fermi–Dirac distribution is [15E.2a–*670*], $f(E) = 1/[e^{(E-\mu)/kT} + 1]$, where $f(E)$ is the probability of occupation of a state with energy E and μ is the chemical potential.

(i) For $E < \mu$ then $\lim_{T\to0} (E-\mu)/kT = -\infty$ so $\lim_{T\to0} f(E) = 1/(e^{-\infty} + 1) = \boxed{1}$

For $E > \mu$ then $\lim_{T\to0} (E-\mu)/kT = +\infty$ so $\lim_{T\to0} f(E) = 1/(e^{\infty} + 1) = 1/\infty = \boxed{0}$

(ii) The integral is evaluated at $T = 0$ by splitting it into two and using the limits obtained in (i).

$$\begin{aligned} N &= \int_0^\infty \rho(E) f(E)\,dE = \int_0^\mu \rho(E)\overbrace{f(E)}^{f(E)=1}\,dE + \int_\mu^\infty \rho(E)\overbrace{f(E)}^{f(E)=0}\,dE \\ &= \int_0^\mu \rho(E)\,dE = \int_0^\mu CE^{1/2}\,dE = \tfrac{2}{3}C\mu^{3/2} \end{aligned}$$

Substituting $C = 4\pi V(2m_e/h^2)^{3/2}$ gives

$$\boxed{N = \frac{8\pi V}{3}\left(\frac{2m_e}{h^2}\right)^{3/2}\mu^{3/2}}$$

(iii) Rearranging the previous equatio to make μ the subject gives

$$\mu = \left(\frac{3N}{8\pi V}\right)^{2/3}\frac{h^2}{2m_e}$$

With $\mathcal{N} = N/V$ gives

$$\boxed{\mu = \left(\frac{3\mathcal{N}}{8\pi}\right)^{2/3}\frac{h^2}{2m_e}}$$

(iv) If each sodium atom contributes one electron to the solid, N is equal to the number of sodium atoms in the solid. The mass density ρ is expressed as $\rho = MN/N_A V = M\mathcal{N}/N_A$, where M is the molar mass of sodium. Hence $\mathcal{N} = \rho N_A/M$

$$\begin{aligned}\mu &= \left(\frac{3\rho N_A}{8\pi M}\right)^{2/3}\frac{h^2}{2m_e}\\ &= \left[\frac{3\times(9.7\times10^5\ \text{g m}^{-3})\times(6.0221\times10^{23}\ \text{mol}^{-1})}{8\pi\times(22.99\ \text{g mol}^{-1})}\right]^{2/3}\\ &\quad\times\frac{(6.6261\times10^{-34}\ \text{J s})^2}{2\times(9.1094\times10^{-31}\ \text{kg})} = 5.049...\times10^{-19}\ \text{J} = \boxed{3.2\ \text{eV}}\end{aligned}$$

P15E.4 The conductance, G, of germanium is predicted to have an Arrhenius-like temperature dependence. The given equation is rearranged to give a straight-line plot

$$G = G_0 e^{-E_g/2kT} \quad \text{hence} \quad \ln G = \ln G_0 - \frac{E_g}{2kT}$$

Hence a plot of $\ln G$ against $(1/T)$ should be a straight line with slope $-E_g/2k$.The data are plotted in Fig. 15.9.

T/K	G/S	$(1/T)/\text{K}^{-1}$	$\ln(G/\text{S})$
312	0.0847	0.00321	−2.469
354	0.4290	0.00282	−0.846
420	2.8600	0.00238	1.051

Linear regression analysis gives the equation for the best-fit line as

$$\ln(G/\text{S}) = (-4.270\times10^3)\times(1/T)/\text{K}^{-1} + 11.22$$

The band gap is computed from the slope

$$\begin{aligned}E_g &= -2k\times(\text{slope})\\ &= -2\times(1.3806\times10^{-23}\ \text{J K}^{-1})\times(-4.270\times10^3\ \text{K}) = 1.179\times10^{-19}\ \text{J}\\ &= \boxed{0.736\ \text{eV}}\end{aligned}$$

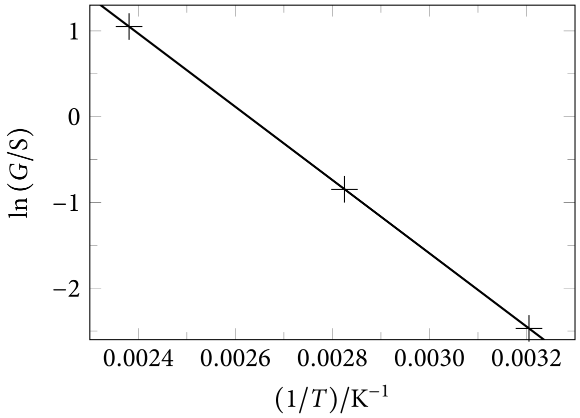


Figure 15.9

P15E.6 It is assumed that the volume of the unit cell does not change on substitution of Ca for Y. A tetragonal unit cell has volume $V = a^2c$, where a and c are the sides of the unit cell. The mass density ρ is given by $\rho = m/V$, where m is the total mass of the unit cell. Therefore $\rho = NM/(N_A V)$ where N is the number of formula units per unit cell and M is the molar mass of a formula unit. It follows that $M = \rho N_A V/N$.

There are two formula units in each unit cell so $N = 2$ and

$$\begin{aligned}M &= 2(200.59) + 2(137.33) + 88.91(1-x) + 40.08x + 2(63.55)\\ &\quad + 7.55(16.00)]\,\mathrm{g\,mol^{-1}} = (1012.65 - 48.83x)\,\mathrm{g\,mol^{-1}}\end{aligned}$$

From the data given

$$\begin{aligned}M &= \tfrac{1}{2}\rho N_A a^2 c\\ &= \tfrac{1}{2}(7.651\times10^{6}\,\mathrm{g\,m^{-3}})\times(6.0221\times10^{23}\,\mathrm{mol^{-1}})\times(0.38606\times10^{-9}\,\mathrm{m})^2\\ &\qquad\times(2.8915\times10^{-9}\,\mathrm{m})\\ &= 992.82\,\mathrm{g\,mol^{-1}}\end{aligned}$$

Equating the expression for M with its numerical value gives $992.82 = (1012.65 - 48.83x)$, hence $x = (1012.65 - 992.82)/48.83 = \boxed{0.406}$.

15F The magnetic properties of solids

Answer to discussion question

Solutions to exercises

E15F.1(b) The magnetic moment m is given by [15F.3–675], $m = g_e[S(S+1)]^{1/2}\mu_B$, where $g_e = 2.0023$ and $\mu_B = e\hbar/(2m_e)$. For Mn^{2+}, $5.3\mu_B = g_e[S(S+1)]^{1/2}\mu_B$, the constant μ_B cancels leaving a quadratic which is solved for S

$$S^2 + S - (5.3/2.0023)^2 = 0 \qquad S = \tfrac{1}{2}\left(-1 \pm \sqrt{1 + 4\times1\times7.006...}\right) = -0.500 \pm 2.693...$$

Of the two solutions, $S = -3.19$ is non-physical, and the solution $S = 2.19$ is reasonably close to $S = 2$. A plausible conclusion is that Mn^{2+} has $\boxed{\text{four}}$ unpaired electrons. Most Mn^{2+} complexes in fact have five unpaired electrons.

E15F.2(b) The molar susceptibility χ_m of a substance is given by [15F.2–*674*], $\chi_m = \chi V_m$, where χ is the volume magnetic susceptibility and V_m is the molar volume. The mass density ρ can be written $\rho = M/V_m$, hence $V_m = M/\rho$. With the data given

$$\chi_m = \chi V_m = \frac{\chi M}{\rho} = \frac{(-7.9\times10^{-7})\times(6\times12.01+12\times1.0079)\,\text{g mol}^{-1}}{0.811\,\text{g cm}^{-3}}$$
$$= \boxed{-8.2\times10^{-11}\,\text{m}^3\,\text{mol}^{-1}}$$

E15F.3(b) The molar susceptibility χ_m of a substance is given by [15F.4b–*675*], the Curie law,

$$\chi_m = \frac{C}{T} \quad \text{where} \quad C = \frac{N_A g_e^2 \mu_0 \mu_B^2 S(S+1)}{3k}$$

This is rearranged to give the spin quantum number as

$$S(S+1) = \frac{3kT\chi_m}{N_A g_e^2 \mu_0 \mu_B^2}$$
$$= \frac{3\times(1.3806\times10^{-23}\,\text{J K}^{-1})\times(298\,\text{K})}{(6.0221\times10^{23}\,\text{mol}^{-1})\times(2.0023)^2}$$
$$\times \frac{6.00\times10^{-8}\,\text{m}^3\,\text{mol}^{-1}}{(1.2566\times10^{-6}\,\text{J s}^2\,\text{C}^{-2}\,\text{m}^{-1})\times(9.2740\times10^{-24}\,\text{J T}^{-1})^2}$$
$$= 2.838...$$

To sort out the units the relations $1\,\text{T} = 1\,\text{kg s}^{-2}\,\text{A}^{-1}$ and $1\,\text{A} = 1\,\text{C s}^{-1}$, hence $1\,\text{C} = 1\,\text{A s}$, are useful. The value of S is found by solving the quadratic

$$S^2 + S - 2.838... = 0 \qquad S = \tfrac{1}{2}\left(-1 \pm \sqrt{1+4\times1\times2.838...}\right) = -0.500 \pm 1.757...$$

The root $S = -2.26$ is non-physical. The other root, $S = 1.26$, implies an effective number of electrons of $2\times1.26 = \boxed{2.5}$ (higher precision is not justified because the expected result is an integer).

The 8 electrons in a Ni^{2+} octahedral complex are arranged in the t_{2g} and e_g orbitals such that there are 2 unpaired electrons. The discrepancy between this and the value of determined above arises because the analysis here considers only the contribution from the electron spins and does not include any possible orbital contribution; in addition, the effect of interactions between the spins is not considered.

E15F.4(b) The spin contribution to the molar magnetic susceptibility is given by equation the Curie law, [15F.4b–*675*]

$$\chi_m = \frac{C}{T} \quad \text{where} \quad C = \frac{N_A g_e^2 \mu_0 \mu_B^2 S(S+1)}{3k}$$

If octahedral coordination and a high-spin arrangement are assumed, the 5 d electrons in Mn^{2+} are arranged as $t_{2g}^3e_g^2$ so theoretically there are 5 unpaired electrons and $S = \frac{5}{2}$

$$\begin{aligned}\frac{N_A g_e^2 \mu_0 \mu_B^2}{3k} &= \frac{(6.0221\times10^{23}\,\mathrm{mol^{-1}})\times(2.0023)^2}{3\times(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})} \\ &\quad\times(1.2566\times10^{-6}\,\mathrm{J\,s^2\,C^{-2}\,m^{-1}})\times(9.2740\times10^{-24}\,\mathrm{J\,T^{-1}})^2 \\ &= 6.302...\times10^{-6}\,\mathrm{m^3\,K\,mol^{-1}}\end{aligned}$$

To sort out the units the relations $1\ \mathrm{T} = 1\ \mathrm{kg\,s^{-2}\,A^{-1}}$ and $1\ \mathrm{A} = 1\ \mathrm{C\,s^{-1}}$, hence $1\ \mathrm{C} = 1\ \mathrm{A\,s}$, are useful. The molar susceptibility follows as

$$\chi_m = \frac{(6.302...\times10^{-6}\,\mathrm{m^3\,K\,mol^{-1}})\times(\frac{5}{2})(\frac{5}{2}+1)}{298\ \mathrm{K}} = \boxed{1.85\times10^{-7}\,\mathrm{m^3\,mol^{-1}}}$$

E15F.5(b) Superconductors classed as *Type I* show abrupt loss of superconductivity when an applied magnetic field exceeds a critical value $\mathcal{H}_c$ characteristic of the material. The dependence of $\mathcal{H}_c$ on T is given by [15F.5–*676*], $\mathcal{H}_c(T) = \mathcal{H}_c(0)\left[1 - T^2/T_c^2\right]$, provided $T \le T_c$. This relationship is rearranged to give T for a given applied field

$$T = T_c\left[1 - \frac{\mathcal{H}_c(T)}{\mathcal{H}_c(0)}\right]^{1/2} = (9.5\ \mathrm{K})\left[1 - \frac{150\ \mathrm{kA\,m^{-1}}}{158\ \mathrm{kA\,m^{-1}}}\right]^{1/2} = \boxed{2.1\ \mathrm{K}}$$

The material must be cooled to 2.1 K or lower to remain superconducting in a magnetic field of $150\ \mathrm{kA\,m^{-1}}$.

Solutions to problems

P15F.2 No data is given in the degeneracy of the electronic levels, so any possible effect of this is ignored in this answer (in fact both the ground and excited states are doubly degenerate, which does not affect the result). Assuming that the ground state has energy zero, and the excited state has energy ε, it follows that $p_1/p_0 = e^{-\varepsilon/kT}$, where p_0 and p_1 are the probability of the ground and excited states being occupied. By definition $p_0 + p_1 = 1$, so it follows that $p_1 = e^{-\varepsilon/kT}/(1 + e^{-\varepsilon/kT})$. Multiplying top and bottom of this expression by $e^{\varepsilon/kT}$ gives $p_1 = 1/(e^{\varepsilon/kT} + 1)$

Since the ground state of NO exhibits no paramagnetism, only molecules in the excited state contribute to the molar magnetic susceptibility. Consequently, [15F.4b–*675*] must be modified to include the probability of the state being occupied

$$\chi_m = \frac{p_1 N_A g_e^2 \mu_0 \mu_B^2 S(S+1)}{3kT} = \frac{N_A g_e^2 \mu_0 \mu_B^2 S(S+1)}{3kT(e^{\varepsilon/kT}+1)}$$

The magnetic moment m is given by [15F.3–*675*], $m = g_e\{S(S+1)\}^{1/2}\mu_B$. Rearranging this gives $S(S+1) = [m/(g_e\mu_B)]^2$, which is substituted into the previous equation to give

$$\chi_m = \frac{N_A\mu_0 m^2}{3kT(e^{\varepsilon/kT}+1)} = \frac{N_A\mu_0 \times (2\mu_B)^2}{3kT(e^{\varepsilon/kT}+1)}$$

where $m = 2\mu_B$ is used, as given in the question.
It is convenient to evaluate the term $\varepsilon/k = hc\tilde{\nu}/k$

$$\frac{hc\tilde{\nu}}{k} = \frac{(6.6261\times10^{-34}\,\text{J s})\times(2.9979\times10^{10}\,\text{cm s}^{-1})\times(121.1\,\text{cm}^{-1})}{1.3806\times10^{-23}\,\text{J K}^{-1}} = 174.24...\,\text{K}$$

and also to evaluate

$$\frac{4N_A\mu_0\mu_B^2}{3k} = \frac{4\times(6.0221\times10^{23}\,\text{mol}^{-1})\times(1.2566\times10^{-6}\,\text{J s}^2\,\text{C}^{-2}\,\text{m}^{-1})}{3\times(1.3806\times10^{-23}\,\text{J K}^{-1})}$$
$$\times(9.2740\times10^{-24}\,\text{J T}^{-1})^2 = 6.286...\times10^{-6}\,\text{m}^3\,\text{mol}^{-1}\,\text{K}$$

The final expression for the molar susceptibility is therefore

$$\chi_m = \frac{(6.286...\times10^{-6}\,\text{m}^3\,\text{mol}^{-1}\,\text{K})}{(T/\text{K})\times(1+e^{(174.2\,\text{K})/(T/\text{K})})}$$

This quantity is plotted as a function of temperature in Fig. 15.10. Initially χ_m increases due to the increasing population of the (paramagnetic) upper state. Eventually, a temperature is reached at which the populations of the two states are pretty much equal, and then χ_m starts to fall off in the way predicted by the Curie law. Thus, there is a maximum in the plot of χ_m against T.

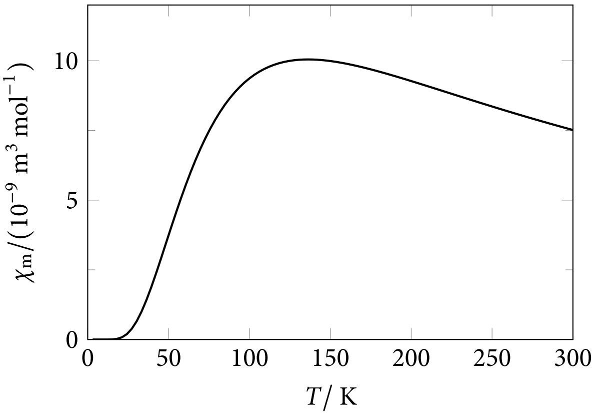


Figure 15.10

15G The optical properties of solids

Answers to discussion questions

D15G.2 See Section 15G.3 on page 680. Significant non-linear effects are only seen when strong (oscillating) electric fields are applied. The intense light available from some lasers provides such a field.

Solutions to exercises

E15G.1(b) The maximum wavelength that allows promotion of electrons is

$$\lambda = \frac{hc}{\Delta\varepsilon} = \frac{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(2.9979\times10^{8}\,\mathrm{m\,s^{-1}})}{(1.12\,\mathrm{eV})\times(1.6022\times10^{-19}\,\mathrm{J\,eV^{-1}})} = 1.10...\times10^{-6}\,\mathrm{m}$$

or $\boxed{1.11\,\mu\mathrm{m}}$

Solutions to problems

P15G.2 (a) The excited states of a dimer have energies $\tilde{\nu}_{\pm} = \tilde{\nu}_{\mathrm{mon}} \pm \tilde{\beta}$. With the given parameters $\tilde{\beta}$ is evaluated as

$$\begin{aligned}\tilde{\beta} &= \frac{\mu_{\mathrm{mon}}^{2}}{4\pi\varepsilon_0 hcr^3}(1-3\cos^2\theta)\\ &= \frac{[4.00\times(3.3356\times10^{-30}\,\mathrm{C\,m})]^2}{4\pi(8.8542\times10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}})\times(6.6261\times10^{-34}\,\mathrm{J\,s})}\\ &\quad\times\frac{(1-3\cos^2\theta)}{(2.9979\times10^{8}\,\mathrm{m\,s^{-1}})\times(0.50\times10^{-9}\,\mathrm{m})^3}\\ &= (6.44...\times10^{4}\,\mathrm{m^{-1}})(1-3\cos^2\theta) = (6.44...\times10^{2}\,\mathrm{cm^{-1}})(1-3\cos^2\theta)\end{aligned}$$

Therefore the energies are

$$\tilde{\nu}_{\pm}/\mathrm{cm^{-1}} = 25\,000 \pm (6.44...\times10^{2})(1-3\cos^2\theta)$$

A plot of these as a function of θ is shown in Fig. 15.11.

(b) By analogy with [15C.1–*658*] the energies are given by

$$\tilde{\nu}_{\mathrm{chain}} = \tilde{\nu}_{\mathrm{mon}} + 2\tilde{V}\cos(k\pi/[N+1])$$

where $k = 1,2,3,\ldots,N$. From part (i) when $\theta = 0$, $\tilde{\beta} = -1.28...\times10^{3}\,\mathrm{cm^{-1}}$; this is the value of $\tilde{V}$.

The lowest-energy spectroscopic transition is from the ground state (defined to have energy zero) to the state with $k = 1$, and therefore occurs at a wavenumber of

$$\begin{aligned}\tilde{\nu}_{\mathrm{min}} &= \tilde{\nu}_{\mathrm{mon}} + 2\tilde{V}\cos(\pi/[N+1])\\ \tilde{\nu}_{\mathrm{min}}/\mathrm{cm^{-1}} &= 25000 - (2.57...\times10^{3})\cos(\pi/[N+1])\end{aligned}$$

This value of k makes $\cos(k\pi/[N+1])$ as close as possible to its maximum value of 1, and because $\tilde{V}$ is negative, this gives the lowest energy.

$N = 5$ $\quad\tilde{\nu}_{\mathrm{min}}/\mathrm{cm^{-1}} = 25000 - (2.57...\times10^{3})\cos(\pi/6) = \boxed{2.277\times10^{4}}$

$N = 10$ $\quad\tilde{\nu}_{\mathrm{min}}/\mathrm{cm^{-1}} = 25000 - (2.57...\times10^{3})\cos(\pi/11) = \boxed{2.253\times10^{4}}$

$N = 15$ $\quad\tilde{\nu}_{\mathrm{min}}/\mathrm{cm^{-1}} = 25000 - (2.57...\times10^{3})\cos(\pi/16) = \boxed{2.247\times10^{4}}$

$N = \infty$ $\quad\tilde{\nu}_{\mathrm{min}}/\mathrm{cm^{-1}} = 25000 - (2.57...\times10^{3})\cos(\pi/\infty) = \boxed{2.242\times10^{4}}$

For large N the cosine term tends to 1 and the transition is as $\tilde{\nu}_{\mathrm{mon}} + 2\tilde{V}$.

(c) Because the model considers only nearest neighbour interactions, the transition dipole moment of the lowest energy transition is $\boxed{\text{independent}}$ of the size of the chain.

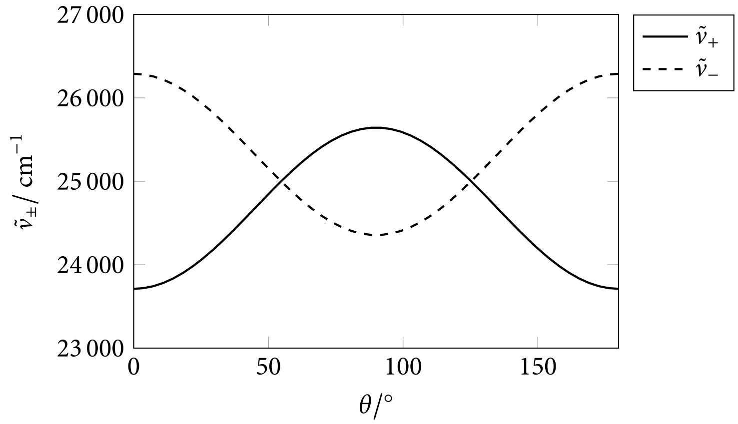


Figure 15.11

Answers to integrated activities

I15.2 The scattering factor $f(\theta)$ is given by [15B.2–*649*]

$$f(\theta) = 4\pi \int_0^\infty \rho(r)\,\frac{\sin kr}{kr}\,r^2\,\mathrm{d}r \qquad k = \frac{4\pi}{\lambda}\sin\theta$$

The quantity $4\pi r^2\rho(r)$ is identified as the radial distribution function $P(r)$, which is given in terms of the radial wavefunction of the orbital, $P(r) = R(r)^2 r^2$

$$f(\theta) = \int_0^\infty P(r)\,\frac{\sin kr}{kr}\,\mathrm{d}r$$

The requested plot is of $f(\theta)$ as a function of $\xi = \sin\theta/\lambda$, hence $k = 4\pi\xi$ and

$$f(\theta) = \int_0^\infty P(r)\,\frac{\sin(4\pi\xi r)}{4\pi\xi r}\,\mathrm{d}r = \frac{1}{4\pi\xi}\int_0^\infty R(r)^2\,\sin(4\pi\xi r)\,r\,\mathrm{d}r$$

From Table 8A.1 on page 306 the 1s hydrogenic orbital the radial wavefunction is $R(r) = 2(Z/a_0)^{3/2}\mathrm{e}^{-Zr/a_0}$, and so the radial distribution function is $P(r) = R(r)^2r^2 = 4(Z/a_0)^3r^2\mathrm{e}^{-2Zr/a_0}$. The integral has to be evaluated numerically using mathematical software. The parameter ξ is some fraction of $1/\lambda$, where λ is the wavelength of the X-rays used. Typically $\lambda = 100$ pm so ξ is less than 10^{10} m^{-1}. The upper limit of the integration can conveniently be set to a modest multiple of the Bohr radius, say $100a_0$, because beyond this distance the electron density will be negligible. The computed scattering factor is shown in Fig. 15.12 for $Z = 1$ and $Z = 2$. As expected, for forward scattering, $\xi = 0$, the scattering factor is equal to the number of electrons, in this case 1. As ξ

increases the scattering factor falls off, but the decay is slower for the more compact orbital with $Z = 2$.

For a 2s hydrogenic orbital

$$R(r) = 8^{-1/2}(Z/a_0)^{3/2}(2 - Zr/a_0)e^{-Zr/2a_0}$$
$$P(r) = 8^{-1}(Z/a_0)^3(2 - Zr/a_0)^2 r^2 e^{-Zr/a_0}$$

The computed scattering factor is shown in Fig. 15.13 for $Z = 1$ and $Z = 2$. As for the 1s orbital the scattering factor is equal to 1 for forward scattering. Compared to the 1s the scattering from 2s falls off more quickly and also shows some small negative excursions.

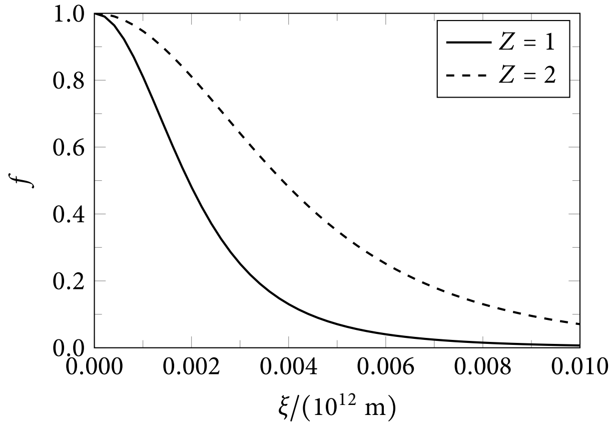


Figure 15.12

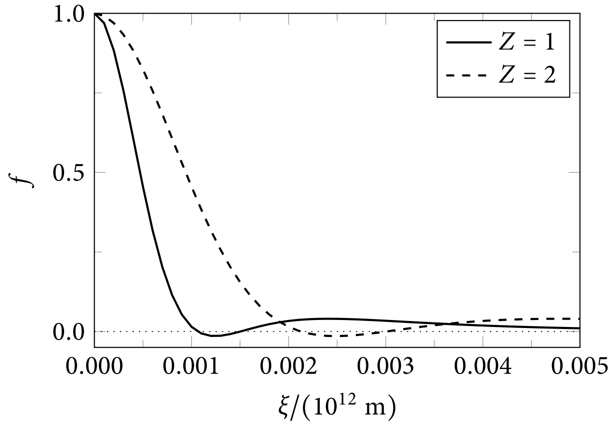


Figure 15.13

16

Molecules in motion

16A Transport properties of a perfect gas

Answers to discussion questions

D16A.2 The diffusion constant is given by [16A.9–*694*], $D = \frac{1}{3}\lambda v_{\text{mean}}$. The mean free path λ decreases as the pressure is increased ([16A.1a–*690*]), so D decreases with increasing pressure and, as a result, the gas molecules diffuse more slowly. The mean speed v_{mean} increases with the temperature ([16A.1b–*690*]), so D also increases with temperature. As a result, molecules in a hot gas diffuse more quickly than those when the gas is cool (for a given concentration gradient). Because the mean free path increases when the collision cross-section σ of the molecules decreases, the diffusion coefficient is greater for small molecules than for large molecules.

The viscosity is given by [16A.11c–*696*], $\eta = \frac{1}{3}v_{\text{mean}}\lambda m\mathcal{N}$. The mean free path is inversely proportional to the pressure and $\mathcal{N}$ is proportional to the pressure, therefore the product $\lambda\mathcal{N}$, and hence the viscosity, is independent of pressure. The physical reason for this pressure-independence is that as the pressure increases more molecules are available to transport the momentum, but they carry it less far on account of the decrease in mean free path. The mean speed goes as $T^{1/2}$ (at constant volume) and so the viscosity increases with temperature. This is because at high temperatures the molecules travel more quickly, so the flux of momentum is greater.

Solutions to exercises

E16A.1(b) For a perfect gas, the collision flux Z_{w} is [16A.7a–*693*], $Z_{\text{w}} = p/(2\pi mkT)^{1/2}$. The number of helium molecule collisions within area A in time interval t is therefore $N = Z_{\text{w}}At$. The mass m is written in terms of the molar mass M: $m = M/N_{\text{A}}$.

$$N = Z_{\text{w}}At = \frac{p}{(2\pi mkT)^{1/2}}At = \frac{pN_{\text{A}}^{1/2}}{(2\pi MkT)^{1/2}}At$$

$$= \frac{(111\ \text{Pa}) \times (6.0221 \times 10^{23}\ \text{mol}^{-1})^{1/2} \times [(3.5 \times 4.0) \times 10^{-4}\ \text{m}^2] \times (10\ \text{s})}{[2\pi \times (0.004\ \text{kg}\,\text{mol}^{-1}) \times (1.3806 \times 10^{-23}\ \text{J}\,\text{K}^{-1}) \times (1500\ \text{K})]^{1/2}}$$

$$= \boxed{5.3 \times 10^{22}} \quad \text{collisions}$$

E16A.2(b) The diffusion constant is given by [16A.9–*694*], $D = \frac{1}{3}\lambda v_{\text{mean}}$, where λ is the mean free path length $\lambda = kT/\sigma p$ [16A.1a–*690*], and v_{mean} is the mean speed $v_{\text{mean}} = (8RT/\pi M)^{1/2}$ [16A.1b–*690*].

$$\begin{aligned}D &= \frac{1}{3}\frac{kT}{\sigma p}\left[\frac{8RT}{\pi M}\right]^{1/2}\\ &= \frac{(1.3806\times10^{-23}\,\text{J}\,\text{K}^{-1})\times(293.15\,\text{K})}{3\times(4.3\times10^{-19}\,\text{m}^2)\times(p/\text{Pa})}\left[\frac{8\times(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})\times(293.15\,\text{K})}{\pi\times(0.02802\,\text{kg}\,\text{mol}^{-1})}\right]^{1/2}\\ &= (1.476...\,\text{m}^2\,\text{s}^{-1})\times\frac{1}{p/\text{Pa}}\end{aligned}$$

The flux of nitrogen molecules atoms J_z is related to the diffusion coefficient D and the concentration gradient $\text{d}\mathcal{N}/\text{d}z$ by [16A.4–*691*], $J_z = -D\text{d}\mathcal{N}/\text{d}z$. From the perfect gas equation, $pV = NkT$, the number density is expressed in terms of the pressure as $\mathcal{N} = N/V = p/kT$. With this, the concentration gradient is written in terms of the pressure gradient: $\text{d}\mathcal{N}/\text{d}z = (1/kT)\text{d}p/\text{d}z$, and hence the flow is $J_z = -(D/kT)\text{d}p/\text{d}z$

$$\begin{aligned}J_z &= \frac{-D}{kT}\frac{\text{d}p}{\text{d}z} = \frac{-1}{p/\text{Pa}}\times\frac{(1.476...\,\text{m}^2\,\text{s}^{-1})\times(1.2\times10^5\,\text{Pa}\,\text{m}^{-1})}{(1.3806\times10^{-23}\,\text{J}\,\text{K}^{-1})\times(293.15\,\text{K})}\\ &= (4.37...\times10^{25}\,\text{m}^2\,\text{s}^{-1})\times\frac{-1}{p/\text{Pa}}\end{aligned}$$

p/Pa	$D/(\text{m}^2\,\text{s}^{-1})$	$J_z/(\text{m}^{-2}\,\text{s}^{-1})$	$(J_z/N_A)/(\text{mol}\,\text{m}^{-2}\,\text{s}^{-1})$
100.0	1.48×10^{-5}	-4.38×10^{23}	-0.73
1.00×10^{5}	1.48×10^{-5}	-4.38×10^{20}	-7.3×10^{-4}
2.00×10^{7}	7.38×10^{-8}	-2.19×10^{18}	-3.6×10^{-6}

E16A.3(b) The thermal conductivity is given by [16A.10c–*695*], $\kappa = \nu p D/T$, where the diffusion coefficient D is given by [16A.9–*694*], $D = \lambda v_{\text{mean}}/3$. The mean free path λ is given by [16A.1a–*690*], $\lambda = kT/\sigma p$, and the mean speed v_{mean} is given by [16A.1b–*690*], $v_{\text{mean}} = (8RT/\pi M)^{1/2}$. The quantity ν is the number of quadratic contributions to the energy, and this is related to the heat capacity by $C_{V,\text{m}} = \nu k N_A$, hence $\nu = C_{V,\text{m}}/kN_A$. The thermal conductivity is therefore expressed as

$$\kappa = \frac{\nu p D}{T} = \frac{\nu p \lambda v_{\text{mean}}}{3T} = \frac{C_{V,\text{m}}}{kN_A}\frac{p}{3T}\frac{kT}{\sigma p}\left(\frac{8RT}{\pi M}\right)^{1/2} = \frac{C_{V,\text{m}}}{3\sigma N_A}\left(\frac{8RT}{\pi M}\right)^{1/2}$$

$$\begin{aligned}\text{hence } \kappa &= \frac{20.8\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}}{3\times(4.3\times10^{-19}\,\text{m}^2)\times(6.0221\times10^{23}\,\text{mol}^{-1})}\\ &\quad\times\left(\frac{8\times(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})\times(298\,\text{K})}{\pi\times(2.802\times10^{-2}\,\text{kg}\,\text{mol}^{-1})}\right)^{1/2}\\ &= \boxed{1.3\times10^{-2}\,\text{J}\,\text{K}^{-1}\,\text{m}^{-1}\,\text{s}^{-1}}\end{aligned}$$

E16A.4(b) The thermal conductivity is given by [16A.10c–*695*], $\kappa = \nu p D/T$, where the diffusion coefficient D is given by [16A.9–*694*], $D = \lambda v_{\text{mean}}/3$. The mean free path λ is given by [16A.1a–*690*], $\lambda = kT/\sigma p$, and the mean speed v_{mean} is given by [16A.1b–*690*], $v_{\text{mean}} = (8RT/\pi M)^{1/2}$. The quantity ν is the number of quadratic contributions to the energy, and this is related to the heat capacity by $C_{V,\text{m}} = \nu k N_\text{A}$, hence $\nu = C_{V,\text{m}}/kN_\text{A}$. The thermal conductivity is therefore expressed as

$$\kappa = \frac{\nu p D}{T} = \frac{\nu p \lambda v_{\text{mean}}}{3T} = \frac{C_{V,\text{m}}}{kN_\text{A}}\frac{p}{3T}\frac{kT}{\sigma p}\left(\frac{8RT}{\pi M}\right)^{1/2} = \frac{C_{V,\text{m}}}{3\sigma N_\text{A}}\left(\frac{8RT}{\pi M}\right)^{1/2} \qquad (16.1)$$

Rearranging gives an expression for σ in terms of the thermal conductivity

$$\sigma = \frac{C_{V,\text{m}}}{3\kappa N_\text{A}}\left(\frac{8RT}{\pi M}\right)^{1/2}$$

The value of $C_{p,\text{m}}$ is given in the *Resource section*; $C_{V,\text{m}}$ is found using $C_{p,\text{m}} - C_{V,\text{m}} = R$ for a perfect gas. The tabulated values of the thermal conductivity are at 273 K. These can be converted to values at 298 K by using the fact that $\kappa \propto T^{1/2}$, which follows from eqn 16.1 provided that the hat capacity can be assumed to be constant over the temperature range of interest. Hence $\kappa_{298\,\text{K}} \approx (298\,\text{K}/273\,\text{K})^{1/2}\,\kappa_{273\,\text{K}}$; with the value from the *Resource section* this gives $\kappa_{298\,\text{K}} = 2.40 \times 10^{-2}(298/273)^{1/2} = 2.50... \times 10^{-2}\,\text{J K}^{-1}\,\text{m}^{-1}\,\text{s}^{-1}$

$$\sigma = \frac{(29.125\,\text{J K}^{-1}\,\text{mol}^{-1}) - (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})}{3 \times (2.50... \times 10^{-2}\,\text{J K}^{-1}\,\text{m}^{-1}\,\text{s}^{-1}) \times (6.0221 \times 10^{23}\,\text{mol}^{-1})}$$
$$\times\left(\frac{8 \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})}{\pi \times (2.802 \times 10^{-2}\,\text{kg mol}^{-1})}\right)^{1/2} = \boxed{0.218\,\text{nm}^2}$$

The value reported in Table 1B.2 on page 17 is 0.43 nm^2.

E16A.5(b) The flux of energy is given by [16A.3–*691*], $J_z = -\kappa\,\text{d}T/\text{d}z$. The value of the thermal conductivity κ for N$_2$ at 298 K is determined in *Exercise* E16A.3(b) as $1.3 \times 10^{-2}\,\text{J K}^{-1}\,\text{m}^{-1}\,\text{s}^{-1}$. As is seen in that *Exercise*, $\kappa \propto T^{1/2}$ provided that the heat capacity is constant over the temperature range of interest. It therefore follows that $\kappa_{290\,\text{K}} = (290\,\text{K}/298\,\text{K})^{1/2}\,\kappa_{298\,\text{K}} = 1.28... \times 10^{-2}\,\text{J K}^{-1}\,\text{m}^{-1}\,\text{s}^{-1}$. With these data the flux is computed as

$$J_z = -\kappa\,\text{d}T/\text{d}z = -(1.28...\times 10^{-2}\,\text{J K}^{-1}\,\text{m}^{-1}\,\text{s}^{-1})\times(8.5\,\text{K m}^{-1}) = \boxed{-0.11\,\text{J m}^{-2}\,\text{s}^{-1}}$$

E16A.6(b) The flux of energy is given by [16A.3–*691*], $J_z = -\kappa\,\text{d}T/\text{d}z$, where κ is the thermal conductivity and the negative sign indicates flow of heat is towards the lower temperature. The rate of energy transfer is $r = J_z A$, where A is the cross-sectional area. The temperature gradient is approximated as $\text{d}T/\text{d}z = \Delta T/\Delta z$. The value of κ is approximated as the value given for N$_2$ in the *Resource section*, 24 mW K^{-1} m^{-1}; because 1 W = 1 J s^{-1} it follows that κ =

$2.4 \times 10^{-2}\ \mathrm{J\,K^{-1}\,m^{-1}\,s^{-1}}$.

$$\begin{aligned} r = J_z A &= -\kappa A \frac{\Delta T}{\Delta z} \\ &= -(2.4 \times 10^{-2}\ \mathrm{J\,K^{-1}\,m^{-1}\,s^{-1}}) \times (2.00\ \mathrm{m^2}) \times \frac{[(0)-(70)]\ \mathrm{K}}{0.0500\ \mathrm{m}} = \boxed{67\ \mathrm{W}} \end{aligned}$$

E16A.7(b) The viscosity η is given by [16A.11c–*696*], $\eta = pMD/RT$. In turn the diffusion constant is given by [16A.9–*694*], $D = \frac{1}{3}\lambda v_{\text{mean}}$, where λ is the mean free path length $\lambda = kT/\sigma p$ [16A.1a–*690*], and v_{mean} is the mean speed $v_{\text{mean}} = (8RT/\pi M)^{1/2}$ [16A.1b–*690*]. The first step is to find an expression for η as a function of temperature

$$\begin{aligned} \eta = \frac{pMD}{RT} &= \frac{pM}{RT}\frac{kT}{3\sigma p}\left(\frac{8RT}{\pi M}\right)^{1/2} = \frac{M}{3\sigma N_A}\left(\frac{8RT}{\pi M}\right)^{1/2} = \frac{1}{3\sigma N_A}\left(\frac{8RM}{\pi}\right)^{1/2} T^{1/2} \\ &= \frac{1}{3 \times (8.8 \times 10^{-19}\ \mathrm{m^2}) \times (6.0221 \times 10^{23}\ \mathrm{mol^{-1}})} \\ &\quad \times \left(\frac{8 \times (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (0.078...\ \mathrm{kg\,mol^{-1}})}{\pi}\right)^{1/2} T^{1/2} \\ &= (8.08... \times 10^{-7}\ \mathrm{kg\,K^{-1/2}\,m^{-1}\,s^{-1}}) \times (T/\mathrm{K})^{1/2} \end{aligned}$$

where $1\ \mathrm{J} = 1\ \mathrm{kg\,m^2\,s^{-2}}$ has been used to arrive at the units on the final line. Using this expression the following table is drawn up (recall that $10^{-7}\ \mathrm{kg\,m^{-1}\,s^{-1}} = 1\ \mu\mathrm{P}$)

T/K	$\eta/(\mathrm{kg\,m^{-1}\,s^{-1}})$	$\eta/(\mu\mathrm{P})$
273	1.34×10^{-5}	134
298	1.40×10^{-5}	140
1000	2.56×10^{-5}	256

E16A.8(b) In the solution to *Exercise* E16A.7(b) it is shown that

$$\eta = \frac{1}{3\sigma N_A}\left(\frac{8RMT}{\pi}\right)^{1/2} \quad \text{hence} \quad \sigma = \frac{1}{3\eta N_A}\left(\frac{8RMT}{\pi}\right)^{1/2}$$

Recalling that $10^{-7}\ \mathrm{kg\,m^{-1}\,s^{-1}} = 1\ \mu\mathrm{P}$, the cross section is computed as

$$\begin{aligned} \sigma &= \frac{1}{3 \times (1.66 \times 10^{-5}\ \mathrm{kg\,m^{-1}\,s^{-1}}) \times (6.0221 \times 10^{23}\ \mathrm{mol^{-1}})} \\ &\quad \times \left(\frac{8 \times (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (0.02802\ \mathrm{kg\,mol^{-1}}) \times (273\ \mathrm{K})}{\pi}\right)^{1/2} \\ &= \boxed{0.424\ \mathrm{nm^2}} \end{aligned}$$

E16A.9(b) The rate of effusion, r is given by [16A.12–*697*], $r = pA_0N_A/(2\pi MRT)^{1/2}$; this rate is the number of molecules escaping through the hole in a particular period of time, divided by that time. The mass loss Δm in period Δt is therefore $\Delta m = \Delta t pA_0N_A/(2\pi MRT)^{1/2} \times m$, where m is the mass of a molecule. This mass is written $m = M/N_A$ and so it follows $\Delta m = \Delta t pA_0M^{1/2}/(2\pi RT)^{1/2}$. Evaluating this with the values given

$$\begin{aligned}\Delta m &= \frac{\Delta t pA_0M^{1/2}}{(2\pi RT)^{1/2}}\\ &= \frac{(86\,400\text{ s}) \times (0.224\text{ Pa}) \times \pi \times (\frac{1}{2} \times 3.00 \times 10^{-3}\text{ m})^2 \times (0.300\text{ kg mol}^{-1})^{1/2}}{[2 \times \pi \times (8.3145\text{ J K}^{-1}\text{ mol}^{-1}) \times (450\text{ K})]^{1/2}}\\ &= 4.89 \times 10^{-4}\text{ kg} = \boxed{489\text{ mg}}\end{aligned}$$

E16A.10(b) The rate of effusion, r is given by [16A.12–*697*], $r = pA_0N_A/(2\pi MRT)^{1/2}$; this rate is the number of molecules escaping through the hole in a particular period of time, divided by that time. The mass loss Δm in period Δt is therefore $\Delta m = \Delta t pA_0N_A/(2\pi MRT)^{1/2} \times m$, where m is the mass of a molecule. This mass is written $m = M/N_A$ and so it follows $\Delta m = \Delta t pA_0M^{1/2}/(2\pi RT)^{1/2}$. This is rearranged to give an expression for p

$$\begin{aligned}p &= \frac{\Delta m(2\pi RT)^{1/2}}{\Delta tA_0M^{1/2}} = \frac{\Delta m}{\Delta tA_0}\left(\frac{2\pi RT}{M}\right)^{1/2}\\ &= \frac{2.77 \times 10^{-4}\text{ kg}}{(500\text{ s}) \times \pi \times (2.5 \times 10^{-4}\text{ m})^2}\left(\frac{2\pi \times (8.3145\text{ J K}^{-1}\text{ mol}^{-1}) \times (573.15\text{ K})}{0.200\text{ kg mol}^{-1}}\right)^{1/2}\\ &= \boxed{1.09 \times 10^3\text{ Pa}}\end{aligned}$$

E16A.11(b) The rate of effusion, r is given by [16A.12–*697*], $r = pA_0N_A/(2\pi MRT)^{1/2}$; this rate is the number of molecules escaping through the hole in a particular period of time, divided by that time. In this experiment the pressure changes so the rate of effusion changes throughout the experiment; nevertheless, the rate is always proportional to $M^{-1/2}$. The two experiments involve comparing the time for the *same* drop in pressure, therefore the only factor that affects this time is the molar mass of the effusing gas. Because the *rate* is proportional to $M^{-1/2}$ the *time* for a given fall in pressure will be proportional to the inverse of this, that is $M^{1/2}$. It follows that

$$\frac{\text{rate for gas A}}{\text{rate for gas B}} = \frac{\text{time for gas B}}{\text{time for gas A}} = \left(\frac{M_B}{M_A}\right)^{1/2}$$

Therefore

$$\frac{82.3\text{ s}}{18.5\text{ s}} = \left(\frac{M_B}{M_{N_2}}\right)^{1/2} \quad \text{hence} \quad M_B = (28.02\text{ g mol}^{-1})\left(\frac{82.3}{18.5}\right)^2 = \boxed{555\text{ g mol}^{-1}}$$

E16A.12(b) The rate of effusion is given by [16A.12–*697*], $\mathrm{d}N/\mathrm{d}t = pA_0N_A/(2\pi MRT)^{1/2}$; this is the rate of change of the number of molecules. If it is assumed that the gas is perfect, the equation of state $pV = NkT$ allows the number to be written as $N = pV/kT$, and therefore $\mathrm{d}N/\mathrm{d}t = (V/kT)\mathrm{d}p/\mathrm{d}t$. The rate of change of the pressure is therefore

$$\frac{\mathrm{d}p}{\mathrm{d}t} = -\frac{kT}{V}\frac{pA_0N_A}{(2\pi MRT)^{1/2}} = -\frac{RTA_0}{V(2\pi MRT)^{1/2}} \times p = -\underbrace{\frac{A_0}{V}\left(\frac{RT}{2\pi M}\right)^{1/2}}_{\alpha} \times p$$

The minus sign is needed because the pressure falls with time. This differential equation is separable and can be integrated between $p = p_i$ and $p = p_f$, corresponding to $t = 0$ and $t = t$.

$$\int_{p_i}^{p_f} (1/p)\,\mathrm{d}p = \int_0^t -\alpha\,\mathrm{d}t \qquad \text{hence} \qquad \ln(p_f/p_i) = -\alpha t$$

The time for the pressure to drop by the specified amount is therefore

$$\begin{aligned} t &= -\ln(p_f/p_i)/\alpha = \ln(p_i/p_f)\frac{V}{A_0}\left(\frac{2\pi M}{RT}\right)^{1/2} \\ &= \ln\left(\frac{1.22\times10^5\ \text{Pa}}{1.05\times10^5\ \text{Pa}}\right)\frac{(22.0\ \text{m}^3)}{[\pi(5.0\times10^{-5}\ \text{m})^2]}\left(\frac{2\pi\times(2.802\times10^{-2}\ \text{kg mol}^{-1})}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(293\ \text{K})}\right)^{1/2} \\ &= 3.57\times10^6\ \text{s} = \boxed{41.4\ \text{days}} \end{aligned}$$

Solutions to problems

P16A.2 The thermal conductivity is given by [16A.10c–*695*], $\kappa = \nu pD/T$, where the diffusion coefficient D is given by [16A.9–*694*], $D = \lambda v_{\text{mean}}/3$. The mean free path λ is given by [16A.1a–*690*], $\lambda = kT/\sigma p$, and the mean speed v_{mean} is given by [16A.1b–*690*], $v_{\text{mean}} = (8RT/\pi M)^{1/2}$. The quantity ν is the number of quadratic contributions to the energy

$$\kappa = \frac{\nu pD}{T} = \frac{\nu p\lambda v_{\text{mean}}}{3T} = \frac{\nu p}{3T}\frac{kT}{\sigma p}\left(\frac{8RT}{\pi M}\right)^{1/2} = \frac{\nu k}{3\sigma}\left(\frac{8RT}{\pi M}\right)^{1/2}$$

At 300 K the expectation is that three translational degrees of freedom and two rotational degrees of freedom will contribute, giving $\nu = 5/2$ (recall that for a linear molecule there is no rotation about the long axis). At 10 K the temperature is far too low for the rotational degrees of freedom to contribute and so $\nu = 3/2$. The ratio $\kappa_{300\,\text{K}}/\kappa_{10\,\text{K}}$ is therefore

$$\frac{\kappa_{300\,\text{K}}}{\kappa_{10\,\text{K}}} = \frac{\nu_{300\,\text{K}}(300\ \text{K})^{1/2}}{\nu_{10\,\text{K}}(10\ \text{K})^{1/2}} = \frac{(5/2)\times(300\ \text{K})^{1/2}}{(3/2)\times(10\ \text{K})^{1/2}} = \boxed{9.13}$$

P16A.4 The rate of effusion, r is given by [16A.12–*697*], $r = pA_0N_A/(2\pi MRT)^{1/2}$; this rate is the number of molecules escaping through the hole in a particular period of time, divided by that time. The mass loss Δm in period Δt is therefore $\Delta m = \Delta t p A_0 N_A/(2\pi MRT)^{1/2} \times m$, where m is the mass of a molecule. This mass is written $m = M/N_A$ and so it follows $\Delta m = \Delta t p A_0 M^{1/2}/(2\pi RT)^{1/2}$. This is rearranged to give an expression for p

$$\begin{aligned} p &= \frac{\Delta m(2\pi RT)^{1/2}}{\Delta t A_0 M^{1/2}} = \frac{\Delta m}{\Delta t A_0}\left(\frac{2\pi RT}{M}\right)^{1/2} \\ &= \frac{(4.3\times10^{-8}\text{ kg})}{(7200\text{ s})\times[\pi(5.0\times10^{-4}\text{ m})^2]}\left(\frac{2\pi\times(8.3145\text{ J K}^{-1}\text{ mol}^{-1})\times(1273.15\text{ K})}{0.07264\text{ kg mol}^{-1}}\right)^{1/2} \\ &= \boxed{7.28\times10^{-3}\text{ Pa}} \end{aligned}$$

P16A.6 The rate of effusion is given by [16A.12–697], $\mathrm{d}N/\mathrm{d}t = pA_0N_A/(2\pi MRT)^{1/2}$; this is the rate of change of the number of molecules. If it is assumed that the gas is perfect, the equation of state $pV = NkT$ allows the number to be written as $N = pV/kT$, and therefore $\mathrm{d}N/\mathrm{d}t = (V/kT)\mathrm{d}p/\mathrm{d}t$. The rate of change of the pressure is therefore

$$\frac{\mathrm{d}p}{\mathrm{d}t} = -\frac{kT}{V}\frac{pA_0N_A}{(2\pi MRT)^{1/2}} = -\frac{RTA_0}{V(2\pi MRT)^{1/2}}\times p = -\underbrace{\frac{A_0}{V}\left(\frac{RT}{2\pi M}\right)^{1/2}}_{\alpha}\times p$$

The minus sign is needed because the pressure falls with time. This differential equation is separable and can be integrated between $p = p_0$ and $p = p$, corresponding to $t = 0$ and $t = t$.

$$\int_{p_0}^{p}(1/p)\,\mathrm{d}p = \int_0^t -\alpha\,\mathrm{d}t \quad \text{hence} \quad \ln(p/p_0) = -\alpha t$$

The time dependence of the pressure is therefore given by

$$\boxed{p = p_0\mathrm{e}^{-\alpha t} \quad \alpha = \frac{A_0}{V}\left(\frac{RT}{2\pi M}\right)^{1/2} \quad \text{or} \quad p = p_0\mathrm{e}^{-t/\tau} \quad \tau = \frac{V}{A_0}\left(\frac{2\pi M}{RT}\right)^{1/2}}$$

The time $t_{1/2}$ for the pressure to fall from p_0 to $p_0/2$ is given by

$$\ln[(p_0/2)/p_0] = -\alpha t_{1/2} \quad \text{hence} \quad t_{1/2} = (\ln 2)/\alpha$$

The half life of the pressure is therefore

$$\boxed{t_{1/2} = \frac{V\ln 2}{A_0}\left(\frac{2\pi M}{RT}\right)^{1/2}}$$

This half-life is independent of the pressure.

16B Motion in liquids

Answers to discussion questions

D16B.2 The Grotthuss mechanism for conduction by protons in water is described in Section 16B.2(a) on page 701 and illustrated in Fig. 16B.2 on page 703. It seems plausible that such a mechanism could also occur in the relatively open hydrogen bonded structure of ice.

Solutions to exercises

E16B.1(b) The temperature dependence of the viscosity η is given by [16B.1–*699*], $\eta = \eta_0 e^{E_a/RT}$, where η_0 is viscosity in the limit of high temperature and E_a is the associated activation energy. Taking the natural logarithm gives $\ln\eta = \ln\eta_0 + E_a/RT$. Hence

$$\ln\eta_1 - \ln\eta_2 = (\ln\eta_0 + E_a/RT_1) - (\ln\eta_0 + E_a/RT_2) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Rearranging gives an expression for the activation energy

$$\begin{aligned} E_a &= R\frac{\ln(\eta_1/\eta_2)}{(T_1^{-1} - T_2^{-1})} \\ &= (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\frac{\ln[(1.554\,\mathrm{cP})/(1.450\,\mathrm{cP})]}{[(293.15\,\mathrm{K})^{-1} - (313.15\,\mathrm{K})^{-1}]} \\ &= \boxed{2.64\,\mathrm{kJ\,mol^{-1}}} \end{aligned}$$

E16B.2(b) According to the law of independent migration of ions, the limiting molar conductivity Λ_m° of an electrolyte is given by the sum of the limiting molar conductivities λ_i of the ions present, [16B.6–*701*], $\Lambda_m^\circ = \nu_+\lambda_+ + \nu_-\lambda_-$; in this expression ν_+ and ν_- are the numbers of cations and anions provided by each formula unit of electrolyte. For each of the given electrolytes it follows that

$$\Lambda^\circ_{\mathrm{KF}} = \lambda_{\mathrm{K^+}} + \lambda_{\mathrm{F^-}} \quad \Lambda^\circ_{\mathrm{KCH_3CO_2}} = \lambda_{\mathrm{K^+}} + \lambda_{\mathrm{CH_3CO_2^-}}$$
$$\Lambda^\circ_{\mathrm{Mg(CH_3CO_2)_2}} = \lambda_{\mathrm{Mg^{2+}}} + 2\lambda_{\mathrm{CH_3CO_2^-}}$$

These expressions are manipulated to give $\Lambda^\circ_{\mathrm{MgF_2}}$

$$\begin{aligned} \Lambda^\circ_{\mathrm{MgF_2}} &= \lambda_{\mathrm{Mg^{2+}}} + 2\lambda_{\mathrm{F^-}} \\ &= (\Lambda^\circ_{\mathrm{Mg(CH_3CO_2)_2}} - 2\lambda_{\mathrm{CH_3CO_2^-}}) + 2(\Lambda^\circ_{\mathrm{KF}} - \lambda_{\mathrm{K^+}}) \\ &= \Lambda^\circ_{\mathrm{Mg(CH_3CO_2)_2}} + 2\Lambda^\circ_{\mathrm{KF}} - 2(\lambda_{\mathrm{CH_3CO_2^-}} + \lambda_{\mathrm{K^+}}) \\ &= \Lambda^\circ_{\mathrm{Mg(CH_3CO_2)_2}} + 2\Lambda^\circ_{\mathrm{KF}} - 2\Lambda^\circ_{\mathrm{KCH_3CO_2}} \\ &= [18.78 + 2(12.89) - 2(11.44)]\,\mathrm{mS\,m^2\,mol^{-1}} = \boxed{21.68\,\mathrm{mS\,m^2\,mol^{-1}}} \end{aligned}$$

E16B.3(b) The ion molar conductivity λ is given in terms of the mobility u by [16B.10–*703*], $\lambda = zuF$, where z is the charge number of the ion (unsigned) and F is Faraday's constant; it follows that $u = \lambda/zF$. Note that $1\ \mathrm{S} = 1\ \mathrm{C\,V^{-1}\,s^{-1}}$.

$$u_{\mathrm{F^-}} = \frac{5.54\ \mathrm{mS\,m^2\,mol^{-1}}}{(1)(96485\ \mathrm{C\,mol^{-1}})} = 5.74\times10^{-5}\ \mathrm{mS\,m^2\,C^{-1}} = \boxed{5.74\times10^{-8}\ \mathrm{m^2\,V^{-1}\,s^{-1}}}$$

$$u_{\mathrm{Cl^-}} = \frac{7.635\ \mathrm{mS\,m^2\,mol^{-1}}}{(1)(96485\ \mathrm{C\,mol^{-1}})} = 7.913\times10^{-5}\ \mathrm{mS\,m^2\,C^{-1}} = \boxed{7.91\times10^{-8}\ \mathrm{m^2\,V^{-1}\,s^{-1}}}$$

$$u_{\mathrm{Br^-}} = \frac{7.81\ \mathrm{mS\,m^2\,mol^{-1}}}{(1)(96485\ \mathrm{C\,mol^{-1}})} = 8.09\times10^{-5}\ \mathrm{mS\,m^2\,C^{-1}} = \boxed{8.09\times10^{-8}\ \mathrm{m^2\,V^{-1}\,s^{-1}}}$$

E16B.4(b) The ion molar conductivity λ is given in terms of the mobility u by [16B.10–*703*], $\lambda = zuF$, where z is the charge number of the ion (unsigned) and F is Faraday's constant. Note that $1\ \mathrm{S} = 1\ \mathrm{C\,V^{-1}\,s^{-1}}$.

$$\lambda = zuF = (1)\times(4.24\times10^{-8}\ \mathrm{m^2\,V^{-1}\,s^{-1}})\times(96485\ \mathrm{C\,mol^{-1}}) = \boxed{4.09\ \mathrm{mS\,m^2\,C^{-1}}}$$

E16B.5(b) The drift speed s of an ion is given by [16B.8b–*702*], $s = u\mathcal{E}$, where $\mathcal{E}$ is the electric field strength. This field strength is given by $\mathcal{E} = \Delta\phi/l$ where $\Delta\phi$ is the potential difference between two electrodes separated by distance l.

$$\begin{aligned} s = u\mathcal{E} = u\frac{\Delta\phi}{l} &= (4.01\times10^{-8}\ \mathrm{m^2\,V^{-1}\,s^{-1}})\times\frac{24.0\ \mathrm{V}}{5.00\times10^{-3}\ \mathrm{m}} \\ &= 1.92\times10^{-4}\ \mathrm{m\,s^{-1}} = \boxed{192\ \mathrm{\mu m\,s^{-1}}} \end{aligned}$$

E16B.6(b) The Einstein relation, [16B.13–*704*], $u = zDF/RT$, gives the relationship between the mobility u, the charge number of the ion z, and the diffusion coefficient D.

$$\begin{aligned} D = \frac{uRT}{zF} &= \frac{(4.24\times10^{-8}\ \mathrm{m^2\,V^{-1}\,s^{-1}})\times(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(298\ \mathrm{K})}{(1)\times(96485\ \mathrm{C\,mol^{-1}})} \\ &= \boxed{1.09\times10^{-9}\ \mathrm{m^2\,s^{-1}}} \end{aligned}$$

Solutions to problems

P16B.2 To fit the data to the expression $\eta = \text{const.}\times e^{E_a/R\theta}$, the natural logarithm is first taken and then the base changed to common logarithms using $\ln x = \log x \times \ln 10$

$$\ln\eta = \ln\text{const.} + \frac{E_a}{RT} \quad \text{hence} \quad \log\eta = \text{const.} + \frac{E_a}{RT\ln 10}$$

The log of the ratio η/η^*, where η^* is the viscosity at temperature T^*, is therefore

$$\log\eta/\eta^* = \log\eta - \log\eta^* = \frac{E_a}{R\ln 10}\left(\frac{1}{T} - \frac{1}{T^*}\right) \qquad (16.2)$$

This expression is compared with that in the question by taking $T^* = (20 + 273) = 293$ K and rewriting the relationship as

$$\log \eta/\eta_{20} = \frac{1.3272[20 - (T/\mathrm{K} - 273)] - 0.001053[20 - (T/\mathrm{K} - 273)]^2}{(T/\mathrm{K} - 273) + 105}$$

where $\theta/°\mathrm{C} = (T/\mathrm{K} - 273)$ is used. One approach is to generate values of $\log \eta/\eta_{20}$ in the range 20 °C to 100 °C and then plot these data against $1/T$; according to eqn 16.2 the slope of such a graph is $E_\mathrm{a}/R \ln 10$. Such a plot is shown in Fig. 16.1.

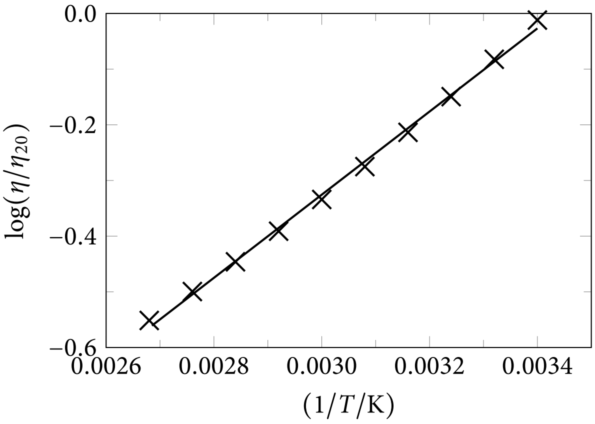


Figure 16.1

The data are a modest fit to a straight line with equation

$$\log(\eta/\eta_{20}) = (7.4667 \times 10^2) \times 1/(T/\mathrm{K}) - 2.5655$$

The activation energy is computed from the slope as

$$\begin{aligned} E_\mathrm{a} &= R \ln 10 \times (\text{slope}) \\ &= (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (\ln 10) \times (7.4667 \times 10^2\ \mathrm{K}) = \boxed{14.3\ \mathrm{kJ\,mol^{-1}}} \end{aligned}$$

P16B.4 The conductance G is the reciprocal of the resistance R, $G = 1/R$. The conductivity of the solution in the cell depends on the measured conductance and the physical dimensions of the cell. However, because in these measurements the same cell is being used, it follows that the conductivity of the solution is given by $\kappa = A/R$, where A is a constant. If the resistance of two solutions are measured in the cell the ratio of the measured resistances is the inverse of the ratio of their conductivities: $R_1/R_2 = \kappa_2/\kappa_1$.

Both solutions are aqueous and hence their conductivities consist of contributions from the water component and acid component. Therefore

$$\frac{\kappa(\text{acid solution})}{\kappa(\text{KCl solution})} = \frac{\kappa(\text{acid}) + \kappa(\text{water})}{\kappa(\text{KCl}) + \kappa(\text{water})} = \frac{R(\text{KCl solution})}{R(\text{acid solution})}$$

Hence

$$\begin{aligned}\kappa(\text{acid}) &= \frac{R(\text{KCl solution})}{R(\text{acid solution})} \times [\kappa(\text{KCl}) + \kappa(\text{water})] - \kappa(\text{water}) \\ &= \frac{33.21\ \Omega}{300.0\ \Omega} \times [(1.1639 + 0.076)\ \text{S m}^{-1}] - (0.076\ \text{S m}^{-1}) \\ &= 61.2...\ \text{mS m}^{-1}\end{aligned}$$

The molar conductivity, Λ_m is defined by equation [16B.4–*700*], $\Lambda_\text{m} = \kappa/c$, where κ is conductivity and c is concentration. Thus for 0.100 mol dm^{-3} ethanoic acid,

$$\begin{aligned}\Lambda_\text{m} &= \frac{\kappa(\text{acid})}{c} = \frac{61.2...\ \text{mS m}^{-1}}{0.100\ \text{mol dm}^{-3}} = \frac{61.2... \times 10^{-3}\ \text{S m}^{-1}}{0.100 \times 10^3\ \text{mol m}^{-3}} \\ &= 0.613\ \text{mS m}^2\ \text{mol}^{-1} = \boxed{6.13\ \text{S cm}^2\ \text{mol}^{-1}}\end{aligned}$$

P16B.6 (a) & (b) The drift speed s of an ion is given by [16B.8b–*702*], $s = u\mathcal{E}$. The electric field strength $\mathcal{E}$ is given by $\mathcal{E} = \Delta\phi/l$ where $\Delta\phi$ is the potential difference between two electrodes separated by distance l. Hence $s = u\mathcal{E} = u\Delta\phi/l$, and the time taken to travel distance l is $t = l/s$.

$$\begin{aligned}\text{For Li}^+ \quad s &= (4.01 \times 10^{-8}\ \text{m}^2\ \text{V}^{-1}\ \text{s}^{-1}) \times \frac{100\ \text{V}}{5.00 \times 10^{-2}\ \text{m}} = \boxed{80.2\ \mu\text{m s}^{-1}} \\ t &= \frac{l}{s} = \frac{5.00 \times 10^{-2}\ \text{m}}{80.2 \times 10^{-6}\ \text{m s}^{-1}} = \boxed{623\ \text{s}} \\ \text{For Na}^+ \quad s &= (5.19 \times 10^{-8}\ \text{m}^2\ \text{V}^{-1}\ \text{s}^{-1}) \times \frac{100\ \text{V}}{5.00 \times 10^{-2}\ \text{m}} = \boxed{104\ \mu\text{m s}^{-1}} \\ t &= \frac{l}{s} = \frac{5.00 \times 10^{-2}\ \text{m}}{104 \times 10^{-6}\ \text{m s}^{-1}} = \boxed{481\ \text{s}} \\ \text{For K}^+ \quad s &= (7.62 \times 10^{-8}\ \text{m}^2\ \text{V}^{-1}\ \text{s}^{-1}) \times \frac{100\ \text{V}}{5.00 \times 10^{-2}\ \text{m}} = \boxed{152\ \mu\text{m s}^{-1}} \\ t &= \frac{l}{s} = \frac{5.00 \times 10^{-2}\ \text{m}}{152 \times 10^{-6}\ \text{m s}^{-1}} = \boxed{329\ \text{s}}\end{aligned}$$

(a) An alternating potential difference with frequency $\nu = 2.0$ kHz requires time $t_{1/2} = 1/2\nu$ to complete a half-cycle. The electric field strength is given by $\mathcal{E} = \mathcal{E}_0 \sin(2\pi\nu t)$ where $\mathcal{E}_0 = (100\ \text{V})/(0.05\ \text{m}) = 2.00 \times 10^3\ \text{V m}^{-1}$

The instantaneous displacement is given by $s\,\text{d}t$, so the net displacement d is found by integrating this over a half cycle with $s = u\mathcal{E}_0 \sin(2\pi\nu t)$; the solvent diameter is taken at 0.3 nm.

$$d = \int_0^{1/2\nu} u\mathcal{E}_0 \sin(2\pi\nu t)\,\mathrm{d}t = \frac{u\mathcal{E}_0}{\pi\nu}$$

$$d(\mathrm{Li}^+) = \frac{(4.01\times10^{-8}\ \mathrm{m^2\,V^{-1}\,s^{-1}})\times(2.00\times10^3\ \mathrm{V\,m^{-1}})}{\pi\times(2\times10^3\ \mathrm{s^{-1}})} = \boxed{12.8\ \mathrm{nm}}$$

$$= \boxed{43}\ \text{solvent diameters}$$

$$d(\mathrm{Na}^+) = \frac{(5.19\times10^{-8}\ \mathrm{m^2\,V^{-1}\,s^{-1}})\times(2.00\times10^3\ \mathrm{V\,m^{-1}})}{\pi\times(2\times10^3\ \mathrm{s^{-1}})} = \boxed{16.5\ \mathrm{nm}}$$

$$= \boxed{55}\ \text{solvent diameters}$$

$$d(\mathrm{K}^+) = \frac{(7.62\times10^{-8}\ \mathrm{m^2\,V^{-1}\,s^{-1}})\times(2.00\times10^3\ \mathrm{V\,m^{-1}})}{\pi\times(2\times10^3\ \mathrm{s^{-1}})} = \boxed{24.3\ \mathrm{nm}}$$

$$= \boxed{81}\ \text{solvent diameters}$$

P16B.8 A spherical particle of radius a and charge ze travelling at a constant speed through a solvent of viscosity η has mobility u given by [16B.9–*702*], $u = ze/f$, where f is the frictional coefficient with Stokes' law value $f = 6\pi\eta a$. It follows that $a = ze/6\pi\eta u$. The mobility is related to the diffusion coefficient D by the Einstein relation, [16B.13–*704*], $u = zDF/RT$, hence $D = uRT/zF$. The viscosity of water is $0.891\times10^{-3}\ \mathrm{kg\,m^{-1}\,s^{-1}}$.

$$a/\mathrm{pm} = \frac{ze}{6\pi\eta u} = \frac{(1)\times(1.6022\times10^{-19}\ \mathrm{C})\times10^{12}}{6\pi\times(0.891\times10^{-3}\ \mathrm{kg\,m^{-1}\,s^{-1}})\times(u/\mathrm{m^2\,V^{-1}\,s^{-1}})}$$

$$= \frac{9.53...\times10^{-6}}{(u/\mathrm{m^2\,V^{-1}\,s^{-1}})}$$

$$D/\mathrm{m^2\,s^{-1}} = \frac{uRT}{zF} = \frac{(u/\mathrm{m^2\,V^{-1}\,s^{-1}})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\ \mathrm{K})}{(1)\times(96485\,\mathrm{C\,mol^{-1}})}$$

$$= (2.56...\times10^{-2})\times(u/\mathrm{m^2\,V^{-1}\,s^{-1}})$$

	Li^+	Na^+	K^+	Rb^+
$u/(10^{-8}\ \mathrm{m^2\,V^{-1}\,s^{-1}})$	4.01	5.19	7.62	7.92
$D/(10^{-9}\ \mathrm{m^2\,s^{-1}})$	1.03	1.33	1.96	2.03
a/pm	238	184	125	120
ionic radius, r_+/pm	59	102	138	149

As commented on in the text, although a 'free' Li^+ is much smaller than a free Na^+ ion the hydrodynamic radius of Li^+ is greater than that of Na^+ on account of the more intense electric field generated by the smaller ion resulting in more solvent molecules be attracted. The number of water molecules being dragged along with an ion is estimated as

$$N_\mathrm{w} = \frac{\text{volume of the solvated ion} - \text{volume of the free ion}}{\text{volume of one water molecule}} = \frac{a^3 - r_+^3}{r_\mathrm{w}^3}$$

The volumes are given by $\frac{4}{3}\pi r^3$ with the relevant radius: a is the hydrodynamic radius, r_+ is the radius of the ion, and r_w is the radius of a water molecule, taken to be 150 pm.

$$N_\text{w}(\text{Li}^+) = \frac{238^3 - 59^3}{150^3} = 3.9 = \boxed{4}$$

$$N_\text{w}(\text{Na}^+) = \frac{184^3 - 102^3}{150^3} = 1.5 = \boxed{1 \text{ to } 2}$$

16C Diffusion

Answers to discussion questions

D16C.2 See the text following [16C.6–*709*].

Solutions to exercises

E16C.1(b) The root mean square displacement in three dimensions is given by [16C.13b–*712*], $\langle r^2\rangle^{1/2} = (6Dt)^{1/2}$, where D is the diffusion coefficient and t is the time period.

$$t = \frac{\langle r^2\rangle}{6D} = \frac{(1.0\times10^{-2}\ \text{m})^2}{6\times(2.26\times10^{-9}\ \text{m}^2\,\text{s}^{-1})} = \boxed{7.4\times10^3\ \text{s}}$$

E16C.2(b) The diffusion in one dimension from a layer of solute is described by [16C.10–*710*]

$$c(x,t) = \frac{n_0}{A(\pi Dt)^{1/2}}\text{e}^{-x^2/4Dt}$$

where $c(x,t)$ is the concentration at time t and distance x from the layer, and n_0 is the amount in moles in the layer of area A placed at $x = 0$. If the mass of I_2 is m, then $n_0 = m/M$, where M is the molar mass (253.8 g mol^{-1}).

$$c(x,t) = \frac{m}{MA(\pi Dt)^{1/2}}\text{e}^{-x^2/4Dt}$$

$$\begin{aligned}
c(5.0\ \text{cm},t) &= \frac{(0.01\ \text{kg})\times\text{e}^{-(5.0\times10^{-2}\ \text{m})^2/4\times(4.05\times10^{-9}\ \text{m}^2\,\text{s}^{-1})t}}{(253.8\ \text{g mol}^{-1})\times(10.0\times10^{-4}\ \text{m}^2)\times[\pi(4.05\times10^{-9}\ \text{m}^2\,\text{s}^{-1})t]^{1/2}}\\
&= [(3.49...\times10^2\ \text{mol dm}^{-3})\times(t/\text{s})^{-1/2}]\text{e}^{-1.54...\times10^5/(t/\text{s})}\\
c(5.0\ \text{cm},10\ \text{s}) &= (3.49...\times10^2\ \text{mol dm}^{-3})\times(10)^{-1/2}\times\text{e}^{-1.54...\times10^5/(10)}\\
&= \boxed{0.00\ \text{mol dm}^{-3}}\\
c(5.0\ \text{cm},24\ \text{h}) &= (3.49...\times10^2\ \text{mol dm}^{-3})[24(3600)]^{-1/2}\times\text{e}^{-1.54...\times10^5/[24(3600)]}\\
&= \boxed{0.199\ \text{mol dm}^{-3}}
\end{aligned}$$

Diffusion is a very slow process: after 10 s the concentration at a height of 10 cm is zero to within the precision of the calculation.

E16C.3(b) The thermodynamic force $\mathcal{F}$ is given by [16C.3b–*706*]

$$\mathcal{F} = -\frac{RT}{c}\left(\frac{\partial c}{\partial x}\right)_{T,p}$$

Substituting $c(x) = c_0 - \beta c_0 x^2$ into the above expression gives

$$\mathcal{F} = -\frac{RT}{c_0 - \beta c_0 x^2}(-2\beta c_0 x) = \frac{2\beta x RT}{1 - \beta x^2}$$

The constant α is found by noting that $c = c_0/2$ at $x = 20$ cm $= 0.20$ m. Hence $c_0/2 = c_0 - \beta c_0 \times (0.20\ \mathrm{m})^2$ and therefore $\beta = 12.5\ \mathrm{m^{-2}}$.

At $T = 298$ K and $x = 8$ cm the force is

$$\begin{aligned}\mathcal{F} &= \frac{2 \times (12.5\ \mathrm{m^{-2}}) \times (8 \times 10^{-2}\ \mathrm{m}) \times (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\ \mathrm{K})}{1 - (12.5\ \mathrm{m^{-2}}) \times (8 \times 10^{-2}\ \mathrm{m})^2} \\ &= \boxed{5.4\ \mathrm{kN\,mol^{-1}}}\end{aligned}$$

A similar calculation at $x = 16$ cm gives $\mathcal{F} = \boxed{7.3\ \mathrm{kN\,mol^{-1}}}$.

E16C.4(b) The thermodynamic force $\mathcal{F}$ is given by [16C.3b–*706*]

$$\mathcal{F} = -\frac{RT}{c}\left(\frac{\partial c}{\partial x}\right)_{T,p}$$

Substituting $c(x) = c_0 e^{-\alpha x^2}$ into the above expression gives

$$\mathcal{F} = -\frac{RT}{c_0 e^{-\alpha x^2}}(-2\alpha c_0 x e^{-\alpha x^2}) = 2\alpha x RT$$

The constant α is found by noting that $c = c_0/2$ at $x = 10$ cm $= 0.10$ m. Hence $c_0/2 = c_0 e^{-\alpha(0.10\ \mathrm{m})^2}$ and therefore $\alpha = \ln 2/(0.10\ \mathrm{m})^2 = 69.3\ \mathrm{m^{-2}}$

The thermodynamic force at $T = 291$ K and $x = 10.0$ cm is

$$\mathcal{F} = 2(69.3\ \mathrm{m^{-2}}) \times (0.10\ \mathrm{m}) \times (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (291\ \mathrm{K}) = \boxed{33.5\ \mathrm{kN\,mol^{-1}}}$$

E16C.5(b) The root mean square displacement in three dimensions is given by [16C.13b–*712*], $\langle r^2 \rangle^{1/2} = (6Dt)^{1/2}$, where D is the diffusion coefficient and t is the time period. Hence,

$$t = \frac{\langle r^2 \rangle}{6D} = \frac{(1.0 \times 10^{-2}\ \mathrm{m})^2}{6 \times (4.05 \times 10^{-9}\ \mathrm{m^2\,s^{-1}})} = \boxed{4.1 \times 10^3\ \mathrm{s}}$$

E16C.6(b) The Stokes–Einstein equation [16C.4b–*708*], $D = kT/6\pi\eta a$, relates the diffusion coefficient D to the viscosity η and the radius a of the diffusing particle, which is modelled as a sphere. Recall that 1 cP $= 10^{-3}\ \mathrm{kg\,m^{-1}\,s^{-1}}$.

$$a = \frac{kT}{6\pi\eta D} = \frac{(1.3806 \times 10^{-23}\ \mathrm{J\,K^{-1}}) \times (298\ \mathrm{K})}{6\pi \times (1.00 \times 10^{-3}\ \mathrm{kg\,m^{-1}\,s^{-1}}) \times (1.055 \times 10^{-9}\ \mathrm{m^2\,s^{-1}})} = \boxed{0.207\ \mathrm{nm}}$$

E16C.7(b) The Einstein–Smoluchowski equation [16C.15–*713*], $D = d^2/2\tau$, relates the diffusion coefficient D to the jump distance d and time τ required for a jump. Approximating the jump length as the molecular diameter, then $d \approx 2a$ where a is the effective molecular radius. This is estimated using the Stokes–Einstein equation [16C.4b–*708*], $D = kT/6\pi\eta a$, to give $2a = 2kT/6\pi\eta D$.

Combining these expressions and using the value $\eta = 0.386 \times 10^{-3}\ \mathrm{kg\,m^{-1}\,s^{-1}}$ for the viscosity of heptane gives

$$\begin{aligned}\tau &= \frac{d^2}{2D} = \frac{1}{2D}\left(\frac{2kT}{6\pi\eta D}\right)^2 = \frac{1}{18D^3}\left(\frac{kT}{\pi\eta}\right)^2 \\ &= \frac{1}{18 \times (3.17 \times 10^{-9}\ \mathrm{m^2\,s^{-1}})^3}\left(\frac{(1.3806 \times 10^{-23}\ \mathrm{J\,K^{-1}}) \times (298\ \mathrm{K})}{\pi \times (0.386 \times 10^{-3}\ \mathrm{kg\,m^{-1}\,s^{-1}})}\right)^2 \\ &= 2.01 \times 10^{-11}\ \mathrm{s} = \boxed{20.1\ \mathrm{ps}}\end{aligned}$$

E16C.8(b) The root mean square displacement in three dimensions is given by equation [16C.13b–*712*], $\langle r^2\rangle^{1/2} = (6Dt)^{1/2}$, where D is the diffusion coefficient and t is the time period. Therefore $t = \langle r^2\rangle/6D$.

For an iodine molecule in benzene, $D = 2.13 \times 10^{-9}\ \mathrm{m^2\,s^{-1}}$

$$t(1.0\ \mathrm{mm}) = \frac{\langle r^2\rangle}{6D} = \frac{(1.0 \times 10^{-3}\ \mathrm{m})^2}{6 \times (2.13 \times 10^{-9}\ \mathrm{m^2\,s^{-1}})} = \boxed{78\ \mathrm{s}}$$

$$t(1.0\ \mathrm{cm}) = \frac{\langle r^2\rangle}{6D} = \frac{(1.0 \times 10^{-2}\ \mathrm{m})^2}{6 \times (2.13 \times 10^{-9}\ \mathrm{m^2\,s^{-1}})} = 7.8 \times 10^3\ \mathrm{s} = \boxed{2.2\ \mathrm{h}}$$

For a sucrose molecule in water, $D = 0.5216 \times 10^{-9}\ \mathrm{m^2\,s^{-1}}$

$$t(1.0\ \mathrm{mm}) = \frac{\langle r^2\rangle}{6D} = \frac{(1.0 \times 10^{-3}\ \mathrm{m})^2}{6 \times (0.5216 \times 10^{-9}\ \mathrm{m^2\,s^{-1}})} = \boxed{320\ \mathrm{s}}$$

$$t(1.0\ \mathrm{cm}) = \frac{\langle r^2\rangle}{6D} = \frac{(1.0 \times 10^{-2}\ \mathrm{m})^2}{6 \times (0.5216 \times 10^{-9}\ \mathrm{m^2\,s^{-1}})} = 3.2 \times 10^4\ \mathrm{s} = \boxed{8.9\ \mathrm{h}}$$

Solutions to problems

P16C.2 The thermodynamic force $\mathcal{F}$ is given by [16C.3b–*706*]

$$\mathcal{F} = -\frac{RT}{c}\left(\frac{\partial c}{\partial x}\right)_{T,p}$$

Substituting $c(x) = c_0\mathrm{e}^{-ax^2}$ into the above expression gives

$$\mathcal{F} = -\frac{RT}{c_0\mathrm{e}^{-ax^2}}(-2ac_0x\mathrm{e}^{-ax^2}) = 2axRT$$

Hence for $a = 0.10\ \text{cm}^{-2} = 0.10 \times 10^4\ \text{m}^{-2}$,

$$\begin{aligned}\mathcal{F} &= 2 \times (0.10 \times 10^4\ \text{m}^{-2}) \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K}) \times (x/\ \text{m}) \\ &= (4.95... \times 10^6\ \text{N mol}^{-1}) \times (x/\ \text{m}) \\ &= \boxed{(5.0\ \text{MN mol}^{-1}) \times (x/\ \text{m})} \\ &= \boxed{(8.2 \times 10^{-18}\ \text{N molecule}^{-1}) \times (x/\ \text{m})}\end{aligned}$$

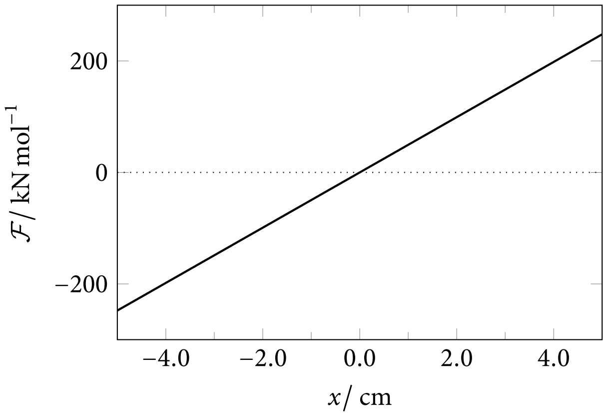


Figure 16.2

A plot of the thermodynamic force per mole against x is shown in Fig. 16.2. It demonstrates that the force is directed such that mass is pushed by the thermodynamic force toward the ends of the tube, down the concentration gradient. A negative force pushes mass toward the left ($x < 0$) and a positive force pushes mass toward the right ($x > 0$).

P16C.4 The concentration c of diffused solute at radius r is give by [16C.11–*711*]. In that equation n_0 is the total amount of solute present, and this can be expressed as $n_0 = m/M$ where m is the mass of solute and M is the molar mass, to give

$$c(r,t) = \frac{n_0 \text{e}^{-r^2/4Dt}}{8(\pi Dt)^{3/2}} = \frac{m\text{e}^{r^2/4Dt}}{8M(\pi Dt)^{3/2}}$$

$$\begin{aligned}c(10\ \text{cm}, t) &= \frac{(10.0\ \text{g}) \times (10^{-3}) \times \text{e}^{-(10\times10^{-2}\ \text{m})^2/[4t\times(5.22\times10^{-10}\ \text{m}^2\ \text{s}^{-1})]}}{8 \times (342.30\ \text{g mol}^{-1}) \times (\pi(5.22 \times 10^{-10}\ \text{m}^2\ \text{s}^{-1})t)^{3/2}} \\ &= (5.49... \times 10^7\ \text{mol dm}^{-3}) \times (t/\text{s})^{-3/2} \times \text{e}^{-4.78...\times10^6/(t/\text{s})} \\ c(10\ \text{cm}, 1.0\ \text{h}) &= (5.49... \times 10^7\ \text{mol dm}^{-3}) \times (3600)^{-3/2} \times \text{e}^{-4.78...\times10^6/3600} \\ &= \boxed{0.00\ \text{mol dm}^{-3}} \\ c(10\ \text{cm}, 1.0\ \text{wk}) &= (5.49... \times 10^7)(6.048 \times 10^5\ \text{s})^{-3/2} \times \text{e}^{-4.78...\times10^6/(6.048\times10^5\ \text{s})} \\ &= \boxed{4.25 \times 10^{-5}\ \text{mol dm}^{-3}}\end{aligned}$$

The process is very slow; even after 1 hour the concentration at a radius of 10 cm is zero to within the precision of the calculation.

P16C.6 (a) The generalised diffusion equation is given by [16C.9–*710*], where c is concentration, t is time, D is the diffusion coefficient, x is displacement and v is the velocity of convective flow.

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x}$$

An expression for $c(x,t)$ is a solution of the diffusion equation if substitution of the expression for $c(x,t)$ into each side of the diffusion equation gives the same result. The proposed solution is

$$c(x,t) = \frac{c_0}{(4\pi Dt)^{1/2}}\mathrm{e}^{-(x-x_0-vt)^2/4Dt}$$

LHS

$$\frac{\partial c}{\partial t} = c(x,t)\left[-\frac{1}{2t} + \frac{(x-x_0)^2}{4Dt^2} - \frac{v^2}{4D}\right]$$

RHS

$$\begin{aligned}
D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} &= D\frac{\partial}{\partial x}\left[\frac{-(x-x_0-vt)}{2Dt}c(x,t)\right] - v\left[\frac{-(x-x_0-vt)}{2Dt}c(x,t)\right]\\
&= D\left[\frac{(x-x_0-vt)^2-2Dt}{(2Dt)^2}c(x,t)\right] + v\left[\frac{(x-x_0-vt)}{2Dt}c(x,t)\right]\\
&= c(x,t)\left[\frac{(x-x_0-vt)^2}{4Dt^2} - \frac{1}{2t} + \frac{v}{2Dt}(x-x_0-vt)\right]\\
&= c(x,t)\left[-\frac{1}{2t} + \frac{(x-x_0)^2}{4Dt^2} - \frac{v^2}{4D}\right]
\end{aligned}$$

The LHS is equal to the RHS, and so the proposed function is indeed a solution to the generalised diffusion equation.

As $t \to 0$ the exponential term $\mathrm{e}^{-x^2/4Dt}$ falls off more and more rapidly, implying that in the limit $t = 0$ all the material is at $x = 0$. The exponential function dominates the term $t^{1/2}$ in the denominator.

(b) Using the values $D = 5\times10^{-10}\ \mathrm{m^2\,s^{-1}}$ and $v = 10^{-6}\ \mathrm{m\,s^{-1}}$, Fig. 16.3 shows the concentration profile against time at different distances $(x - x_0) =$ 0.5 mm, 1.0 mm, 5.0 mm. As expected, the initial concentration at a given distance is zero. As time passes, the concentration begins to increase to a maximum value when $(x - x_0 = vt)$ and then, as diffusion continues in the x-direction, the concentration begins to decrease toward zero at longer times. The value of $c(x,t)/c_0$ reaches its maximum value at longer times as the value of $(x-x_0)$ is increased since it takes longer for the solute to reach distance $(x - x_0)$.

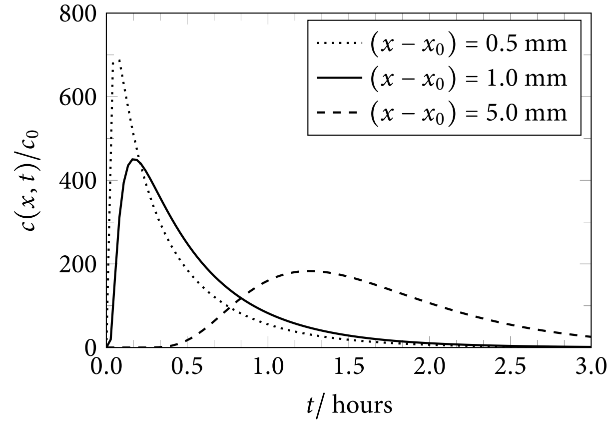


Figure 16.3

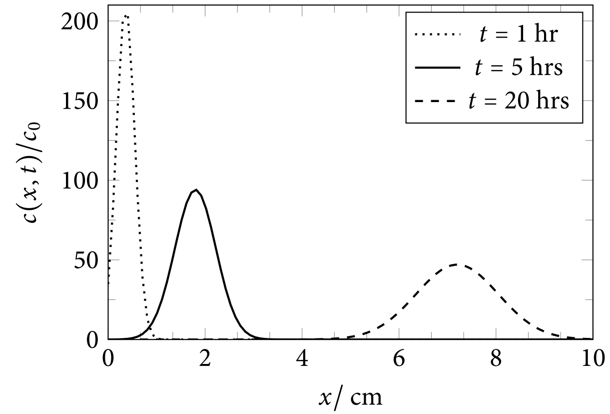


Figure 16.4

Setting $x_0 = 0$, Fig. 16.4 shows the concentration profile against distance x at different 1 hour, 5 hours and 20 hours. The shorter the time, the closer the maximum is to the origin; for longer times, the maximum moves out to larger distances as a result of the convective flow. In addition, as time proceeds diffusion occurs and this causes the bell-shaped curves to widen and spread. Because the amount of material is conserved, the area under each curve must be the same: this is why their maximum amplitude decreases as they spread out.

(c) Defining $x_c = x_0 + vt$ and $z = (x - x_c)/(4D)^{1/2}$ allows a general set of concentration profiles at different times to be plotted without specifying either x_0, v or D.

$$c(x,t) = \frac{c_0 e^{-(x-x_0-vt)^2/4Dt}}{(4\pi Dt)^{1/2}} = \frac{c_0 e^{-(x-x_c)^2/4Dt}}{(4\pi D)^{1/2}\, t^{1/2}} = \frac{c_0 e^{-z^2/t}}{(4\pi D)^{1/2}\, t^{1/2}}$$

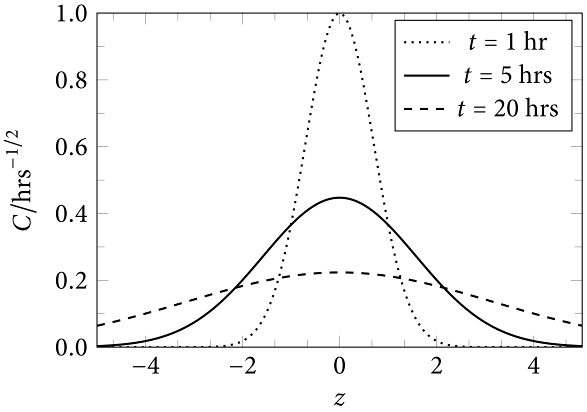


Figure 16.5

Hence

$$C(z,t) = \frac{(4\pi D)^{1/2} c(x,t)}{c_0} = \frac{1}{t^{1/2}} e^{-z^2/t}$$

as required.

A plot of C as a function of z for times 1, 5, and 20 hours is shown in Fig. 16.5. These long times have been chosen unit because of the slow rate of diffusion.

P16C.8 The probability of being n steps from the origin is $P(nd) = N!/(N-N_R)!N_R!2^N$ where N_R is the number of steps taken to the right and N is the total number of steps. Note that $n = N_R - N_L$ and $N = N_R + N_L$, where N_L is the number of steps taken to the left.

$$N_R = N - N_L = N_L + n \quad \text{hence} \quad N_L = \frac{N-n}{2}$$

$$N_L = N - N_R = N_R - n \quad \text{hence} \quad N_R = \frac{N+n}{2}$$

$$\text{therefore } P(nd) = \frac{N!}{[N - (\frac{N-n}{2})]! \ (\frac{N-n}{2})! \ 2^N} = \frac{N!}{(\frac{N+n}{2})! \ (\frac{N-n}{2})! \ 2^N}$$

The combination $N = 4$ and $n = 6$ is physically impossible, so $P(6d) = \boxed{0}$. The combination $N = 6$ and $n = 6$ has probability

$$P(6d) = \frac{6!}{(\frac{6+6}{2})! \ (\frac{6-6}{2})! \, 2^6} = \boxed{0.0156}$$

The combination $N = 12$ and $n = 6$ has probability

$$P(6d) = \frac{12!}{(\frac{12+6}{2})! \ (\frac{12-6}{2})! \, 2^{12}} = \boxed{0.0537}$$

P16C.10 The root-mean-square-displacement in three dimensions is given by [16C.13b–*712*], $\langle r^2\rangle^{1/2} = (6Dt)^{1/2}$, where t is the time period and D is the diffusion coefficient. It follows that $t = \langle r^2\rangle/6D$

$$t = \frac{\langle r^2\rangle}{6D} = \frac{(1.0\times10^{-6}\ \mathrm{m})^2}{6\times(1.0\times10^{-11}\ \mathrm{m^2\,s^{-1}})} = \boxed{1.7\times10^{-2}\ \mathrm{s}}$$

Answers to integrated activities

I16.2 (a) The diffusion equation is [16C.6–*709*].

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

The proposed solution is

$$c(x,t) = c_0 + (c_s - c_0)[1-\mathrm{erf}(\xi)]$$

where $\xi(x,t) = x/(4Dt)^{1/2}$ and $\mathrm{erf}(\xi) = 2\pi^{-1/2}\int_0^{\xi}\mathrm{e}^{-y^2}\,\mathrm{d}y$. Note that, by definition, $\partial[\mathrm{erf}(\xi)]/\partial\xi = 2\pi^{-1/2}\mathrm{e}^{-\xi^2}$.

The first step is to examine the initial and boundary conditions. At $t = 0$, $\xi(x,0) = \infty$. Hence $\mathrm{erf}(\xi) = 2\pi^{-1/2}\int_0^{\infty}\mathrm{e}^{-y^2}\,\mathrm{d}y = (2\pi^{-1/2})\times(\tfrac{1}{2}\pi^{1/2}) = 1$ and $c(x,0) = c_0 + (c_s - c_0)[1-1] = c_0$ for $0 < x < \infty$. At $x = 0$, $\xi(0,t) = 0$. Hence $\mathrm{erf}(\xi) = 2\pi^{-1/2}\int_0^{0}\mathrm{e}^{-y^2}\,\mathrm{d}y = (2\pi^{-1/2})\times 0 = 0$ and $c(0,t) = c_0 + (c_s - c_0)[1-0] = c_s$ for $0 \le t \le \infty$. Therefore, this expression for $c(x,t)$ satisfies the initial and boundary conditions.

To determine whether or not the proposed solution solves the diffusion equation it is substituted into the each side. For the LHS

$$\frac{\partial c}{\partial t} = \frac{\partial(c_0 + (c_s - c_0)[1-\mathrm{erf}(\xi)])}{\partial t} = -(c_s - c_0)\frac{\partial[\mathrm{erf}(\xi)]}{\partial\xi}\frac{\partial\xi}{\partial t}$$

$$= -(c_s - c_0)(2\pi^{-1/2}\mathrm{e}^{-\xi^2})\frac{\partial[x/(4Dt)^{1/2}]}{\partial t}$$

$$= -(c_s - c_0)(2\pi^{-1/2}\mathrm{e}^{-x^2/4Dt})\left[\frac{x}{(4D)^{1/2}t^{3/2}}\right] = \frac{x(c_s - c_0)}{(4\pi D)^{1/2}t^{3/2}}\mathrm{e}^{x^2/4Dt}$$

For the RHS

$$D\frac{\partial^2 c}{\partial x^2} = D\frac{\partial}{\partial x}\left[-(c_s - c_0)\frac{\partial[\mathrm{erf}(\xi)]}{\partial\xi}\frac{\partial\xi}{\partial x}\right]$$

$$= -\frac{2D(c_s - c_0)}{(4\pi Dt)^{1/2}}\frac{\partial[\mathrm{e}^{-x^2/4Dt}]}{\partial x} = -\frac{2D(c_s - c_0)}{(4\pi Dt)^{1/2}}\left(\frac{-x}{2Dt}\mathrm{e}^{-x^2/4Dt}\right)$$

$$= \frac{x(c_s - c_0)}{(4\pi D)^{1/2}(t)^{3/2}}\mathrm{e}^{x^2/4Dt}$$

Therefore the LHS is equal to the RHS and the proposed form of $c(x,t)$ does indeed satisfy the diffusion equation, as well as the initial and boundary conditions.

(b) Diffusion through aveoli sites (about 1 cell thick) of oxygen and carbon dioxide between lungs and blood capillaries (also about 1 cell thick) occurs through about 75 μm (the diameter of a red blood cell). Thus, the range $0 \le x \le 100$ μm is reasonable for concentration profiles for the diffusion of oxygen into water. Given the maximum distance, the longest time is estimated using [16C.12–*711*].

$$t_{\text{max}} \approx \frac{\pi x_{\text{max}}^2}{4D} = \frac{\pi(0.1\times10^{-3}\ \text{m})^2}{4(2.10\times10^{-9}\ \text{m}^2\,\text{s}^{-1})} = 3.74\ \text{s}$$

The plots shown in Fig. 16.6 are with $c_0 = 0$, $c_s = 2.9\times10^{-4}$ mol dm^{-3}, and $D = 2.10\times10^{-9}$ m^2 s^{-1}.

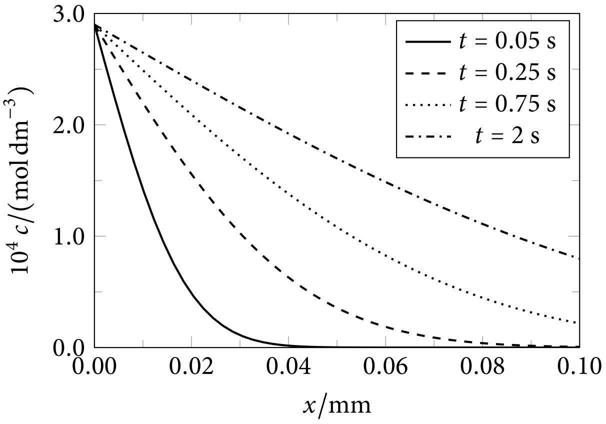


Figure 16.6

17

Chemical kinetics

17A The rates of chemical reactions

Answers to discussion questions

D17A.2 A reaction order for a particular species can only be ascribed when the rate is simply proportional to a power of the concentration of that species. For example, if the rate law is of the form $v = k_r[\mathrm{A}]^a[\mathrm{B}]^b \ldots$ an order is ascribable to both A and B, but if the rate law is of the form $v = (k_1[\mathrm{A}])/(k_2 + k_3[\mathrm{B}])$, an order is ascribable to A, but not to B.

D17A.4 This is discussed in Section 17A.1 on page 723.

Solutions to exercises

E17A.1(b) Assuming perfect gas behaviour the total pressure is proportional to the amount in moles of gas present, provided that the temperature is constant and the volume of the container is fixed. Imagine that a certain amount of N_2 is consumed so that its partial pressure falls by Δp. Due to the stoichiometry of the reaction the partial pressure of H_2 will fall by $3\Delta p$, and the partial pressure of NH_3 will increase by $2\Delta p$. The overall change in the total pressure will by $-\Delta p - 3\Delta p + 2\Delta p = -2\Delta p$.

If the initial pressure is p_0 then, because the reactant gases are in their stoichiometric ratios, the partial pressure of N_2 is $\tfrac{1}{4}p_0$. If a fraction α of the N_2 is consumed, its partial pressure falls to $\tfrac{1}{4}p_0(1-\alpha)$, thus $\Delta p = \tfrac{1}{4}p_0\alpha$. It has already been established that the total pressure changes by $-2\Delta p$, therefore the final pressure is

$$p_\mathrm{f} = p_0 - 2\Delta p = p_0 - 2(\tfrac{1}{4}p_0\alpha) = p_0(1 - \tfrac{1}{2}\alpha)$$

When the reaction is complete, $\alpha = 1$ and hence $p_\mathrm{f} = \tfrac{1}{2}p_0$, which is in accord with the overall stoichiometry of the reaction in which four moles of gas go to two.

E17A.2(b) The stoichiometry of the reaction shows that one mole of CH_3CH_3 is formed for every two moles of CH_3 consumed. The rate of formation of CH_3CH_3 is therefore half the rate of consumption of CH_3. As explained in Section 17A.2(a) on page 725 the rate of consumption of a reactant R is given by $-\mathrm{d}[\mathrm{R}]/\mathrm{d}t$. Therefore the rate of formation of CH_3CH_3 is

$$\frac{\mathrm{d}[\mathrm{CH_3CH_3}]}{\mathrm{d}t} = \tfrac{1}{2}\times -\frac{\mathrm{d}[\mathrm{CH_3}]}{\mathrm{d}t} = \tfrac{1}{2}\times -(-1.2\ \mathrm{mol\,dm^{-3}\,s^{-1}}) = +0.6\ \mathrm{mol\,dm^{-3}\,s^{-1}}$$

E17A.3(b) For a homogeneous reaction in a constant volume system the rate of reaction is given by [17A.3b–*726*], $v = (1/\nu_J)\mathrm{d}[J]/\mathrm{d}t$, which is rearranged to $\mathrm{d}[J]/\mathrm{d}t = \nu_J v$. In these expressions ν_J is the stoichiometric number of species J, which is negative for reactants and positive for products. For this reaction $\nu_A = -1$, $\nu_B = -3$, $\nu_C = +1$ and $\nu_D = +2$.

$$\begin{aligned}
&\text{For A} \quad \mathrm{d}[A]/\mathrm{d}t = \nu_A v = (-1) \times (2.7\ \mathrm{mol\,dm^{-3}\,s^{-1}}) = -2.7\ \mathrm{mol\,dm^{-3}\,s^{-1}}\\
&\text{For B} \quad \mathrm{d}[B]/\mathrm{d}t = \nu_B v = (-3) \times (2.7\ \mathrm{mol\,dm^{-3}\,s^{-1}}) = -8.1\ \mathrm{mol\,dm^{-3}\,s^{-1}}\\
&\text{For C} \quad \mathrm{d}[C]/\mathrm{d}t = \nu_C v = (+1) \times (2.7\ \mathrm{mol\,dm^{-3}\,s^{-1}}) = +2.7\ \mathrm{mol\,dm^{-3}\,s^{-1}}\\
&\text{For D} \quad \mathrm{d}[D]/\mathrm{d}t = \nu_D v = (+2) \times (2.7\ \mathrm{mol\,dm^{-3}\,s^{-1}}) = +5.4\ \mathrm{mol\,dm^{-3}\,s^{-1}}
\end{aligned}$$

The rate of consumption of A is $\boxed{2.7\ \mathrm{mol\,dm^{-3}\,s^{-1}}}$, the rate of consumption of B is $\boxed{8.1\ \mathrm{mol\,dm^{-3}\,s^{-1}}}$, the rate of formation of C is $\boxed{2.7\ \mathrm{mol\,dm^{-3}\,s^{-1}}}$, and the rate of formation of D is $\boxed{5.4\ \mathrm{mol\,dm^{-3}\,s^{-1}}}$.

E17A.4(b) For a homogeneous reaction in a constant volume system the rate of reaction is given by [17A.3b–*726*], $v = (1/\nu_J)\mathrm{d}[J]/\mathrm{d}t$, where ν_J is the stoichiometric number of species J which is negative for reactants and positive for products. For species B, which has $\nu_B = -3$, this gives

$$v = \frac{1}{\nu_B}\frac{\mathrm{d}[B]}{\mathrm{d}t} = \frac{1}{-3} \times (-2.7\ \mathrm{mol\,dm^{-3}\,s^{-1}}) = \boxed{0.90\ \mathrm{mol\,dm^{-3}\,s^{-1}}}$$

Because B is consumed in the reaction, the rate of change in the concentration of B, $\mathrm{d}[B]/\mathrm{d}t$, is negative and equal to minus the rate of consumption of B. Rearranging [17A.3b–*726*] then gives

$$\begin{aligned}
&\text{For A} \quad \mathrm{d}[A]/\mathrm{d}t = \nu_A v = (-1) \times (0.90\ \mathrm{mol\,dm^{-3}\,s^{-1}}) = -0.90\ \mathrm{mol\,dm^{-3}\,s^{-1}}\\
&\text{For B} \quad \mathrm{d}[C]/\mathrm{d}t = \nu_C v = (+1) \times (0.90\ \mathrm{mol\,dm^{-3}\,s^{-1}}) = +0.90\ \mathrm{mol\,dm^{-3}\,s^{-1}}\\
&\text{For D} \quad \mathrm{d}[D]/\mathrm{d}t = \nu_D v = (+2) \times (0.90\ \mathrm{mol\,dm^{-3}\,s^{-1}}) = +1.8\ \mathrm{mol\,dm^{-3}\,s^{-1}}
\end{aligned}$$

The rate of consumption of A is $\boxed{0.90\ \mathrm{mol\,dm^{-3}\,s^{-1}}}$, the rate of formation of C is $\boxed{0.90\ \mathrm{mol\,dm^{-3}\,s^{-1}}}$, and the rate of formation of D is $\boxed{1.8\ \mathrm{mol\,dm^{-3}\,s^{-1}}}$.

E17A.5(b) As explained in Section 17A.2(b) on page 726 the units of k_r are always such as to convert the product of concentrations, each raised to the appropriate power, into a rate expressed as a change in concentration divided by time. In this case the rate is given in $\mathrm{mol\,dm^{-3}\,s^{-1}}$, so if the concentrations are expressed in $\mathrm{mol\,dm^{-3}}$ the units of k_r will be $\boxed{\mathrm{dm^{6}\,mol^{-2}\,s^{-1}}}$ because

$$\overbrace{(\mathrm{dm^{6}\,mol^{-2}\,s^{-1}})}^{k_r} \times \overbrace{(\mathrm{mol\,dm^{-3}})}^{[A]} \times \overbrace{(\mathrm{mol\,dm^{-3}})^{2}}^{[B]^2} = \mathrm{mol\,dm^{-3}\,s^{-1}}$$

The rate of reaction is given by [17A.3b–*726*], $v = (1/\nu_J)(\mathrm{d}[J]/\mathrm{d}t)$, where ν_J is the stoichiometric number of species J. Rearranging gives $\mathrm{d}[J]/\mathrm{d}t = \nu_J v$. In this case $\nu_C = +1$, $\nu_A = -1$, and $v = k_r[A][B]^2$ so

$$\frac{\mathrm{d}[C]}{\mathrm{d}t} = \nu_C v = k_r[A][B]^2 \qquad \frac{\mathrm{d}[A]}{\mathrm{d}t} = \nu_A v = -k_r[A][B]^2$$

The rate of formation of C is therefore $\mathrm{d[C]}/\mathrm{d}t = \boxed{k_r[\mathrm{A}][\mathrm{B}]^2}$ and the rate of consumption of A is $-\mathrm{d[A]}/\mathrm{d}t = \boxed{k_r[\mathrm{A}][\mathrm{B}]^2}$.

E17A.6(b) The rate of reaction is given by [17A.3b–*726*], $v = (1/\nu_J)(\mathrm{d[J]}/\mathrm{d}t)$. In this case $\nu_C = +1$ so

$$v = \frac{1}{\nu_J}\frac{\mathrm{d[C]}}{\mathrm{d}t} = \frac{1}{+1}k_r[\mathrm{A}][\mathrm{B}][\mathrm{C}]^{-1} = \boxed{k_r[\mathrm{A}][\mathrm{B}][\mathrm{C}]^{-1}}$$

As explained in Section 17A.2(b) on page 726 the units of k_r are always such as to convert the product of concentrations, each raised to the appropriate power, into a rate expressed as a change in concentration divided by time. In this case the rate is given in $\mathrm{mol\,dm^{-3}\,s^{-1}}$, so if the concentrations are expressed in $\mathrm{mol\,dm^{-3}}$ the units of k_r will be $\boxed{\mathrm{s^{-1}}}$ because

$$\overbrace{(\mathrm{s^{-1}})}^{k_r} \times \overbrace{(\mathrm{mol\,dm^{-3}})}^{[\mathrm{A}]} \times \overbrace{(\mathrm{mol\,dm^{-3}})}^{[\mathrm{B}]} \times \overbrace{(\mathrm{mol\,dm^{-3}})^{-1}}^{[\mathrm{C}]^{-1}} = \mathrm{mol\,dm^{-3}\,s^{-1}}$$

E17A.7(b) As explained in Section 17A.2(b) on page 726 the units of k_r are always such as to convert the product of concentrations, each raised to the appropriate power, into a rate expressed as a change in concentration divided by time.

(i) A second-order reaction expressed with concentrations in molecules per cubic metre is one with a rate law such as $v = k_r[\mathrm{A}]^2$. If the rate is given in $\mathrm{molecules\,m^{-3}\,s^{-1}}$ then the units of k_r will be $\boxed{\mathrm{m^3\,molecules^{-1}\,s^{-1}}}$ because

$$\overbrace{(\mathrm{m^3\,molecules^{-1}\,s^{-1}})}^{k_r} \times \overbrace{(\mathrm{molecules\,m^{-3}})^2}^{[\mathrm{A}]^2} = \mathrm{molecules\,m^{-3}\,s^{-1}}$$

A third-order reaction expressed with concentrations in molecules per cubic metre is one with a rate law such as $v = k_r[\mathrm{A}]^2[\mathrm{B}]$. The units of k_r will then be $\boxed{\mathrm{m^6\,molecules^{-2}\,s^{-1}}}$ because

$$\overbrace{(\mathrm{m^6\,molecules^{-2}\,s^{-1}})}^{k_r} \times \overbrace{(\mathrm{molecules\,m^{-3}})^2}^{[\mathrm{A}]^2} \times \overbrace{(\mathrm{molecules\,m^{-3}})}^{[\mathrm{B}]}$$
$$= \mathrm{molecules\,m^{-3}\,s^{-1}}$$

(ii) If the rate laws are expressed with pressures in pascals then a second-order reaction is one with a rate law such as $v = k_r p_A p_B$ and a third-order reaction is one with a rate law such as $v = k_r p_A p_B p_C$. If the rate is given in $\mathrm{Pa\,s^{-1}}$ then the units of k_r will be $\boxed{\mathrm{Pa^{-1}\,s^{-1}}}$ and $\boxed{\mathrm{Pa^{-2}\,s^{-1}}}$ respectively.

$$\text{For second-order}\quad \overbrace{(\mathrm{Pa^{-1}\,s^{-1}})}^{k_r} \times \overbrace{(\mathrm{Pa})}^{p_A} \times \overbrace{(\mathrm{Pa})}^{p_B} = \mathrm{Pa\,s^{-1}}$$

$$\text{For third-order}\quad \overbrace{(\mathrm{Pa^{-2}\,s^{-1}})}^{k_r} \times \overbrace{(\mathrm{Pa})}^{p_A} \times \overbrace{(\mathrm{Pa})}^{p_B} \times \overbrace{(\mathrm{Pa})}^{p_C} = \mathrm{Pa\,s^{-1}}$$

E17A.8(b) If $k_a'[A] \gg k_b$, which might occur when the concentration of A is very high, then the term k_b in the denominator of the rate law is negligible compared to the $k_a'[A]$ term and so the rate law becomes

$$v = k_a k_b [A]^2 / k_a'[A] = k_{r,\text{eff}}[A] \quad \text{where } k_{r,\text{eff}} = k_a k_b / k_a'$$

Under these conditions the concentration of A appears raised to the power +1 so the reaction is first order in A.

If instead $k_a'[A] \ll k_b$, which might occur when the concentration of A is very low, the term $k_a'[A]$ is negligible in the denominator and so the rate law becomes

$$v = k_a k_b [A]^2 / k_b = k_a [A]^2$$

Under these conditions the order with respect to A is +2.

In between these two limits, when $k_a'[A]$ and k_b are comparable, no order with respect to A can be defined.

E17A.9(b) The gaseous species is denoted A and the order with respect to A as a. The rate law expressed in terms of partial pressure is then $v = k_r p_A^a$. Taking (common) logarithms gives

$$\log v = \log k_r + \log p_A^a = \log k_r + a \log p_A$$

where the properties of logarithms $\log(xy) = \log x + \log y$ and $\log x^a = a \log x$ are used.

This expression implies that a graph of $\log v$ against $\log p_A$ will be a straight line of slope a, from which the order can be determined. However, because there are only two data points a graph is not necessary so an alternative approach is used.

If the initial partial pressure of the compound is $p_{A,0}$ then the partial pressure when a fraction f has reacted, so that a fraction $1 - f$ remains, is $(1 - f)p_{A,0}$. Data are given for two points, $f_1 = 0.100$ and $f_2 = 0.200$. Denoting the rates at these points by v_1 and v_2 and using the expression $\log v = \log k_r + a \log p_A$ from above gives the equations

$$\log v_1 = \log k_r + a \log[(1 - f_1)p_{A,0}] \qquad \log v_2 = \log k_r + a \log[(1 - f_2)p_{A,0}]$$

Subtracting the second equation from the first gives

$$\log v_1 - \log v_2 = a \log[(1 - f_1)p_{A,0}] - a \log[(1 - f_2)p_{A,0}]$$

Hence

$$\log\left(\frac{v_1}{v_2}\right) = a \log\left(\frac{(1 - f_1)p_{A,0}}{(1 - f_2)p_{A,0}}\right) = a \log\left(\frac{1 - f_1}{1 - f_2}\right)$$

where the property of logarithms $\log x - \log y = \log(x/y)$ is used and the factor of $p_{A,0}$ is cancelled.

Rearranging for a gives

$$a = \frac{\log(v_1/v_2)}{\log[(1 - f_1)/(1 - f_2)]} = \frac{\log[(10.01\ \text{Pa s}^{-1})/(8.90\ \text{Pa s}^{-1})]}{\log[(1 - 0.100)/(1 - 0.200)]} = \boxed{1.00}$$

Solutions to problems

P17A.2 The rate law is assumed to take the form $v_0 = k_r[\mathrm{Y}]^a[\mathrm{complex}]^b$ where v_0 is the initial rate, and a and b are the orders with respect to Y and the complex. Denoting $k_r[\mathrm{Y}]^a$ by $k_{r,\mathrm{eff}}$ gives $v_0 = k_{r,\mathrm{eff}}[\mathrm{complex}]^b$, which on taking logarithms gives

$$\log v_0 = \log k_{r,\mathrm{eff}} + \log[\mathrm{complex}]^b = \log k_{r,\mathrm{eff}} + b\log[\mathrm{complex}]$$

where the properties of logarithms $\log(xy) = \log x + \log y$ and $\log x^a = a\log x$ are used.

This expression implies that a graph of $\log v_0$ against $\log[\mathrm{complex}]$ will be a straight line of slope b and intercept $\log k_{r,\mathrm{eff}}$. The data are plotted in Fig. 17.1 for both initial concentrations of Y

Case (i): $[\mathrm{Y}] = 2.7\times10^{-3}\ \mathrm{mol\,dm^{-3}}$

$[\mathrm{complex}]$ $/\mathrm{mol\,dm^{-3}}$	v_0 $/\mathrm{mol\,dm^{-3}\,s^{-1}}$	$\log([\mathrm{complex}]$ $/\mathrm{mol\,dm^{-3}})$	$\log(v_0$ $/\mathrm{mol\,dm^{-3}\,s^{-1}})$
0.008 01	125	−2.096	2.097
0.009 22	144	−2.035	2.158
0.012 11	190	−1.917	2.279

Case (ii): $[\mathrm{Y}] = 6.1\times10^{-3}\ \mathrm{mol\,dm^{-3}}$

$[\mathrm{complex}]$ $/\mathrm{mol\,dm^{-3}}$	v_0 $/\mathrm{mol\,dm^{-3}\,s^{-1}}$	$\log([\mathrm{complex}]$ $/\mathrm{mol\,dm^{-3}})$	$\log(v_0$ $/\mathrm{mol\,dm^{-3}\,s^{-1}})$
0.008 01	640	−2.096	2.806
0.009 22	730	−2.035	2.863
0.012 11	960	−1.917	2.982

Both sets of data fall on good straight lines, the equations for which are

$$\text{case (i): } \log(v_0/\mathrm{mol\,dm^{-3}\,s^{-1}}) = 1.014\times\log([\mathrm{complex}]/\mathrm{mol\,dm^{-3}}) + 4.222$$
$$\text{case (ii): } \log(v_0/\mathrm{mol\,dm^{-3}\,s^{-1}}) = 0.984\times\log([\mathrm{complex}]/\mathrm{mol\,dm^{-3}}) + 4.868$$

Both lines have a slope of approximately 1, so it is concluded that the order with respect to the complex is $\boxed{1}$. Hence the rate law is $v_0 = k_{r,\mathrm{eff}}[\mathrm{complex}]$.

The intercepts are identified with $\log k_{r,\mathrm{eff}}$ in each case. For case (i), the intercept at $\log([\mathrm{complex}]/\mathrm{mol\,dm^{-3}}) = 0$ is $\log v_0/\mathrm{mol\,dm^{-3}\,s^{-1}} = 4.222$, which on taking the antilogarithm corresponds to $v_0 = 1.66...\times10^4\ \mathrm{mol\,dm^{-3}\,s^{-1}}$ when $[\mathrm{complex}] = 1\ \mathrm{mol\,dm^{-3}}$. Because the rate law has already been established to be $v_0 = k_{r,\mathrm{eff}}[\mathrm{complex}]$, it follows that

$$k_{r,\mathrm{eff,i}} = \frac{v_0}{[\mathrm{complex}]} = \frac{1.66...\times10^4\ \mathrm{mol\,dm^{-3}\,s^{-1}}}{1\ \mathrm{mol\,dm^{-3}}} = 1.66...\times10^4\ \mathrm{s^{-1}}$$

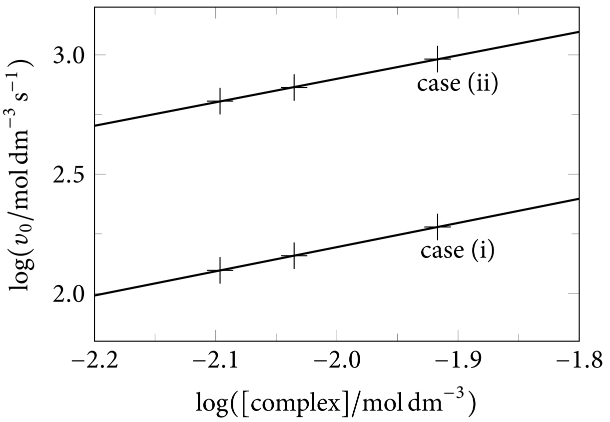


Figure 17.1

Similarly, for case (ii) the intercept is $\log v_0/\mathrm{mol\,dm^{-3}\,s^{-1}} = 4.868$ which corresponds to $v_0 = 7.37... \times 10^4\ \mathrm{mol\,dm^{-3}\,s^{-1}}$ when $[\mathrm{complex}] = 1\ \mathrm{mol\,dm^{-3}}$. Hence

$$k_{\mathrm{r,eff,ii}} = \frac{v_0}{[\mathrm{complex}]} = \frac{7.37... \times 10^4\ \mathrm{mol\,dm^{-3}\,s^{-1}}}{1\ \mathrm{mol\,dm^{-3}}} = 7.37... \times 10^4\ \mathrm{s^{-1}}$$

Because $k_{\mathrm{r,eff}} = k_{\mathrm{r}}[\mathrm{Y}]^b$, taking the logarithm gives

$$\log k_{\mathrm{r,eff}} = \log k_{\mathrm{r}} + \log[\mathrm{Y}]^b = \log k_{\mathrm{r}} + b\log[\mathrm{Y}]$$

where the properties of logarithms $\log(xy) = \log x + \log y$ and $\log x^a = a\log x$ are used.

This expression implies that a graph of $\log k_{\mathrm{r,eff}}$ against $\log[\mathrm{Y}]$ will be a straight line of slope b. However, because there are only two data points, one for $[\mathrm{Y}] = 2.7\ \mathrm{mmol\,dm^{-3}}$ and one for $[\mathrm{Y}] = 6.1\ \mathrm{mmol\,dm^{-3}}$, a graph is not necessary and an alternative approach is used. The two data points give the equations

$$\log k_{\mathrm{r,eff,i}} = \log k_{\mathrm{r}} + b\log[\mathrm{Y}]_{\mathrm{i}} \quad \text{and} \quad \log k_{\mathrm{r,eff,ii}} = \log k_{\mathrm{r}} + b\log[\mathrm{Y}]_{\mathrm{ii}}$$

Subtracting the second equation from the first gives

$$\log k_{\mathrm{r,eff,i}} - \log k_{\mathrm{r,eff,ii}} = b\log[\mathrm{Y}]_{\mathrm{i}} - b\log[\mathrm{Y}]_{\mathrm{ii}}$$

Hence, using $\log x - \log y = \log(x/y)$,

$$\log\left(\frac{k_{\mathrm{r,eff,i}}}{k_{\mathrm{r,eff,ii}}}\right) = b\log\left(\frac{[\mathrm{Y}]_{\mathrm{i}}}{[\mathrm{Y}]_{\mathrm{ii}}}\right)$$

Rearranging for b gives

$$b = \frac{\log(k_{\mathrm{r,eff,i}}/k_{\mathrm{r,eff,ii}})}{\log([\mathrm{Y}]_{\mathrm{i}}/[\mathrm{Y}]_{\mathrm{ii}})} = \frac{\log\left[(1.66... \times 10^4\ \mathrm{s^{-1}})/(7.37... \times 10^4\ \mathrm{s^{-1}})\right]}{\log\left[(2.7\ \mathrm{mmol\,dm^{-3}})/(6.1\ \mathrm{mmol\,dm^{-3}})\right]} = 1.83\ldots$$

This value is moderately close to 2, implying that the reaction is $\boxed{\text{second-order}}$ with respect to Y.

The value of k_r is found using $k_{r,\text{eff}} = k_r[\text{Y}]^b$ with the value of b just found. Taking $b = 2$ and rearranging gives $k_r = k_{r,\text{eff}}/[\text{Y}]^2$.

$$\text{For case (i)}\quad k_r = \frac{1.66... \times 10^4\ \text{s}^{-1}}{(2.7 \times 10^{-3}\ \text{mol dm}^{-3})^2} = 2.28... \times 10^9\ \text{dm}^6\ \text{mol}^{-2}\ \text{s}^{-1}$$

$$\text{For case (ii)}\quad k_r = \frac{7.37... \times 10^4\ \text{s}^{-1}}{(6.1 \times 10^{-3}\ \text{mol dm}^{-3})^2} = 1.98... \times 10^9\ \text{dm}^6\ \text{mol}^{-2}\ \text{s}^{-1}$$

The average value of k_r from these two results is $\boxed{2.1 \times 10^9\ \text{dm}^6\ \text{mol}^{-2}\ \text{s}^{-1}}$.

17B Integrated rate laws

Answers to discussion questions

D17B.2 In general the rate of a reaction depends on the concentration of the various species involved. If all but one of the species is placed in large excess, such that their concentrations do not vary with time, the rate law may reduce to the simple form $v = k_r'[\text{A}]^a$, where A is the species not in excess. If this is the case, the power a is the order with respect to A: if $a = 1$ the reaction is said to be pseudofirst order with respect to A, if $a = 2$ it is pseudosecond order. It is also possible that under certain conditions a more complex rate law will simplify to pseudofirst or pseudosecond order. For example if the rate law is of the form $v = (k_1[\text{A}]^2)/(k_2+k_3[\text{A}])$, when $k_3[\text{A}] \gg k_2$ the rate law becomes pseudofirst order in A, but when $k_3[\text{A}] \ll k_2$, the rate law is pseudosecond order in A.

Solutions to exercises

E17B.1(b) The integrated rate law for a first-order reaction of ethanol CH_3CH_2OH is given by [17B.2b–*732*], $\ln([CH_3CH_2OH]/[CH_3CH_2OH]_0) = -k_r t$. Rearranging for k_r and taking $[CH_3CH_2OH] = 56.0\ \text{mmol dm}^{-3}$ when $t = 1.22 \times 10^4$ s gives

$$k_r = -\frac{1}{t}\ln\left(\frac{[CH_3CH_2OH]}{[CH_3CH_2OH]_0}\right) = -\frac{1}{1.22 \times 10^4\ \text{s}}\ln\left(\frac{56.0 \times 10^{-3}\ \text{mol dm}^{-3}}{220 \times 10^{-3}\ \text{mol dm}^{-3}}\right)$$
$$= \boxed{1.12 \times 10^{-4}\ \text{s}^{-1}}$$

E17B.2(b) The fact that the two half lives are not the same establishes that the reaction is not first-order because, as explained in Section 17B.2 on page 731, a first-order reaction has a constant half-life. For orders $n \neq 1$ the half-life is given by [17B.6–*734*], $t_{1/2} = (2^{n-1} - 1)/[(n-1)k_r[\text{A}]_0^{n-1}]$. Denoting the two measurements by

$t_{1/2,\mathrm{i}}$ and $t_{1/2,\mathrm{ii}}$ and expressing concentration in terms of partial pressure gives the two equations

$$t_{1/2,\mathrm{i}} = \frac{2^{n-1}-1}{(n-1)k_\mathrm{r}p_{\mathrm{A,i}}^{n-1}} \qquad t_{1/2,\mathrm{ii}} = \frac{2^{n-1}-1}{(n-1)k_\mathrm{r}p_{\mathrm{A,ii}}^{n-1}}$$

The second equation is divided by the first to give

$$\frac{t_{1/2,\mathrm{ii}}}{t_{1/2,\mathrm{i}}} = \left(\frac{p_{\mathrm{A,i}}}{p_{\mathrm{A,ii}}}\right)^{n-1} \quad \text{hence} \quad \log\left(\frac{t_{1/2,\mathrm{ii}}}{t_{1/2,\mathrm{i}}}\right) = (n-1)\log\left(\frac{p_{\mathrm{A,i}}}{p_{\mathrm{A,ii}}}\right)$$

where $\log x^a = a\log x$ is used. Rearranging for n gives

$$n = \frac{\log\left(t_{1/2,\mathrm{ii}}/t_{1/2,\mathrm{i}}\right)}{\log\left(p_{\mathrm{A,i}}/p_{\mathrm{A,ii}}\right)} + 1 = \frac{\log[(178\ \mathrm{s})/(340\ \mathrm{s})]}{\log[(55.5\ \mathrm{kPa})/(28.9\ \mathrm{kPa})]} + 1 = 8.24\times10^{-3}$$

This is very close to zero, so the reaction is $\boxed{\text{zeroth-order}}$.

E17B.3(b) For the reaction $2\mathrm{A(g)} \rightarrow$ products the rate, as given by [17A.3b–*726*], $v = (1/\nu_\mathrm{J})(\mathrm{d}[\mathrm{J}]/\mathrm{d}t)$, is

$$v = \frac{1}{-2}\frac{\mathrm{d}p_\mathrm{A}}{\mathrm{d}t}$$

where concentrations are expressed in terms of partial pressures. It is given that the reaction is first-order in A, so $v = k_\mathrm{r}p_\mathrm{A}$. Combining this with the above expression for v gives

$$\frac{1}{-2}\frac{\mathrm{d}p_\mathrm{A}}{\mathrm{d}t} = k_\mathrm{r}p_\mathrm{A} \quad \text{hence} \quad \frac{\mathrm{d}p_\mathrm{A}}{\mathrm{d}t} = -2k_\mathrm{r}p_\mathrm{A}$$

This has the same form, except with $2k_\mathrm{r}$ instead of k_r, as [17B.2a–*731*], $(\mathrm{d}[\mathrm{A}]/\mathrm{d}t) = -k_\mathrm{r}[\mathrm{A}]$, for which it is shown in Section 17B.2 on page 731 that the half-life and the integrated rate law are

$$t_{1/2} = \frac{\ln 2}{k_\mathrm{r}} \qquad [\mathrm{A}] = [\mathrm{A}]_0\mathrm{e}^{-k_\mathrm{r}t}$$

The expressions for the reaction in question are analogous, but with k_r replaced by $2k_\mathrm{r}$.

$$t_{1/2} = \frac{\ln 2}{2k_\mathrm{r}} \qquad p_\mathrm{A} = (p_{\mathrm{A},0})\mathrm{e}^{-2k_\mathrm{r}t}$$

The half-life is

$$t_{1/2} = \frac{\ln 2}{2k_\mathrm{r}} = \frac{\ln 2}{2\times3.56\times10^{-7}\ \mathrm{s}^{-1}} = \boxed{9.74\times10^{5}\ \mathrm{s}}$$

The partial pressures at the specified times are calculated from the above integrated form of the rate law. Hence

$$t = 50\ \mathrm{s} \quad p_\mathrm{A} = (33.0\ \mathrm{kPa})\times\mathrm{e}^{-2\times(3.56\times10^{-7}\ \mathrm{s}^{-1})\times(50\ \mathrm{s})} = \boxed{33.0\ \mathrm{kPa}}$$

$$t = 20\ \mathrm{min} \quad p_\mathrm{A} = (33.0\ \mathrm{kPa})\times\mathrm{e}^{-2\times(3.56\times10^{-7}\ \mathrm{s}^{-1})\times([20\times60]\ \mathrm{s})} = \boxed{33.0\ \mathrm{kPa}}$$

E17B.4(b) The reaction is of the form A + 2B → P. From Table 17B.3 on page 735 the integrated rate law for this reaction, assuming that it has rate law $v = k_r[A][B]$, is

$$[P] = \frac{[A]_0[B]_0(1 - e^{([B]_0 - 2[A]_0)k_r t})}{2[A]_0 - [B]e^{([B]_0 - 2[A]_0)k_r t}}$$

The equation gives the concentration of a product P produced in 1 : 1 stoichiometry with the reactant A. It therefore applies to the species C in the reaction A + 2B → C + D. Hence

$$[C] = \frac{[A]_0[B]_0(1 - e^{\lambda})}{2[A]_0 - [B]_0 e^{\lambda}} \qquad \lambda = ([B]_0 - 2[A]_0)k_r t$$

For $t = 20$ s

$$\begin{aligned}\lambda &= \left[(0.130 \text{ mol dm}^{-3}) - 2 \times (0.027 \text{ mol dm}^{-3})\right] \times (0.34 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \\ &\quad \times (20 \text{ s}) = 0.516... \\ [C] &= \frac{(0.027 \text{ mol dm}^{-3}) \times (0.130 \text{ mol dm}^{-3}) \left(1 - e^{0.516...}\right)}{2 \times (0.027 \text{ mol dm}^{-3}) - (0.130 \text{ mol dm}^{-3}) \times e^{0.516...}} \\ &= \boxed{0.014 \text{ mol dm}^{-3}}\end{aligned}$$

For $t = 15$ min

$$\begin{aligned}\lambda &= \left[(0.130 \text{ mol dm}^{-3}) - 2 \times (0.027 \text{ mol dm}^{-3})\right] \times (0.34 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \\ &\quad \times ([15 \times 60] \text{ s}) = 23.2... \\ [C] &= \frac{(0.027 \text{ mol dm}^{-3}) \times (0.130 \text{ mol dm}^{-3}) \left(1 - e^{23.2...}\right)}{2 \times (0.027 \text{ mol dm}^{-3}) - (0.130 \text{ mol dm}^{-3}) \times e^{23.2...}} \\ &= \boxed{0.027 \text{ mol dm}^{-3}}\end{aligned}$$

E17B.5(b) Using [17A.3b–*726*], $v = (1/\nu_J)(d[J]dt)$, the rate of the reaction 2A → P is $v = -\frac{1}{2}(d[A]/dt)$. Combining this with the rate law $v = k_r[A]^3$ gives

$$-\frac{1}{2}\frac{d[A]}{dt} = k_r[A]^3 \quad \text{hence} \quad \frac{d[A]}{dt} = -2k_r[A]^3$$

This rate law is integrated following the method in Section 17B.3 on page 733. The equation is first rearranged to

$$-\frac{d[A]}{[A]^3} = 2k_r \quad \text{hence} \quad \overbrace{-\int_{[A]_0}^{[A]} [A]^{-3}\, d[A]}^{\text{Integral A.1}} = 2k_r \int_0^t dt$$

where the limits of the integration arise because the concentration is $[A]_0$ at $t = 0$ and at a later time t it is $[A]$. Performing the integration gives

$$\tfrac{1}{2}[A]^{-2}\Big|_{[A]_0}^{[A]} = 2k_r\, t\Big|_0^t \quad \text{hence} \quad \tfrac{1}{2}\left(\frac{1}{[A]^2} - \frac{1}{[A]_0^2}\right) = 2k_r t$$

Rearranging for t gives

$$t = \frac{1}{4k_r}\left(\frac{1}{[A]^2} - \frac{1}{[A]_0^2}\right)$$
$$= \frac{1}{4 \times \left(6.50 \times 10^{-4}\ \text{dm}^6\ \text{mol}^{-2}\ \text{s}^{-1}\right)}$$
$$\times \left(\frac{1}{\left(0.015\ \text{mol}\,\text{dm}^{-3}\right)^2} - \frac{1}{\left(0.067\ \text{mol}\,\text{dm}^{-3}\right)^2}\right) = \boxed{1.6 \times 10^6\ \text{s}} \text{ or 19 days}$$

E17B.6(b) From Table 17B.3 on page 735, the integrated rate law for a second-order reaction of the type A + 2B → P is

$$k_r t = \frac{1}{[B]_0 - 2[A]_0} \ln \frac{[A]_0\left([B]_0 - 2[P]\right)}{\left([A]_0 - [P]\right)[B]_0}$$

Because one mole of P is formed for every mole of A that reacts, it follows that $[P] = [A]_0 - [A]$, because the quantity $[A]_0 - [A]$ is equal to the amount of A that has reacted. The term $[A]_0 - [P]$ in the above expression is therefore simply equal to $[A]$. Similarly, $[P] = \frac{1}{2}([B]_0 - [B])$ because one mole of P is formed for every two moles of B that react. Rearranging gives $[B]_0 - 2[P] = [B]$. It follows that the integrated rate equation can be written as

$$k_r t = \frac{1}{[B]_0 - 2[A]_0} \ln \frac{[A]_0[B]}{[A][B]_0} \quad \text{hence} \quad k_r t = \frac{1}{[B]_0 - 2[A]_0} \ln \frac{[B]/[B]_0}{[A]/[A]_0}$$

(i) After 1 hour the amount of A has fallen by 0.010 $\text{mol}\,\text{dm}^{-3}$ from 0.050 $\text{mol}\,\text{dm}^{-3}$ to 0.040 $\text{mol}\,\text{dm}^{-3}$. The stoichiometry of the reaction means that B must have fallen by twice this amount, that is by 0.020 $\text{mol}\,\text{dm}^{-3}$, from its initial value of 0.030 $\text{mol}\,\text{dm}^{-3}$ to 0.010 $\text{mol}\,\text{dm}^{-3}$. Rearranging the above integrated rate equation for k_r and using these values, together with $t = 1\ \text{h} \times (60^2\ \text{s}\,\text{h}^{-1}) = 3600\ \text{s}$, gives

$$k_r = \frac{1}{\left([B]_0 - 2[A]_0\right)t} \ln \frac{[B]/[B]_0}{[A]/[A]_0}$$
$$= \frac{1}{\left[\left(0.030\ \text{mol}\,\text{dm}^{-3}\right) - 2 \times \left(0.050\ \text{mol}\,\text{dm}^{-3}\right)\right] \times (3600\ \text{s})}$$
$$\times \ln\left(\frac{\left(0.010\ \text{mol}\,\text{dm}^{-3}\right)/\left(0.030\ \text{mol}\,\text{dm}^{-3}\right)}{\left(0.040\ \text{mol}\,\text{dm}^{-3}\right)/\left(0.050\ \text{mol}\,\text{dm}^{-3}\right)}\right)$$
$$= 3.47... \times 10^{-3}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} = \boxed{3.5\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}$$

(ii) The half-life of a reactant is the time taken for the concentration of that reactant to fall to half its initial value. Thus the half-life of A is the time taken for $[A]$ to fall to $\frac{1}{2}[A]_0 = (0.050\ \text{mol}\,\text{dm}^{-3})/2 = 0.0250\ \text{mol}\,\text{dm}^{-3}$. However, this is not possible from the given starting conditions, because the stoichiometry of the reaction requires the concentration of B to fall by twice this amount, that is, by 0.050 $\mathrm{mol\,dm^{-3}}$, but the concentration of B is only 0.030 $\mathrm{mol\,dm^{-3}}$ to start with. The half-life of A is therefore $\boxed{\text{infinite}}$, since the condition $[\mathrm{A}] = 0.0250\ \mathrm{mol\,dm^{-3}}$ can never be reached. The half-life of B is the time at which $[\mathrm{B}] = \frac{1}{2}[\mathrm{B}]_0 = (0.030\ \mathrm{mol\,dm^{-3}})/2 = 0.015\ \mathrm{mol\,dm^{-3}}$. To achieve this the concentration of B must fall by 0.015 $\mathrm{mol\,dm^{-3}}$, which from the stoichiometry of the reaction means that the concentration of A must fall by $\frac{1}{2}\times(0.015\ \mathrm{mol\,dm^{-3}}) = 0.0075\ \mathrm{mol\,dm^{-3}}$. The concentration of A will therefore be

$$[\mathrm{A}] = \overbrace{(0.050\ \mathrm{mol\,dm^{-3}})}^{[\mathrm{A}]_0} - (0.0075\ \mathrm{mol\,dm^{-3}}) = 0.0425\ \mathrm{mol\,dm^{-3}}$$

Rearranging the integrated rate equation for t and using these concentrations for A and B gives

$$\begin{aligned} t &= \frac{1}{k_\mathrm{r}}\frac{1}{[\mathrm{B}]_0 - 2[\mathrm{A}]_0}\ln\frac{[\mathrm{B}]/[\mathrm{B}]_0}{[\mathrm{A}]/[\mathrm{A}]_0} \\ &= \frac{1}{3.47...\times10^{-3}\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}}\times\frac{1}{(0.030\ \mathrm{mol\,dm^{-3}}) - 2\times(0.050\ \mathrm{mol\,dm^{-3}})} \\ &\quad\times\ln\left(\frac{(0.015\ \mathrm{mol\,dm^{-3}})/(0.030\ \mathrm{mol\,dm^{-3}})}{(0.0425\ \mathrm{mol\,dm^{-3}})/(0.050\ \mathrm{mol\,dm^{-3}})}\right) = \boxed{2.2\times10^3\ \mathrm{s}}\ \text{or 0.61 h} \end{aligned}$$

Solutions to problems

P17B.2 The concentration of B is given in the question as

$$[\mathrm{B}] = \frac{nk_\mathrm{r}t[\mathrm{A}]_0^2}{1+k_\mathrm{r}t[\mathrm{A}]_0} \quad \text{hence} \quad \frac{[\mathrm{B}]}{[\mathrm{A}]_0} = \frac{nk_\mathrm{r}t[\mathrm{A}]_0}{1+k_\mathrm{r}t[\mathrm{A}]_0}$$

The concentration of A for a second-order reaction is given by [17B.4b–*733*],

$$[\mathrm{A}] = \frac{[\mathrm{A}]_0}{1+k_\mathrm{r}t[\mathrm{A}]_0} \quad \text{hence} \quad \frac{[\mathrm{A}]}{[\mathrm{A}]_0} = \frac{1}{1+k_\mathrm{r}t[\mathrm{A}]_0}$$

These expressions are plotted in Fig. 17.2 as $[\mathrm{A}]/[\mathrm{A}]_0$ or $[\mathrm{B}]/[\mathrm{A}]_0$ against $k_\mathrm{r}t[\mathrm{A}]_0$.

P17B.4 The order is determined by testing the fit of the data to integrated rate law expressions. A zeroth-order reaction of the form A → P has an integrated rate law given by [17B.1–*731*], $[\mathrm{A}] = [\mathrm{A}]_0 - k_\mathrm{r}t$, so if the reaction is zeroth-order then a plot of $[\mathrm{A}]$ against t will be a straight line of slope $-k_\mathrm{r}$. In this case, A is $(\mathrm{CH_3})_3\mathrm{CBr}$. On the other hand, a first-order reaction has an integrated rate law given by [17B.2b–*732*], $\ln([\mathrm{A}]/[\mathrm{A}]_0) = -k_\mathrm{r}t$, so if the reaction is first-order then a plot of $\ln[\mathrm{A}]/[\mathrm{A}]_0$ against t will be a straight line of slope $-k_\mathrm{r}$. Finally, if the order is $n \geq 2$ the integrated rate law is given in Table 17B.3 on page 735 as

$$k_\mathrm{r}t = \frac{1}{n-1}\left(\frac{1}{([\mathrm{A}]_0-[\mathrm{P}])^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right) \text{ hence } \frac{1}{[\mathrm{A}]^{n-1}} = (n-1)k_\mathrm{r}t + \frac{1}{[\mathrm{A}]_0^{n-1}}$$

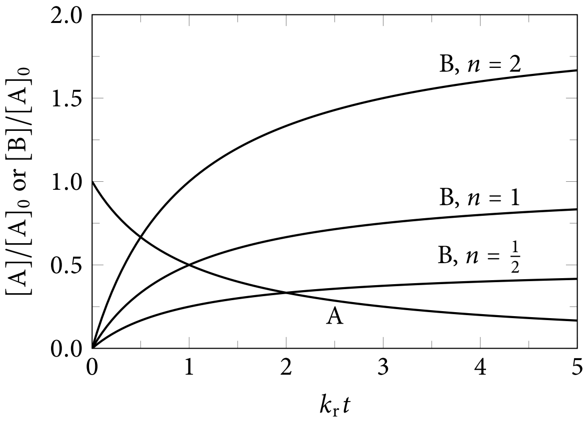


Figure 17.2

where to obtain the second expression the relation $[P] = [A]_0 - [A]$ is substituted and the equation rearranged. This expression implies that if the reaction has order $n \geq 2$ a plot of $1/[A]^{n-1}$ against t will be a straight line of slope $(n-1)k_r$.

The data are plotted assuming zeroth-, first-, second-, and third-order in Fig. 17.3. The first-order plot shows the best fit to a straight line, so it is concluded that the reaction is $\boxed{\text{first-order}}$.

t/h	$[A]$ /mol dm^{-3}	$\ln \frac{[A]}{[A]_0}$	$1/[A]$ /dm^3 mol^{-1}	$1/[A]^2$ /dm^6 mol^{-2}
0	0.1039	0.000	9.62	9.263×10^1
3	0.0896	−0.148	11.16	1.246×10^2
6	0.0776	−0.292	12.89	1.661×10^2
10	0.0639	−0.486	15.65	2.449×10^2
18	0.0353	−1.080	28.33	8.025×10^2
31	0.0207	−1.613	48.31	2.334×10^3

The equation of the line in the first-order plot is

$$\ln([A]/[A]_0) = -5.42 \times 10^{-2} \times (t/\text{h}) + 1.54 \times 10^{-2}$$

Identifying the slope with $-k_r$ as discussed above gives the first-order rate constant as $k_r = \boxed{5.42 \times 10^{-2}\ \text{h}^{-1}}$.

The concentration of $(CH_3)_3CB_4$ remaining after 43.8 h is calculated using the integrated rate law for a first-order reaction, [17B.2b–*732*], $[A] = [A]_0 e^{-k_r t}$

$$\begin{aligned}[A] &= (10.39 \times 10^{-2}\ \text{mol dm}^{-3}) \times e^{-(5.42\times10^{-2}\ \text{h}^{-1})\times(43.8\ \text{h})} \\ &= \boxed{0.97 \times 10^{-2}\ \text{mol dm}^{-3}}\end{aligned}$$

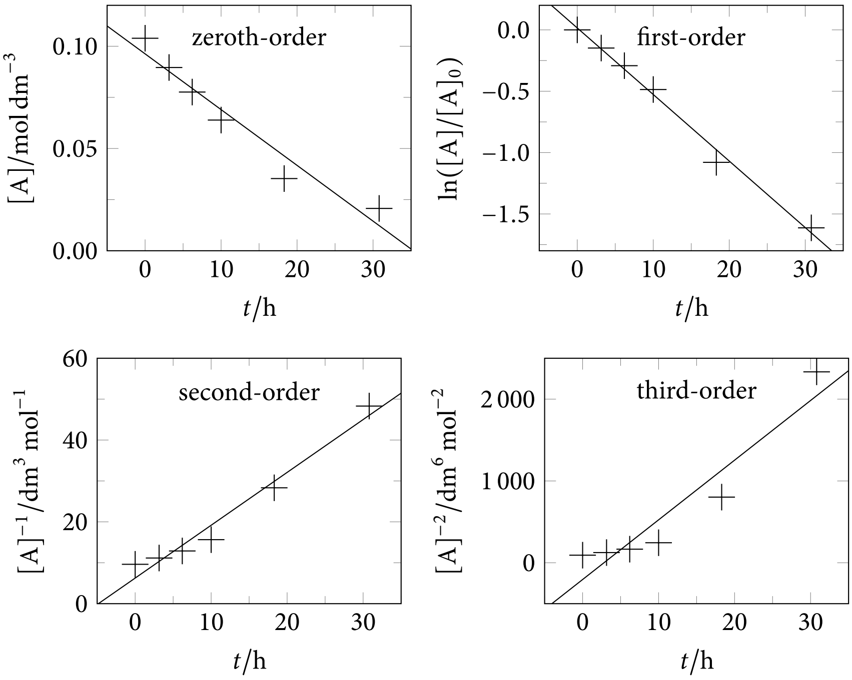


Figure 17.3

P17B.6 Noting from the definition pH = $-\log([H^+]/\text{mol dm}^{-3})$ that the H^+ concentration is given by $([H^+]/\text{mol dm}^{-3}) = 10^{-\text{pH}}$, the initial rate is

$$\begin{aligned} v &= k_r[HSO_3{}^-]^2[H^+]^2 \\ &= (3.6\times10^6\ \text{dm}^9\,\text{mol}^{-3}\,\text{s}^{-1})\times(50\times10^{-6}\ \text{mol dm}^{-3})^2\times(10^{-5.6}\ \text{mol dm}^{-3})^2 \\ &= \boxed{5.7\times10^{-14}\ \text{mol dm}^{-3}\,\text{s}^{-1}} \end{aligned}$$

From the definition of reaction rate [17A.3b–*726*], $v = (1/\nu_J)(\text{d}[J]/\text{d}t)$, the rate is written in terms of the $HSO_3{}^-$ concentration as $v = -\frac{1}{2}\text{d}[HSO_3{}^-]/\text{d}t$. Combining this with the rate law $v = k_r[HSO_3{}^-]^2[H^+]^2$ gives

$$-\tfrac{1}{2}\frac{\text{d}[HSO_3{}^-]}{\text{d}t} = k_r[HSO_3{}^-]^2[H^+]^2 \quad \text{hence} \quad \frac{\text{d}[HSO_3{}^-]}{\text{d}t} = -2k_r[H^+]^2[HSO_3{}^-]^2$$

Because the pH and hence $[H^+]$ is assumed constant, this is written as

$$\frac{\text{d}[H^+]}{\text{d}t} = -k_{r,\text{eff}}[HSO_3{}^-]^2 \quad \text{where} \quad k_{r,\text{eff}} = 2k_r[H^+]^2$$

This expression corresponds to the rate law of an effective second-order reaction, for which the half-life is given by [17B.5–*734*], $t_{1/2} = 1/(k_{r,\text{eff}}[A]_0)$. Hence the time taken for the $HSO_3{}^-$ concentration to fall to half its initial value is

$$t_{1/2} = \frac{1}{k_{r,\text{eff}}[HSO_3{}^-]_0} = \frac{1}{2k_r[H^+]^2[HSO_3{}^-]_0}$$
$$= \frac{1}{2 \times (3.6 \times 10^6\ \text{dm}^9\ \text{mol}^{-3}\ \text{s}^{-1}) \times (10^{-5.6})^2 \times (50 \times 10^{-6}\ \text{mol dm}^{-3})^2}$$
$$= \boxed{4.4 \times 10^8\ \text{s}} \text{ or 14 years}$$

P17B.8 Visual inspection of the data suggests that the half-life is constant at about 2 minutes. This indicates that the reaction is $\boxed{\text{first-order}}$ because first order reactions have a constant half-life.

Using [17A.3b–*726*], $v = (1/\nu_J)(\text{d}[J]/\text{d}t)$, the rate is written as $v = -\frac{1}{2}\text{d}[N_2O_5]/\text{d}t$. Combining this with $v = k_r[N_2O_5]$, the rate law for a first-order reaction, gives

$$-\tfrac{1}{2}\frac{\text{d}[N_2O_5]}{\text{d}t} = k_r[N_2O_5] \quad \text{hence} \quad \frac{\text{d}[N_2O_5]}{\text{d}t} = -k_{r,\text{eff}}[N_2O_5] \text{ where } k_{r,\text{eff}} = 2k_r$$

The integrated form of this rate law is given by [17B.2b–*732*]

$$\ln([N_2O_5]/[N_2O_5]_0) = -k_{r,\text{eff}}t \quad \text{or} \quad \ln[N_2O_5] = \ln[N_2O_5]_0 - k_r t$$

This expression implies that a graph of $\ln[N_2O_5]$ against t will be a straight line of slope $-k_{r,\text{eff}} = -2k_r$. To estimate k_r without drawing a graph, pairs of data are considered and used to estimate the slope according to

$$\text{slope} = \frac{\Delta \ln[N_2O_5]}{\Delta t} = \frac{\ln[N_2O_5]_{t+\Delta t} - \ln[N_2O_5]_t}{\Delta t}$$

Taking $\Delta t = 1$ min the results are

t/min	$[N_2O_5]$/mol dm^{-3}	$\ln([N_2O_5]$/mol dm$^{-3})$	slope/min^{-1}
0	1.000	0.000	−0.350
1	0.705	−0.350	−0.350
2	0.497	−0.699	−0.354
3	0.349	−1.053	−0.350
4	0.246	−1.402	−0.352
5	0.173	−1.754	

The approximately constant value of the slope confirms that the reaction is first-order. The average value of the slope is −0.350... min^{-1}; identifying this with $-2k_r$ as described above gives $\boxed{k_r = 0.175\ \text{min}^{-1}}$.

In an alternative approach, $\ln[N_2O_5]$ is plotted against t, as shown in Fig. 17.4.

The data lie on a good straight line, thus confirming that the reaction is first-order. The equation of the line is

$$\ln([N_2O_5]/\text{mol dm}^{-3}) = -0.351 \times (t/\text{min}) + 1.077 \times 10^{-3}$$

Identifying the slope with $-2k_r$ gives $\boxed{k_r = 0.175\ \text{min}^{-1}}$.

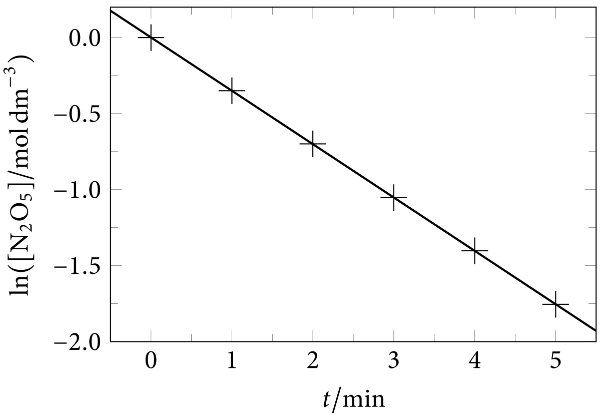


Figure 17.4

P17B.10 The reaction is confirmed to be first-order by fitting the data to an integrated rate law. The integrated rate law for a first order reaction is given by [17B.2b–*732*], $\ln([A]/[A]_0) = -k_r t$; this expression implies that if the hydrolysis of sucrose is first order then a graph of $\ln([\text{sucrose}]/[\text{sucrose}]_0)$ against t should be a straight line of slope $-k_r$. The data are plotted in Fig. 17.5

$t/10^3$ s	$[\text{sucrose}]$ $/\text{mol dm}^{-3}$	$\ln\dfrac{[\text{sucrose}]}{[\text{sucrose}]_0}$
0	0.316	0.000
14	0.300	−0.052
39	0.274	−0.143
60	0.256	−0.211
80	0.238	−0.283
110	0.211	−0.404
140	0.190	−0.509
170	0.170	−0.620
210	0.146	−0.772

The data lie on a good straight line, thus confirming that the reaction is first-order. The equation of the line is

$$\ln([\text{sucrose}]/[\text{sucrose}]) = -3.670\times10^{-3}\times(t/\text{min}) + 3.052\times10^{-3}$$

Identifying the slope with $-k_r$ gives = $\boxed{k_r = 3.670\times10^{-3}\ \text{min}^{-1}}$. The half-life of a first-order reaction is given by [17B.3–*732*], $t_{1/2} = \ln 2/k_r$.

$$t_{1/2} = \frac{\ln 2}{k_r} = \frac{\ln 2}{3.670\times10^{-3}\ \text{min}^{-1}} = \boxed{189\ \text{min}}$$

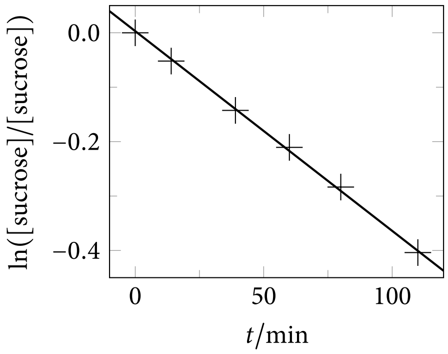


Figure 17.5

P17B.12 The order is determined by testing the fit of the data to integrated rate law expressions. If the rate law is $v = k_r[\mathrm{ClO}]^n$, where n is the order to be determined, expressing v in terms of the rate of change of concentration of [ClO] using [17A.3b–*726*], $v = (1/\nu_J)(\mathrm{d[J]}/\mathrm{d}t)$ gives

$$v = \frac{1}{-2}\frac{\mathrm{d[ClO]}}{\mathrm{d}t} = k_r[\mathrm{ClO}]^n \quad \text{hence} \quad \frac{\mathrm{d[ClO]}}{\mathrm{d}t} = -2k_r[\mathrm{ClO}]^n$$

Integrated rate laws are given in Table 17B.3 on page 735, but care is needed because these are for reactions of the form A → P but here the reaction is 2ClO → products.

For $n = 0$, Table 17B.3 on page 735 shows that a reaction A → P with rate law $v = \mathrm{d[P]}/\mathrm{d}t = k_r$ has integrated rate law $\mathrm{A} = \mathrm{A}_0 - k_r t$. To adapt this expression for the reaction in question, the rate law for the reaction in the table is first written as $\mathrm{d[A]}/\mathrm{d}t = -k_r$ using $\mathrm{d[P]}/\mathrm{d}t = -\mathrm{d[A]}/\mathrm{d}t$ for a reaction of the form A → P. This rate law matches that found above, $\mathrm{d[ClO]}/\mathrm{d}t = -2k_r[\mathrm{ClO}]^n$, for $n = 0$ and A = ClO, except that k_r is replaced by $2k_r$. The integrated rate law will therefore be the same except with k_r replaced by $2k_r$, that is, $[\mathrm{ClO}] = [\mathrm{ClO}]_0 - 2k_r t$. This expression implies that if the reaction is zeroth-order a plot of [ClO] against t will give a straight line of slope $-2k_r$.

Similarly Table 17B.3 on page 735 gives the integrated rate law for a first-order reaction A → P with rate law $v = \mathrm{d[P]}/\mathrm{d}t = k_r[\mathrm{A}]$ as $\ln([\mathrm{A}]_0/[\mathrm{A}]) = k_r t$, equivalent to [17B.2b–*732*], $\ln([\mathrm{A}]/[\mathrm{A}]_0) = -k_r t$. By the same reasoning as above the integrated rate law for the reaction will be $\ln([\mathrm{ClO}]/[\mathrm{ClO}]_0) = -2k_r t$, implying that a plot of $\ln([\mathrm{ClO}]/[\mathrm{ClO}]_0)$ against t will give a straight line of slope $-2k_r$.

Finally, if the order is $n \geq 2$ the integrated rate law for a reaction A → P with rate law $v = \mathrm{d[P]}/\mathrm{d}t = k_r[\mathrm{A}]^n$ is given in Table 17B.3 on page 735 as

$$k_r t = \frac{1}{n-1}\left(\frac{1}{([\mathrm{A}]_0 - [\mathrm{P}])^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right) \text{ hence } \frac{1}{[\mathrm{A}]^{n-1}} = (n-1)k_r t + \frac{1}{[\mathrm{A}]_0^{n-1}}$$

where to obtain the second expression the relation $[\mathrm{P}] = [\mathrm{A}]_0 - [\mathrm{A}]$ is substituted and the equation rearranged. Adapting this expression for the reaction in question gives $1/[\mathrm{ClO}]^{n-1} = 2(n-1)k_r t + 1/[\mathrm{ClO}]_0^{n-1}$. This expression implies that if the reaction has order $n \geq 2$ a plot of $1/[\mathrm{ClO}]^{n-1}$ against t will be a straight line of slope $2(n-1)k_r$.

The data are plotted assuming zeroth-, first-, second-, and third-order in Fig. 17.6.

t/ms	$[\mathrm{ClO}]$ $/\mu\mathrm{mol\,dm^{-3}}$	$\ln \dfrac{[\mathrm{ClO}]}{[\mathrm{ClO}]_0}$	$1/[\mathrm{ClO}]$ $/\mathrm{dm^3\,\mu mol^{-1}}$	$1/[\mathrm{ClO}]^2$ $/\mathrm{dm^6\,\mu mol^{-2}}$
0.12	8.49	0.000	0.118	0.013 9
0.62	8.09	−0.048	0.124	0.015 3
0.96	7.10	−0.179	0.141	0.019 8
1.60	5.79	−0.383	0.173	0.029 8
3.20	5.20	−0.490	0.192	0.037 0
4.00	4.77	−0.577	0.210	0.044 0
5.75	3.95	−0.765	0.253	0.064 1

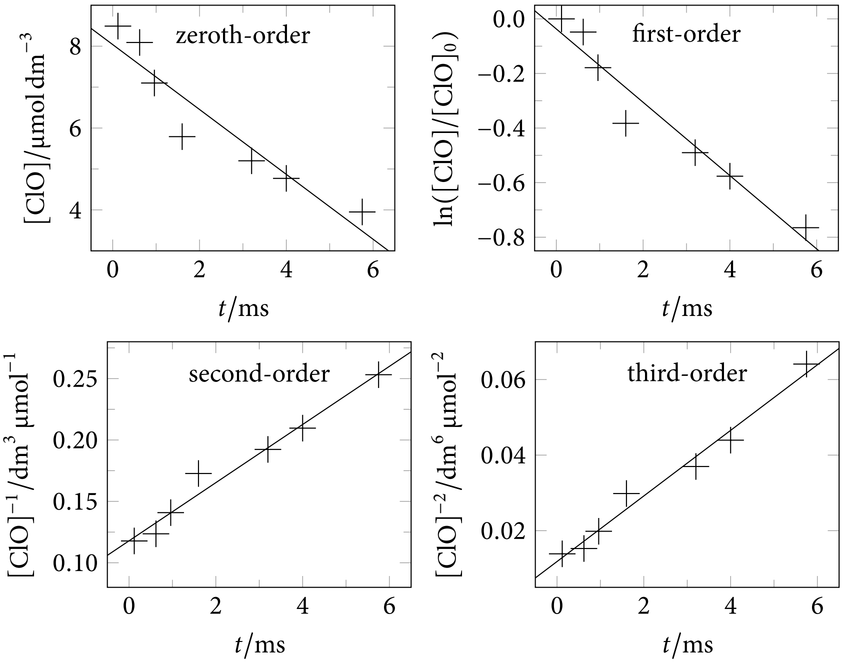


Figure 17.6

None of the plots give a perfect straight line due to experimental scatter in the data. The values of the product moment correlation coefficient for each of the plots are −0.945, −0.971, 0.987 and 0.989 for zeroth-, first-, second-, and third-order respectively, suggesting that the second-, third- or a higher order plot gives the best fit.

If the reaction is second-order, the rate constant is found from the equation of the line in the second-order plot

$$[\mathrm{ClO}]^{-1}/\mathrm{dm^3\,\mu mol^{-1}} = 2.368\times10^{-2}\times(t/\mathrm{ms}) + 0.118$$

Identifying the slope with $-2(n-1)k_\mathrm{r}$ as discussed above, noting that $n = 2$ for a second-order plot, gives gives the second-order rate constant as

$$\begin{aligned} k_\mathrm{r} &= -\tfrac{1}{2}\times(-2.368\times10^{-2}\ \mathrm{dm^3\,\mu mol^{-1}\,ms^{-1}}) \\ &= 1.18...\times10^{-2}\ \mathrm{dm^3\,\mu mol^{-1}\,ms^{-1}} \\ &= (1.18...\times10^{-2}\ \mathrm{dm^3\,\mu mol^{-1}\,ms^{-1}})\times\frac{10^6\ \mathrm{\mu mol}}{1\ \mathrm{mol}}\times\frac{10^3\ \mathrm{ms}}{1\ \mathrm{s}} \\ &= \boxed{1.18\times10^7\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}} \end{aligned}$$

The half-life of a non-first-order reaction depends on the initial concentration, and for a reaction with order $n > 1$ is given by [17B.6–*734*], $t_{1/2} = (2^{n-1} - 1)/([n-1]k_\mathrm{r}[\mathrm{A}]_0^{n-1})$. However, this is for a reaction of the form A → products. In this case the reaction is 2A → products, so k_r must be replaced by $2k_\mathrm{r}$ as explained earlier. The half-life is then given by

$$t_{1/2} = \frac{2^{n-1}-1}{2(n-1)k_\mathrm{r}[\mathrm{ClO}]_0^{n-1}}$$

If the reaction is second-order, using $[\mathrm{ClO}]_0 = 8.49\ \mathrm{\mu mol\,dm^{-3}}$ and the value of k_r from above gives

$$\begin{aligned} t_{1/2} &= \frac{2^{2-1}-1}{2(2-1)k_\mathrm{r}[\mathrm{ClO}]_0^{2-1}} = \frac{1}{2\times1\times(1.18...\times10^{-2}\ \mathrm{dm^3\,\mu mol^{-1}})\times(8.49\ \mathrm{\mu mol})} \\ &= \boxed{4.97\ \mathrm{ms}} \end{aligned}$$

P17B.14 (a) If the reaction A + B → P is mth order in A and nth order in B the rate law is

$$v = \frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = k_\mathrm{r}[\mathrm{A}]^m[\mathrm{B}]^n$$

For a short time period the derivative is approximated by finite changes

$$\frac{\delta[\mathrm{P}]}{\delta t} = k_\mathrm{r}[\mathrm{A}]^m[\mathrm{B}]^n \quad \text{hence} \quad \delta[\mathrm{P}] = k_\mathrm{r}[\mathrm{A}]^m[\mathrm{B}]^n\delta t$$

The concentration of P at a time δt after the start of the reaction is therefore

$$[\mathrm{P}] = [\mathrm{P}]_0 + \delta[\mathrm{P}] = 0 + \delta[\mathrm{P}] = k_\mathrm{r}[\mathrm{A}]^m[\mathrm{B}]^n\delta t$$

Dividing by [A], which is assumed to be approximately constant over the short time range δt, then gives $[\mathrm{P}]/[\mathrm{A}] = k_\mathrm{r}[\mathrm{A}]^{m-1}[\mathrm{B}]^n\delta t$ as required.

(b) The reaction propene+HCl → chloropropane has the form of the reaction A + B → P analysed in part (a). Setting A as propene, B as HCl and P as chloropropane, and expressing concentrations in terms of partial pressures, the result derived in part (a) becomes

$$\frac{p_{\text{chloropropane}}}{p_{\text{propene}}} = k_r p_{\text{propene}}^{m-1} p_{\text{HCl}}^{n} \delta t \propto p_{\text{propene}}^{m-1}$$

The fact that $p_{\text{chloropropane}}/p_{\text{propene}}$ is independent of p_{propene} implies that $m - 1 = 0$ and hence $m = 1$. Therefore the reaction is $\boxed{\text{first-order}}$ in propene.

If instead HCl is treated as A and propene as B, the result from part (a) becomes

$$\frac{p_{\text{chloropropane}}}{p_{\text{HCl}}} = k_r p_{\text{HCl}}^{m-1} p_{\text{propene}} \delta t$$

where the order with respect to propene has been set to 1 as deduced above. Taking common logarithms gives

$$\log \frac{p_{\text{chloropropane}}}{p_{\text{HCl}}} = \log\left(k_r p_{\text{propene}} \delta t\right) + (n-1)\log p_{\text{HCl}}$$

where $\log(xy) = \log x + \log y$ and $\log x^a = a \log x$ are used. This expression implies that a plot of $\log(p_{\text{chloropropane}}/p_{\text{HCl}})$ against $\log p_{\text{HCl}}$ will be a straight line of slope $n - 1$. Such a plot is shown in Fig. 17.7.

$p_{\text{HCl}}/\text{atm}$	$\dfrac{p_{\text{chloropropane}}}{p_{\text{HCl}}}$	$\log(p_{\text{HCl}}/\text{atm})$	$\log\left(\dfrac{p_{\text{chloropropane}}}{p_{\text{HCl}}}\right)$
10.0	0.05	1.00	−1.30
7.5	0.03	0.88	−1.52
5.0	0.01	0.70	−2.00

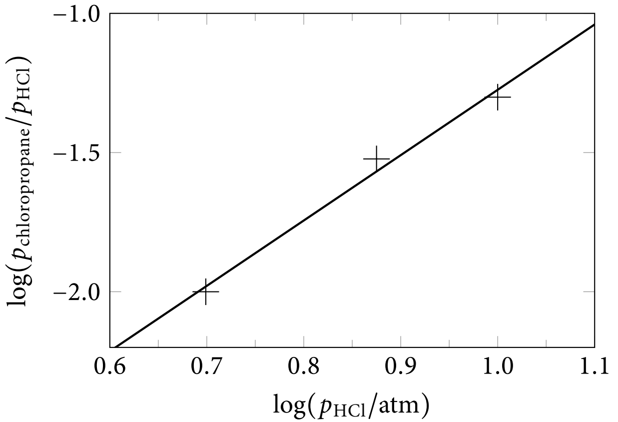


Figure 17.7

The data lie on a modest straight line, the equation of which is

$$\log(p_{\text{chloropropane}}/p_{\text{HCl}}) = 2.3 \times \log(p_{\text{HCl}}/\text{atm}) - 3.6$$

The slope is moderately close to 2, suggesting that $n-1=2$ and hence $n=3$. Therefore the reaction may be $\boxed{\text{third-order}}$ in HCl. However there are only three data points, they do not lie very close to a straight line, and slope of the line is not very close to 2, so the conclusion should be treated with caution in the absence of further data.

P17B.16 The stoichiometry of the reaction $2A + 3B \rightarrow P$ implies that when the concentration of P has increased from 0 to x, the concentration of A has fallen to $[A]_0 - 2x$ and the concentration of B has fallen to $[B]_0 - 3x$. This is because each P that forms entails the disappearance of two A and three B. The rate law $v = d[P]/dt = k_r[A][B]$ then becomes

$$\frac{d[P]}{dt} = k_r([A]_0 - 2x)([B]_0 - 3x) \quad \text{hence} \quad \frac{dx}{dt} = k_r([A]_0 - 2x)([B] - 3x)$$

where to go to the second expression $[P] = x$ is used, which implies that $d[P]dt = dx/dt$. The expression is rearranged and the initial condition $x = 0$ when $t = 0$ is applied. This gives the integrations required as

$$\int_0^x \frac{1}{([A]_0 - 2x)([B]_0 - 3x)}\,dx = \int_0^t k_r\,dt$$

The right-hand side evaluates to $k_r t$. The left-hand side is evaluated using the integrals from the *Resource section*

$$\begin{aligned}\int_0^x \frac{1}{([A]_0 - 2x)([B]_0 - 3x)}\,dx &= \int_0^x \frac{1}{2(\tfrac{1}{2}[A]_0 - x) \times 3(\tfrac{1}{3}[B]_0 - x)}\,dx \\ &= \frac{1}{6}\overbrace{\int_0^x \frac{1}{(\tfrac{1}{2}[A]_0 - x)(\tfrac{1}{3}[B]_0 - x)}\,dx}^{\text{Integral A.3}} \\ &= \frac{1}{6} \times \frac{1}{\tfrac{1}{3}[B]_0 - \tfrac{1}{2}[A]_0} \times \ln \frac{(\tfrac{1}{3}[B]_0 - x)(\tfrac{1}{2}[A]_0)}{(\tfrac{1}{2}[A]_0 - x)(\tfrac{1}{3}[B]_0)} \\ &= \frac{1}{2[B]_0 - 3[A]_0} \ln \frac{([B]_0 - 3x)[A]_0}{([A]_0 - 2x)[B]_0}\end{aligned}$$

Combining this with the right-hand side the integrated rate law is

$$\boxed{\frac{1}{2[B]_0 - 3[A]_0} \ln \frac{([B]_0 - 3x)[A]_0}{([A]_0 - 2x)[B]_0} = k_r t}$$

P17B.18 A reaction of the form $A \rightarrow P$ that is nth order in A has rate law $v = k_r[A]^n$. Combining this with [17A.3b–*726*], $v = (1/\nu_J)(d[J]/dt)$ gives

$$\frac{1}{-1}\frac{d[A]}{dt} = k_r[A]^n \quad \text{hence} \quad -[A]^{-n}\,d[A] = k_r\,dt$$

Initially, at $t = 0$, the concentration of A is $[\mathrm{A}]_0$, and at a later time t it is $[\mathrm{A}]$. These are used as the limits of the integration to give

$$\overbrace{\int_{[\mathrm{A}]_0}^{[\mathrm{A}]} -[\mathrm{A}]^{-n}\,\mathrm{d}[\mathrm{A}]}^{\text{Integral A.1}} = \int_0^t k_\mathrm{r}\,\mathrm{d}t \quad \text{hence} \quad \frac{1}{n-1}[\mathrm{A}]^{-(n-1)}\bigg|_{[\mathrm{A}]_0}^{[\mathrm{A}]} = k_\mathrm{r}t\bigg|_0^t$$

$$\text{hence} \quad \frac{1}{n-1}\left(\frac{1}{[\mathrm{A}]^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right) = k_\mathrm{r}t \qquad (\text{for } n \neq 1)$$

This integrated rate law is equivalent to that given in Table 17B.3 on page 735 and is valid for all values of n, including fractional values, except for $n = 1$. Dividing through by k_r gives

$$t = \frac{1}{(n-1)k_\mathrm{r}}\left(\frac{1}{[\mathrm{A}]^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right)$$

Setting $t = t_{1/2}$ when $[\mathrm{A}] = \tfrac{1}{2}[\mathrm{A}]_0$ gives

$$t_{1/2} = \frac{1}{(n-1)k_\mathrm{r}}\left(\frac{1}{(\tfrac{1}{2}[\mathrm{A}])^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right) = \frac{2^{n-1}-1}{(n-1)k_\mathrm{r}[\mathrm{A}]_0^{n-1}}$$

Similarly, setting $t = t_{3/4}$ when $[\mathrm{A}] = \tfrac{3}{4}[\mathrm{A}]_0$ gives

$$t_{3/4} = \frac{1}{(n-1)k_\mathrm{r}}\left(\frac{1}{(\tfrac{3}{4}[\mathrm{A}])^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right) = \frac{(\tfrac{4}{3})^{n-1}-1}{(n-1)k_\mathrm{r}[\mathrm{A}]_0^{n-1}}$$

Hence

$$\frac{t_{1/2}}{t_{3/4}} = \frac{(2^{n-1}-1)/(n-1)k_\mathrm{r}[\mathrm{A}]_0^{n-1}}{[(\tfrac{4}{3})^{n-1}-1]/(n-1)k_\mathrm{r}[\mathrm{A}]_0^{n-1}} = \boxed{\frac{2^{n-1}-1}{(\tfrac{4}{3})^{n-1}-1}}$$

17C **Reactions approaching equilibrium**

Answers to discussion questions

D17C.2 If the equilibrium position shifts with pressure, a pressure jump can be used to alter the rate of the reaction. For such an effect on equilibrium, the volume change of the reaction must be non-zero.

Solutions to exercises

E17C.1(b) The binding of the drug to protein is represented by the equilibrium

$$\text{Protein} + \text{Drug} \underset{k_\mathrm{r}'}{\overset{\mathrm{k_r}}{\rightleftharpoons}} \text{Complex}$$

The equilibrium constant in terms of rate constants is given by [17C.8–*738*], $K = k_\mathrm{r}c^\ominus/k_\mathrm{r}'$. Because the forward and backward reactions are of different order, the

$c^\ominus$ is included so that the ratio of k_r, with units $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, to k'_r, with units $\mathrm{s^{-1}}$, is turned into a dimensionless quantity. Rearranging for k'_r gives

$$k'_r = \frac{k_r c^\ominus}{K} = \frac{(1.5\times10^8\ \mathrm{dm^3\,mol^{-1}\,s^{-1}})\times(1\ \mathrm{mol\,dm^{-3}})}{200}$$
$$= \boxed{7.5\times10^5\ \mathrm{s^{-1}}}$$

E17C.2(b) The relaxation time in a jump experiment is given by [17C.9a–*739*], $\tau = 1/(k_r + k'_r)$. Both forward and reverse reactions are first-order, so their rate constants are related to their half-lives according to [17B.3–*732*], $t_{1/2} = \ln 2/k_r$, which is rearranged to $k_r = \ln 2/t_{1/2}$. This is used to replace k_r and k'_r in the expression for τ to give

$$\tau = (k_r + k'_r)^{-1} = \left(\frac{\ln 2}{t_{1/2}} + \frac{\ln 2}{t'_{1/2}}\right)^{-1} = \left(\frac{\ln 2}{24\ \mathrm{ms}} + \frac{\ln 2}{39\ \mathrm{ms}}\right)^{-1} = \boxed{21\ \mathrm{ms}}$$

Solutions to problems

P17C.2 The forward and backward reactions are

$$\mathrm{A}\rightarrow 2\mathrm{B} \quad \frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_r[\mathrm{A}] \qquad\qquad 2\mathrm{B}\rightarrow\mathrm{A} \quad \frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k'_r[\mathrm{B}]^2$$

The concentration of A is reduced by the forward reaction at a rate $k_r[\mathrm{A}]$ but is increased by the backward reaction at a rate $k'_r[\mathrm{B}]^2$. The net rate of change is therefore $\mathrm{d}[\mathrm{A}]/\mathrm{d}t = -k_r[\mathrm{A}] + k'_r[\mathrm{B}]^2$. If the initial concentration of A is $[\mathrm{A}]_0$, the stoichiometry of the reaction implies that $[\mathrm{B}] = 2([\mathrm{A}]_0 - [\mathrm{A}])$. Therefore

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_r[\mathrm{A}] + 4k'_r([\mathrm{A}]_0 - [\mathrm{A}])^2$$

To solve this differential equation, it is convenient to define a new variable $x = [\mathrm{A}]/[\mathrm{A}]_0$, so that $[\mathrm{A}] = [\mathrm{A}]_0 x$ and $\mathrm{d}[\mathrm{A}]/\mathrm{d}t = [\mathrm{A}]_0\mathrm{d}x/\mathrm{d}t$. Making these substitutions gives

$$[\mathrm{A}]_0\frac{\mathrm{d}x}{\mathrm{d}t} = -k_r[\mathrm{A}]_0 x + 4k'_r([\mathrm{A}]_0 - [\mathrm{A}]_0 x)^2 = -k_r[\mathrm{A}]_0 x + 4k'_r[\mathrm{A}]_0^2(1-x)^2$$

Dividing this expression through by $[\mathrm{A}]_0$ and then taking out a factor of $4k'_r[\mathrm{A}]_0$ gives

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -k_r x + 4k'_r[\mathrm{A}]_0(1-x)^2 = 4k'_r[\mathrm{A}]_0\left[-\frac{k_r}{4k'_r[\mathrm{A}]_0} + (1-x)^2\right]$$
$$= 4k'_r[\mathrm{A}]_0\left[-\frac{k_r}{4k'_r[\mathrm{A}]_0} + 1 - 2x + x^2\right]$$
$$= 4k'_r[\mathrm{A}]_0\left[x^2 + \left(2 - \frac{k_r}{4k'_r[\mathrm{A}]_0}\right)x + 1\right]$$

The term in square brackets is a quadratic in x which may therefore be written $(a-x)(b-x)$, where a and b are the roots of $x^2-(2+k_r/4k_r'[A]_0)x+1=0$, that is

$$a=\frac{-(2+k_r/4k_r'[A]_0)+\sqrt{(2+k_r/4k_r'[A]_0)^2-4}}{2}$$

and b is the same but with the negative square root. Therefore

$$\frac{dx}{dt}=4k_r'[A]_0(a-x)(b-x) \;\text{ hence }\; \int_1^x \frac{1}{(a-x)(b-x)}\,dx=\int_0^t 4k_r'[A]_0\,dt$$

where the initial condition that $x=[A]/[A]_0=1$ when $t=0$ is applied. The integral on the right is $4k_r'[A]_0t$, while the integral on the left is evaluated using integral A.3 in the *Resource section* to give

$$\frac{1}{b-a}\ln\frac{(b-x)(a-1)}{(a-x)(b-1)}=4k_r'[A]_0t$$

Rearranging for x gives

$$\frac{(b-x)(a-1)}{(a-x)(b-1)}=e^{4(b-a)k_r'[A]_0t}$$

$$\text{hence}\quad (b-x)=(a-x)\frac{b-1}{a-1}e^{4k_r'[A]_0t}$$

$$\text{hence}\quad b-\frac{a(b-1)}{a-1}e^{4(b-a)k_r'[A]_0t}=x\left(1-\frac{b-1}{a-1}e^{4(b-a)k_r'[A]_0t}\right)$$

$$\text{hence}\quad x=\frac{b-[a(b-1)/(a-1)]e^{4(b-a)k_r'[A]_0t}}{1-[(b-1)/(a-1)]e^{4(b-a)k_r'[A]_0t}}$$

This expression gives $x=[A]/[A]_0$ as a function of time; as defined above a and b are constants that depend on the relative values of k_r, k_r', and $[A]_0$.

As an example, for the specific case $k_r=k_r'[A]_0$ evaluation of the expression for a and b given above yields $a=1.64...$ and $b=0.609...$. Putting these into the expression for x and replacing $k_r'[A]_0$ by k_r in the exponents for clarity in this specific case gives

$$x=\frac{\overbrace{(0.609...)}^{b}+\overbrace{(1.00...)}^{a(b-1)/(a-1)}\times\exp[\overbrace{(-4.12...)}^{4(b-a)}k_rt]}{1+\underbrace{(0.609...)}_{(b-1)/(a-1)}\times\exp[\underbrace{(-4.12...)}_{4(b-a)}k_rt]}$$

The dimensionless quantity $x=[A]/[A]_0$ is plotted against the likewise dimensionless quantity k_rt in Fig. 17.8. The graph shows that initially the concentration of A decreases, because the backwards reaction is unimportant compared to the forwards reaction due to little product B being present, but then levels off as the system comes to equilibrium. An expression for [B] is found by recalling from above that $[B]=2([A]_0-[A])$. Therefore

$$\frac{[B]}{[A]_0}=2(1-x)=2\left(1-\frac{(0.609...)+(1.00...)e^{(-4.12...)k_rt}}{1-(0.609...)e^{(-4.12...)k_rt}}\right)$$

This expression for $[B]/[A]_0$ is also plotted on Fig. 17.8.

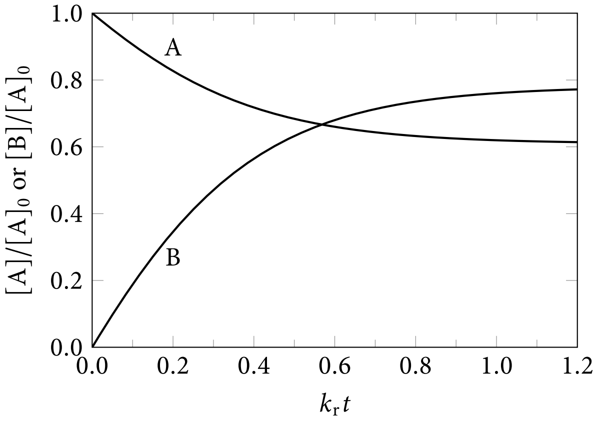


Figure 17.8

P17C.4 A mechanism containing three steps is

$$A \underset{k'_a}{\overset{k_a}{\rightleftharpoons}} B \underset{k'_b}{\overset{k_b}{\rightleftharpoons}} C \underset{k'_c}{\overset{k_c}{\rightleftharpoons}} D$$

At equilibrium, the forward and backward reactions of each step are equal.

$$\text{Step 1} \quad k_a[A]_{eq} = k'_a[B]_{eq} \quad \text{hence} \quad [B]_{eq} = [A]_{eq} \times \frac{k_a}{k'_a}$$

$$\text{Step 2} \quad k_b[B]_{eq} = k'_b[C]_{eq}$$

$$\text{hence} \quad [C]_{eq} = [B]_{eq} \times \frac{k_b}{k'_b} = [A]_{eq} \times \frac{k_a}{k'_a} \times \frac{k_b}{k'_b}$$

$$\text{Step 3} \quad k_c[C]_{eq} = k'_c[D]_{eq}$$

$$\text{hence} \quad [D]_{eq} = [C]_{eq} \times \frac{k_c}{k'_c} = [A]_{eq} \times \frac{k_a}{k'_a} \times \frac{k_b}{k'_b} \times \frac{k_c}{k'_c}$$

Generalising this process it is clear that for a reaction

$$A \underset{k'_a}{\overset{k_a}{\rightleftharpoons}} B \underset{k'_b}{\overset{k_b}{\rightleftharpoons}} C \underset{k'_c}{\overset{k_c}{\rightleftharpoons}} D \rightleftharpoons \ldots \rightleftharpoons P$$

the equilibrium concentration of the final product P, and the equilibrium constant for the overall reaction $A \rightleftharpoons P$, are

$$[P]_{eq} = [A]_{eq} \times \frac{k_a}{k'_a} \times \frac{k_b}{k'_b} \times \frac{k_c}{k'_c} \times \ldots \quad \text{hence} \quad K = \frac{[P]_{eq}}{[A]_{eq}} = \boxed{\frac{k_a}{k'_a} \times \frac{k_b}{k'_b} \times \frac{k_c}{k'_c} \times \ldots}$$

P17C.6 The reaction $A \rightleftharpoons B+C$ is analysed in *How is that done?* 17C.1 on page 738 where it is shown that the relaxation time τ is given by $1/\tau = k_r + k'_r([B]_{eq} + [C]_{eq})$. In addition, the equilibrium constant is given by [17C.8–*738*], $K = (k_a/k'_a) \times$

$(k_b/k_b') \times \ldots$, but in this case in order for K to be dimensionless it is necessary to include a factor of $1/c^{\ominus}$ because k_r is a first-order rate constant with units $\mathrm{s^{-1}}$ while k_r' is a second-order rate constant with units $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$.

$$K = \frac{k_r}{k_r' c^{\ominus}} \quad \text{hence} \quad k_r = k_r' c^{\ominus} K$$

This is substituted into the expression for $1/\tau$ to give

$$1/\tau = k_r' c^{\ominus} K + k_r'([\mathrm{B}]_{\mathrm{eq}} + [\mathrm{C}]_{\mathrm{eq}})$$

which is then rearranged for k_r'

$$k_r' = \frac{1}{\tau} \times \frac{1}{c^{\ominus}K + [\mathrm{B}]_{\mathrm{eq}} + [\mathrm{C}]_{\mathrm{eq}}} = \frac{1}{3.0 \times 10^{-6}\ \mathrm{s}}$$

$$\times \frac{1}{(1\ \mathrm{mol\,dm^{-3}}) \times (2.0 \times 10^{-16}) + (0.20 \times 10^{-3}\ \mathrm{mol\,dm^{-3}}) + (0.20 \times 10^{-3}\ \mathrm{mol\,dm^{-3}})}$$

$$= 8.33\ldots \times 10^{8}\ \mathrm{dm^3\,mol^{-1}\,s^{-1}} = \boxed{8.3 \times 10^{8}\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}}$$

The rearranged expression for K above is then used to find k_r

$$k_r = k_r' c^{\ominus} K = (8.33\ldots \times 10^{8}\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}) \times (1\ \mathrm{mol\,dm^{-3}}) \times (2.0 \times 10^{-16})$$

$$= \boxed{1.7 \times 10^{-7}\ \mathrm{s^{-1}}}$$

17D The Arrhenius equation

Answers to discussion questions

D17D.2 The temperature dependence of some reactions is not Arrhenius-like, in the sense that a straight line is not obtained when $\ln k_r$ is plotted against $1/T$. However, it is still possible to define an activation energy using [17D.3–*742*], $E_a = RT^2(\mathrm{d}\ln k_r/\mathrm{d}T)$. 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 $\ln k_r$ against $1/T$ even if the Arrhenius plot is not a straight line. Non Arrhenius behaviour is sometimes a sign that quantum mechanical tunnelling is playing a significant role in the reaction. A reaction with a very small or zero activation energy, so that $k_r = A$, such as for some radical recombination reactions in the gas phase, has a rate that is largely temperature independent.

Solutions to exercises

E17D.1(b) The rate constant k_r for the decomposition is calculated at each temperature using the Arrhenius equation [17D.4–*743*], $k_r = A\mathrm{e}^{-E_a/RT}$. The half-life is given by [17B.3–*732*], $t_{1/2} = \ln 2/k_r$. Combining these expressions gives

$$t_{1/2} = \frac{\ln 2}{A\mathrm{e}^{-E_a/RT}} = \frac{\ln 2}{A}\mathrm{e}^{E_a/RT}$$

(i) At 20 °C

$$t_{1/2}=\frac{\ln 2}{4.00\times10^{15}\,\mathrm{s}^{-1}}\times\exp\left(\frac{261\times10^{3}\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times([20+273.15]\,\mathrm{K})}\right)$$

$$=\boxed{5.6\times10^{30}\,\mathrm{s}}\text{ or }1.8\times10^{23}\text{ years}$$

(ii) At 500 °C

$$t_{1/2}=\frac{\ln 2}{4.00\times10^{15}\,\mathrm{s}^{-1}}\times\exp\left(\frac{261\times10^{3}\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times([500+273.15]\,\mathrm{K})}\right)$$

$$=\boxed{74\,\mathrm{s}}$$

E17D.2(b) The relationship between the values of a rate constant at two different temperatures is given by [17D.2–*742*], $\ln(k_{r,2}/k_{r,1})=(E_a/R)(1/T_1-1/T_2)$. Rearranging for E_a gives

$$E_a=\frac{R\ln(k_{r,2}/k_{r,1})}{1/T_1-1/T_2}=\frac{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times\ln\left[(4.01\times10^{-2})/(2.25\times10^{-2})\right]}{1/([29+273.15]\,\mathrm{K})-1/([37+273.15]\,\mathrm{K})}$$

$$=5.62...\times10^{4}\,\mathrm{J\,mol^{-1}}=\boxed{56.3\,\mathrm{kJ\,mol^{-1}}}$$

The frequency factor is found by rearranging the Arrhenius equation [17D.4–*743*], $k_r=Ae^{-E_a/RT}$, for A. The data for both temperatures gives the same result.

At T_1 $\quad A=k_r e^{E_a/RT_1}$

$$=(2.25\times10^{-2}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}})\times\exp\frac{5.62...\times10^{4}\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times([29+273.15]\,\mathrm{K})}$$

$$=\boxed{1.21\times10^{8}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}}$$

At T_2 $\quad A=k_r e^{E_a/RT_2}$

$$=(4.01\times10^{-2}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}})\times\exp\frac{5.62...\times10^{4}\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times([37+273.15]\,\mathrm{K})}$$

$$=1.21\times10^{8}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$$

E17D.3(b) The relationship between the values of a rate constant at two different temperatures is given by [17D.2–*742*], $\ln(k_{r,2}/k_{r,1})=(E_a/R)(1/T_1-1/T_2)$. Rearranging for E_a, and using $k_{r,2}/k_{r,1}=2$ because the rate constant doubles between the two temperatures, gives

$$E_a=\frac{R\ln(k_{r,2}/k_{r,1})}{1/T_1-1/T_2}=\frac{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times\ln 2}{1/([25+273.15]\,\mathrm{K})-1/([35+273.15]\,\mathrm{K})}=\boxed{53\,\mathrm{kJ\,mol^{-1}}}$$

E17D.4(b) The relationship between the values of a rate constant at two different temperatures is given by [17D.2–*742*], $\ln(k_{r,2}/k_{r,1}) = (E_a/R)(1/T_1 - 1/T_2)$. Rearranging gives

$$\frac{R}{E_a}\ln\frac{k_{r,2}}{k_{r,1}} = \frac{1}{T_1} - \frac{1}{T_2} \quad \text{hence} \quad T_2 = \left(\frac{1}{T_1} - \frac{R}{E_a}\ln\frac{k_{r,2}}{k_{r,1}}\right)^{-1}$$

If k_r is to increase by 10 % then $k_{r,2} = k_{r,1} + 0.10 \times k_{r,1} = 1.10 \times k_{r,1}$, so $k_{r,2}/k_{r,1} = 1.10$. Hence, taking $T_1 = 25\ °\text{C}$,

$$T_2 = \left(\frac{1}{[25 + 273.15]\ \text{K}} - \frac{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}{99.1 \times 10^3\ \text{J mol}^{-1}}\ln 1.10\right)^{-1} = \boxed{298.9\ \text{K}} = \boxed{25.7\ °\text{C}}$$

E17D.5(b) As explained in Section 17D.2(a) on page 743 the fraction f of collisions that are sufficiently energetic to be successful is given by the exponential factor $e^{-E_a/RT}$.

$$f = e^{-E_a/RT} = \exp\left(-\frac{80 \times 10^3\ \text{J mol}^{-1}}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (500\ \text{K})}\right) = \boxed{4.4 \times 10^{-9}}$$

Solutions to problems

P17D.2 The Arrhenius equation [17D.1–*741*], $\ln k_r = \ln A - E_a/RT$, implies that a plot of $\ln k_r$ against $1/T$ should give a straight line of slope $-E_a/R$ and intercept $\ln A$. The data are plotted in Fig. 17.9.

$\theta/°\text{C}$	T/K	k_r/s^{-1}	$1/(T/\text{K})$	$\ln(k_r/\text{s}^{-1})$
0.0	273.2	2.46×10^{-3}	0.003 66	−6.01
20.0	293.2	4.51×10^{-2}	0.003 41	−3.10
40.0	313.2	5.76×10^{-1}	0.003 19	−0.55

The data fall on a good straight line, the equation for which is

$$\ln(k_r/\text{s}^{-1}) = (-1.167 \times 10^4) \times 1/(T/\text{K}) + 36.71$$

Identifying the slope with $-E_a/R$ gives the activation energy as

$$E_a = -\textit{slope} \times R = -(-1.167 \times 10^4\ \text{K}) \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) = \boxed{97.0\ \text{kJ mol}^{-1}}$$

P17D.4 The Arrhenius equation [17D.1–*741*], $\ln k_r = \ln A - E_a/RT$, implies that a plot of $\ln k_r$ against $1/T$ should give a straight line of slope $-E_a/R$ and intercept $\ln A$. The data are plotted in Fig. 17.10.

T/K	$k_r/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$	$1/(T/\text{K})$	$\ln(k_r/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$
300.3	1.44×10^7	0.003 33	16.48
341.2	3.03×10^7	0.002 93	17.23
392.2	6.90×10^7	0.002 55	18.05

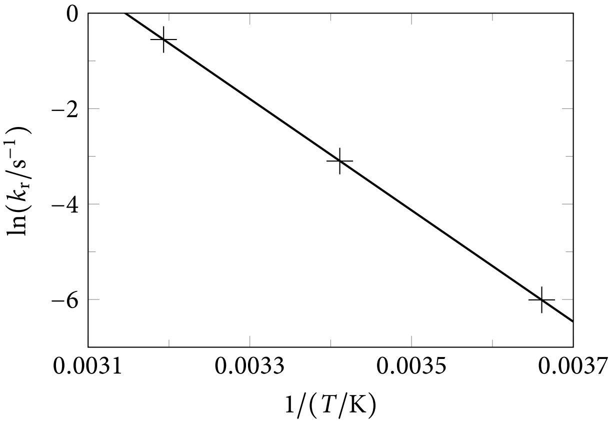


Figure 17.9

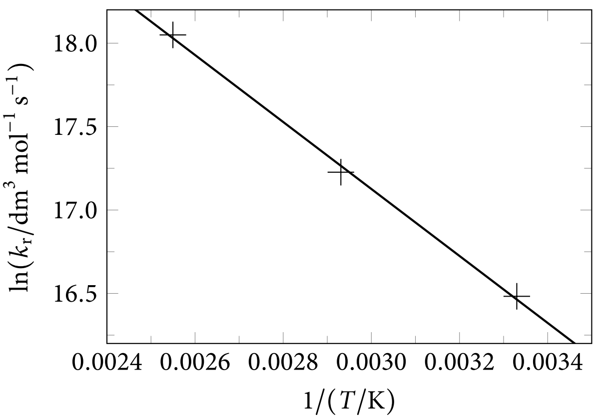


Figure 17.10

The data fall on a good straight line, the equation for which is

$$\ln(k_r/\mathrm{dm^3\,mol^{-1}\,s^{-1}}) = (-2.007\times10^3)\times 1/(T/\mathrm{K}) + 23.15$$

Identifying the slope with $-E_a/R$ gives the activation energy as

$$E_a = -slope\times R = -(-2.007\times10^3\ \mathrm{K})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) = \boxed{16.7\ \mathrm{kJ\,mol^{-1}}}$$

Identifying the intercept with $\ln A$ gives the frequency factor as

$$A = e^{23.15}\ \mathrm{dm^3\,mol^{-1}\,s^{-1}} = \boxed{1.13\times10^{10}\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}}$$

The units of A are the same as the units of k_r.

P17D.6 (a) The rate constant is estimated using the Arrhenius equation [17D.4–*743*],

$k_r = Ae^{-E_a/RT}$.

$$k_r = (1.13 \times 10^9\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}) \times \exp\left(\frac{-14.1 \times 10^3\ \mathrm{J\,mol^{-1}}}{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (263\ \mathrm{K})}\right)$$
$$= 1.79... \times 10^6\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$$

The rate equation for the bimolecular reaction $CH_4 + OH \rightarrow CH_3 + H_2O$ is $v = -d[CH_4]/dt = k_r[CH_4][OH]$, so the rate of consumption of methane is

$$-\frac{d[CH_4]}{dt} = k_r[CH_4][OH]$$
$$= (1.79... \times 10^6\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}) \times (40 \times 10^{-9}\ \mathrm{mol\,dm^{-3}}) \times (3.5 \times 10^{-15}\ \mathrm{mol\,dm^{-3}})$$
$$= 2.51... \times 10^{-16}\ \mathrm{mol\,dm^{-3}\,s^{-1}} = \boxed{2.5 \times 10^{-16}\ \mathrm{mol\,dm^{-3}\,s^{-1}}}$$

(b) Multiplication of the rate in $\mathrm{mol\,dm^{-3}\,s^{-1}}$ by the volume of the atmosphere gives the rate in $\mathrm{mol\,s^{-1}}$, and multiplication by the molar mass of methane, $16.0416\ \mathrm{g\,mol^{-1}}$, gives the rate in $\mathrm{g\,s^{-1}}$. Finally, multiplication by the length of a year in seconds, $365 \times 24 \times 60^2 = 31536000$ s, gives the mass consumed anually.

$$m = (2.51... \times 10^{-16}\ \mathrm{mol\,dm^{-3}\,s^{-1}}) \times (4 \times 10^{21}\ \mathrm{dm^3}) \times (16.0416\ \mathrm{g\,mol^{-1}}) \times (31536000\ \mathrm{s}) \times \frac{1\ \mathrm{kg}}{1000\ \mathrm{g}} = \boxed{5.1 \times 10^{11}\ \mathrm{kg}}$$

17E Reaction mechanisms

Answers to discussion questions

D17E.2 The rate-determining step is what it says it is, the step whose rate determines the overall rate of reaction. Any steps subsequent to the rate-determining step cannot, by definition, go any faster than the rate-determining step, and in fact they proceed at the same rate as the rate-determining step. A step prior to the rate-determining step may proceed faster that the rate-determining step.

D17E.4 If several steps are involved in a reaction mechanism it is possible that changes in the concentrations of the species involved will result in a change in the rate-determining step, and hence a change in the rate law. This may result in a change of order. A simple example is the Lindemann–Hinshelwood mechanism considered in Section 17F.1 on page 753 where there is a change for first- to second-order kinetics depending on the pressure of the reactants.

D17E.6 In a multi-step mechanism it is possible that the overall rate constant for the reaction will be a composite of the rate constants for different steps. If, in this expression for the overall rate constant, a rate constant for an individual step appears to a negative power, k_r^{-a}, then this term will decrease with increasing temperature and so make a negative contribution to the overall activation energy. If this effect is the dominant one, the overall activation energy may be negative. A simple example of this behaviour is possible for reactions involving pre-equilibrium, as discussed in Section 17E.5 on page 750.

Solutions to exercises

E17E.1(b) (i) The pre-equilibrium $A + B \rightleftharpoons U$ is described by the equilibrium constant K given by

$$K = \frac{[U]/c^\ominus}{([A]/c^\ominus)([B]/c^\ominus)} = \frac{[U]c^\ominus}{[A][B]} \quad \text{hence} \quad [U] = \frac{K[A][B]}{c^\ominus}$$

The equilibrium constant K is written in terms of rate constants using [17C.8–*738*], $K = (k_a/k'_a) \times (k_b/k'_b) \times ....$ However, in order to make K dimensionless it is necessary in this case to include a factor of $1/c^\ominus$ because k_a is a second-order rate constant with units $\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ while k'_a is a first-order rate constant with units s^{-1}. Thus $K = k_a c^\ominus/k'_a$, which, on substituting into the above expression for $[U]$ yields

$$[U] = \frac{k_a c^\ominus}{k'_a} \times \frac{[A][B]}{c^\ominus} = \frac{k_a}{k'_a}[A][B]$$

This expression is alternatively obtained by noting that at equilibrium the rates of the forward and reverse reactions are the same (provided the formation of H can be ignored)

$$k_a[A][B] = k'_a[U] \quad \text{hence} \quad [U] = \frac{k_a}{k'_a}[A][B]$$

The rate of formation of H is $d[H]/dt = k_b[U]$; substituting the expression for $[U]$ into this gives

$$\frac{d[H]}{dt} = k_b[U] = \boxed{\frac{k_a k_b}{k'_a}[A][B]}$$

(ii) The net rate of change in the concentration of U is

$$\frac{d[U]}{dt} = k_a[A][B] - k'_a[U] - k_b[U]$$

In the steady-state approximation this is assumed to be zero

$$k_a[A][B] - k'_a[U] - k_b[U] = 0 \quad \text{hence} \quad k_a[A][B] = [U](k'_a + k_b)$$

$$\text{hence}[U] = \frac{k_a[A][B]}{k'_a + k_b}$$

The rate of formation of H is given by $\mathrm{d}[\mathrm{H}]/\mathrm{d}t = k_\mathrm{b}[\mathrm{U}]$; substituting the above expression for $[\mathrm{U}]$ into this gives

$$\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t} = k_\mathrm{b}[\mathrm{U}] = \frac{k_\mathrm{a}k_\mathrm{b}[\mathrm{A}][\mathrm{B}]}{k'_\mathrm{a} + k_\mathrm{b}}$$

If the rate of decay of U back to A + B is much faster than the decay of U to H, that is if $k'_\mathrm{a}[\mathrm{U}] \gg k_\mathrm{b}[\mathrm{U}]$, the k_b term in the denominator is neglected in comparison to k'_a and the expression becomes

$$\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t} \approx \frac{k_\mathrm{a}k_\mathrm{b}[\mathrm{A}][\mathrm{B}]}{k'_\mathrm{a}} = \frac{k_\mathrm{a}k_\mathrm{b}}{k'_\mathrm{a}}[\mathrm{A}][\mathrm{B}]$$

which is the same as the rate law derived in part (i) assuming a pre-equilibrium. This is because under these assumptions the removal of U to form product is then too slow to affect the maintenance of the equilibrium between A, B and U.

On the other hand, if the rate of conversion of U to H with rate $k_\mathrm{b}[\mathrm{U}]$ is much faster than the decay back to starting materials with rate $k'_\mathrm{a}[\mathrm{U}]$, that is if $k_\mathrm{b} \gg k'_\mathrm{a}$, the denominator of the rate law is approximated by k_b and the rate law becomes

$$\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t} \approx \frac{k_\mathrm{a}k_\mathrm{b}[\mathrm{A}][\mathrm{B}]}{k_\mathrm{b}} = k_\mathrm{a}[\mathrm{A}][\mathrm{B}]$$

This rate law corresponds to the first step A+B → U being rate-determining: once U has formed from A and B in this step it immediately goes on to form product.

E17E.2(b) If step (1) forms a pre-equilibrium, the equilibrium constant K is given by

$$K = \frac{([\mathrm{CH_2ClCH_2O^-}]/c^\ominus)}{([\mathrm{CH_2ClCH_2OH}]/c^\ominus)([\mathrm{OH^-}]/c^\ominus)} = \frac{[\mathrm{CH_2ClCH_2O^-}]c^\ominus}{[\mathrm{CH_2ClCH_2OH}][\mathrm{OH^-}]}$$

This is rearranged to $\quad [\mathrm{CH_2ClCH_2O^-}] = \dfrac{K[\mathrm{CH_2ClCH_2OH}][\mathrm{OH^-}]}{c^\ominus}$

The rate of formation of $\mathrm{(CH_2CH_2)_2O}$ is given by the rate of step (2),

$$\frac{\mathrm{d}[\mathrm{(CH_2CH_2)_2O}]}{\mathrm{d}t} = k_2[\mathrm{CH_2ClCH_2O^-}]$$

Substituting the above expression for $[\mathrm{CH_2ClCH_2O^-}]$ into this gives

$$v = \frac{\mathrm{d}[\mathrm{(CH_2CH_2)_2O}]}{\mathrm{d}t} = \frac{k_2K}{c^\ominus}[\mathrm{CH_2ClCH_2OH}][\mathrm{OH^-}]$$

This is the required expression. The factor of $1/c^\ominus$ is necessary for the rate equation to be dimensionally consistent.

E17E.3(b) The overall activation energy for a reaction consisting of a pre-equilibrium followed by a rate-limiting elementary step is given by [17E.13–*751*], $E_\mathrm{a} = E_\mathrm{a,a} + E_\mathrm{a,b} - E_\mathrm{a,a'}$, where $E_\mathrm{a,a}$ and $E_\mathrm{a,a'}$ are the forward and reverse activation energies for the pre-equilibrium and $E_\mathrm{a,b}$ is the activation energy for the following elementary step. In this case

$$E_\mathrm{a} = (27\ \mathrm{kJ\,mol^{-1}}) + (15\ \mathrm{kJ\,mol^{-1}}) - (35\ \mathrm{kJ\,mol^{-1}}) = \boxed{+7\ \mathrm{kJ\,mol^{-1}}}$$

Solutions to problems

P17E.2 The concentrations of A, I, and P in the reaction mechanism $A \xrightarrow{k_a} I \xrightarrow{k_b} P$ are given by [17E.4a–*747*], [17E.4b–*747*], and [17E.4c–*747*].

$$[A] = [A]_0 e^{-k_a t} \qquad [I] = \frac{k_a}{k_b - k_a}\left(e^{-k_a t} - e^{-k_b t}\right)[A]_0$$

$$[P] = \left\{1 + \frac{k_a e^{-k_b t} - k_b e^{-k_a t}}{k_b - k_a}\right\}[A]_0$$

These expressions are plotted for $[A]_0 = 1\ \text{mol dm}^{-3}$, $k_b = 1\ \text{s}^{-1}$, and four different values of k_a in Fig. 17.11. Note that the final plot has a different horizontal scale to the others.

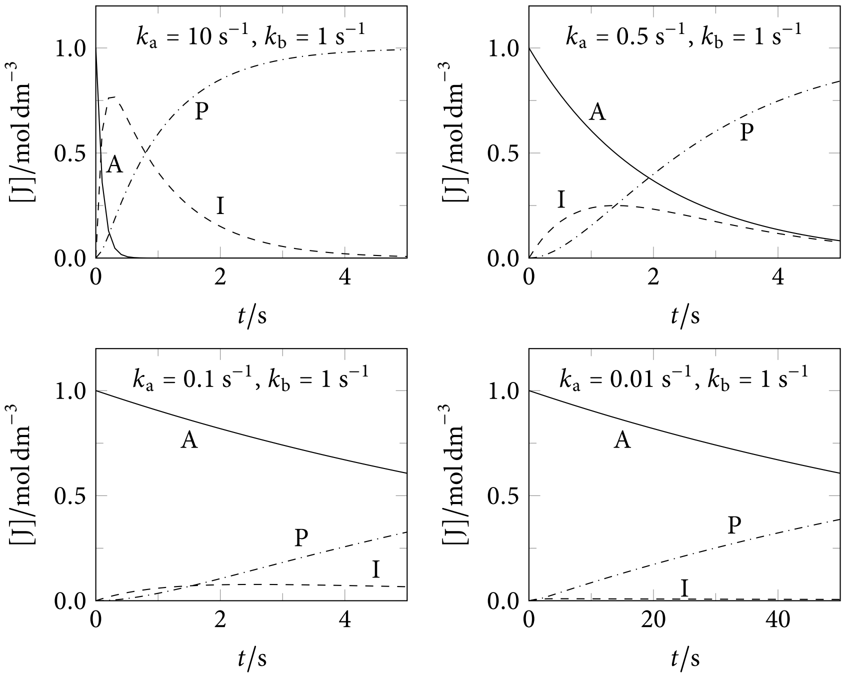


Figure 17.11

In the first plot, $k_a \gg k_b$, so A is quickly converted to I, and I is then converted more slowly to P. The rise in P mirrors the fall in I. On the other hand, in the last plot $k_a \ll k_b$, so as soon as I is formed it immediately goes on to P. Consequently the concentration of I remains low and approximately constant, and the rise in P mirrors the fall in A. This latter situation is the one to which the steady-state approximation applies. The maximum concentration reached by I decreases, and moves to later times, as the ratio k_a/k_b decreases.

P17E.4 For the scheme $A \underset{k_a'}{\overset{k_a}{\rightleftarrows}} B \underset{k_b'}{\overset{k_b}{\rightleftarrows}} C$ the net rates of change of the concentrations of A, B, and C are

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_\mathrm{a}[\mathrm{A}] + k'_\mathrm{a}[\mathrm{B}] \qquad \frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_\mathrm{a}[\mathrm{A}] - k'_\mathrm{a}[\mathrm{B}] - k_\mathrm{b}[\mathrm{B}] + k'_\mathrm{b}[\mathrm{C}]$$
$$\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = k_\mathrm{b}[\mathrm{B}] - k'_\mathrm{b}[\mathrm{C}]$$

If B is a reactive intermediate that reacts almost as soon as it is formed, the steady-state approximation applies to B and $\mathrm{d}[\mathrm{B}]/\mathrm{d}t = 0$. Therefore

$$k_\mathrm{a}[\mathrm{A}] - k'_\mathrm{a}[\mathrm{B}] - k_\mathrm{b}[\mathrm{B}] + k'_\mathrm{b}[\mathrm{C}] = 0 \quad \text{hence} \quad \underbrace{k_\mathrm{a}[\mathrm{A}] - k'_\mathrm{a}[\mathrm{B}]}_{\text{term 1}} = \underbrace{k_\mathrm{b}[\mathrm{B}] - k'_\mathrm{b}[\mathrm{C}]}_{\text{term 2}}$$

From the discussion above, it is evident that term 1 is equal to $-\mathrm{d}[\mathrm{A}]/\mathrm{d}t$ and term 2 is equal to $\mathrm{d}[\mathrm{C}]/\mathrm{d}t$. Therefore

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t}$$

which is precisely what is expected for the scheme $\mathrm{A} \underset{k'_\mathrm{r}}{\overset{k_\mathrm{r}}{\rightleftarrows}} \mathrm{C}$.

P17E.6 Application of the steady-state approximation to the intermediate $\mathrm{N_2O_2}$ gives

$$\frac{\mathrm{d}[\mathrm{N_2O_2}]}{\mathrm{d}t} = k_\mathrm{a}[\mathrm{NO}]^2 - k'_\mathrm{a}[\mathrm{N_2O_2}] - k_\mathrm{b}[\mathrm{N_2O_2}][\mathrm{O_2}] = 0$$

This is rearranged for $[\mathrm{N_2O_2}]$.

$$[\mathrm{N_2O_2}]\,(k'_\mathrm{a} + k_\mathrm{b}[\mathrm{O_2}]) = k_\mathrm{a}[\mathrm{NO}]^2 \quad \text{hence} \quad [\mathrm{N_2O_2}] = \frac{k_\mathrm{a}[\mathrm{NO}]^2}{k'_\mathrm{a} + k_\mathrm{b}[\mathrm{O_2}]}$$

The rate of formation of $\mathrm{NO_2}$ is then

$$\frac{\mathrm{d}[\mathrm{NO_2}]}{\mathrm{d}t} = 2k_\mathrm{b}[\mathrm{N_2O_2}][\mathrm{O_2}] = \boxed{\frac{2k_\mathrm{a}k_\mathrm{b}[\mathrm{NO}]^2[\mathrm{O_2}]}{k'_\mathrm{a} + k_\mathrm{b}[\mathrm{O_2}]}}$$

The factor of 2 arises because two $\mathrm{NO_2}$ molecules are formed in the final step. To go to the final expression, the concentration of $\mathrm{N_2O_2}$ from above is substituted in.

P17E.8 (a) The rate equations for the mechanism $hhhh... \underset{k'_\mathrm{a}}{\overset{k_\mathrm{a}}{\rightleftarrows}} hchh... \underset{k'_\mathrm{b}}{\overset{k_\mathrm{b}}{\rightleftarrows}} cccc...$ 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) Applying the steady-state approximation to *hchh...* so that $\mathrm{d}[hchh...]/\mathrm{d}t = 0$ gives

$$k_\mathrm{a}[hhhh...] - k_\mathrm{a}'[hchh...] - k_\mathrm{b}[hchh...] + k_\mathrm{b}'[cccc...] = 0$$

$$\text{hence}\quad [hchh...] = \frac{k_\mathrm{a}[hhhh...] + k_\mathrm{b}'[cccc...]}{k_\mathrm{a}' + k_\mathrm{b}}$$

Substituting this into the expression for $\mathrm{d}[hhhh...]/\mathrm{d}t$ gives

$$\begin{aligned}\frac{\mathrm{d}[hhhh...]}{\mathrm{d}t} &= -k_\mathrm{a}[hhhh...] + k_\mathrm{a}'\left(\frac{k_\mathrm{a}[hhhh...] + k_\mathrm{b}'[cccc...]}{k_\mathrm{a}' + k_\mathrm{b}}\right)\\ &= -\left(k_\mathrm{a} - \frac{k_\mathrm{a}'k_\mathrm{a}}{k_\mathrm{a}' + k_\mathrm{b}}\right)[hhhh...] + \frac{k_\mathrm{a}'k_\mathrm{b}'[cccc...]}{k_\mathrm{a}' + k_\mathrm{b}}\\ &= -\underbrace{\frac{k_\mathrm{a}k_\mathrm{b}}{k_\mathrm{a}' + k_\mathrm{b}}}_{k_\mathrm{r}}[hhhh...] + \underbrace{\frac{k_\mathrm{a}'k_\mathrm{b}'}{k_\mathrm{a}' + k_\mathrm{b}}}_{k_\mathrm{r}'}[cccc...]\end{aligned}$$

Similarly for $\mathrm{d}[cccc...]/\mathrm{d}t$

$$\begin{aligned}\frac{\mathrm{d}[cccc...]}{\mathrm{d}t} &= k_\mathrm{b}\left(\frac{k_\mathrm{a}[hhhh...] + k_\mathrm{b}'[cccc...]}{k_\mathrm{a}' + k_\mathrm{b}}\right)[hchh...] - k_\mathrm{b}'[cccc...]\\ &= \frac{k_\mathrm{a}k_\mathrm{b}[hhhh...]}{k_\mathrm{a}' + k_\mathrm{b}} - \left(k_\mathrm{b}' - \frac{k_\mathrm{b}k_\mathrm{b}'}{k_\mathrm{a}' + k_\mathrm{b}}\right)[cccc...]\\ &= \underbrace{\frac{k_\mathrm{a}k_\mathrm{b}}{k_\mathrm{a}' + k_\mathrm{b}}}_{k_\mathrm{r}}[hhhh...] - \underbrace{\frac{k_\mathrm{a}'k_\mathrm{b}'}{k_\mathrm{a}' + k_\mathrm{b}}}_{k_\mathrm{r}'}[cccc...]\end{aligned}$$

These expressions have precisely the same form as those for the mechanism *hhhh...* $\underset{k_\mathrm{r}'}{\overset{k_\mathrm{r}}{\rightleftarrows}}$ *cccc...* for which the expressions are

$$\frac{\mathrm{d}[hhhh...]}{\mathrm{d}t} = -k_\mathrm{r}[hhhh...] + k_\mathrm{r}'[cccc...] \qquad \frac{\mathrm{d}[cccc...]}{\mathrm{d}t} = k_\mathrm{r}[hhhh...] - k_\mathrm{r}'[cccc...]$$

Thus the two mechanisms are equivalent provided *hchh...* can be regarded as being a steady-state intermediate, that is, if the rate of its breakdown is much faster than the rate of its formation.

An alternative, and rather simpler approach, is to use the same argument as deployed in *Problem* P17E.4.

P17E.10 The reaction is shown schematically in Fig. 17.12.

As explained in Section 17E.6 on page 752, thermodynamic control arises when the reaction is allowed to reach equilibrium. The reactant R is therefore considered to be in equilibrium with both $\mathrm{P_1}$ and with $\mathrm{P_2}$

$$\mathrm{R} \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \mathrm{P_1} \qquad \mathrm{R} \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} \mathrm{P_2}$$

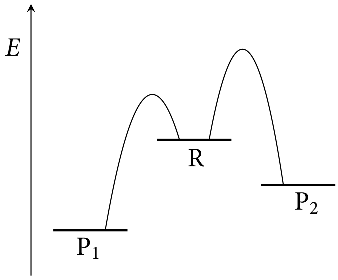


Figure 17.12

At equilibrium, the rates of the forward and backward reactions of R to P_1 are equal, as are those to P_2. Therefore

$$k_1[\mathrm{R}] = k_1'[\mathrm{P}_1] \quad \text{hence} \quad [\mathrm{P}_1] = \frac{k_1[\mathrm{R}]}{k_1'}; \quad k_2[\mathrm{R}] = k_2'[\mathrm{P}_2] \quad \text{hence} \quad [\mathrm{P}_2] = \frac{k_2[\mathrm{R}]}{k_2'}$$

The ratio of the two products is therefore

$$\frac{[\mathrm{P}_2]}{[\mathrm{P}_1]} = \frac{k_2[\mathrm{R}]/k_2'}{k_1[\mathrm{R}]/k_1'} = \boxed{\frac{k_2k_1'}{k_2'k_1}} = \boxed{\frac{K_2}{K_1}}$$

where K_1 and K_2 are the equilibrium constants for $\mathrm{R} \rightleftharpoons \mathrm{P}_1$ and $\mathrm{R} \rightleftharpoons \mathrm{P}_2$, respectively.

17F Examples of reaction mechanisms

Answers to discussion questions

D17F.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 [17F.12b–*756*], $\langle N\rangle = 1 + k_\mathrm{r}t[\mathrm{A}]_0$. 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.

As discussed in Section 17F.2(b) on page 756, chain polymerization involves initiation, propagation, and termination steps. 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 ([17F.15–*757*]) $\langle N\rangle = 2k_\mathrm{r}[\mathrm{M}][\mathrm{In}]^{-1/2}$ where $k_\mathrm{r} = k_\mathrm{p}(4fk_\mathrm{i}k_\mathrm{t})^{-1/2}$, and 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. It is seen 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.

D17F.4 As temperature increases, the rate of an enzyme-catalyzed reaction is expected 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.

Solutions to exercises

E17F.1(b) The effective rate constant for the Lindemann–Hinshelwood mechanism is given by [17F.8–*754*], $1/k_\mathrm{r} = k_\mathrm{a}'/k_\mathrm{a}k_\mathrm{b} + 1/k_\mathrm{a}[\mathrm{A}]$. The difference between the effective rate constant at two pressures is therefore

$$\frac{1}{k_{\mathrm{r},2}} - \frac{1}{k_{\mathrm{r},1}} = \frac{1}{k_\mathrm{a}}\left(\frac{1}{[\mathrm{A}]_2} - \frac{1}{[\mathrm{A}]_1}\right) \quad \text{hence} \quad k_\mathrm{a} = \frac{1/[\mathrm{A}]_2 - 1/[\mathrm{A}]_1}{1/k_{\mathrm{r},2} - 1/k_{\mathrm{r},1}}$$

The rate constant for the activation step, k_a, is therefore

$$k_\mathrm{a} = \frac{1/(25\ \mathrm{Pa}) - 1/(1.09\times10^{3}\ \mathrm{Pa})}{1/(2.2\times10^{-4}\ \mathrm{s}^{-1}) - 1/(1.7\times10^{-3}\ \mathrm{s}^{-1})} = \boxed{9.9\times10^{-6}\ \mathrm{Pa}^{-1}\ \mathrm{s}^{-1}}$$

or $\boxed{9.9\ \mathrm{MPa}^{-1}\ \mathrm{s}^{-1}}$.

E17F.2(b) The fraction of condensed groups at time t of a stepwise polymerisation is given by [17F.11–*755*], $p = k_\mathrm{r}t[\mathrm{A}]_0/(1 + k_\mathrm{r}t[\mathrm{A}]_0)$. Hence, after 10.00 h, or 10.00 h × $(60^2\ \mathrm{s})/(1\ \mathrm{h}) = 3.60\times10^4\ \mathrm{s}$,

$$\begin{aligned} p &= \frac{k_\mathrm{r}t[\mathrm{A}]_0}{1 + k_\mathrm{r}t[\mathrm{A}]_0} \\ &= \frac{(2.80\times10^{-2}\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1})\times(3.60\times10^{4}\ \mathrm{s})\times(50.0\times10^{-3}\ \mathrm{mol\,dm}^{-3})}{1+(2.80\times10^{-2}\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1})\times(3.60\times10^{4}\ \mathrm{s})\times(50.0\times10^{-3}\ \mathrm{mol\,dm}^{-3})} \\ &= 0.980... = \boxed{0.981} \end{aligned}$$

The degree of polymerisation in a stepwise polymerisation is given by [17F.12a–*755*], $\langle N\rangle = 1/(1-p)$.

$$\langle N\rangle = \frac{1}{1-p} = \frac{1}{1-0.980...} = \boxed{51}$$

E17F.3(b) The kinetic chain length in a chain polymerisation reaction is given by [17F.14c–*757*], $\lambda = k_r[\mathrm{M}][\mathrm{In}]^{-1/2}$. The ratio of chain length under the two different sets of conditions is therefore

$$\frac{\lambda_2}{\lambda_1} = \frac{k_r[\mathrm{M}]_2[\mathrm{In}]_2^{-1/2}}{k_r[\mathrm{M}]_1[\mathrm{In}]_1^{-1/2}} = \left(\frac{[\mathrm{M}]_2}{[\mathrm{M}]_1}\right) \times \left(\frac{[\mathrm{In}]_2}{[\mathrm{In}]_1}\right)^{-1/2} = 5.0 \times \left(\frac{1}{10.0}\right)^{-1/2} = \boxed{15.8}$$

E17F.4(b) The Michaelis–Menten equation for the rate of an enzyme-catalysed reaction is given by [17F.18a–*759*], $v = v_{\max}/(1 + K_\mathrm{M}/[\mathrm{S}]_0)$. Rearranging for $v_{\max}$ gives

$$v_{\max} = v\left(1 + \frac{K_\mathrm{M}}{[\mathrm{S}]_0}\right) = (0.205\ \mathrm{mmol\,dm^{-3}\,s^{-1}}) \times \left(1 + \frac{0.032\ \mathrm{mol\,dm^{-3}}}{0.875\ \mathrm{mol\,dm^{-3}}}\right)$$
$$= \boxed{0.212\ \mathrm{mmol\,dm^{-3}\,s^{-1}}}$$

E17F.5(b) The catalytic efficiency is defined in the exercise as $k_\mathrm{b}/K_\mathrm{M}$, and $v_{\max}$ is related to k_b according to [17F.17b–*759*], $v_{\max} = k_\mathrm{b}[\mathrm{E}]_0$, hence $k_\mathrm{b} = v_{\max}/[\mathrm{E}]_0$. Therefore, the catalytic efficiency is

$$\frac{k_\mathrm{b}}{K_\mathrm{M}} = \frac{v_{\max}}{K_\mathrm{M}[\mathrm{E}]_0} = \frac{4.25\times10^{-4}\ \mathrm{mol\,dm^{-3}\,s^{-1}}}{(0.032\ \mathrm{mol\,dm^{-3}}) \times (3.60\times10^{-9}\ \mathrm{mol\,dm^{-3}})}$$
$$= \boxed{3.7\times10^{6}\ \mathrm{dm^{3}\,mol^{-1}\,s^{-1}}}$$

Solutions to problems

P17F.2 The kinetic chain length in a chain polymerization is given by [17F.14c–*757*], $\lambda = k_r[\mathrm{M}][\mathrm{In}]^{-1/2}$. This represents the average number of molecules in a chain produced by one initiating radical, at the point at which the chain is terminated. Disproportionation termination does not change the number of monomers in the chain, so the average polymer length is equal to the kinetic chain length

$$\langle N\rangle = \lambda = \boxed{k_r[\mathrm{M}][\mathrm{In}]^{-1/2}}$$

This is in contrast to mutual termination, where as explained in Section 17F.2(b) on page 756 the average number of monomers in a terminated polymer is the sum of the numbers of monomers in the two combining polymer chains.

P17F.4 The Michaelis–Menten mechanism is

$$\mathrm{E} + \mathrm{S} \underset{k_\mathrm{a}'}{\overset{k_\mathrm{a}}{\rightleftharpoons}} \mathrm{ES} \xrightarrow{k_\mathrm{b}} \mathrm{E} + \mathrm{P}$$

If E, S and ES form a pre-equilibrium, then the rate of the forward step in this equilibrium, $k_\mathrm{a}[\mathrm{A}][\mathrm{S}]$, must be equal to the rate of the reverse step, $k_\mathrm{a}'[\mathrm{ES}]$. Hence $k_\mathrm{a}[\mathrm{E}][\mathrm{S}] = k_\mathrm{a}'[\mathrm{ES}]$. The total concentration of enzyme is $[\mathrm{E}]_0 = [\mathrm{E}] +$

[ES], so $[\mathrm{E}] = [\mathrm{E}]_0 - [\mathrm{ES}]$. Substituting this into the expression previously found gives

$$k_\mathrm{a}\left([\mathrm{E}]_0 - [\mathrm{ES}]\right)[\mathrm{S}] = k_\mathrm{a}'[\mathrm{ES}] \quad \text{hence} \quad [\mathrm{ES}] = \frac{k_\mathrm{a}[\mathrm{E}]_0[\mathrm{S}]}{k_\mathrm{a}[\mathrm{S}] + k_\mathrm{a}'}$$

The rate of product formation is given by the rate of the second step, $v = k_\mathrm{b}[\mathrm{ES}]$, hence

$$v = \frac{k_\mathrm{b}k_\mathrm{a}[\mathrm{E}]_0[\mathrm{S}]}{k_\mathrm{a}[\mathrm{S}] + k_\mathrm{a}'} = \frac{k_\mathrm{b}[\mathrm{E}]_0}{1 + k_\mathrm{a}'/k_\mathrm{a}[\mathrm{S}]} = \boxed{\frac{k_\mathrm{b}[\mathrm{E}]_0}{1 + k_\mathrm{a}'/k_\mathrm{a}[\mathrm{S}]_0}}$$

To go to the final expression, the fact that the substrate is typically in large excess compared to the enzyme, so that the free substrate concentration [S] is approximately equal to the initial substrate concentration $[\mathrm{S}]_0$, is used.

The equation based on the steady-state approximation is given by [17F.16–*759*],

$$v = \frac{k_\mathrm{b}[\mathrm{E}]_0}{1 + K_\mathrm{M}/[\mathrm{S}]_0} \quad \text{where} \quad K_\mathrm{M} = \frac{k_\mathrm{a}' + k_\mathrm{b}}{k_\mathrm{a}}$$

This is the same as the pre-equilibrium equation if $k_\mathrm{a}' \gg k_\mathrm{b}$, that is, if the ES complex is much more likely to revert to E + S than to react onward to products. This condition is assumed in applying the pre-equilibrium hypothesis, which requires that the reaction of ES to products is too slow relative to the reversion of ES to E + S to significantly affect the setting up of the pre-equilibrium.

P17F.6 The rate of product formation is $v = k_\mathrm{c}[\mathrm{ES}']$, so the task is to find an expression for $[\mathrm{ES}']$. The steady-state approximation is applied to the two intermediates ES and ES′

$$\frac{\mathrm{d}[\mathrm{ES}]}{\mathrm{d}t} = k_\mathrm{a}[\mathrm{E}][\mathrm{S}] - k_\mathrm{a}'[\mathrm{ES}] - k_\mathrm{b}[\mathrm{ES}] \approx 0 \quad \text{and} \quad \frac{\mathrm{d}[\mathrm{ES}']}{\mathrm{d}t} = k_\mathrm{b}[\mathrm{ES}] - k_\mathrm{c}[\mathrm{ES}'] \approx 0$$

The concentration of free enzyme E is given by $[\mathrm{E}] = [\mathrm{E}]_0 - [\mathrm{ES}] - [\mathrm{ES}']$. Substituting this into the steady-state expression for [ES] gives

$$\begin{aligned} &k_\mathrm{a}\left([\mathrm{E}]_0 - [\mathrm{ES}] - [\mathrm{ES}']\right)[\mathrm{S}] - k_\mathrm{a}'[\mathrm{ES}] - k_\mathrm{b}[\mathrm{ES}] = 0 \\ \text{hence}\quad &k_\mathrm{a}[\mathrm{S}][\mathrm{E}]_0 - k_\mathrm{a}[\mathrm{S}][\mathrm{ES}] - k_\mathrm{a}[\mathrm{S}][\mathrm{ES}'] - k_\mathrm{a}'[\mathrm{ES}] - k_\mathrm{b}[\mathrm{ES}] = 0 \end{aligned}$$

The steady-state expression for $[\mathrm{ES}']$ implies that $[\mathrm{ES}] = k_\mathrm{c}[\mathrm{ES}']/k_\mathrm{b}$. This is used to substitute for [ES] in the above expression to give

$$k_\mathrm{a}[\mathrm{S}][\mathrm{E}]_0 - k_\mathrm{a}[\mathrm{S}]\frac{k_\mathrm{c}}{k_\mathrm{b}}[\mathrm{ES}'] - k_\mathrm{a}[\mathrm{S}][\mathrm{ES}'] - k_\mathrm{a}'\frac{k_\mathrm{c}}{k_\mathrm{b}}[\mathrm{ES}'] - k_\mathrm{c}[\mathrm{ES}'] = 0$$

This expression is multiplied through by k_b and divided through by $k_\mathrm{a}[\mathrm{S}]$

$$\begin{aligned} &k_\mathrm{b}[\mathrm{E}]_0 - k_\mathrm{c}[\mathrm{ES}'] - k_\mathrm{b}[\mathrm{ES}'] - \frac{k_\mathrm{a}'k_\mathrm{c}}{k_\mathrm{a}[\mathrm{S}]}[\mathrm{ES}'] - \frac{k_\mathrm{b}k_\mathrm{c}}{k_\mathrm{a}[\mathrm{S}]}[\mathrm{ES}'] = 0 \\ \text{hence}\quad &k_\mathrm{b}[\mathrm{E}]_0 = [\mathrm{ES}']\left(k_\mathrm{c} + k_\mathrm{b} + \frac{k_\mathrm{a}'k_\mathrm{c}}{k_\mathrm{a}[\mathrm{S}]} + \frac{k_\mathrm{b}k_\mathrm{c}}{k_\mathrm{a}[\mathrm{S}]}\right) \\ &\phantom{k_\mathrm{b}[\mathrm{E}]_0} = [\mathrm{ES}']\left((k_\mathrm{b} + k_\mathrm{c}) + \frac{k_\mathrm{c}(k_\mathrm{a}' + k_\mathrm{b})}{k_\mathrm{a}[\mathrm{S}]}\right) \end{aligned}$$

Dividing through by $(k_b + k_c)$ gives $\dfrac{k_b[E]_0}{k_b + k_c} = [ES']\left(1 + \dfrac{k_c(k'_a + k_b)}{k_a(k_b + k_c)[S]}\right)$

$$\text{hence}\quad [ES'] = \frac{(k_b/[k_b + k_c])\,[E]_0}{1 + (k_c[k'_a + k_b]/k_a[k_b + k_c])\,/[S]}$$

This expression is substituted into $v = k_c[ES']$ to give

$$v = k_c[ES'] = \frac{(k_b k_c/[k_b + k_c])\,[E]_0}{1 + (k_c[k'_a + k_b]/k_a[k_b + k_c])\,/[S]_0}$$

Note that $[S]$ is replaced by $[S]_0$ because the substrate is typically in large excess relative to the enzyme so that $[S] \approx [S]_0$. The final rate equation has the same form as the Michaelis–Menten equation [17F.18a–*759*], with

$$v = \frac{v_{max}}{1 + K_M/[S]_0}, \quad \text{with} \quad v_{max} = \frac{k_b k_c[E]_0}{k_b + k_c} \quad \text{and} \quad K_M = \frac{k_c(k'_a + k_b)}{k_a(k_b + k_c)}$$

P17F.8 (a) The Michaelis–Menten equation [17F.16–*759*] is $v = k_b[E]_0/(1+K_M/[S]_0)$, or [17F.18a–*759*] $v = v_{max}/(1 + K_M/[S]_0)$. Rearranging gives

$$v\left(1 + \frac{K_M}{[S]_0}\right) = v_{max}$$

$$\text{hence}\quad v + \frac{vK_M}{[S]_0} = v_{max}$$

$$\text{hence}\quad \frac{v}{[S]_0} = -\frac{1}{K_M}v + \frac{v_{max}}{K_M}$$

This expression implies that a plot of $v/[S]_0$ against v should be a straight line of slope $-1/K_M$ and intercept v_{max}/K_M.

(b) Note that the question should read *a Hanes plot of* $[S]_0/v$ *against* $[S]_0$, not $v/[S]_0$ *against* $[S]_0$.

The Michaelis–Menten equation [17F.18a–*759*] is inverted and then multiplied through by $[S]_0$ to give

$$\frac{1}{v} = \frac{1 + K_M/[S]_0}{v_{max}} \quad \text{hence} \quad \frac{[S]_0}{v} = \frac{[S]_0}{v_{max}} + \frac{K_M}{v_{max}}$$

This expression implies that a plot of $[S]_0/v$ against $[S]_0$ should be a straight line of slope $1/v_{max}$ and intercept K_M/v_{max}.

(c) The data are plotted as a Lineweaver–Burk plot in Fig. 17.13, as an Eadie–Hofstee plot in Fig. 17.14, and as a Hanes plot in Fig. 17.15. In all cases the data lie on a good straight line.

$[H_2O_2]/\text{mol dm}^{-3}$	$v/\text{mol dm}^{-3}\,\text{s}^{-1}$	$1/([H_2O_2]/\text{mol dm}^{-3})$	$1/(v/\text{mol dm}^{-3}\,\text{s}^{-1})$	$v/[H_2O_2]\ /\text{s}^{-1}$	$[H_2O_2]/v\ /\text{s}$
0.300	4.431	3.333	0.2257	14.77	0.0677
0.400	4.518	2.500	0.2213	11.30	0.0885
0.500	4.571	2.000	0.2188	9.14	0.1094
0.600	4.608	1.667	0.2170	7.68	0.1302
0.700	4.634	1.429	0.2158	6.62	0.1511

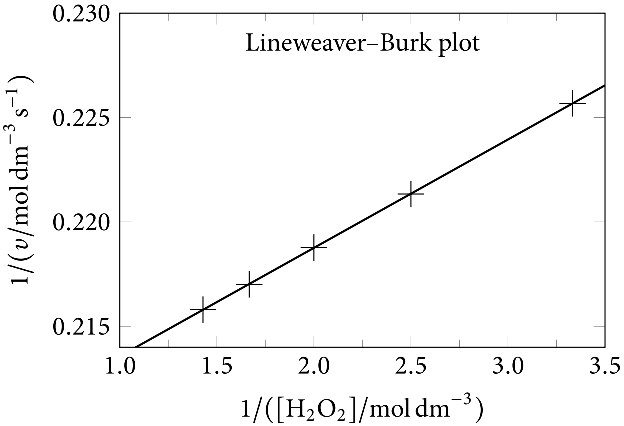


Figure 17.13

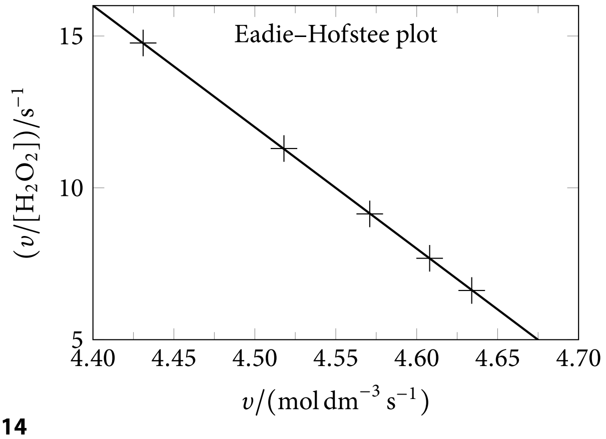


Figure 17.14

For the Lineweaver–Burk plot, the equation of the line is

$$1/(v/\text{mol dm}^{-3}\,\text{s}^{-1}) = 5.190 \times 10^{-3} \times 1/([H_2O_2]/\text{mol dm}^{-3}) + 0.2084$$

The intercept is identified with $1/v_{\text{max}}$ so that

$$v_{\text{max}} = \frac{1}{0.2084\ \text{mol dm}^{-3}\,\text{s}^{-1}} = 4.79...\ \text{mol dm}^{-3}\,\text{s}^{-1} = \boxed{4.80\ \text{mol dm}^{-3}\,\text{s}^{-1}}$$

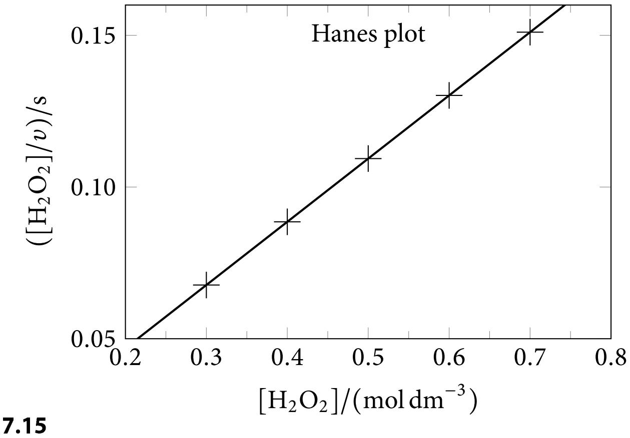


Figure 17.15

The slope is identified with K_M/v_{max} so that

$$K_M = (\overbrace{5.190\times10^{-3}}^{\text{slope}}\ \text{s})\times(\overbrace{4.79...\ \text{mol dm}^{-3}\,\text{s}^{-1}}^{v_{max}}) = \boxed{0.0249\ \text{mol dm}^{-3}}$$

For the Eadie–Hofstee plot, the equation of the line is

$$(v/[H_2O_2])/\text{s}^{-1} = -40.02\times(v/\text{mol dm}^{-3}\,\text{s}^{-1}) + 192.1$$

The slope is identified with $-1/K_M$ so that

$$K_M = \frac{-1}{-40.02\ \text{dm}^3\,\text{mol}^{-1}} = 0.0249...\ \text{mol dm}^{-3} = \boxed{0.0250\ \text{mol dm}^{-3}}$$

The intercept is identified with v_{max}/K_M so that

$$v_{max} = (\overbrace{192.1}^{\text{intercept}}\ \text{s}^{-1})\times(\overbrace{0.0249...\ \text{mol dm}^{-3}}^{K_M}) = \boxed{4.80\ \text{mol dm}^{-3}\,\text{s}^{-1}}$$

For the Hanes plot, the equation of the line is

$$([H_2O_2]/v)/\text{s} = 0.2084\times([H_2O_2]/\text{mol dm}^{-3}) + 5.189\times10^{-3}$$

The slope is identified with $1/v_{max}$ so that

$$v_{max} = \frac{1}{0.2084\ \text{dm}^3\,\text{mol}^{-1}\,\text{s}} = 4.79...\ \text{mol dm}^{-3}\,\text{s}^{-1} = \boxed{4.80\ \text{mol dm}^{-3}\,\text{s}^{-1}}$$

The intercept is identified with K_M/v_{max} so that

$$K_M = (\overbrace{5.189\times10^{-3}}^{\text{intercept}}\ \text{s})\times(\overbrace{4.79...\ \text{mol dm}^{-3}\,\text{s}^{-1}}^{v_{max}}) = \boxed{0.0249\ \text{mol dm}^{-3}}$$

The three plots thus give essentially the same values of K_M and v_{max} for these data.

17G **Photochemistry**

Answer to discussion question

Solutions to exercises

E17G.1(b) The primary quantum yield is defined by [17G.1a–*763*], $\phi = N_{\text{events}}/N_{\text{abs}}$. In this equation N_{abs} is the number of photons absorbed and N_{events} is, in this case, the number of molecules of A that decompose, $N_{\text{decomposed}}$. Rearranging gives

$$N_{\text{abs}} = \frac{N_{\text{decomposed}}}{\phi} = \frac{n_{\text{decomposed}}N_{\text{A}}}{\phi} = \frac{n_{\text{formed}}N_{\text{A}}}{\phi}$$

In the final expression, n_{formed} is the amount in moles of B that is formed, which from the stoichiometry of the reaction A → B + C is equal to the amount of A that decomposes. The quantum yield is 120 mmol einstein^{-1}, or 0.120 mol mol^{-1} = 0.120, hence

$$N_{\text{abs}} = \frac{n_{\text{formed}}N_{\text{A}}}{\phi} = \frac{(1.77\times10^{-3}\ \text{mol})\times(6.0221\times10^{23}\ \text{mol}^{-1})}{0.120} = \boxed{8.88\times10^{21}}$$

E17G.2(b) The fluorescence quantum yield is given by [17G.4–*765*], $\phi_{\text{F},0} = k_{\text{F}}\tau_0$. The observed lifetime τ_0 is given by [17G.3b–*764*], $\tau_0 = 1/(k_{\text{F}} + k_{\text{ISC}} + k_{\text{IC}})$, which is written as $\tau_0 = 1/k_{\text{r}}$ where $k_{\text{r}} = k_{\text{F}} + k_{\text{ISC}} + k_{\text{IC}}$ is the effective first-order rate constant for the decay of the excited state of the fluorescing species. For a first-order process k_{r} is related to the half-life according to [17B.3–*732*], $t_{1/2} = \ln 2/k_{\text{r}}$, and combining this expression with $\tau_0 = 1/k_{\text{r}}$ gives $t_{1/2} = \ln 2/(1/\tau_0) = \ln 2\tau_0$. Hence $\tau_0 = t_{1/2}/\ln 2$.

Rearranging [17G.4–*765*] then gives

$$k_{\text{F}} = \frac{\phi_{\text{F},0}}{\tau_0} = \frac{\phi_{\text{F},0}}{t_{1/2}/\ln 2} = \frac{\phi_{\text{F},0}\ln 2}{t_{1/2}} = \frac{0.16\times\ln 2}{1.5\times10^{-9}\ \text{s}} = \boxed{7.4\times10^{7}\ \text{s}^{-1}}$$

E17G.3(b) The Stern–Volmer equation [17G.5–*765*] is $\phi_{\text{F},0}/\phi_{\text{F}} = 1 + \tau_0 k_{\text{Q}}[\text{Q}]$, where ϕ_{F} and $\phi_{\text{F},0}$ are the fluorescence quantum yields with and without the quencher. The rate of fluorescence v, and hence the fluorescence intensity, is directly proportional to the fluorescence quantum yield according to [17G.1b–*763*], $\phi = v/I_{\text{abs}}$. Therefore to reduce the fluorescence intensity to 75% of the unquenched value requires $\phi_{\text{F}} = \frac{3}{4}\phi_{\text{F},0}$ and hence $\phi_{\text{F},0}/\phi_{\text{F}} = \frac{4}{3}$. Rearranging the Stern–Volmer equation then gives

$$[\text{Q}] = \frac{\phi_{\text{F},0}/\phi_{\text{F}} - 1}{\tau_0 k_{\text{Q}}} = \frac{4/3 - 1}{(3.5\times10^{-9}\ \text{s})\times(2.5\times10^{9}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})}$$

$$= \boxed{0.038\ \text{mol dm}^{-3}}$$

E17G.4(b) The efficiency of resonance energy transfer η_T is defined by [17G.6–*767*], $\eta_T = 1 - \phi_F/\phi_{F,0}$, and the distance-dependence of the efficiency is given by [17G.7–*767*], $\eta_T = R_0^6/(R_0^6 + R^6)$, where R is the donor–acceptor distance and R_0 is a constant characteristic of the particular donor–acceptor pair.

In this case a decrease of the fluorescence quantum yield by 15% implies that $\phi_F = (1-0.15)\phi_{F,0} = 0.85\phi_{F,0}$. Hence the efficiency is $\eta_T = 1 - \phi_F/\phi_{F,0} = 1 - 0.85 = 0.15$. Rearranging [17G.7–*767*] for R, and taking $R_0 = 2.2$ nm from Table 17G.3 on page 767, gives

$$R = R_0\left(\frac{1-\eta_T}{\eta_T}\right)^{1/6} = (2.2\text{ nm}) \times \left(\frac{1-0.15}{0.15}\right)^{1/6} = \boxed{2.9\text{ nm}}$$

Solutions to problems

P17G.2 The quantum yield in terms of the rates of processes is given by [17G.1b–*763*],

$$\phi = \frac{\text{rate of process, } v}{\text{rate of photon absorption}} \quad \text{hence} \quad v = \phi \times (\text{rate of photon absorption})$$

The rate of photon absorption is calculated by first finding the fraction of photons that are absorbed by the layer of stratosphere. This is done using the Beer–Lambert law [11A.8–*421*], which states that the intensity of transmitted radiation I is related to the intensity of incident radiation I_0 according to $I = I_0 10^{-\varepsilon[\text{J}]L}$, where [J] is the concentration of the absorbing substance, L is the thickness of the sample through which the radiation is passed, and ε is the the molar absorption coefficient. The fraction of photons that are transmitted through the layer of stratosphere is therefore $I/I_0 = 10^{-\varepsilon[\text{O}_3]L}$, and the fraction f that are absorbed is

$$\begin{aligned} f &= 1 - I/I_0 = 1 - 10^{-\varepsilon[\text{O}_3]L} \\ &= 1 - 10^{-(260\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1})\times(8\times10^{-9}\text{ mol dm}^{-3})\times(1.0\text{ km})\times[(10^5\text{ cm})/(1\text{ km})]} = 0.380... \end{aligned}$$

The rate of photon absorption is then calculated by considering a column of the stratosphere with a cross sectional area of 1 cm^2 and a height of 1 km = 10^5 cm. A flux of 1×10^{14} photons cm^{-2} s^{-1} means that each second 1×10^{14} photons arrive at the top of this column. Of these photons, a fraction $f = 0.380...$ are absorbed as they pass through the column, so the column absorbs $0.380...\times10^{14}$ photons per second. The rate of photon absorption per dm^3 of stratosphere is found by dividing by the volume of the column, which is $(1\text{ cm}^2)\times(10^5\text{ cm}) = 10^5\text{ cm}^3$, or 10^2 dm^3. Hence

$$\text{rate of photon absorption} = \frac{0.380...\times10^{14}\text{ s}^{-1}}{10^2\text{ dm}^3} = 0.380...\times10^{12}\text{ dm}^{-3}\text{ s}^{-1}$$

Multiplication by the quantum yield ϕ gives the rate of ozone consumption in molecules dm^{-3} s^{-1}, and division by N_A then gives the rate in mol dm^{-3} s^{-1}.

$$v = \overbrace{0.94}^{\phi} \times \frac{0.380...\times10^{12}\text{ dm}^{-3}\text{ s}^{-1}}{6.0221\times10^{23}\text{ mol}^{-1}} = \boxed{5.9\times10^{-13}\text{ mol dm}^{-3}\text{ s}^{-1}}$$

P17G.4 The Stern–Volmer equation [17G.5–*765*] is $\phi_{F,0}/\phi_F = 1 + \tau_0 k_Q[Q]$. By analogy with this expression, the effect of a quencher on the phosphorescence quantum yield ϕ_P is $\phi_{P,0}/\phi_P = 1 + \tau_0 k_Q[\mathrm{Q}]$, where $\phi_{P,0}$ is the phosphorescence quantum yield in the absence of the quencher.

By analogy with [17G.4–*765*], $\phi_{F,0} = k_F\tau_0$, the phosphorescence quantum yield is $\phi_{P,0} = k_P\tau_0$, where k_P is the rate constant for phosphorescence. This implies that the rate constant for phosphorescence, and hence the rate of phosphorescence, which in turn determines the intensity of the phosphorescence, is proportional to the quantum yield. Therefore $I_{P,0}/I_P = \phi_{P,0}/\phi_P$, which on substitution into the equation $\phi_{P,0}/\phi_P = 1 + \tau_0 k_Q[\mathrm{Q}]$ above gives

$$\frac{I_{P,0}}{I_P} = 1 + \tau_0 k_Q[\mathrm{Q}] \quad \text{hence} \quad \frac{1}{I_P} = \frac{1}{I_{P,0}} + \frac{\tau_0 k_Q}{I_{P,0}}[\mathrm{Q}]$$

This expression implies that a plot of $1/I_P$ against $[\mathrm{Q}]$ should be a straight line of slope $\tau_0 k_Q/I_{P,0}$ and intercept $1/I_{P,0}$. The data are plotted in Fig. 17.16.

$[\mathrm{Q}]/(\mathrm{mol\,dm^{-3}})$	$I_P/(\text{arbitrary units})$	$I_P^{-1}/(\text{arbitrary units})^{-1}$
0.001 0	0.41	2.44
0.005 0	0.25	4.00
0.010 0	0.16	6.25

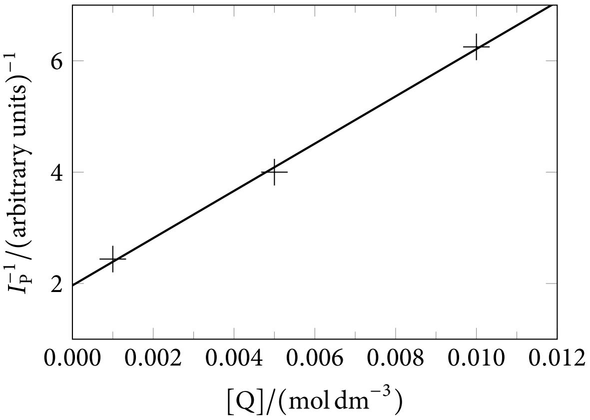


Figure 17.16

The data lie on a good straight line, the equation of which is

$$I_P^{-1}/(\text{arbitrary units})^{-1} = (4.25\times10^2)\times([\mathrm{Q}]/\mathrm{mol\,dm^{-3}}) + 1.97$$

The intercept is identified with $1/I_{P,0}$ so that

$$I_{P,0} = \frac{1}{1.97\ (\text{arbitrary units})^{-1}} = 0.507...\ \text{arbitrary units}$$

The slope is identified with $\tau_0 k_Q / I_{P,0}$

$$\frac{\tau_0 k_Q}{I_{P,0}} = 4.25 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ (arbitrary units)}^{-1}$$

The value of $I_{P,0}$ is known from the intercept, but it is necessary to find τ_0 before this expression can be used to calculate k_Q. This is done using [17G.3a–*764*], $[S^*] = [S^*]_0 e^{-t/\tau_0}$, for the decay of the excited species in the absence of a quencher. The half-life of the phosphorescent species S^*, and therefore of the phosphorescence, is the time taken for $[S^*]$ to reach half its initial value. Therefore

$$\tfrac{1}{2}[S^*]_0 = [S^*]e^{-t_{1/2}/\tau_0} \quad \text{hence} \quad 2 = e^{t_{1/2}/\tau_0} \quad \text{hence} \quad \tau_0 = t_{1/2}/\ln 2$$

Substituting this into the expression above involving the slope of the graph gives

$$\frac{t_{1/2} k_Q}{I_{P,0} \ln 2} = 4.25 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ (arbitrary units)}^{-1}\text{, hence}$$

$$k_Q = \frac{(0.507\ldots \text{ arbitrary units}) \times \ln 2 \times (4.25 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{(arbitrary units)}^{-1})}{29 \times 10^{-6} \text{ s}}$$

$$= \boxed{5.1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

P17G.6 The efficiency of energy transfer in terms of the donor–acceptor distance is given by [17G.7–*767*], $\eta_T = R_0^6/(R_0^6 + R^6)$. Taking the reciprocal of both sides gives

$$\frac{1}{\eta_T} = \frac{R_0^6 + R^6}{R_0^6} = 1 + \frac{R^6}{R_0^6}$$

This expression implies that a plot of η_T against R^6 should be a straight line of intercept 1 and slope $1/R_0^6$. The data are plotted in Fig. 17.17.

R/nm	η_T	R^6/nm^6	$1/\eta_T$
1.2	0.99	3.0	1.01
1.5	0.94	11	1.06
1.8	0.97	34	1.03
2.8	0.82	4.8×10^2	1.22
3.1	0.74	8.9×10^2	1.35
3.4	0.65	1.5×10^3	1.54
3.7	0.40	2.6×10^3	2.50
4.0	0.28	4.1×10^3	3.57
4.3	0.24	6.3×10^3	4.17
4.6	0.16	9.5×10^3	6.25

The data lie on a modest straight line with intercept close to 1, so it is concluded that these data are consistent with [17G.7–*767*]. The equation of the line is

$$1/\eta_T = (5.5 \times 10^{-4}) \times R^6/\text{nm}^6 + 0.97$$

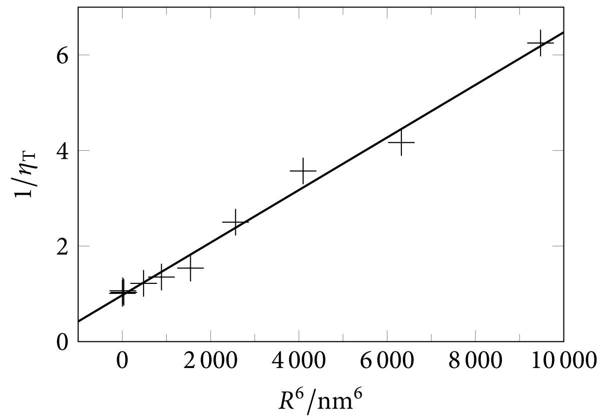


Figure 17.17

The slope is identified with $1/R_0^6$, so R_0 for the naphthyl–dansyl pair is

$$R_0 = \left(\frac{1}{5.5\times10^{-4}\ \text{nm}^{-6}}\right)^{1/6} = \boxed{3.5\ \text{nm}}$$

Solutions to integrated activities

I17.2 The step $\boxed{S \to I}$ is autocatalytic because the rate of this step, $\mathrm{d}S/\mathrm{d}t = rSI$, is proportional to I which is a product of the step. The step $I \to R$ is not autocatalytic because its rate $\mathrm{d}R/\mathrm{d}t = aI$ does not depend on the product R of the step.

Whether the disease spreads or dies out depends on whether the number infectives I increases or decreases with time. For the disease to spread,

$$\frac{\mathrm{d}I}{\mathrm{d}t} = rSI - aI > 0 \quad \text{hence} \quad \boxed{a/r < S}$$

Similarly, for the disease to die out,

$$\frac{\mathrm{d}I}{\mathrm{d}t} = rSI - aI < 0 \quad \text{hence} \quad \boxed{a/r > S}$$

The total rate of change of all species present is

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{\mathrm{d}S}{\mathrm{d}t} + \frac{\mathrm{d}I}{\mathrm{d}t} + \frac{\mathrm{d}R}{\mathrm{d}t} = (-rSI) + (rSI - aI) + (aI) = 0$$

The result $\mathrm{d}N/\mathrm{d}t = 0$ implies that the total population is constant.

I17.4 It is supposed that each monomer has one end group A with which it can join to another monomer. In a polymer, only the terminal monomer unit in the chain has a free end group.

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 fraction of end groups that have reacted is p and the fraction of free end groups remaining is $1-p$, so the probability that a polymer contains $N-1$ reacted groups and one unreacted group is $p^{N-1} \times (1-p)$. The average value of N is then given by

$$\langle N \rangle = \sum_{N=1}^{\infty} N P_N = \sum_{N=1}^{\infty} N p^{N-1}(1-p) = (1-p) \sum_{N=1}^{\infty} N p^{N-1}$$

To evaluate the sum, it is noted that Np^{N-1} corresponds to the derivative of p^N. Hence

$$\sum_{N=1}^{\infty} N p^{N-1} = \sum_{N=1}^{\infty} \frac{\mathrm{d}}{\mathrm{d}p} p^N = \frac{\mathrm{d}}{\mathrm{d}p}\left[\sum_{N=1}^{\infty} p^N\right] = \frac{\mathrm{d}}{\mathrm{d}p}\left[p + p^2 + p^3 + \dots\right]$$

The expression in square brackets is a geometric series with first term p and common ratio p; the sum to infinity of this series is therefore $p/(1-p)$. Hence

$$\sum_{N=1}^{\infty} N p^{N-1} = \frac{\mathrm{d}}{\mathrm{d}p}\left[\frac{p}{1-p}\right] = \frac{(1-p)+p}{(1-p)^2} = \frac{1}{(1-p)^2}$$

The average value of N is therefore

$$\langle N \rangle = (1-p) \sum_{N=1}^{\infty} N p^{N-1} = (1-p) \times \frac{1}{(1-p)^2} = \frac{1}{1-p}$$

This is the same result as [17F.12a–*755*] which is derived in Section 17F.2(a) on page 755 by a different method. However the approach used here is more easily generalised to find an expression for $\langle N^2 \rangle$.

$$\langle N^2 \rangle = \sum_{N=1}^{\infty} N^2 P_N = \sum_{N=1}^{\infty} N^2 p^{N-1}(1-p) = (1-p) \sum_{N=1}^{\infty} N \times N p^{N-1}$$

The quantity Np^{N-1} is recognised as the derivative of p^N

$$\begin{aligned}\langle N^2 \rangle &= (1-p) \sum_{N=1}^{\infty} N \times \frac{\mathrm{d}}{\mathrm{d}p} p^N = (1-p) \frac{\mathrm{d}}{\mathrm{d}p}\left[\sum_{N=1}^{\infty} N p^N\right] \\ &= (1-p) \frac{\mathrm{d}}{\mathrm{d}p}\left[p \sum_{N=1}^{\infty} N p^{N-1}\right]\end{aligned}$$

The sum $\sum_{N=1}^{\infty} Np^{N-1}$ was already evaluated above; its value is $1/(1-p)^2$. Hence

$$\langle N^2 \rangle = (1-p) \frac{\mathrm{d}}{\mathrm{d}p}\left[p \times \frac{1}{(1-p)^2}\right] = (1-p) \times \frac{1+p}{(1-p)^3} = \frac{1+p}{(1-p)^2}$$

The average values of M and M^2 are found by noting that the molar mass of a polymer with N monomers is given by $M = NM_1$ where M_1 is the mass of a single polymer unit. Hence

$$\langle M\rangle = \langle NM_1\rangle = M_1\langle N\rangle = M_1 \times \frac{1}{1-p} = \frac{M_1}{1-p}$$

$$\langle M^2\rangle = \langle (NM_1)^2\rangle = \langle M_1^2N^2\rangle = M_1^2\langle N^2\rangle = M_1^2 \times \frac{1+p}{(1-p)^2} = \frac{M_1^2(1+p)}{(1-p)^2}$$

Therefore

$$\left(\langle M^2\rangle - \langle M\rangle^2\right)^{1/2} = \left(\frac{M_1^2(1+p)}{(1-p)^2} - \frac{M_1^2}{(1-p)^2}\right) = \left(M_1^2\frac{p}{(1-p)^2}\right) = \boxed{\frac{M_1p^{1/2}}{1-p}}$$

The root mean square deviation of the polymer mass is then

$$\begin{aligned}(\langle M^2\rangle - \langle M\rangle^2)^{1/2} &= \left(\langle (M_1N)^2\rangle - \langle M_1N\rangle^2\right)^{1/2} = \left(M_1^2\langle N^2\rangle - M_1^2\langle N\rangle^2\right)^{1/2}\\ &= M_1\underbrace{\left(\langle N^2\rangle - \langle N\rangle^2\right)^{1/2}}_{\mathrm{var}(N)} = M_1 \times \left(\frac{p}{(1-p)^2}\right)^{1/2} = \boxed{\frac{M_1p^{1/2}}{1-p}}\end{aligned}$$

as before.

The time dependence of p is given by [17F.11–*755*], $p = k_\mathrm{r}t[\mathrm{A}]_0/(1+k_\mathrm{r}t[\mathrm{A}]_0)$. Substituting this into the expression for $(\langle M^2\rangle - \langle M\rangle^2)^{1/2}$ gives the root mean square deviation as a function of time as

$$\begin{aligned}\frac{M_1p^{1/2}}{1-p} &= M_1p^{1/2}(1-p)^{-1} = M_1\left(\frac{k_\mathrm{r}t[\mathrm{A}]_0}{1+k_\mathrm{r}t[\mathrm{A}]_0}\right)^{1/2}\left(1-\frac{k_\mathrm{r}t[\mathrm{A}]_0}{1+k_\mathrm{r}t[\mathrm{A}]_0}\right)^{-1}\\ &= M_1\left(\frac{k_\mathrm{r}t[\mathrm{A}]_0}{1+k_\mathrm{r}t[\mathrm{A}]_0}\right)^{1/2}\left(\frac{1}{1+k_\mathrm{r}t[\mathrm{A}]_0}\right)^{-1}\\ &= \boxed{M_1\left\{k_\mathrm{r}t[\mathrm{A}]_0(1+k_\mathrm{r}t[\mathrm{A}]_0)\right\}^{1/2}}\end{aligned}$$

I17.6 The rate of the forward and backward steps are

$$\mathrm{A}\rightarrow\mathrm{B} \quad \frac{\mathrm{d[B]}}{\mathrm{d}t} = I_\mathrm{A} \qquad\qquad \mathrm{B}\rightarrow\mathrm{A} \quad \frac{\mathrm{d[B]}}{\mathrm{d}t} = -k_\mathrm{r}[\mathrm{B}]^2$$

The overall rate of change of [B] is therefore $\mathrm{d[B]}/\mathrm{d}t = I_\mathrm{A} - k_\mathrm{r}[\mathrm{B}]^2$. In the steady state, $\mathrm{d[B]}/\mathrm{d}t = 0$, hence

$$k_\mathrm{r}[\mathrm{B}]^2 = I_\mathrm{a} \quad \text{hence} \quad [\mathrm{B}] = \boxed{\left(\frac{I_\mathrm{a}}{k_\mathrm{r}}\right)^{1/2}}$$

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. This is in contrast to corresponding equilibrium expression, in which the ratio [B]/[A] depends on a ratio of rate constants for the forward and reverse reactions as explained in Section 17C.1 on page 737.

18

Reaction dynamics

18A Collision theory

Answers to discussion questions

D18A.2 To the extent that real gases deviate from perfect gas behaviour, 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. Similarly, repulsive interactions might reduce the frequency of collisions compared to what would be predicted for perfect gases.

D18A.4 Reactions between complex molecules might be expected to have strong steric requirements (small steric factors) as a result of the reaction requiring a particular orientation and approach of the reacting parts of the molecule: the more complex the molecules, the smaller the fraction of collisions which are potentially reactive.

In the RRK theory of unimolecular reactions molecular complexity plays a different role in that it governs the distribution of energy in the excited molecule. In this theory the rate constant for the unimolecular decay of an energized molecule A* is given by [18A.11–*785*],

$$k_\mathrm{b}(E) = \left(1 - \frac{E^*}{E}\right)^{s-1} k_\mathrm{b}$$

Here E^* is the minimum energy that must be accumulated in a bond for it to break, E is the total energy, and s is the number of modes of motion (modelled as harmonic oscillators) that the molecule possesses. The term in parentheses is less than 1, therefore the expression implies that the more complex the molecule (the greater s), the smaller the rate constant becomes.

Solutions to exercises

E18A.1(b) The collision frequency is given by [1B.12b–*17*], $z = \sigma v_\mathrm{rel} p/kT$, where σ is the collision cross-section, given in terms of the collision diameter d as $\sigma = \pi d^2$, and v_rel is the mean relative speed of the colliding molecules. This speed is given by [1B.11b–*16*], $v_\mathrm{rel} = (8kT/\pi\mu)^{1/2}$, with $\mu = m_\mathrm{A}m_\mathrm{B}/(m_\mathrm{A} + m_\mathrm{B})$. For collisions between like molecules $\mu = m/2$ and $v_{\text{rel}} = (16kT/\pi m)^{1/2}$.

$$\begin{aligned} z &= \frac{\sigma v_{\text{rel}} p}{kT} = \frac{\pi d^2 p}{kT}\left(\frac{16kT}{\pi m}\right)^{1/2} = 4d^2 p\left(\frac{\pi}{mkT}\right)^{1/2} \\ &= 4 \times (360 \times 10^{-12}\ \text{m})^2 \times (120 \times 10^3\ \text{Pa}) \\ &\quad \times \left(\frac{\pi}{(28.01 \times 1.6605 \times 10^{-27}\ \text{kg}) \times (1.3806 \times 10^{-23}\ \text{J K}^{-1}) \times (303\ \text{K})}\right)^{1/2} \\ &= \boxed{7.90 \times 10^9\ \text{s}^{-1}} \end{aligned}$$

To confirm the units of z it is useful to recall that $1\ \text{J} = 1\ \text{kg m}^2\ \text{s}^{-2}$ and $1\ \text{Pa} = 1\ \text{kg m}^{-1}\ \text{s}^{-2}$.

The collision density between identical molecules is given by [18A.4b–*781*]

$$Z_{\text{AA}} = \sigma\left(\frac{4kT}{\pi m}\right)^{1/2} N_{\text{A}}^2[\text{A}]^2$$

where $[\text{A}]$ is the molar concentration of the gas. In turn, this is expressed in terms of the pressure using the perfect gas equation to give $[\text{A}] = n_{\text{A}}/V = p_{\text{A}}/RT$.

$$\begin{aligned} Z_{\text{AA}} &= \pi d^2\left(\frac{4kT}{\pi m}\right)^{1/2}\frac{N_{\text{A}}^2 p_{\text{A}}^2}{R^2T^2} = 2d^2\left(\frac{\pi kT}{m}\right)^{1/2}\frac{p_{\text{A}}^2}{k^2T^2} = 2d^2\left(\frac{\pi}{mk^3T^3}\right)^{1/2} p_{\text{A}}^2 \\ &= 2 \times (360 \times 10^{-12}\ \text{m})^2 \times (120 \times 10^3\ \text{Pa})^2 \\ &\quad \times \left(\frac{\pi}{(28.01 \times 1.6605 \times 10^{-27}\ \text{kg}) \times (1.3806 \times 10^{-23}\ \text{J K}^{-1})^3 \times (303\ \text{K})^3}\right)^{1/2} \\ &= \boxed{1.13 \times 10^{35}\ \text{m}^{-3}\ \text{s}^{-1}} \end{aligned}$$

The above expression shows that $z \propto pT^{-1/2}$, but at constant volume $p \propto T$, therefore the overall temperature dependence is $z \propto T^{1/2}$. The percentage increase in z on increasing T by 10 K is therefore

$$\frac{313^{1/2} - 303^{1/2}}{303^{1/2}} = 0.0163... = \boxed{1.6\%}$$

Similarly the final expression for the collision density shows $Z_{\text{AA}} \propto p^2T^{-3/2}$ which, with $p \propto T$, gives $Z_{\text{AA}} \propto T^2T^{-3/2} \propto T^{1/2}$. This is the same dependence as z, so the same percentage increase will result.

E18A.2(b) The collision theory expression for the rate constant is given in [18A.9–*783*]. In this expression, the factor $e^{-E_a/RT}$ is identified as the fraction of collisions f having at least kinetic energy E_a along the flight path. For example with $E_a = 15\ \text{kJ mol}^{-1}$ and $T = 300\ \text{K}$

$$\frac{E_a}{RT} = \frac{15 \times 10^3\ \text{J mol}^{-1}}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (300\ \text{K})} = 6.01... \quad f = e^{-6.01...} = \boxed{2.45 \times 10^{-3}}$$

A similar calculation gives $\boxed{f = 0.105}$ at $T = 800$ K. With $E_a = 150\ \text{kJ mol}^{-1}$ the result is $\boxed{f = 7.64 \times 10^{-27}}$ at $T = 300$ K, and $\boxed{f = 1.61 \times 10^{-10}}$ at $T = 800$ K.

E18A.3(b) The method for calculating the fractions is shown in the solution to *Exercise* E18A.2(b). For $E_a = 15\,\mathrm{kJ\,mol^{-1}}$ and $T = 300\,\mathrm{K}$ it is found that $f = 2.44... \times 10^{-3}$ and increasing the temperature to 310 K gives $f = 2.96... \times 10^{-3}$. The percentage increase is

$$100 \times \frac{(2.96... \times 10^{-3}) - (2.44... \times 10^{-3})}{2.44... \times 10^{-3}} = \boxed{21\%}$$

A similar calculation gives an increase by $\boxed{2.8\%}$ at 800 K. With $E_a = 150\,\mathrm{kJ\,mol^{-1}}$ the result is $\boxed{596\%}$ at $T = 300\,\mathrm{K}$, and $\boxed{32\%}$ at $T = 800\,\mathrm{K}$.

E18A.4(b) The collision theory expression for the rate constant is given in [18A.9–*783*].

$$\begin{aligned} k_r &= \sigma N_A \left(\frac{8kT}{\pi\mu}\right)^{1/2} e^{-E_a/RT} \\ &= (0.30 \times 10^{-18}\,\mathrm{m^2}) \times (6.0221 \times 10^{23}\,\mathrm{mol^{-1}}) \\ &\quad \times \left(\frac{8 \times (1.3806 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (450\,\mathrm{K})}{\pi(3.930 \times 1.6605 \times 10^{-27}\,\mathrm{kg})}\right)^{1/2} \\ &\quad \times e^{-(200\times10^3\,\mathrm{J\,mol^{-1}})/[(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(450\,\mathrm{K})]} \\ &= \boxed{1.7 \times 10^{-15}\,\mathrm{mol^{-1}\,m^3\,s^{-1}}} \end{aligned}$$

The units are best resolved by realising that $(8kT/\pi\mu)^{1/2}$ is a speed, with units $\mathrm{m\,s^{-1}}$. Note that $0.30\,\mathrm{nm^2}$ is $0.30 \times 10^{-18}\,\mathrm{m^2}$.

E18A.5(b) As described in Section 18A.1(b) on page 781, the reactive cross section may be estimated from the (non-reactive) collision cross sections of A and B: $\sigma_{\mathrm{est}} = \frac{1}{4}(\sigma_A^{1/2} + \sigma_B^{1/2})^2$. The steric factor is given by the ratio of the experimental reactive cross section, σ_{exp}, to the estimated cross section

$$\begin{aligned} P &= \frac{\sigma_{\mathrm{exp}}}{\sigma_{\mathrm{est}}} = \frac{8.7 \times 10^{-22}\,\mathrm{m^2}}{[(0.88 \times 10^{-18}\,\mathrm{m^2})^{1/2} + (0.40 \times 10^{-18}\,\mathrm{m^2})^{1/2}]^2/4} \\ &= \boxed{1.4 \times 10^{-3}} \end{aligned}$$

E18A.6(b) In the RRK theory the rate constant for the unimolecular decay of an energized molecule A* is given by [18A.11–*785*],

$$k_b(E) = \left(1 - \frac{E^*}{E}\right)^{s-1} k_b = (1 - x)^{s-1} k_b$$

where $x = E^*/E$. For a linear molecule with 4 atoms there are $3N-5 = 3\times4-5 = 7$ normal modes, so $s = 7$. This expression is rearranged for x to give

$$\begin{aligned} x &= 1 - [k_b(E)/k_b]^{1/(s-1)} \\ &= 1 - [0.025]^{1/(7-1)} = \boxed{0.46} \end{aligned}$$

E18A.7(b) In the RRK theory the rate constant for the unimolecular decay of an energized molecule A* is given by [18A.11–*785*],

$$\frac{k_b(E)}{k_b} = \left(1 - \frac{E^*}{E}\right)^{s-1}$$

where E^* is the minimum energy needed to break the bond, and E is the energy available from the collision. With the data given

$$\frac{k_b(E)}{k_b} = \left(1 - \frac{300\ \text{kJ mol}^{-1}}{500\ \text{kJ mol}^{-1}}\right)^{12-1} = \boxed{4.19 \times 10^{-5}}$$

Solutions to problems

P18A.2 The first step is to analyse the given rate constant data in terms of the Arrhenius equation, $k_r = Ae^{-E_a/RT}$. A plot of $\ln k_r$ against $1/T$ has slope $-E_a/R$ and intercept $\ln A$. The data are tabulated below and the plot is shown in Fig. 18.1.

T/K	$(10^3/T)/\text{K}^{-1}$	$k_r/(\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$	$\ln[k_r/(\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1})]$
600	1.67	4.6×10^2	6.13
700	1.43	9.7×10^3	9.18
800	1.25	1.3×10^5	11.8
1 000	1.00	3.1×10^6	14.9

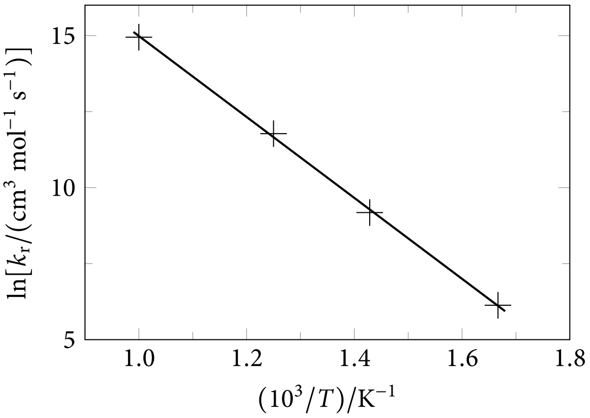


Figure 18.1

The data are a good fit to the line

$$\ln[k_r/(\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1})] = -1.331 \times 10^4/(T/\text{K}) + 28.30$$

From the intercept $\ln A = 28.30$ and hence $A = 1.944 \times 10^{12}\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$; for the next part of the calculation this is conveniently expressed as $1.944 \times 10^6\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}$.

The collision theory expression for the rate constant is given in [18A.9–*783*]

$$k_r = \sigma^* N_A \left(\frac{8kT}{\pi\mu}\right)^{1/2} e^{-E_a/RT}$$

Here σ^* is interpreted as the reactive cross-section, related to the collision cross-section σ by $\sigma^* = P\sigma$, where P is the steric factor. Comparison of the above expression for k_r with the Arrhenius equation, $k_r = Ae^{-E_a/RT}$, gives the frequency factor as $A = \sigma^* N_A\,(8kT/\pi\mu)^{1/2}$; this is rearranged to give an expression for σ^*. The mass of the NO_2 radical is 46.01 m_u, therefore the reduced mass of the collision is $\mu = \frac{1}{2} \times 46.01\ m_u = 3.81... \times 10^{-26}$ kg. For the calculation the temperature is taken to be in the middle of the data, which is 750 K.

$$\begin{aligned}\sigma^* &= \frac{A}{N_A}\left(\frac{\pi\mu}{8kT}\right)^{1/2}\\ &= \frac{1.944 \times 10^6\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}}{6.0221 \times 10^{23}\ \text{mol}^{-1}}\left(\frac{\pi(3.81... \times 10^{-26}\ \text{kg})}{8 \times (1.3806 \times 10^{-23}\ \text{J K}^{-1}) \times (750\ \text{K})}\right)^{1/2}\\ &= 3.88... \times 10^{-21}\ \text{m}^2 = \boxed{0.0039\ \text{nm}^2}\end{aligned}$$

The units are best resolved by realising that $(8kT/\pi\mu)^{1/2}$ is a speed, with units m s^{-1}. The steric factor is $P = \sigma^*/\sigma = (3.88... \times 10^{-21}\ \text{m}^2)/(0.60 \times 10^{-18}\ \text{m}^2) = \boxed{0.0065}$.

P18A.4 In *Example* 18A.1 on page 785 it is shown that for the harpoon mechanism the reactive cross-section σ^* can be estimated as

$$\sigma^* = \pi R^{*2} = \pi\left(\frac{e^2}{4\pi\varepsilon_0(I - E_{ea})}\right)^2$$

With the data for Na and Cl_2, and using the conversion 1 eV = 1.6022×10^{-19} J from inside the font cover

$$\begin{aligned}\sigma^* &= \pi\left(\frac{(1.6022 \times 10^{-19}\ \text{C})^2}{4\pi(8.8542 \times 10^{-12}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^{-1}) \times (5.1 - 1.3) \times (1.6022 \times 10^{-19}\ \text{J})}\right)^2\\ &= 4.51... \times 10^{-19}\ \text{m}^2 = \boxed{0.45\ \text{nm}^2}\end{aligned}$$

The results of similar calculations for the other combinations of alkali metal and halogen are given in the table. All the values of σ^* in the table are smaller than the experimental values, but they do show the correct trends down the columns. The variation with E_{ea} across the table is not so good.

σ^*/nm^2	Cl_2	Br_2	I_2
Na	0.45	0.43	0.56
K	0.72	0.68	0.96
Rb	0.77	0.72	1.04
Cs	0.96	0.89	1.35

18B Diffusion-controlled reactions

Answers to discussion questions

D18B.2 In the cage effect, a pair of molecules may be held in close proximity for an extended period of time by the presence of other neighbouring molecules, typically solvent molecules. Such a pair is called an encounter pair, and their time near each other is called an 'encounter' as opposed to a simple collision. An encounter may include a series of collisions. Furthermore, as a result of collisions with neighbouring molecules, an encounter pair may pick up enough energy to react, even though the pair may not have had enough energy when first formed.

Solutions to exercises

E18B.1(b) The second-order rate constant for a diffusion-controlled reaction is given by [18B.3–*789*], $k_\mathrm{d} = 4\pi R^* D N_\mathrm{A}$, where R^* is the critical distance and D is the diffusion constant. As explained in the text, D is the sum of the diffusion constants of the two species, therefore in this case D is twice the value given. With the data given

$$\begin{aligned} k_\mathrm{d} &= 4\pi \times (0.4\times10^{-9}\ \mathrm{m}) \times (2\times5.2\times10^{-9}\ \mathrm{m^2\,s^{-1}}) \times (6.0221\times10^{23}\ \mathrm{mol^{-1}}) \\ &= \boxed{3.1\times10^{7}\ \mathrm{m^3\,mol^{-1}\,s^{-1}}} \end{aligned}$$

E18B.2(b) For a diffusion-controlled reaction the rate constant is approximated by [18B.4–*789*], $k_\mathrm{d} = 8RT/3\eta$, where η is the viscosity. Recall that 1 P = $10^{-1}\ \mathrm{kg\,m^{-1}\,s^{-1}}$, so that 1 cP = $10^{-3}\ \mathrm{kg\,m^{-1}\,s^{-1}}$.

(i) For decylbenzene

$$k_\mathrm{d} = \frac{8\times(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(298\ \mathrm{K})}{3\times(3.36\times10^{-3}\ \mathrm{kg\,m^{-1}\,s^{-1}})} = \boxed{1.97\times10^{6}\ \mathrm{m^3\,mol^{-1}\,s^{-1}}}$$

In sorting out the units it is useful to recall 1 J = 1 $\mathrm{kg\,m^2\,s^{-2}}$.

(ii) For sulfuric acid

$$k_\mathrm{d} = \frac{8\times(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(298\ \mathrm{K})}{3\times(27\times10^{-3}\ \mathrm{kg\,m^{-1}\,s^{-1}})} = \boxed{2.4\times10^{5}\ \mathrm{m^3\,mol^{-1}\,s^{-1}}}$$

E18B.3(b) For a diffusion-controlled reaction the rate constant is approximated by [18B.4–*789*], $k_\mathrm{d} = 8RT/3\eta$, where η is the viscosity. Recall that 1 P = $10^{-1}\ \mathrm{kg\,m^{-1}\,s^{-1}}$, so that 1 cP = $10^{-3}\ \mathrm{kg\,m^{-1}\,s^{-1}}$. Therefore the rate constant is

$$\begin{aligned} k_\mathrm{d} &= \frac{8\times(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(320\ \mathrm{K})}{3\times(0.601\times10^{-3}\ \mathrm{kg\,m^{-1}\,s^{-1}})} \\ &= 1.18...\times10^{6}\ \mathrm{m^3\,mol^{-1}\,s^{-1}} = \boxed{1.18\times10^{6}\ \mathrm{m^3\,mol^{-1}\,s^{-1}}} \end{aligned}$$

The half-life of a second-order reaction is given by [17B.5–*734*], $t_{1/2} = 1/k_r[\mathrm{A}]_0$. The initial concentration is 2.0 mmol dm^{-3} which is 2.0 mol m^{-3}. With the data given

$$t_{1/2} = \frac{1}{(1.18... \times 10^6\ \mathrm{m^3\ mol^{-1}\ s^{-1}}) \times (2.0\ \mathrm{mol\ m^{-3}})} = \boxed{42\ \mathrm{ns}}$$

E18B.4(b) The second-order rate constant for a diffusion-controlled reaction is given by [18B.3–*789*], $k_d = 4\pi R^* D N_A$, where R^* is the critical distance and D is the diffusion constant. As explained in the text D is the sum of the diffusion constants of the two species. The value of D is estimated using the Stokes–Einstein equation, $D = kT/6\pi\eta R$, and with the data given separate values of D are computed for the two species. The critical distance is taken as $R^* = R_A + R_B$. Recall that 1 P = 10^{-1} kg m^{-1} s^{-1}, so that 1 cP = 10^{-3} kg m^{-1} s^{-1}.

$$\begin{aligned}
k_d &= 4\pi(R_A + R_B)(D_A + D_B)N_A \\
&= 4\pi N_A(R_A + R_B)\frac{kT}{6\pi\eta}\left(\frac{1}{R_A} + \frac{1}{R_B}\right) \\
&= 4\pi \times (6.0221 \times 10^{23}\ \mathrm{mol^{-1}}) \times (421 + 945) \\
&\quad \times \frac{(1.3806 \times 10^{-23}\ \mathrm{J\,K^{-1}}) \times (293\ \mathrm{K})}{6\pi \times (1.35 \times 10^{-3}\ \mathrm{kg\,m^{-1}\,s^{-1}})}\left(\frac{1}{421} + \frac{1}{945}\right) \\
&= 5.64... \times 10^6\ \mathrm{m^3\ mol^{-1}\ s^{-1}}
\end{aligned}$$

The initial concentrations are $[\mathrm{A}] = 0.155\ \mathrm{mol\,dm^{-3}} = 0.155 \times 10^3\ \mathrm{mol\ m^{-3}}$ and $[\mathrm{B}] = 0.195\ \mathrm{mol\,dm^{-3}} = 0.195 \times 10^3\ \mathrm{mol\ m^{-3}}$. The initial rate is therefore

$$\begin{aligned}
\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} &= k_d[\mathrm{A}][\mathrm{B}] \\
&= (5.64... \times 10^6\ \mathrm{m^3\ mol^{-1}\ s^{-1}}) \\
&\quad \times (0.155 \times 10^3\ \mathrm{mol\ m^{-3}}) \times (0.195 \times 10^3\ \mathrm{mol\ m^{-3}}) \\
&= \boxed{1.71 \times 10^{11}\ \mathrm{mol\ m^{-3}\ s^{-1}}}
\end{aligned}$$

Using [18B.4–*789*], $k_d = 8RT/3\eta$, the rate constant is

$$k_d = \frac{8 \times (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (293\ \mathrm{K})}{3 \times (1.35 \times 10^{-3}\ \mathrm{kg\,m^{-1}\,s^{-1}})} = 4.81 \times 10^6\ \mathrm{m^3\ mol^{-1}\ s^{-1}}$$

This value would result in a somewhat slower initial rate, casting some doubt therefore on the validity of the approximations used.

Solutions to problems

P18B.2 It is convenient to plot the function as

$$\frac{[\mathrm{J}]^* A}{n_0} = \frac{\mathrm{e}^{-x^2/4Dt - k_r t}}{(\pi D t)^{1/2}}$$

For the plots shown in Fig. 18.2 the diffusion constant is chosen as $D = 4.1 \times 10^{-9}\ \mathrm{m^2\,s^{-1}}$, the value suggested in *Brief illustration* 18B.3 on page 790. The plot on the left is for $k_r = 0$. As expected, as time increases the material spreads further from the origin and the profile flattens. The plot on the right is for $k_r = 2 \times 10^{-3}\ \mathrm{s^{-1}}$. Now, because reaction also consumes the material, the curves are all at lower values with the longer time curves being more affected because more material has been consumed by the reaction.

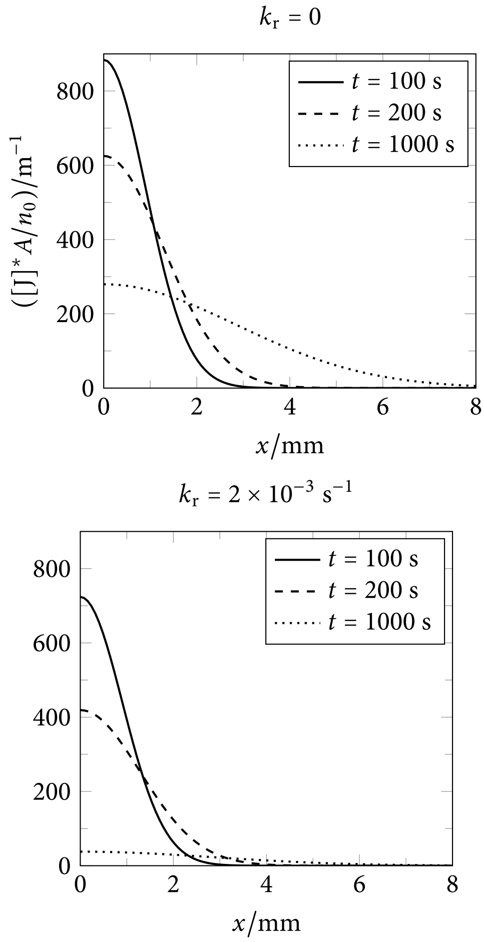


Figure 18.2

P18B.4 (a) For a diffusion-controlled reaction the rate constant is approximated by [18B.4–*789*], $k_d = 8RT/3\eta$, where η is the viscosity, given at 298 K as $1.06 \times 10^{-3}\ \mathrm{kg\,m^{-1}\,s^{-1}}$ in the *Resource section*

$$k_d = \frac{8 \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})}{3 \times (1.06 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}})} = \boxed{6.23 \times 10^{6}\ \mathrm{m^3\,mol^{-1}\,s^{-1}}}$$

(b) The second-order rate constant for a diffusion-controlled reaction is also given by [18B.3–*789*], $k_d = 4\pi R^* D N_A$, where R^* is the critical distance and D is the sum of the diffusion constants of the two species. It is convenient to express the rate constant as $2.77 \times 10^6\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}$. Rearranging the expression gives

$$R^* = \frac{k_d}{4\pi D N_A} = \frac{2.77 \times 10^6\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}}{4\pi \times (1 \times 10^{-9}\ \text{m}^2\ \text{s}^{-1}) \times (6.0221 \times 10^{23}\ \text{mol}^{-1})}$$
$$= \boxed{0.4\ \text{nm}}$$

18C Transition-state theory

Answers to discussion questions

D18C.2 The Eyring equation, [18C.10–*794*], results from activated complex theory which is an attempt to account for the rate constants of bimolecular reactions by considering the scheme $\text{A} + \text{B} \rightleftharpoons \text{C}^{\ddagger} \longrightarrow \text{P}$, where $\text{C}^{\ddagger}$ is an activated complex. In the formulation of the theory, it is assumed that the activated complex and the reactants are in equilibrium. The concentration of the activated complex is calculated in terms of an equilibrium constant, which in turn is calculated from the partition functions of the reactants and a postulated form of the activated complex. It is further supposed that one normal mode of the activated complex, the one corresponding to displacement along the reaction coordinate, has a very low force constant. Displacement along this mode leads to products, provided that the complex enters a certain configuration of its atoms, known as the transition state.

D18C.4 The primary kinetic isotope effect is the change in rate constant of a reaction in which the breaking of a bond involving the isotope occurs in the rate-determining step. 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. 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, so there is little zero-point energy associated with this vibration of the complex, and hence little change in its zero-point energy upon deuteration. The net effect is an increase in the activation energy of the reaction. It is then expected that the rate constant for the reaction will be lowered in the deuterated molecule, and this is what is observed.

Sometimes the rate of reaction is lowered upon deuteration to an extent even greater than can be accounted for by this analysis. In such cases, quantum-mechanical tunneling 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

E18C.1(b) The empirical expression is compared to the Arrhenius equation $k_r = Ae^{-E_a/RT}$, allowing the activation energy to be determined from $E_a/R = 5925$ K; hence $E_a = (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (5925\ \text{K}) = 49.2...\ \text{kJ mol}^{-1}$. The frequency factor is $A = 6.92 \times 10^{12}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} = 6.92 \times 10^{9}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}$.

The relationship between E_a and $\Delta^{\ddagger}H$ for a bimolecular solution-phase reaction is given by [18C.17–*796*], $\Delta^{\ddagger}H = E_a - RT = (49.2... \times 10^3\ \text{J mol}^{-1}) - (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K}) = \boxed{46.8\ \text{kJ mol}^{-1}}$. The relationship between A and $\Delta^{\ddagger}S$ for a bimolecular solution-phase reaction is given by [18C.19b–*796*]

$$A = e\frac{kT}{h}\frac{RT}{p^{\ominus}}e^{\Delta^{\ddagger}S/R}$$

$$\begin{aligned}\text{hence } \Delta^{\ddagger}S &= R\ln\frac{Ap^{\ominus}h}{ekRT^2}\\ &= (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\\ &\quad\times\ln\frac{(6.92\times10^{9}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1})\times(10^5\ \text{Pa})\times(6.6261\times10^{-34}\ \text{J s})}{e(1.3806\times10^{-23}\ \text{J K}^{-1})\times(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(298\ \text{K})^2}\\ &= \boxed{-34.1\ \text{J K}^{-1}\ \text{mol}^{-1}}\end{aligned}$$

Note the conversion of the units of A to $\text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}$.

E18C.2(b) The empirical expression is compared to the Arrhenius equation $k_r = Ae^{-E_a/RT}$, allowing the activation energy to be determined from $E_a/R = 4972$ K; hence $E_a = (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (4972\ \text{K}) = 41.3...\ \text{kJ mol}^{-1}$. The frequency factor is $A = 4.98 \times 10^{13}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} = 4.98 \times 10^{10}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}$.

The relationship between E_a and $\Delta^{\ddagger}H$ for a bimolecular solution-phase reaction is given by [18C.17–*796*], $\Delta^{\ddagger}H = E_a - RT = (41.3... \times 10^3\ \text{J mol}^{-1}) - (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K}) = +38.8...\ \text{kJ mol}^{-1}$. The relationship between A and $\Delta^{\ddagger}S$ for a bimolecular solution-phase reaction is given by [18C.19b–*796*]

$$A = e\frac{kT}{h}\frac{RT}{p^{\ominus}}e^{\Delta^{\ddagger}S/R}$$

$$\begin{aligned}\text{hence } \Delta^{\ddagger}S &= R\ln\frac{Ap^{\ominus}h}{ekRT^2}\\ &= (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\\ &\quad\times\ln\frac{(4.98\times10^{10}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1})\times(10^5\ \text{Pa})\times(6.6261\times10^{-34}\ \text{J s})}{e(1.3806\times10^{-23}\ \text{J K}^{-1})\times(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(298\ \text{K})^2}\\ &= -17.6...\ \text{J K}^{-1}\ \text{mol}^{-1}\end{aligned}$$

Note the conversion of the units of A to $\text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}$. $\Delta^{\ddagger}G$ is found by combining the values of $\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$ in the usual way

$$\begin{aligned}\Delta^{\ddagger}G &= \Delta^{\ddagger}H - T\Delta^{\ddagger}S\\ &= (+38.8\ldots \times 10^3\ \text{J mol}^{-1}) - (298\ \text{K}) \times (-17.6\ldots\ \text{J K}^{-1}\ \text{mol}^{-1})\\ &= \boxed{+44.1\ \text{kJ mol}^{-1}}\end{aligned}$$

E18C.3(b) The rate constant for a bimolecular gas phase reaction is given by [18C.18a–*796*]

$$k_r = e^2 \frac{kT}{h}\frac{RT}{p^{\ominus}} e^{\Delta^{\ddagger}S/R} e^{-E_a/RT}$$

This rearranges to

$$\begin{aligned}\Delta^{\ddagger}S &= R\ln\left(k_r \frac{hp^{\ominus}}{e^2 kRT^2} e^{E_a/RT}\right) = R\ln\left(\frac{k_r hp^{\ominus}}{e^2 kRT^2}\right) + \frac{E_a}{T}\\ &= (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\\ &\quad \times \ln\left(\frac{(0.35\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}) \times (6.6261 \times 10^{-34}\ \text{J s}) \times (10^5\ \text{Pa})}{e^2(1.3806 \times 10^{-23}\ \text{J K}^{-1}) \times (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (338\ \text{K})^2}\right)\\ &\quad + \frac{39.7 \times 10^3\ \text{J mol}^{-1}}{338\ \text{K}}\\ &= \boxed{-124\ \text{J K}^{-1}\ \text{mol}^{-1}}\end{aligned}$$

E18C.4(b) In *Example* 18C.1 on page 794 the following expression for the rate constant for a reaction between structureless particles is derived

$$k_r = N_A\left(\frac{8kT}{\pi\mu}\right)^{1/2} \sigma^* e^{-\Delta E_0/RT}$$

The activation energy is obtained from its usual definition, [17D.3–*742*]

$$\begin{aligned}E_a &= RT^2 \frac{d\ln k_r}{dT}\\ &= RT^2 \frac{d}{dT}\left\{\ln\left[N_A\left(\frac{8kT}{\pi\mu}\right)^{1/2} \sigma^*\right] - \frac{\Delta E_0}{RT}\right\}\\ &= RT^2\left(\frac{1}{2T} + \frac{\Delta E_0}{RT^2}\right) = \tfrac{1}{2}RT + \Delta E_0\end{aligned}$$

Therefore $\Delta E_0 = E_a - \frac{1}{2}RT$ and hence

$$k_r = N_A\left(\frac{8kT}{\pi\mu}\right)^{1/2} \sigma^* e^{1/2} e^{-\Delta E_a/RT}$$

The rate constant for a bimolecular gas phase reaction is given by [18C.18a–*796*]

$$k_\mathrm{r} = \mathrm{e}^2 \frac{kT}{h}\frac{RT}{p^\ominus}\mathrm{e}^{\Delta^\ddagger S/R}\mathrm{e}^{-E_\mathrm{a}/RT}$$

Comparing these two expressions gives

$$N_\mathrm{A}\left(\frac{8kT}{\pi\mu}\right)^{1/2}\sigma^*\mathrm{e}^{1/2} = \mathrm{e}^2\frac{kT}{h}\frac{RT}{p^\ominus}\mathrm{e}^{\Delta^\ddagger S/R}$$

This is rearranged to give $\Delta^\ddagger S$, noting that for a collision between like molecules $\mu = \frac{1}{2}m$

$$\begin{aligned}\Delta^\ddagger S &= R\ln\left(N_\mathrm{A}\left(\frac{8kT}{\pi\mu}\right)^{1/2}\sigma^*\frac{hp^\ominus}{\mathrm{e}^{3/2}kRT^2}\right)\\ &= (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\\ &\quad\times\ln\left[(6.0221\times10^{23}\,\mathrm{mol^{-1}})\times\left(\frac{8\times(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(450\,\mathrm{K})}{\pi\times\frac{1}{2}\times92\times(1.6605\times10^{-27}\,\mathrm{kg})}\right)^{1/2}\right.\\ &\quad\times(0.45\times10^{-18}\,\mathrm{m^2})\\ &\quad\left.\times\frac{(6.6261\times10^{-34}\,\mathrm{J\,s})\times(10^5\,\mathrm{Pa})}{\mathrm{e}^{3/2}(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(450\,\mathrm{K})^2}\right]\\ &= \boxed{-79\,\mathrm{J\,K^{-1}\,mol^{-1}}}\end{aligned}$$

E18C.5(b) It is convenient to convert the units of the frequency factor and express it as $A = 2.3\times10^{10}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$. The relationship between E_a and $\Delta^\ddagger H$ for a bimolecular gas-phase reaction is given by [18C.17–*796*], $\Delta^\ddagger H = E_\mathrm{a} - 2RT = (30.0\times10^3\,\mathrm{J\,mol^{-1}}) - 2\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K}) = +25.0...\,\mathrm{kJ\,mol^{-1}} = \boxed{+25\,\mathrm{kJ\,mol^{-1}}}$. The relationship between A and $\Delta^\ddagger S$ for a bimolecular gas-phase reaction is given by [18C.19a–*796*]

$$A = \mathrm{e}^2\frac{kT}{h}\frac{RT}{p^\ominus}\mathrm{e}^{\Delta^\ddagger S/R}$$

$$\begin{aligned}\text{hence } \Delta^\ddagger S &= R\ln\frac{Ap^\ominus h}{\mathrm{e}^2kRT^2}\\ &= (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\\ &\quad\times\ln\frac{(2.3\times10^{10}\,\mathrm{m^3\,mol^{-1}\,s^{-1}})\times(10^5\,\mathrm{Pa})\times(6.6261\times10^{-34}\,\mathrm{J\,s})}{\mathrm{e}^2(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})^2}\\ &= -32.4...\,\mathrm{J\,K^{-1}\,mol^{-1}} = \boxed{-32\,\mathrm{J\,K^{-1}\,mol^{-1}}}\end{aligned}$$

$\Delta^\ddagger G$ is found by combining the values of $\Delta^\ddagger H$ and $\Delta^\ddagger S$ in the usual way

$$\begin{aligned}\Delta^\ddagger G &= \Delta^\ddagger H - T\Delta^\ddagger S\\ &= (+25.0...\times10^3\,\mathrm{J\,mol^{-1}}) - (298\,\mathrm{K})\times(-32.4...\,\mathrm{J\,K^{-1}\,mol^{-1}})\\ &= \boxed{+35\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

E18C.6(b) The variation of the rate constant with ionic strength is given by [18C.23–*797*], $\lg k_r = \lg k_r^\circ + 2\mathcal{A}z_A z_B I^{1/2}$; at 298 K and for aqueous solutions $\mathcal{A} = 0.509$. In the absence of further information assume $z_A = +1$ and $z_A = +1$. Rearranging for $\lg k_r^\circ$ gives

$$\begin{aligned}\lg k_r^\circ &= \lg k_r - 2\mathcal{A}z_A z_B I^{1/2}\\ &= \lg(1.55\ \text{dm}^6\ \text{mol}^{-2}\ \text{min}^{-1}) - 2\times(0.509)\times(+1)\times(+1)\times(0.0241)^{1/2}\\ &= 0.0322...\end{aligned}$$

Therefore $\boxed{k_r^\circ = 1.08\ \text{dm}^6\ \text{mol}^{-2}\ \text{min}^{-1}}$.

E18C.7(b) The effect of deuteration on the rate constant is given by [18C.25–*799*]

$$\frac{k_r(\text{C–D})}{k_r(\text{C–H})} = e^{-\zeta} \quad \zeta = \frac{\hbar\omega(\text{C–H})}{2kT}\left\{1-\left(\frac{\mu_{\text{CH}}}{\mu_{\text{CD}}}\right)^{1/2}\right\}$$

In this expression $\omega(\text{C–H}) = (k_f/\mu_{\text{CH}})^{1/2}$. It can be adapted for other pairs of isotopes by changing the effective masses and the force constant.

The effective mass for $^{12}\text{C–}^{16}\text{O}$ is

$$\mu_{\text{CO}} = \frac{m_C m_O}{m_C + m_O} = \frac{12\times15.9949}{12+15.9949}\,m_u = 6.85...\,m_u = 1.13...\times10^{-26}\ \text{kg}$$

Likewise for $^{12}\text{C–}^{18}\text{O}$ (denoted C–O′) the effective mass is

$$\mu_{\text{CO}'} = \frac{m_C m_{O'}}{m_C + m_{O'}} = \frac{12\times17.9992}{12+17.9992}\,m_u = 7.19...\,m_u$$

With the given force constant

$$\omega(\text{C–O}) = \left(\frac{1750\ \text{N m}^{-1}}{1.13...\times10^{-26}\ \text{kg}}\right)^{1/2} = 3.92...\times10^{14}\ \text{s}^{-1}$$

At 298 K

$$\begin{aligned}\zeta &= \frac{(1.0546\times10^{-34}\ \text{J s})\times(3.92...\times10^{14}\ \text{s}^{-1})}{2\times(1.3806\times10^{-23}\ \text{J K}^{-1})\times(298\ \text{K})}\left\{1-\left(\frac{6.85...}{7.19...}\right)^{1/2}\right\}\\ &= 0.121...\end{aligned}$$

$$\frac{k_r(\text{C–O}')}{k_r(\text{C–O})} = e^{-\zeta} = e^{-.121...} = \boxed{0.86}$$

Raising the temperature will decrease ζ which will have the effect of increasing the ratio $k_r(\text{C–O}')/k_r(\text{C–O})$ and so moving it closer to 1. That is, the isotope effect will be reduced.

Solutions to problems

P18C.2 The first step is to analyse the given rate constant data in terms of the Arrhenius equation, $k_r = Ae^{-E_a/RT}$. A plot of $\ln k_r$ against $1/T$ has slope $-E_a/R$ and intercept $\ln A$. The data are tabulated below and the plot is shown in Fig. 18.3.

$\theta/°\mathrm{C}$	T/K	$(10^3/T)/\mathrm{K}^{-1}$	k_r/s^{-1}	$\ln(k_r/\mathrm{s}^{-1})$
−24.82	248.33	4.027	1.22×10^{-4}	−9.011
−20.73	252.42	3.962	2.31×10^{-4}	−8.373
−17.02	256.13	3.904	4.39×10^{-4}	−7.731
−13.00	260.15	3.844	8.50×10^{-4}	−7.070
−8.95	264.20	3.785	1.43×10^{-3}	−6.550

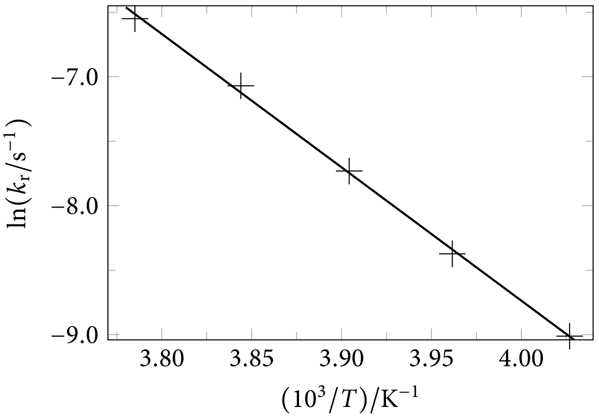


Figure 18.3

The data are a good fit to the line

$$\ln(k_r/\mathrm{s}^{-1}) = -1.035 \times 10^4/(T/\mathrm{K}) + 32.66$$

From the intercept $\ln A = 32.66$ and hence $A = 1.526 \times 10^{14}\ \mathrm{s}^{-1}$. From the slope $-E_a/R = 1.035 \times 10^4$ K, hence $E_a = 86.3...\ \mathrm{kJ\,mol^{-1}} = \boxed{86.3\ \mathrm{kJ\,mol^{-1}}}$.

This reaction is first order, so the argument leading to the expression for the rate constant in terms of partition functions needs to be modified. Crucially, the equilibrium constant for the formation of the activated complex, $K^{\ddagger} = p_{\mathrm{C}^{\ddagger}}/p_{\mathrm{A}}$, no longer includes a $p^{\ominus}$ term. Similarly, for this equilibrium the conversion from partial pressures to concentrations does not involve an RT term because in this case these terms cancel between products and reactants: in other words the equilibrium constant has the same value regardless of whether partial pressures or concentrations are used. Following this through, the argument in the text leads to a modified version of [18C.10–*794*]

$$k_{r,1\mathrm{st}} = \kappa \frac{kT}{h} \overline{K}^{\ddagger}$$

The activation energy is obtained from its usual definition, [17D.3–*742*]

$$\begin{aligned} E_a &= RT^2 \frac{\mathrm{d}\ln k_{r,1\mathrm{st}}}{\mathrm{d}T} = RT^2 \frac{\mathrm{d}}{\mathrm{d}T} \ln\left[\kappa \frac{kT}{h} \overline{K}^{\ddagger}\right] \\ &= RT^2 \left(\frac{1}{T} + \frac{\mathrm{d}\ln \overline{K}^{\ddagger}}{\mathrm{d}T}\right) \\ &= RT^2 \left(\frac{1}{T} + \frac{\Delta^{\ddagger}H}{RT^2}\right) = RT + \Delta^{\ddagger}H \end{aligned}$$

where to go to the last line the equivalent of $\mathrm{d}\ln K/\mathrm{d}T = \Delta_r H^{\ominus}/RT^2$ is used. The expression for $k_{r,1\mathrm{st}}$ is then written in terms of $\Delta^{\ddagger}G$, $\Delta^{\ddagger}H$, and $\Delta^{\ddagger}S$

$$\begin{aligned} k_{r,1\mathrm{st}} &= \kappa \frac{kT}{h} \overline{K}^{\ddagger} = \kappa \frac{kT}{h} \mathrm{e}^{-\Delta^{\ddagger}G/RT} \\ &= \kappa \frac{kT}{h} \mathrm{e}^{\Delta^{\ddagger}S/R}\, \mathrm{e}^{-\Delta^{\ddagger}H/RT} = \left[\kappa \frac{kT}{h} \mathrm{e}^{\Delta^{\ddagger}S/R}\, \mathrm{e}\right] \mathrm{e}^{-E_a/RT} \end{aligned}$$

where to go to the final expression $\Delta^{\ddagger}H = E_a - RT$ is used. The quantity in the bracket is identified as the frequency factor A.

From the graph $E_a = 86.3...\ \mathrm{kJ\,mol^{-1}}$, therefore

$$\begin{aligned} \Delta^{\ddagger}H &= E_a - RT = (86.3... \times 10^3\ \mathrm{kJ\,mol^{-1}}) - (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (253\ \mathrm{K}) \\ &= +84.2...\ \mathrm{kJ\,mol^{-1}} = \boxed{+84.2\ \mathrm{kJ\,mol^{-1}}} \end{aligned}$$

Assuming $\kappa = 1$

$$A = \frac{kT}{h} \mathrm{e}^{\Delta^{\ddagger}S/R}\, \mathrm{e}$$

hence $\Delta^{\ddagger}S = R \ln \dfrac{Ah}{kT\mathrm{e}}$

$$\begin{aligned} &= (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \ln \frac{(1.526 \times 10^{14}\ \mathrm{s^{-1}}) \times (6.6261 \times 10^{-34}\ \mathrm{J\,s})}{(1.3806 \times 10^{-23}\ \mathrm{J\,K^{-1}}) \times (253\ \mathrm{K}) \times \mathrm{e}} \\ &= +19.6...\ \mathrm{J\,K^{-1}\,mol^{-1}} = \boxed{+19.7\ \mathrm{J\,K^{-1}\,mol^{-1}}} \end{aligned}$$

$\Delta^{\ddagger}G$ is found by combining the values of $\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$ in the usual way

$$\begin{aligned} \Delta^{\ddagger}G &= \Delta^{\ddagger}H - T\Delta^{\ddagger}S \\ &= (+84.2... \times 10^3\ \mathrm{J\,mol^{-1}}) - (253\ \mathrm{K}) \times (+19.6...\ \mathrm{J\,K^{-1}\,mol^{-1}}) \\ &= \boxed{+79.2\ \mathrm{kJ\,mol^{-1}}} \end{aligned}$$

P18C.4 The suggested starting point, [18C.9–*794*], is an expression for the equilibrium constant for the formation of the activated complex in terms of the partition functions

$$\overline{K}^{\ddagger} = \frac{N_A \overline{q}^{\ominus}_{C^{\ddagger}}}{q^{\ominus}_A q^{\ominus}_B} \mathrm{e}^{-\Delta E_0/RT}$$

For reactions with the same activation energy their relative rate constants will depend only on the ratio of partition functions, so attention is focused on this quantity. To simplify the notation, the overline, double dagger and standard symbols will be omitted. The translational contribution to the partition function is written q^{T}, and the rotational contribution is written q^{R} for each degree of rotational freedom; similarly, the vibrational contribution is written q^{V} for each normal mode.

For the reaction between atoms, the reactants only have translational contributions, but the activated complex has both translational and rotational contributions (two rotational degrees of freedom as the species is linear). There is no vibrational contribution because the only vibration corresponds to the reaction coordinate.

$$\left(\frac{q_{\mathrm{C}}}{q_{\mathrm{A}}q_{\mathrm{B}}}\right)_{\mathrm{atom}}=\frac{q^{\mathrm{T}}\times(q^{\mathrm{R}})^2}{q^{\mathrm{T}}\times q^{\mathrm{T}}}=\frac{(q^{\mathrm{R}})^2}{q^{\mathrm{T}}}$$

If the reactant A is non-linear and has N atoms it has three rotational degrees of freedom and $3N-6$ normal modes; similar considerations apply to B which has N' atoms. The activated complex also has three rotational degrees of freedom and $N_{\mathrm{act}}=3(N+N')-5$ normal modes, the one corresponding to the reaction coordinate being omitted.

$$\begin{aligned}\left(\frac{q_{\mathrm{C}}}{q_{\mathrm{A}}q_{\mathrm{B}}}\right)_{\mathrm{mol}}&=\frac{q^{\mathrm{T}}\times(q^{\mathrm{R}})^3\times(q^{\mathrm{V}})^{N_{\mathrm{act}}}}{q^{\mathrm{T}}\times(q^{\mathrm{R}})^3\times(q^{\mathrm{V}})^{3N-6}\times q^{\mathrm{T}}\times(q^{\mathrm{R}})^3\times(q^{\mathrm{V}})^{3N'-6}}\\&=\frac{(q^{\mathrm{V}})^7}{q^{\mathrm{T}}\times(q^{\mathrm{R}})^3}\end{aligned}$$

where to go to the last line the calculation $[3(N+N')-5]-(3N-6)-(3N'-6)=7$ is used.

The ratio of the rates for the molecular and atomic reactants is therefore

$$\frac{k_{\mathrm{r,mol}}}{k_{\mathrm{r,atom}}}=\frac{(q^{\mathrm{V}})^7}{q^{\mathrm{T}}\times(q^{\mathrm{R}})^3}\,\frac{q^{\mathrm{T}}}{(q^{\mathrm{R}})^2}=\frac{(q^{\mathrm{V}})^7}{(q^{\mathrm{R}})^5}=\frac{(1)^7}{(10^{1.5})^5}=\boxed{3\times10^{-8}}$$

The reaction with molecules is indeed very much slower.

P18C.6 The variation of the rate constant with ionic strength is given by [18C.23–*797*], $\lg k_{\mathrm{r}}=\lg k_{\mathrm{r}}^{\circ}+2\mathcal{A}z_{\mathrm{A}}z_{\mathrm{B}}I^{1/2}$; at 298 K and for aqueous solutions $\mathcal{A}=0.509$. A plot of $\lg k_{\mathrm{r}}$ against $I^{1/2}$ is used to explore whether or not this relationship applies; for the solution given $I=3[\mathrm{Na_2SO_4}]/\mathrm{mol\,kg^{-1}}$.

$[\mathrm{Na_2SO_4}]/\mathrm{mol\,kg^{-1}}$	$I^{1/2}$	$k_{\mathrm{r}}/(\mathrm{dm^{3/2}\,mol^{-1/2}\,s^{-1}})$	$\lg[k_{\mathrm{r}}/(\mathrm{dm^{3/2}\,mol^{-1/2}\,s^{-1}})]$
0.2	0.775	0.462	−0.335
0.15	0.671	0.430	−0.367
0.1	0.548	0.390	−0.409
0.05	0.387	0.321	−0.493
0.025	0.274	0.283	−0.548
0.012 5	0.194	0.252	−0.599
0.005	0.122	0.224	−0.650

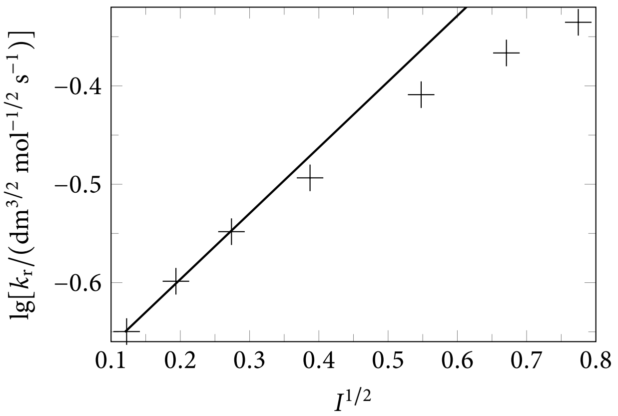


Figure 18.4

The plot is shown in Fig 18.4: it is evident that the data do not fall on a straight line. This is perhaps not surprising as the ionic strengths used are considerably in excess of those for which the Debye–Hückel limiting law is expected to apply. The three data points at lowest ionic strength do fall on a good line, as is shown in the plot, and these have a slope of +0.67. Such a value implies

$$2 \times (0.509) \times (z_A z_B) = +0.67 \quad \text{hence} \quad (z_A z_B) = +0.658$$

This result makes no sense in terms of the theory, so little can be deduced other than the fact that the two species have charges with the same sign.

P18C.8 The variation of the rate constant with ionic strength is given by [18C.23–*797*], $\lg k_r = \lg k_r^\circ + 2\mathcal{A} z_A z_B I^{1/2}$; at 298 K and for aqueous solutions $\mathcal{A} = 0.509$. A plot of $\lg k_r$ against $I^{1/2}$ is used to explore whether or not this relationship applies.

I	$I^{1/2}$	$k_r/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})$	$\lg[k_r/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})]$
0.002 5	0.050 0	1.05	0.021
0.003 7	0.060 8	1.12	0.049
0.004 5	0.067 1	1.16	0.064
0.006 5	0.080 6	1.18	0.072
0.008 5	0.092 2	1.26	0.100

The plot is shown in Fig 18.5; the data do not fall on a straight line. The limiting slope, taken from the first three points, is +2.54. Such a value implies

$$2 \times (0.509) \times (z_A z_B) = +2.54 \quad \text{hence} \quad (z_A z_B) = +2.5$$

This result implies that both ions have charges with the same sign, and if one has charge 1 the other may have a charge of 2 or 3.

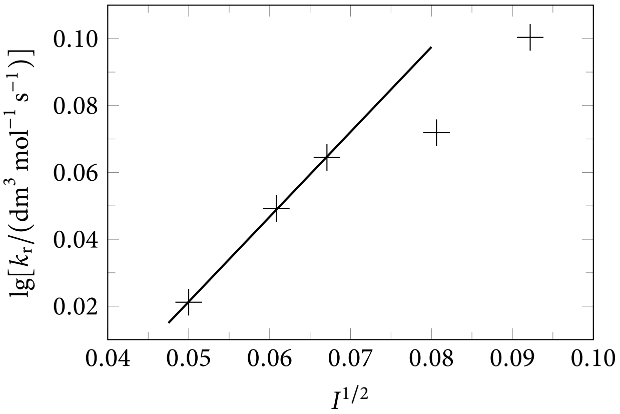


Figure 18.5

P18C.10 The equilibrium constant for the dissociation of the weak acid HA according to $\mathrm{HA} \rightleftharpoons \mathrm{H^+ + A^-}$ is written in terms of activities, and then in terms of activity coefficients and concentrations; it is assumed that the activity coefficient for the neutral species is unity.

$$K_a = \frac{a_{\mathrm{H^+}}a_{\mathrm{A^-}}}{a_{\mathrm{HA}}} = \frac{\gamma_{\mathrm{H^+}}[\mathrm{H^+}]\gamma_{\mathrm{A^-}}[\mathrm{A^-}]}{\gamma_{\mathrm{HA}}[\mathrm{HA}]c^{\ominus}} = \frac{\gamma_\pm^2[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]c^{\ominus}}$$

Taking logarithms gives

$$\lg K_a = \lg[\mathrm{H^+}] + 2\lg\gamma_\pm + \lg\frac{[\mathrm{A^-}]}{[\mathrm{HA}]c^{\ominus}}$$

Inserting the Debye–Hückel limiting law, $\lg\gamma_\pm = -\mathcal{A}|z_+z_-|I^{1/2}$, and taking $z_+ = +1$ and $z_- = -1$, gives

$$\lg K_a = \lg[\mathrm{H^+}] - 2\mathcal{A}I^{1/2} + \lg\frac{[\mathrm{A^-}]}{[\mathrm{HA}]c^{\ominus}}$$

$$\text{hence } \lg[\mathrm{H^+}] = \lg K_a - \lg\frac{[\mathrm{A^-}]}{[\mathrm{HA}]c^{\ominus}} + 2\mathcal{A}I^{1/2}$$

The rate is written $r = k_r[\mathrm{H^+}][\mathrm{B}]$, hence

$$\begin{aligned}\lg r &= \lg(k_r[\mathrm{B}]) + \lg[\mathrm{H^+}]\\ &= \lg(k_r[\mathrm{B}]) + \lg K_a - \lg\frac{[\mathrm{A^-}]}{[\mathrm{HA}]c^{\ominus}} + 2\mathcal{A}I^{1/2}\\ &= \lg\frac{k_rK_a[\mathrm{B}][\mathrm{HA}]c^{\ominus}}{[\mathrm{A^-}]} + 2\mathcal{A}I^{1/2}\end{aligned}$$

The prediction is that the log of the rate will go as $I^{1/2}$.

18D The dynamics of molecular collisions

Answers to discussion questions

D18D.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.

D18D.4 Molecular beams may be used to prepare molecules in specific rotational and vibrational states, and then to examine the results of collisions between such precisely prepared species. Section 18D.1(a) on page 801 describes how molecular beams are prepared such that the molecules in them have a very narrow range of velocities and therefore relatively few collisions to redistribute their energies. Molecules in such beams can be prepared in specific vibrational states, for example, by using lasers to excite vibrations. Crossing two molecular beams allows collisions to be staged between two sets of precisely characterized molecules. Detectors can then be used to study the results of those collisions, recording the number of molecules in which particular states that are scattered in a given direction.

Solutions to exercises

E18D.1(b) Refer to Fig. 18D.19 on page 808, 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 as ‡ ○). 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. This 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.

In contrast, the successful trajectory is able to turn the 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 reactant is relatively high in vibrational energy. Once this successful trajectory passes through the transition state, it follows a straight course into the valley representing products, so the product is high in translational energy and low in vibrational energy.

E18D.2(b) The numerator of [18D.6–*809*] is integrated with the assumption that $\overline{P}(E) = 1$ for $E < V$, and zero otherwise. Effectively this means computing the integral over the range $E = 0$ to $E = V$ with $\overline{P}(E) = 1$

$$\begin{aligned}\int_0^{\infty} \overline{P}(E)\,\mathrm{e}^{-E/kT}\,\mathrm{d}E &= \int_0^{V} \mathrm{e}^{-E/kT}\,\mathrm{d}E \\ &= -kT\,\mathrm{e}^{-E/kT}\Big|_0^V \\ &= -kT(\mathrm{e}^{-V/kT} - 1) = \boxed{kT(1 - \mathrm{e}^{-V/kT})}\end{aligned}$$

When $kT \ll V$ the exponential term goes to zero, leaving a linear dependence on T. When $kT \gg V$ the exponential is expanded as $(1 - V/kT)$, which leads to a result independent of T.

Solutions to problems

P18D.2 The change in intensity of the beam, $\mathrm{d}I$, is proportional to the number of scatterers per unit volume, $\mathcal{N}$, the intensity of the beam, I, and the path length $\mathrm{d}L$. The constant of proportionality is the collision cross-section σ, the 'target area' of each scatterer.

$$\mathrm{d}I = -\sigma\mathcal{N}I\,\mathrm{d}L \quad \text{hence} \quad \frac{1}{I}\,\mathrm{d}I = -\sigma\mathcal{N}\,\mathrm{d}L \quad \text{hence} \quad \mathrm{d}\ln I = -\sigma\mathcal{N}\,\mathrm{d}L$$

If the incident intensity at $L = 0$ is I_0, and the intensity after scattering through length L is I, integration gives

$$\int_{I_0}^{I} \mathrm{d}\ln I = \int_0^{L} -\sigma\mathcal{N}\,\mathrm{d}L \quad \text{hence} \quad \ln I/I_0 = -\sigma\mathcal{N}L$$

For scattering by CH_2F_2 $I/I_0 = 0.60$, whereas for scattering over the same length by Ar $I/I_0 = 0.90$ at the same pressure. The ratio of the logarithms of these fractions is the ratio of the collision cross sections.

$$\frac{\ln 0.60}{\ln 0.90} = \frac{\sigma_{\mathrm{CH_2F_2}}}{\sigma_{\mathrm{Ar}}} = \boxed{4.8}$$

The very polar species CsCl is scattered more strongly by the polar CH_2F_2 than by atomic Ar.

P18D.4 For a collinear approach the potential energy surface is described in terms of that for HOD, the H–O distance $R_{\mathrm{H-O}}$, and the D–O distance $R_{\mathrm{D-O}}$. When the H–O distance is large the variation of the potential energy is essentially that of an isolated OD molecule with $R_{\mathrm{D-O}}$. When the D–O distance is large the variation of the potential energy is essentially that of an isolated OH molecule with the distance $R_{\mathrm{H-O}}$.

18E Electron transfer in homogeneous systems

Answers to discussion questions

D18E.2 Electron tunnelling plays an important role in electron transfer. As is discussed in Section 7D.4 on page 268, it is expected that tunnelling will be more important for electrons than any other particles that participate in chemical reactions because electrons are so much lighter than atoms or ions. Tunnelling is responsible for the exponential distance dependence of the factor $H_{\mathrm{et}}(d)^2$, given by [18E.4–*812*], and the electron-transfer rate constant, given by [18E.5–*812*], is directly proportional to $H_{\mathrm{et}}(d)^2$. A full discussion is found in Section 18E.2 on page 811.

Solutions to exercises

E18E.1(b) The distance dependence of $H_{\mathrm{et}}(d)^2$ given by [18E.4–*812*], $H_{\mathrm{et}}(d)^2 = H_{\mathrm{et}}^{\circ 2}\mathrm{e}^{-\beta d}$.

$$\begin{aligned}\frac{H_{\mathrm{et}}(d_2)^2}{H_{\mathrm{et}}(d_1)^2} &= \mathrm{e}^{-\beta(d_2-d_1)} \\ &= \mathrm{e}^{-(30\ \mathrm{nm}^{-1})[(2.0\ \mathrm{nm})-(1.0\ \mathrm{nm})]} = 9.35... \times 10^{-14}\end{aligned}$$

Increasing the distance from 1.0 nm to 2.0 nm reduces $H_{\mathrm{et}}(d)^2$ by $\boxed{\text{13 orders}}$ of magnitude.

E18E.2(b) The rate constant for electron-transfer is given by [18E.5–*812*] together with [18E.6–*813*]

$$k_{\mathrm{et}} = \frac{1}{h}\left(\frac{\pi^3}{RT\Delta E_{\mathrm{R}}}\right)^{1/2} H_{\mathrm{et}}(d)^2\,\mathrm{e}^{-\Delta^{\ddagger}G/RT} \qquad \Delta^{\ddagger}G = \frac{(\Delta_{\mathrm{r}}G^{\ominus} + \Delta E_{\mathrm{R}})^2}{4\Delta E_{\mathrm{R}}}$$

For the two reactions given, ΔE_{R} and $H_{\mathrm{et}}(d)^2$ are assumed to be the same, therefore

$$\frac{k_{\mathrm{et},2}}{k_{\mathrm{et},1}} = \mathrm{e}^{-(\Delta^{\ddagger}G_2-\Delta^{\ddagger}G_1)/RT} \quad \text{hence} \quad \ln k_{\mathrm{et},2}/k_{\mathrm{et},1} = -(\Delta^{\ddagger}G_2 - \Delta^{\ddagger}G_1)/RT$$

The term $(\Delta^{\ddagger}G_2 - \Delta^{\ddagger}G_1)/RT$ is then developed as

$$\begin{aligned}\frac{\Delta^{\ddagger}G_2 - \Delta^{\ddagger}G_1}{RT} &= \frac{(\Delta_{\mathrm{r}}G_2^{\ominus} + \Delta E_{\mathrm{R}})^2 - (\Delta_{\mathrm{r}}G_1^{\ominus} + \Delta E_{\mathrm{R}})^2}{4\Delta E_{\mathrm{R}}RT} \\ &= \frac{(\Delta_{\mathrm{r}}G_2^{\ominus})^2 - (\Delta_{\mathrm{r}}G_1^{\ominus})^2 + 2\Delta E_{\mathrm{R}}(\Delta_{\mathrm{r}}G_2^{\ominus} - \Delta_{\mathrm{r}}G_1^{\ominus})}{4\Delta E_{\mathrm{R}}RT} \\ &= \frac{1}{4RT}\left[\frac{(\Delta_{\mathrm{r}}G_2^{\ominus})^2 - (\Delta_{\mathrm{r}}G_1^{\ominus})^2}{\Delta E_{\mathrm{R}}} + 2(\Delta_{\mathrm{r}}G_2^{\ominus} - \Delta_{\mathrm{r}}G_1^{\ominus})\right]\end{aligned}$$

Putting this with the expression for $\ln k_{\mathrm{r},2}/k_{\mathrm{r},1}$ gives

$$\ln k_{\mathrm{et},2}/k_{\mathrm{et},1} = \frac{-1}{4RT}\left[\frac{(\Delta_{\mathrm{r}}G_2^{\ominus})^2 - (\Delta_{\mathrm{r}}G_1^{\ominus})^2}{\Delta E_{\mathrm{R}}} + 2(\Delta_{\mathrm{r}}G_2^{\ominus} - \Delta_{\mathrm{r}}G_1^{\ominus})\right]$$

This expression is then rearranged for ΔE_R

$$-4RT\ln k_{\mathrm{et},2}/k_{\mathrm{et},1} - 2(\Delta_\mathrm{r}G_2^\ominus - \Delta_\mathrm{r}G_1^\ominus) = \frac{(\Delta_\mathrm{r}G_2^\ominus)^2 - (\Delta_\mathrm{r}G_1^\ominus)^2}{\Delta E_\mathrm{R}}$$

$$\Delta E_\mathrm{R} = \frac{(\Delta_\mathrm{r}G_2^\ominus)^2 - (\Delta_\mathrm{r}G_1^\ominus)^2}{-4RT\ln k_{\mathrm{et},2}/k_{\mathrm{et},1} - 2(\Delta_\mathrm{r}G_2^\ominus - \Delta_\mathrm{r}G_1^\ominus)}$$

$$\Delta E_\mathrm{R} = \frac{(\Delta_\mathrm{r}G_1^\ominus)^2 - (\Delta_\mathrm{r}G_2^\ominus)^2}{4RT\ln k_{\mathrm{et},2}/k_{\mathrm{et},1} + 2(\Delta_\mathrm{r}G_2^\ominus - \Delta_\mathrm{r}G_1^\ominus)}$$

The data are given in eV so it is convenient to express $4RT$ in eV with the help of the conversion factors inside the front cover

$$4RT = 4\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\ \mathrm{K})\times\frac{1\ \mathrm{eV}}{96.485\times10^3\ \mathrm{J\,mol^{-1}}} = 0.102...\ \mathrm{eV}$$

With the data given

$$\begin{aligned}\Delta E_\mathrm{R} &= \frac{(\Delta_\mathrm{r}G_1^\ominus)^2 - (\Delta_\mathrm{r}G_2^\ominus)^2}{4RT\ln k_{\mathrm{et},2}/k_{\mathrm{et},1} + 2(\Delta_\mathrm{r}G_2^\ominus - \Delta_\mathrm{r}G_1^\ominus)}\\ &= \frac{(-0.665\ \mathrm{eV})^2 - (-0.975\ \mathrm{eV})^2}{(0.102...\ \mathrm{eV})\times\ln\frac{(3.33\times10^6\ \mathrm{s^{-1}})}{(2.02\times10^5\ \mathrm{s^{-1}})} + 2[(-0.975\ \mathrm{eV}) - (-0.665\ \mathrm{eV})]}\\ &= 1.53...\ \mathrm{eV} = \boxed{1.53\ \mathrm{eV}}\end{aligned}$$

Using the data for the first value of the rate constant

$$\Delta^\ddagger G = \frac{(\Delta_\mathrm{r}G^\ominus + \Delta E_\mathrm{R})^2}{4\Delta E_\mathrm{R}} = \frac{[(-0.665\ \mathrm{eV}) + (1.53...\ \mathrm{eV})]^2}{4\times(1.53...\ \mathrm{eV})} = 0.122...\ \mathrm{eV}$$

The expression for k_r given by [18E.5–*812*] is then rearranged to find $H_\mathrm{et}(d)^2$

$$H_\mathrm{et}(d)^2 = hk_\mathrm{et}\left(\frac{RT\Delta E_\mathrm{R}}{\pi^3}\right)^{1/2} \mathrm{e}^{\Delta^\ddagger G/RT}$$

As the values of ΔE_R and $\Delta^\ddagger G$ have already been found in eV, it is convenient to express the term RT also in eV; following the same process as above gives $RT = 0.0256...$ eV.

$$\begin{aligned}H_\mathrm{et}(d)^2 &= (6.6261\times10^{-34}\ \mathrm{J\,s})\times(2.02\times10^5\ \mathrm{s^{-1}})\\ &\quad\times\left(\frac{(0.0256...\ \mathrm{eV})\times(1.53...\ \mathrm{eV})}{\pi^3}\right)^{1/2} \mathrm{e}^{(0.122...\ \mathrm{eV})/(0.0256...\ \mathrm{eV})}\\ &= 5.59...\times10^{-28}\ \mathrm{J\,eV} = 8.97...\times10^{-47}\ \mathrm{J^2}\end{aligned}$$

On the final line the units are converted using 1 eV = 1.6021×10^{-19} J. Hence $\boxed{H_\mathrm{et}(d) = 9.47\times10^{-24}\ \mathrm{J}}$.

E18E.3(b) The rate constant for electron-transfer is given by [18E.5–*812*] together with [18E.6–*813*]

$$k_{\rm et} = \frac{1}{h}\left(\frac{\pi^3}{RT\Delta E_{\rm R}}\right)^{1/2} H_{\rm et}(d)^2\, e^{-\Delta^{\ddagger}G/RT} \qquad \Delta^{\ddagger}G = \frac{(\Delta_{\rm r}G^{\ominus} + \Delta E_{\rm R})^2}{4\Delta E_{\rm R}}$$

For the two reactions given, $\Delta E_{\rm R}$ and $\Delta^{\ddagger}G$ are assumed to be the same. The distance dependence of $H_{\rm et}(d)^2$ is given by [18E.4–*812*], $H_{\rm et}(d)^2 = H_{\rm et}^{\circ 2} e^{-\beta d}$, therefore

$$\frac{k_{\rm et,2}}{k_{\rm et,1}} = \frac{(H_{\rm et}(d)^2)_2}{(H_{\rm et}(d)^2)_1} = e^{-\beta(d_2-d_1)}$$

hence $\ln(k_{\rm et,2}/k_{\rm et,1}) = -\beta(d_2 - d_1)$

$$\text{therefore } \beta = -\frac{\ln(k_{\rm et,2}/k_{\rm et,1})}{(d_2 - d_1)}$$

$$\beta = -\frac{\ln[(4.51\times10^4\ {\rm s}^{-1})/(2.02\times10^5\ {\rm s}^{-1})]}{(1.23\ {\rm nm}) - (1.11\ {\rm nm})} = 12.5...\ {\rm nm}^{-1}$$

The rate constant for $d_3 = 1.59$ nm is then found using the result above

$$\begin{aligned} k_{\rm et,3} &= k_{\rm et,1} e^{-\beta(d_3-d_1)} \\ &= (2.02\times10^5\ {\rm s}^{-1}) \times e^{-(12.5...\ {\rm nm}^{-1})\times[(1.59\ {\rm nm})-(1.11\ {\rm nm})]} \\ &= \boxed{498\ {\rm s}^{-1}} \end{aligned}$$

Solutions to problems

P18E.2 Using the Marcus cross-relation, and assuming $f = 1$, the rate constant may be expressed $k_{\rm r} = (k_{\rm AA}k_{\rm DD}K)^{1/2}$, where in this case A is the $\rm Ru^{3+}$ complex and D is the $\rm Fe^{3+}$ complex. The equilibrium constant K for the overall reaction is found from the standard potentials. Subtracting the second half-cell reaction from the first gives (omitting the ligands for brevity)

$$\mathrm{Ru^{3+} + Fe^{2+} \longrightarrow Ru^{2+} + Fe^{3+}} \qquad E^{\ominus} = +1.26\ {\rm V} - (+0.77\ {\rm V}) = +0.49\ {\rm V}$$

In this reaction one electron is involved, therefore the standard Gibbs energy change is given by [6C.3–*221*], $\Delta_{\rm r}G^{\ominus} = -FE^{\ominus}$, and the equilibrium constant by $\Delta_{\rm r}G^{\ominus} = -RT\ln K$, hence

$$\begin{aligned} K &= e^{-\Delta_{\rm r}G^{\ominus}/RT} = e^{FE^{\ominus}/RT} \\ &= e^{(96485\,{\rm C\,mol^{-1}})\times(+0.49\ {\rm V})/[(8.3145\,{\rm J\,K^{-1}\,mol^{-1}})\times(298\ {\rm K})]} \\ &= 1.93\ldots\times10^8 \end{aligned}$$

The rate constant for the overall process is therefore

$$\begin{aligned} k_{\rm r} &= (k_{\rm AA}k_{\rm DD}K)^{1/2} \\ &= [(4.0\times10^8\ {\rm dm^3\,mol^{-1}\,s^{-1}})\times(4.2\ {\rm dm^3\,mol^{-1}\,s^{-1}})\times(1.93\ldots\times10^8)]^{1/2} \\ &= \boxed{5.7\times10^8\ {\rm dm^3\,mol^{-1}\,s^{-1}}} \end{aligned}$$

P18E.4 The variation of the electron-transfer rate constant with $\Delta_r G^\ominus$ is given by [18E.8–*814*]

$$\ln k_{et} = -\frac{RT}{4\Delta E_R}\left(\frac{\Delta_r G^\ominus}{RT}\right)^2 - \tfrac{1}{2}\left(\frac{\Delta_r G^\ominus}{RT}\right) + \text{const.}$$

A plot of $\ln k_{et}$ against $-\Delta_r G^\ominus$ is expected to be an inverted parabola and, as described in the text, the maximum occurs at $-\Delta_r G^\ominus = \Delta E_R$. The plot is shown in Fig 18.6.

$-\Delta_r G^\ominus/\text{eV}$	$k_{et}/(10^6\ \text{s}^{-1})$	$\lg[k_{et}/(10^6\ \text{s}^{-1})]$
0.665	0.657	−0.182
0.705	1.52	0.182
0.745	1.12	0.049
0.975	8.99	0.954
1.015	5.76	0.760
1.055	10.1	1.004

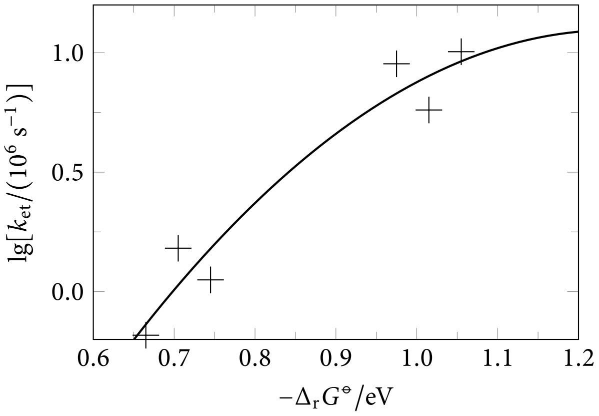


Figure 18.6

The data are rather poor fit to the second-order polynomial

$$\lg[k_{et}/(10^6\ \text{s}^{-1})] = -3.682 \times (-\Delta_r G^\ominus/\text{eV})^2 + 9.157 \times (-\Delta_r G^\ominus/\text{eV}) - 4.5983$$

which is shown on the plot. The maximum of this function occurs when the derivative is zero, that is when $2\times -3.682 \times (-\Delta_r G^\ominus/\text{eV}) + 9.157 = 0$; this occurs at $(-\Delta_r G^\ominus/\text{eV}) = 1.24....$ Therefore $\boxed{\Delta E_R = 1.2\ \text{eV}}$.

P18E.6 The theoretical treatment given in the text applies only at relatively high temperatures. At temperatures above 130 K, the reaction in question is observed to follow a temperature dependence consistent with [18E.5–*812*], namely increasing rate with increasing temperature. Below 130 K, the temperature dependent terms in the equation are replaced by Franck–Condon factors (Topic 11F); that is, temperature-dependent terms are replaced by temperature-independent wavefunction overlap integrals.

Answers to integrated activities

I18.2 Typical orders of magnitudes are $q_{\text{m}}^{\text{T}}/N_{\text{A}} \approx 10^7$, $q^{\text{R}} \approx 10$ per rotational degree of freedom, $q^{\text{V}} \approx 1$ per vibrational degree of freedom, and $q^{\text{E}} \approx 1$. Vibrational and electronic contributions will therefore be ignored from now on. According to transition-state theory the rate constant is given by ([18C.10–*794*] and [18C.9–*794*])

$$k_{\text{r}} = \kappa \frac{kT}{h}\frac{RT}{p^{\ominus}}\frac{N_{\text{A}}q_{\text{C}^{\ddagger}}^{\ominus}}{q_{\text{C}}^{\ominus}q_{\text{B}}^{\ominus}}\,\text{e}^{-\Delta E_0/RT}$$

At 298 K the factors in from the the ratio of partition functions evaluate to $1.5\times10^{11}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}$, assuming $\kappa = 1$.

For a reaction between structureless particles A, B, and C‡ all have contributions from translation; in addition, C‡ has two rotational degrees of freedom, therefore

$$\begin{aligned}
k_{\text{r}} &= (1.5\times10^{11}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1})\times\frac{N_{\text{A}}\times q_{\text{m}}^{\text{T}}\times(q^{\text{R}})^2}{q_{\text{m}}^{\text{T}}\times q_{\text{m}}^{\text{T}}}\,\text{e}^{-\Delta E_0/RT}\\
&= (1.5\times10^{11}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1})\times\frac{(q^{\text{R}})^2}{q_{\text{m}}^{\text{T}}/N_{\text{A}}}\,\text{e}^{-\Delta E_0/RT}\\
&= (1.5\times10^{11}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1})\times\frac{(10)^2}{10^7}\\
&= (1.5\times10^{6}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1})\times\text{e}^{-\Delta E_0/RT}
\end{aligned}$$

In collision theory the rate constant is given by [18A.9–*783*]

$$k_{\text{r}} = \sigma N_{\text{A}}\left(\frac{8kT}{\pi\mu}\right)^{1/2}\text{e}^{-E_{\text{a}}/RT}$$

For a typical value $\sigma = 0.4\ \text{nm}^2$ and a mass of 2×10^{-26} kg, at 298 K

$$k_{\text{r}} = (1.7\times10^{8}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1})\times\text{e}^{-E_{\text{a}}/RT}$$

Assuming that $E_{\text{a}} \approx \Delta E_0$, collision theory gives a rate constant greater by about a factor of 100, implying a steric factor of about 0.01; this is a plausible result.

If A and B are non-linear triatomics, then A, B and C‡ all have three rotational degrees of freedom

$$\begin{aligned}
k_{\text{r}} &= (1.5\times10^{11}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1})\times\frac{N_{\text{A}}\times q_{\text{m}}^{\text{T}}\times(q^{\text{R}})^3}{q_{\text{m}}^{\text{T}}\times(q^{\text{R}})^3\times q_{\text{m}}^{\text{T}}\times(q^{\text{R}})^3}\,\text{e}^{-\Delta E_0/RT}\\
&= (1.5\times10^{11}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1})\times\frac{1}{(q^{\text{R}})^3\times q_{\text{m}}^{\text{T}}/N_{\text{A}}}\,\text{e}^{-\Delta E_0/RT}\\
&= (1.5\times10^{11}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1})\times\frac{1}{(10)^3\times10^7}\\
&= (15\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1})\times\text{e}^{-\Delta E_0/RT}
\end{aligned}$$

The steric factor is now 9×10^{-8} – very much smaller than for the reaction between structureless particles.

19

Processes at solid surfaces

19A An introduction to solid surfaces

Answers to discussion questions

D19A.2 The Auger effect is described in Section 19A.3(b) on page 828. In Auger electron spectroscopy the electron beam is only able to affect species on the surface and perhaps a few layers into the bulk, and therefore the emitted electrons are characteristic of the surface and the species adsorbed onto it. The energies of the emitted electrons are characteristic of the material present and so provide a fingerprint of the sample.

In scanning Auger microscopy (SAM) the electron beam is narrowly focused so that electrons are excited only from a small region (of dimension about 50 nm). By scanning the beam across the sample it is possible to build up a map of the composition.

In scanning tunnelling microscopy (STM) a topological map of the surface is built up, and under favourable circumstances individual atoms may be identified; the resolution is thus much greater than that achieved in SAM. However, STM gives no clues as to the identity of the atoms on the surface, in contrast to SAM.

Solutions to exercises

E19A.1(b) The collision flux, Z_w, is given by [19A.1–*825*], $Z_w = p/(2\pi MkT/N_A)^{1/2}$ where p is the pressure of gas, M is the molar mass of the molecule, k is Boltzmann's constant, T is the temperature and N_A is Avogadro's constant. From inside the front cover, 760 Torr = 1 atm = 1.01325×10^5 Pa, therefore 1 Torr is 133.32 Pa.

(i) For a nitrogen molecule, the molar mass $M = 2 \times (14.01\ \text{g mol}^{-1}) = 28.02\ \text{g mol}^{-1}$, therefore for $p = 10.0$ Pa

$$
\begin{aligned}
Z_w &= \frac{p}{(2\pi MkT/N_A)^{1/2}} \\
&= \frac{(10.0\ \text{Pa}) \times (6.0221 \times 10^{23}\ \text{mol}^{-1})^{1/2}}{\left[2\pi \times (28.02 \times 10^{-3}\ \text{kg mol}^{-1}) \times (1.3806 \times 10^{-23}\ \text{J K}^{-1}) \times (298.15\ \text{K})\right]^{1/2}} \\
&= 2.88... \times 10^{23}\ \text{m}^{-2}\,\text{s}^{-1} = \boxed{2.88 \times 10^{19}\ \text{cm}^{-2}\,\text{s}^{-1}}
\end{aligned}
$$

For $p = 0.150\ \mu\text{Torr}$

$$
\begin{aligned}
Z_\text{w} &= \frac{p}{(2\pi MkT/N_\text{A})^{1/2}}\\
&= \frac{(0.150\times10^{-6}\ \text{Torr})\times(133.32\ \text{Pa Torr}^{-1})\times(6.0221\times10^{23}\ \text{mol}^{-1})^{1/2}}{\left[2\pi\times(28.02\times10^{-3}\ \text{kg mol}^{-1})\times(1.3806\times10^{-23}\ \text{J K}^{-1})\times(298.15\ \text{K})\right]^{1/2}}\\
&= 5.76...\times10^{17}\ \text{m}^{-2}\,\text{s}^{-1} = \boxed{5.76\times10^{13}\ \text{cm}^{-2}\,\text{s}^{-1}}
\end{aligned}
$$

(ii) For methane, the molar mass $M = (12.011\ \text{g mol}^{-1}) + 4\times(1.0079\ \text{g mol}^{-1}) = 16.043\ \text{g mol}^{-1}$, therefore for $p = 10.0\ \text{Pa}$

$$
\begin{aligned}
Z_\text{w} &= \frac{p}{(2\pi MkT/N_\text{A})^{1/2}}\\
&= \frac{(10.0\ \text{Pa})\times(6.0221\times10^{23}\ \text{mol}^{-1})^{1/2}}{\left[2\pi\times(16.043\times10^{-3}\ \text{kg mol}^{-1})\times(1.3806\times10^{-23}\ \text{J K}^{-1})\times(298.15\ \text{K})\right]^{1/2}}\\
&= 3.80...\times10^{23}\ \text{m}^{-2}\,\text{s}^{-1} = \boxed{3.81\times10^{19}\ \text{cm}^{-2}\,\text{s}^{-1}}
\end{aligned}
$$

For $p = 0.150\ \mu\text{Torr}$,

$$
\begin{aligned}
Z_\text{w} &= \frac{p}{(2\pi MkT/N_\text{A})^{1/2}}\\
&= \frac{(0.150\times10^{-6}\ \text{Torr})\times(133.32\ \text{Pa Torr}^{-1})\times(6.0221\times10^{23}\ \text{mol}^{-1})^{1/2}}{\left[2\pi\times(16.043\times10^{-3}\ \text{kg mol}^{-1})\times(1.3806\times10^{-23}\ \text{J K}^{-1})\times(298.15\ \text{K})\right]^{1/2}}\\
&= 7.61...\times10^{17}\ \text{m}^{-2}\,\text{s}^{-1} = \boxed{7.62\times10^{13}\ \text{cm}^{-2}\,\text{s}^{-1}}
\end{aligned}
$$

E19A.2(b) The collision flux, Z_w, is given by [19A.1–*825*], $Z_\text{w} = p/(2\pi MkT/N_\text{A})^{1/2}$ where p is the pressure of gas, M is the molar mass of the molecule, k is Boltzmann's constant, T is the temperature and N_A is Avogadro's constant.

The collision rate, z, is given by $z = AZ_\text{w}$ where A is the surface area. Hence,

$$z = AZ_\text{w} = \frac{Ap}{(2\pi MkT/N_\text{A})^{1/2}}$$

For N_2 the molar mass $M = 2\times(14.01\ \text{g mol}^{-1}) = 28.02\ \text{g mol}^{-1}$. Thus, for $A = \pi(d/2)^2$, where d is the diameter of the circular surface, rearranging the above expression gives

$$
\begin{aligned}
p &= \frac{r(2\pi MkT/N_\text{A})^{1/2}}{A}\\
&= \frac{5.00\times10^{19}\ \text{s}^{-1}}{\pi\times(0.5\times2.0\times10^{-3}\ \text{m})^2}\\
&\quad\times\left(\frac{2\pi\times(28.02\times10^{-3}\ \text{kg mol}^{-1})\times(1.3806\times10^{-23}\ \text{J K}^{-1})\times(525\ \text{K})}{6.0221\times10^{23}\ \text{mol}^{-1}}\right)^{1/2}\\
&= \boxed{7.3\times10^{2}\ \text{Pa}}
\end{aligned}
$$

E19A.3(b) For a perfect gas, and at constant temperature, $p \propto 1/V$, where V is the volume occupied by the gas at pressure p. Therefore

$$\frac{p_2}{p_1} = \frac{V_1}{V_2} \quad \text{hence} \quad V_2 = \frac{V_1 p_1}{p_2}$$

The surface coverage θ is given by $\theta = V/V_\infty$ where V is the volume of gas adsorbed at a particular pressure p and V_∞ is the volume of gas which gives a complete monolayer, but where the volume has been corrected to the same pressure p.

At 5.0 bar, the volume adsorbed is a complete monolayer and thus $V_\infty = 6.6\ \text{cm}^3$ at 5.0 bar. At 0.30 bar, this same volume is

$$V_{\infty,0.3\ \text{bar}} = \frac{(6.6\ \text{cm}^3) \times (5.0\ \text{bar})}{0.3\ \text{bar}} = 110\ \text{cm}^3$$

Hence the surface coverage is

$$\theta = \frac{11\ \text{cm}^3}{110\ \text{cm}^3} = \boxed{0.1}$$

E19A.4(b) For a process to be spontaneous it must be accompanied by a reduction in the Gibbs energy, that is $\Delta G < 0$, where $\Delta G = \Delta H - T\Delta S$. If adsorption is endothermic, $\Delta H > 0$, but nevertheless observed to be spontaneous, it must be that $\Delta S > 0$. This is unusual for adsorption of a gas because such a process involves the loss of translational degrees of freedom. However, if the adsorbed molecule dissociates on binding it is possible for the entropy to increase, $\Delta S > 0$.

Solutions to problems

P19A.2 The collision flux, Z_W, is given by [19A.1–*825*], $Z_\text{W} = p/(2\pi MkT/N_\text{A})^{1/2}$ where p is the pressure of gas, M is the molar mass of the molecule, k is Boltzmann's constant, T is the temperature and N_A is Avogadro's constant.

(a) For an oxygen molecule, the molar mass $M = 2 \times (16.00\ \text{g mol}^{-1}) = 32.00\ \text{g mol}^{-1}$, therefore at $T = 300$ K and $p = 100$ kPa,

$$\begin{aligned} Z_\text{W} &= \frac{p}{(2\pi MkT/N_\text{A})^{1/2}} \\ &= \frac{(100 \times 10^3\ \text{Pa}) \times (6.0221 \times 10^{23}\ \text{mol}^{-1})^{1/2}}{\left[2\pi \times (32.00 \times 10^{-3}\ \text{kg mol}^{-1}) \times (1.3806 \times 10^{-23}\ \text{J K}^{-1}) \times (300\ \text{K})\right]^{1/2}} \\ &= 2.68... \times 10^{27}\ \text{m}^{-2}\,\text{s}^{-1} = \boxed{2.69 \times 10^{23}\ \text{cm}^{-2}\,\text{s}^{-1}} \end{aligned}$$

(b) At $p = 1.00$ Pa the collision rate is reduced by a factor of 10^5 compared to (a): $\boxed{Z_\text{W} = 2.69 \times 10^{18}\ \text{cm}^{-2}\,\text{s}^{-1}}$

Assume that on the surface the atoms are centred on a square grid of side a_0, the lattice spacing, with the atoms in contact (a face of a simple cubic lattice). It follows that the radius of each atom is half the lattice spacing $r = a_0/2$. Hence, the area, A, of a single surface atom is approximated by $A = \pi r^2 = \pi(\frac{1}{2}a_0)^2 = \frac{1}{4}\pi a_0^2$.

For $p = 100$ kPa, the number of collisions made with a single surface atom in each second by oxygen is

$$\begin{aligned} n_{\text{col}} &= AZ_{\text{w}}\Delta t = \tfrac{1}{4}\pi Z_{\text{w}} a_0^2 \Delta t \\ &= \tfrac{1}{4}\pi \times (2.68... \times 10^{27}\ \text{m}^{-2}\,\text{s}^{-1}) \times (291 \times 10^{-12}\ \text{m})^2 \times (1\ \text{s}) = \boxed{1.79 \times 10^8} \end{aligned}$$

For $p = 1.00$ Pa, the number of collisions is reduced by a factor of 10^5 compared to the calculation just made: $\boxed{AZ_{\text{w}} = 1.79 \times 10^3}$.

P19A.4 Using Bragg's law, $\lambda = 2d\sin\theta$, it is observed that for a given wavelength, the greater the separation d of atomic layers within a lattice, the smaller the scattering angle θ.Therefore, in terms of the LEED pattern, the farther apart the atoms responsible for the pattern, the closer the spots appear in the LEED pattern.

Therefore, tripling the horizontal separation between the atoms corresponds to the spot separation reducing to a third of the original separation between the spots. The vertical separation between atoms is unchanged, therefore the vertical separation of LEED spots in that dimension remains unchanged. The result is shown in Fig. 19.1.

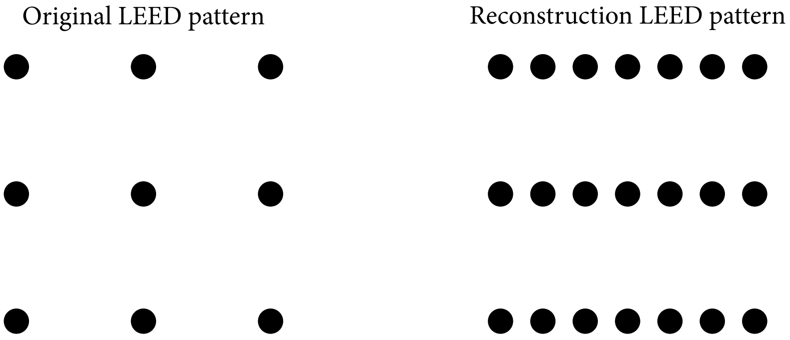


Figure 19.1

19B Adsorption and desorption

Answers to discussion questions

D19B.2 The assumptions made in deriving the Langmuir isotherm are:

(1) Adsorption cannot proceed beyond monolayer coverage.

(2) All sites are equivalent and the surface is uniform.

(3) The ability of a molecule to adsorb at a given site is independent of the occupation of neighbouring sites.

For the BET isotherm assumption (1) is removed so that multi-layer coverage is possible. In the derivation of this isotherm a distinction is made between the energetics involved in forming the first and subsequent layers.

Solutions to exercises

E19B.1(b) There is an error in the *Exercise*: the volume at the lower pressure should be $1.52\ \text{cm}^3$.

The Langmuir isotherm is [19B.2–*833*], $\theta = \alpha p/(1+\alpha p)$, with $\alpha = k_a/k_d$. The surface coverage may be written in terms of the volume of gas adsorbed V, $\theta = V/V_\infty$, where V_∞ is the volume corresponding to complete coverage. For two different pressures

$$\frac{V_1}{V_\infty} = \frac{\alpha p_1}{1+\alpha p_1} \qquad \frac{V_2}{V_\infty} = \frac{\alpha p_2}{1+\alpha p_2}$$

Inverting both sides

$$\frac{V_\infty}{V_1} = \frac{1}{\alpha p_1} + 1 \qquad \frac{V_\infty}{V_2} = \frac{1}{\alpha p_2} + 1$$

To eliminate α first multiply the left-hand equation by $1/p_2$ and the right-hand equation by $1/p_1$

$$\frac{V_\infty}{p_2 V_1} = \frac{1}{\alpha p_1 p_2} + \frac{1}{p_2} \qquad \frac{V_\infty}{p_1 V_2} = \frac{1}{\alpha p_1 p_2} + \frac{1}{p_1}$$

Subtracting the two equations gives then eliminates α

$$\frac{V_\infty}{p_2 V_1} - \frac{V_\infty}{p_1 V_2} = \frac{1}{p_2} - \frac{1}{p_1}$$

$$\text{hence} \quad V_\infty = \frac{1/p_2 - 1/p_1}{1/p_2 V_1 - 1/p_1 V_2} = \frac{p_1 - p_2}{p_1/V_1 - p_2/V_2}$$

where for the last step top and bottom are multiplied by $p_1 p_2$.

With the data given

$$V_\infty = \frac{p_1 - p_2}{p_1/V_1 - p_2/V_2} = \frac{(56.4\ \text{kPa}) - (108\ \text{kPa})}{(56.4\ \text{kPa})/(1.52\ \text{cm}^3) - (108\ \text{kPa})/(2.77\ \text{cm}^3)} = \boxed{27.4\ \text{cm}^3}$$

E19B.2(b) The residence half-life is given by [19B.14–*839*], $t_{1/2} = \tau_0 \mathrm{e}^{E_{\mathrm{a,des}}/RT}$. The activation energy for desorption, $E_{\mathrm{a,des}}$, is approximated as minus the enthalpy of adsorption.

$$\begin{aligned} t_{1/2} &= (1.0 \times 10^{-14}\ \mathrm{s})\,\mathrm{e}^{(155\times10^{3}\ \mathrm{J\,mol^{-1}})/[(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(500\ \mathrm{K})]} \\ &= \boxed{1.6 \times 10^{2}\ \mathrm{s}} \end{aligned}$$

E19B.3(b) The Langmuir isotherm is [19B.2–*833*], $\theta = \alpha p/(1+\alpha p)$. The surface coverage may be written in terms of the volume of gas adsorbed V, $\theta = V/V_\infty$, where V_∞ is the volume corresponding to complete coverage. Equivalently, θ may be expressed in terms of the mass adsorbed, $\theta = m/m_\infty$, where m_∞ is the mass corresponding to complete coverage. For two different pressures

$$\frac{m_1}{m_\infty} = \frac{\alpha p_1}{1+\alpha p_1} \qquad \frac{m_2}{m_\infty} = \frac{\alpha p_2}{1+\alpha p_2}$$

The aim is to find m_∞, and the algebra to do this is just the same as the method for finding V_∞ in *Exercise* E19B.1(b) with volumes replaced by masses. The result is

$$\begin{aligned} m_\infty &= \frac{p_1 - p_2}{p_1/m_1 - p_2/m_2} \\ &= \frac{(36.0\ \mathrm{kPa}) - (4.0\ \mathrm{kPa})}{(36.0\ \mathrm{kPa})/(0.63\ \mathrm{mg}) - (4.0\ \mathrm{kPa})/(0.21\ \mathrm{mg})} = 0.84\ \mathrm{mg} \end{aligned}$$

The surface coverage at the first pressure is therefore

$$\theta_1 = \frac{m_1}{m_\infty} = \frac{0.63\ \mathrm{mg}}{0.84\ \mathrm{mg}} = \boxed{0.75}$$

At the second pressure $\theta_2 = (0.21\ \mathrm{mg})/(0.84\ \mathrm{mg}) = \boxed{0.25}$.

E19B.4(b) The Langmuir isotherm is [19B.2–*833*], $\theta = \alpha p/(1+\alpha p)$, inverting both sides gives

$$\frac{1}{\theta} = \frac{1}{\alpha p} + 1 \quad \text{hence} \quad \frac{1}{\alpha p} = \frac{1}{\theta} - 1 = \frac{1-\theta}{\theta}$$

Inverting again gives

$$\alpha p = \frac{\theta}{1-\theta} \quad \text{hence} \quad p = \frac{\theta}{\alpha(1-\theta)}$$

With the data given

$$p = \frac{0.20}{(0.548\ \mathrm{kPa^{-1}}) \times (1 - 0.20)} = \boxed{0.46\ \mathrm{kPa}}$$

A similar calculation for $\theta = 0.75$ gives $\boxed{5.5\ \mathrm{kPa}}$.

E19B.5(b) The isosteric enthalpy of adsorption is define as [19B.5b–*834*]

$$\left(\frac{\partial \ln(\alpha p^{\ominus})}{\partial(1/T)}\right)_{\theta} = -\frac{\Delta_{\text{ad}}H^{\ominus}}{R}$$

From the Langmuir isotherm is follows that $\alpha = \theta/p(1-\theta)$ but, because an isosteric process is being considered (θ is constant), this reduces to $\alpha = C/p$, where C is a constant. With just two sets of data the derivative is approximated as the finite interval to give

$$\frac{\ln(Cp^{\ominus}/p_2) - \ln(Cp^{\ominus}/p_1)}{(1/T_2) - (1/T_1)} = -\frac{\Delta_{\text{ad}}H^{\ominus}}{R}$$

$$\text{hence } \ln p_1/p_2 = -\frac{\Delta_{\text{ad}}H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\text{hence } \ln p_2 = \ln p_1 + \frac{\Delta_{\text{ad}}H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

The data gives the enthalpy of desorption as +12.2 J for 1.00 mmol of gas, therefore the molar enthalpy of adsorption is $-12.2\ \text{kJ mol}^{-1}$.

$$\ln(p_2/\text{kPa}) = \ln(8.86\ \text{kPa}) + \frac{-12.2\ \text{kJ mol}^{-1}}{8.3145\ \text{J K}^{-1}\,\text{mol}^{-1}}\left(\frac{1}{318\ \text{K}} - \frac{1}{298\ \text{K}}\right) = 2.49...$$

Therefore $(p_2/\text{kPa}) = e^{2.49\cdots}$, giving $\boxed{p_2 = 12.1\ \text{kPa}}$.

E19B.6(b) The isosteric enthalpy of adsorption is define as [19B.5b–*834*]

$$\left(\frac{\partial \ln(\alpha p^{\ominus})}{\partial(1/T)}\right)_{\theta} = -\frac{\Delta_{\text{ad}}H^{\ominus}}{R}$$

From the Langmuir isotherm is follows that $\alpha = \theta/p(1-\theta)$ but, because an isosteric process is being considered (θ is constant), this reduces to $\alpha = C/p$, where C is a constant. With just two sets of data the derivative is approximated as the finite interval to give

$$\frac{\ln(Cp^{\ominus}/p_2) - \ln(Cp^{\ominus}/p_1)}{(1/T_2) - (1/T_1)} = -\frac{\Delta_{\text{ad}}H^{\ominus}}{R}$$

$$\text{hence } \ln(p_1/p_2) = -\frac{\Delta_{\text{ad}}H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\text{hence } \Delta_{\text{ad}}H^{\ominus} = \frac{R\ln(p_2/p_1)}{1/T_2 - 1/T_1}$$

With the data given

$$\Delta_{\text{ad}}H^{\ominus} = \frac{(8.3145\ \text{J K}^{-1}\,\text{mol}^{-1}) \times \ln[(1.02\times10^{6}\ \text{Pa})/(350\times10^{3}\ \text{Pa})]}{1/(240\ \text{K}) - 1/(180\ \text{K})}$$

$$= \boxed{-6.40\ \text{kJ mol}^{-1}}$$

E19B.7(b) The rate constant for desorption is assumed to follow an Arrhenius law, $k_{\text{des}} = Ae^{-E_{\text{a,des}}/RT}$. Recall that for a first order process the half life is simply proportional to the inverse of the rate constant, therefore the time needed for a certain amount to desorb is also inversely proportional to the rate constant. Thus

$$\tau_1/\tau_2 = e^{-(E_{\text{a,des}}/R)(1/T_2-1/T_1)}$$
$$\text{hence } \ln(\tau_1/\tau_2) = -\frac{E_{\text{a,des}}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$
$$\text{hence } E_{\text{a,des}} = \frac{-R\ln(\tau_1/\tau_2)}{(1/T_2-1/T_1)}$$

With the data given

$$E_{\text{a,des}} = \frac{-(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\ln[(1856\,\text{s})/(8.44\,\text{s})]}{1/(1012\,\text{K})-1/(873\,\text{K})}$$
$$= 2.85... \times 10^5\,\text{J mol}^{-1} = \boxed{285\,\text{kJ mol}^{-1}}$$

The times for desorption at different temperatures are computed using

$$\tau_1/\tau_2 = e^{-(E_{\text{a,des}}/R)(1/T_2-1/T_1)} \quad \text{hence} \quad \tau_2 = \tau_1 e^{(E_{\text{a,des}}/R)(1/T_2-1/T_1)}$$

The time needed at 298 K is related to that at 873 K

$$\tau_2 = (1856\,\text{s})\,e^{[(2.85...\times10^5\,\text{J mol}^{-1})/(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})][1/(298\,\text{K})-1/(873\,\text{K})]}$$
$$= 1.5 \times 10^{36}\,\text{s}$$

Effectively, the gas does not desorb at this temperature. Repeating the calculation at 1500 K

$$\tau_2 = (1856\,\text{s})\,e^{[(2.85...\times10^5\,\text{J mol}^{-1})/(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})][1/(1500\,\text{K})-1/(873\,\text{K})]}$$
$$= \boxed{0.14\,\text{ms}}$$

E19B.8(b) The average time that a species remains adsorbed is proportional to its half-life, given by [19B.14–*839*], $t_{1/2} = \tau_0 e^{E_{\text{a,des}}/RT}$. Therefore, if the two times are τ_1 and τ_2 at temperatures T_1 and T_2

$$\tau_2/\tau_1 = e^{(E_{\text{a,des}}/R)(1/T_2-1/T_1)}$$
$$\text{hence } \ln(\tau_2/\tau_1) = \frac{E_{\text{a,des}}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$
$$\text{hence } E_{\text{a,des}} = \frac{R\ln(\tau_2/\tau_1)}{1/T_2-1/T_1}$$

The data gives the lifetime at the higher temperature as $\tau_2 = \tau_1(1-0.35) = 0.65\,\tau_1$

$$E_{\text{a,des}} = \frac{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\ln[(0.65\tau_1)/(\tau_1)]}{1/(1000\,\text{K})-1/(600\,\text{K})}$$
$$= \boxed{5.4\,\text{kJ mol}^{-1}}$$

E19B.9(b) The half-life for a species on the surface is given by [19B.14–*839*], $t_{1/2} = \tau_0 \mathrm{e}^{E_{\mathrm{a,des}}/RT}$.

(i) With $E_{\mathrm{a,des}} = 20\ \mathrm{kJ\,mol^{-1}}$

$$\text{at 298 K}\quad t_{1/2} = (0.12\ \mathrm{ps})\ \mathrm{e}^{(20\times10^{3}\ \mathrm{J\,mol^{-1}})/[(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(298\ \mathrm{K})]}$$

$$= \boxed{3.8\times10^{2}\ \mathrm{ps}}$$

$$\text{at 800 K}\quad t_{1/2} = (0.12\ \mathrm{ps})\ \mathrm{e}^{(20\times10^{3}\ \mathrm{J\,mol^{-1}})/[(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(800\ \mathrm{K})]}$$

$$= \boxed{2.4\ \mathrm{ps}}$$

(ii) With $E_{\mathrm{a,des}} = 200\ \mathrm{kJ\,mol^{-1}}$

$$\text{at 298 K}\quad t_{1/2} = (0.12\ \mathrm{ps})\ \mathrm{e}^{(200\times10^{3}\ \mathrm{J\,mol^{-1}})/[(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(298\ \mathrm{K})]}$$

$$= 1.36...\times10^{34}\ \mathrm{ps} = \boxed{1.4\times10^{22}\ \mathrm{s}}$$

$$\text{at 800 K}\quad t_{1/2} = (0.12\ \mathrm{ps})\ \mathrm{e}^{(200\times10^{3}\ \mathrm{J\,mol^{-1}})/[(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(800\ \mathrm{K})]}$$

$$= 1.37...\times10^{12}\ \mathrm{ps} = \boxed{1.4\ \mathrm{s}}$$

Solutions to problems

P19B.2 As is shown in *Example* 19B.1 on page 833, a suitable plot to test the Langmuir isotherm is of p/V against p; such a plot has intercept $1/\alpha V_\infty$ and slope $1/V_\infty$. The table of data is given below and the plot is shown in Fig. 19.2.

p/Pa	$V/\mathrm{cm^3}$	$(p/V)/(\mathrm{Pa\,cm^{-3}})$
25	0.042	595
129	0.163	791
253	0.221	1 145
540	0.321	1 682
1 000	0.411	2 433
1 593	0.471	3 382

Omitting the data points for the two highest pressures gives a reasonable straight line with equation

$$(p/V)/(\mathrm{Pa\,cm^{-3}}) = 2.135\times(p/\mathrm{Pa}) + 547.9$$

V_∞ is found from the slope as $V_\infty = 1/\text{slope} = 1/(2.135)\ \mathrm{cm^3} = \boxed{0.47\ \mathrm{cm^3}}$. The value of α is found from (slope)/(intercept), $\alpha = (2.135)/(547.9)\ \mathrm{Pa^{-1}} = \boxed{3.9\times10^{-3}\ \mathrm{Pa^{-1}}}$.

P19B.4 Note: the volume data given in the *Problem* is in error. The values in the table should be, reading left to right, 1.22 1.33 1.31 1.36 1.40 in $\mathrm{cm^3}$.

As is shown in *Example* 19B.1 on page 833, a suitable plot to fit data to the Langmuir isotherm is of p/V against p; such a plot has intercept $1/\alpha V_\infty$ and slope $1/V_\infty$. The table of data is given below and the plot is shown in Fig. 19.3.

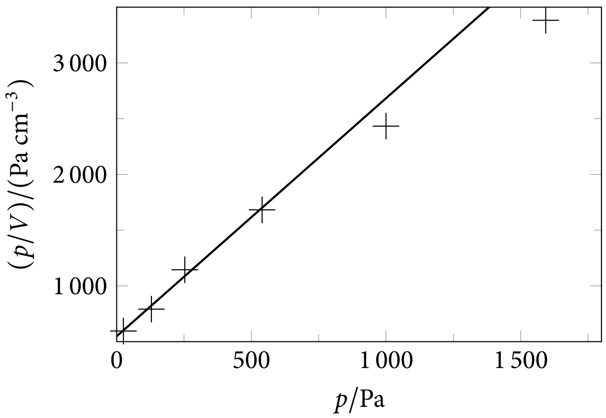


Figure 19.2

p/atm	V/cm^3	$(p/V)/(\text{atm cm}^{-3})$
0.050	1.22	0.0410
0.100	1.33	0.0752
0.150	1.31	0.115
0.200	1.36	0.147
0.250	1.40	0.179

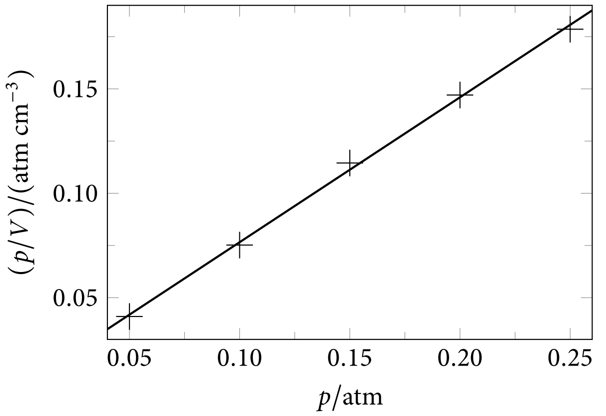


Figure 19.3

The data fall on a reasonable straight line with equation

$$(p/V)/(\text{atm cm}^{-3}) = 0.6941 \times (p/\text{atm}) + 7.147 \times 10^{-3}$$

V_∞ is found from the slope as $V_\infty = 1/\text{slope} = 1/(0.6941)\ \text{cm}^3 = \boxed{1.44\ \text{cm}^3}$.

The number of H_2 molecules in this volume is found using the perfect gas law

$$\begin{aligned} N &= \frac{N_A pV}{RT} \\ &= \frac{(6.0221\times10^{23}\ \text{mol}^{-1})\times(1.01325\times10^{5}\ \text{Pa})\times(1.44\times10^{-6}\ \text{m}^3)}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(273.15\ \text{K})} \\ &= 3.86...\times10^{19} \end{aligned}$$

The area of a molecule is estimated from the mass density of the liquid in the following way. Consider a volume V of the liquid which has mass density ρ; the mass of the liquid is $V\rho$ and this corresponds to $V\rho/M$ moles, where M is the molar mass. The number of molecules in the volume is $N = N_A V\rho/M$, therefore the volume occupied by one molecule is $V/N = M/N_A\rho$.

If the molecule is considered to be a sphere of radius R, then $\frac{4}{3}\pi R^3 = M/N_A\rho$, from which it follows that $R = (3M/4N_A\rho\pi)^{1/3}$. Therefore the area of the 'silhouette' of the sphere is $A = \pi R^2 = \pi(3M/4N_A\rho\pi)^{2/3}$. With the data given

$$\begin{aligned} A &= \pi\left(\frac{3\times(2.0158\ \text{g mol}^{-1})}{4\times(6.0221\times10^{23}\ \text{mol}^{-1})\times(0.708\ \text{g cm}^{-3})\times\pi}\right)^{2/3} \\ &= 3.40...\times10^{-16}\ \text{cm}^2 = 3.40...\times10^{-20}\ \text{m}^2 \end{aligned}$$

The surface area is therefore $(3.86...\times10^{19})\times(3.40...\times10^{-20}\ \text{m}^2) = \boxed{1.3\ \text{m}^2}$.

P19B.6 (a) As is shown in *Example* 19B.1 on page 833, a suitable plot to fit data to the Langmuir isotherm is of p/V against p; such a plot has intercept $1/\alpha V_\infty$ and slope $1/V_\infty$. The table of data is given below and the plot is shown in Fig. 19.4; it is clear from this that the data do not conform to the Langmuir isotherm.

p/kPa	V/cm^3	$(p/V)/(\text{kPa cm}^{-3})$	z	$y/(10^{-3}\ \text{cm}^{-3})$
13.3	17.9	0.743	0.067	3.980
26.7	33.0	0.809	0.134	4.669
40.0	47.0	0.851	0.200	5.319
53.3	60.8	0.877	0.267	5.976
66.7	75.3	0.886	0.334	6.645
80.0	91.3	0.876	0.400	7.302

(b) In [19B.7–*836*] the BET isotherm is manipulated into a straight-line plot

$$\frac{z}{(1-z)V} = \frac{1}{cV_{\text{mon}}} + \frac{(c-1)}{cV_{\text{mon}}}z \qquad z = p/p^*$$

Thus a plot of $z/(1-z)V$ against z is expected to be a straight line with slope $(c-1)/cV_{\text{mon}}$ and intercept $1/cV_{\text{mon}}$; note that (slope)/(intercept) $= c - 1$. For brevity the term $z/(1-z)V$ is denoted y. The manipulated data is shown in the table above and the plot is shown in Fig. 19.5.

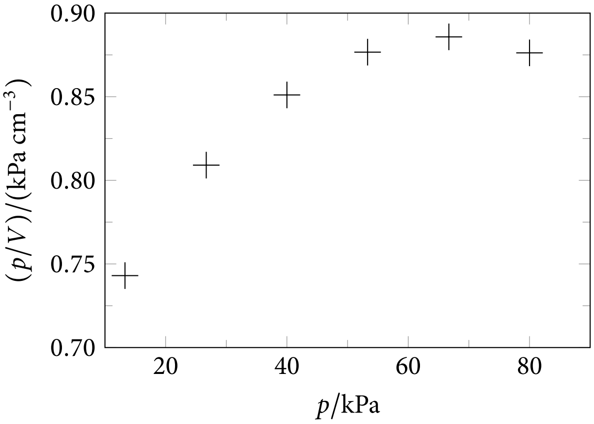


Figure 19.4

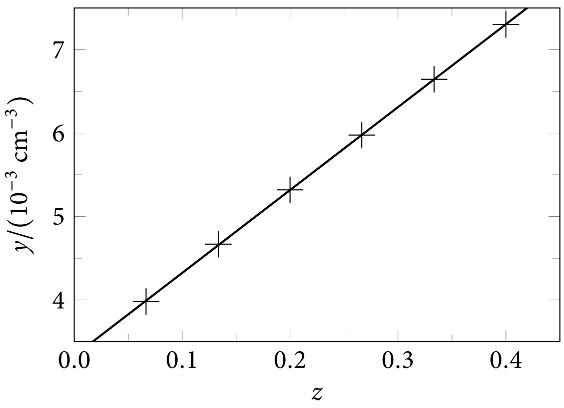


Figure 19.5

The data are a good fit to a straight line with equation

$$y/(10^{-3}\ \text{cm}^{-3}) = 9.939 \times (z) + 3.329$$

The parameter c is found using

$$\frac{\text{slope}}{\text{intercept}} = c - 1 \quad \text{hence} \quad c = 1 + \frac{9.939}{3.329} = \boxed{3.99}$$

The intercept is $1/cV_{\text{mon}}$, therefore

$$V_{\text{mon}} = \frac{1}{c \times (\text{intercept})} = \frac{1}{3.99 \times 10^{-3} \times (3.329\ \text{cm}^{-3})} = \boxed{75.3\ \text{cm}^3}$$

P19B.8 Note: there is missing data from this *Problem*, which is that the two temperatures referred to are 400 °C and 500 °C.

The isosteric enthalpy of adsorption is defined as [19B.5b–*834*]

$$\left(\frac{\partial \ln(\alpha p^{\ominus})}{\partial(1/T)}\right)_{\theta} = -\frac{\Delta_{\text{ad}}H^{\ominus}}{R}$$

With just two sets of data the derivative is approximated as the finite interval to give

$$\begin{aligned}\frac{\ln(\alpha_2 p^{\ominus}) - \ln(\alpha_1 p^{\ominus})}{(1/T_2) - (1/T_1)} &= -\frac{\Delta_{\text{ad}}H^{\ominus}}{R}\\ \text{hence } \ln \alpha_2/\alpha_1 &= -\frac{\Delta_{\text{ad}}H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\end{aligned}$$

With the data given

$$\begin{aligned}\ln \alpha_2/\alpha_1 &= -\frac{(-160 \times 10^3\ \text{J mol}^{-1})}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}\left(\frac{1}{773\ \text{K}} - \frac{1}{673\ \text{K}}\right)\\ &= -3.69...\end{aligned}$$

Therefore $\alpha_2/\alpha_1 = e^{-3.69...} = \boxed{0.0247}$.

P19B.10 The Freundlich isotherm is written $c_{\text{ads}} = Kc_{\text{sol}}^{1/n}$; taking logarithms gives $\ln c_{\text{ads}} = \ln K + (1/n)\ln c_{\text{sol}}$. This implies that a plot of $\ln c_{\text{ads}}$ against $\ln c_{\text{sol}}$ should be a straight line of slope $1/n$ and intercept $\ln K$. The data are given below and the plot is shown in Fig. 19.6.

$c_{\text{sol}}/(\text{mg g}^{-1})$	$c_{\text{ads}}/(\text{mg g}^{-1})$	$\ln[c_{\text{sol}}/(\text{mg g}^{-1})]$	$\ln[c_{\text{ads}}/(\text{mg g}^{-1})]$
8.26	4.41	2.111	1.48
15.65	9.20	2.750	2.22
25.43	35.20	3.236	3.56
31.74	52.00	3.458	3.95
40.00	67.20	3.689	4.21

The data fall on a modest straight line, the equation of which is

$$\ln[c_{\text{ads}}/(\text{mg g}^{-1})] = 1.849 \times \ln[c_{\text{sol}}/(\text{mg g}^{-1})] - 2.554$$

The slope is $1/n$, therefore $n = 1/\text{slope} = 1/(1.849) = \boxed{0.54}$. The intercept gives $\ln K$ and hence $\boxed{K = 0.078\ \text{mg g}^{-1}}$.

To compute the fractional coverage θ it would be necessary to know the mass needed for a monolayer. This is of no particular significance for this isotherm.

P19B.12 The Langmuir isotherm would be different in the three cases.

(a) For adsorption without dissociation [19B.2–*833*], $\theta = \alpha p/(1 + \alpha p)$

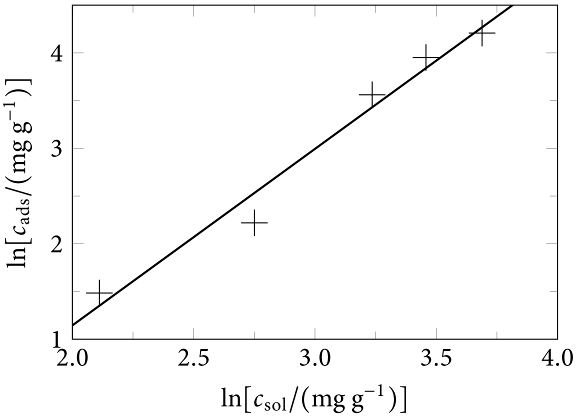


Figure 19.6

(b) For adsorption with dissociation into two species the isotherm is [19B.4–*833*], $\theta = (\alpha p)^{1/2}/[1 + (\alpha p)^{1/2}]$

(c) By extension, for adsorption with dissociation into three species the isotherm is $\theta = (\alpha p)^{1/3}/[1 + (\alpha p)^{1/3}]$

A plot of θ against p at low pressures (where the denominator is approximately 1) would show progressively weaker dependence on p for dissociation into two or three species.

19C Heterogeneous catalysis

Answers to discussion questions

D19C.2 The two relevant equations derived in *How is that done?* 19C.1 on page 842 are

$$(\alpha_A p_A + 1)\theta_A + \alpha_A p_A \theta_B = \alpha_A p_A \qquad \alpha_B p_B \theta_A + (\alpha_B p_B + 1)\theta_B = \alpha_B p_B$$

The first is multiplied by $\alpha_B p_B$ and the second by $(\alpha_A p_A + 1)$ to give

$$\alpha_B p_B(\alpha_A p_A + 1)\theta_A + \alpha_B p_B \alpha_A p_A \theta_B = \alpha_B p_B \alpha_A p_A$$
$$(\alpha_A p_A + 1)\alpha_B p_B \theta_A + (\alpha_A p_A + 1)(\alpha_B p_B + 1)\theta_B = (\alpha_A p_A + 1)\alpha_B p_B$$

The terms in θ_A are now the same, and so will disappear when the two equations are subtracted to give

$$\alpha_B p_B \alpha_A p_A \theta_B - (\alpha_A p_A + 1)(\alpha_B p_B + 1)\theta_B = \alpha_B p_B \alpha_A p_A - (\alpha_A p_A + 1)\alpha_B p_B$$

The expression for θ_B then follows with some rearrangement and simplification

$$\begin{aligned}\theta_B &= \frac{\alpha_B p_B \alpha_A p_A - (\alpha_A p_A + 1)\alpha_B p_B}{\alpha_B p_B \alpha_A p_A - (\alpha_A p_A + 1)(\alpha_B p_B + 1)} \\ &= \frac{-\alpha_B p_B}{\alpha_B p_B \alpha_A p_A - \alpha_A p_A \alpha_B p_B - \alpha_A p_A - \alpha_B p_B - 1} \\ &= \frac{\alpha_B p_B}{\alpha_A p_A + \alpha_B p_B + 1}\end{aligned}$$

which is the required expression. That for θ_B is simply found by swapping the indices A and B: the equations all remain valid under such a change.

Solutions to exercises

E19C.1(b) The amount in moles of CO gas is found using the perfect gas law.

$$\begin{aligned}n &= \frac{pV}{RT} = \frac{(1\ \text{bar})\times(10^5\ \text{Pa})}{1\ \text{bar}} \times \frac{3.75 \times 10^{-6}\ \text{m}^3}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (273.15\ \text{K})} \\ &= 1.65... \times 10^{-4}\ \text{mol}\end{aligned}$$

which corresponds to $N_A n = (6.0221 \times 10^{23}\ \text{mol}^{-1}) \times (1.65 \times 10^{-4}\ \text{mol}) = 9.94... \times 10^{19}$ molecules.

A rough calculation of the surface area notes that the collision cross section is $\sigma = \pi d^2$, where d is the diameter of the colliding spheres. Therefore $d = (\sigma/\pi)^{1/2}$, and hence $r = \frac{1}{2}(\sigma/\pi)^{1/2}$. The area of one molecule is $\pi r^2 = \pi \frac{1}{4}\sigma/\pi = \frac{1}{4}\sigma$. In the tables, no value for the collision cross section of CO is given, so the value for N_2 is used. The surface area is therefore $(9.94... \times 10^{19}) \times \frac{1}{4} \times (0.43 \times 10^{-18}\ \text{m}^2) = \boxed{11\ \text{m}^2}$.

In fact circles do not cover a plane completely, and it can be shown that the highest coverage which can be achieved is one in which the circles cover 0.91 of the area of the plane. The estimate of the area therefore needs to be scaled up by a factor of $1/0.91 \approx 1.1$ to give 12 m^2.

Solutions to problems

P19C.2 The rate law for a unimolecular decomposition occurring on a surface is given by [19C.1–*841*]

$$v = \frac{k_r \alpha p}{1 + \alpha p}$$

HI is adsorbed strongly on gold, implying that $\alpha p \gg 1$, and so the rate law reduces to $v = k_r$: that is, zeroth order and thus independent of pressure. On platinum, absorption is weaker implying that $\alpha p \ll 1$. In this limit the rate law becomes $v = k_r \alpha p$: that is, first order in the pressure.

19D Processes at electrodes

Answers to discussion questions

D19D.2 This is discussed in Section 19D.3 on page 850.

Solutions to exercises

E19D.1(b) If the anodic process is dominant, the current density is given by [19D.5a–*850*], $\ln j = \ln j_0 + (1-\alpha)f\eta$, where $f = F/RT$. At 298.15 K

$$f = (96485\,\mathrm{C\,mol^{-1}})/[(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298.15\,\mathrm{K})] = 38.921\,\mathrm{V^{-1}}$$

where the units are resolved by recalling $1\,\mathrm{V} = 1\,\mathrm{J\,C^{-1}}$. Taking the difference of two expressions for $\ln j$ for different overpotentials gives

$$\begin{aligned}\ln(j_2/j_1) &= (1-\alpha)f(\eta_2-\eta_1)\\ \text{hence } \eta_2 &= \frac{\ln(j_2/j_1)}{(1-\alpha)f} + \eta_1\\ &= \frac{\ln(72/17.0)}{(1-0.42)\times(38.921\,\mathrm{V^{-1}})} + 0.105\,\mathrm{V} = \boxed{0.17\,\mathrm{V}}\end{aligned}$$

E19D.2(b) If the anodic process is dominant, the current density is given by [19D.5a–*850*], $j = j_0 e^{(1-\alpha)f\eta}$, where $f = F/RT$. At 298.15 K, $f = 38.921\,\mathrm{V^{-1}}$. Rearranging for j_0 and then using the data given

$$\begin{aligned}j_0 &= j\,e^{-(1-\alpha)f\eta}\\ &= (17.0\,\mathrm{mA\,cm^{-2}})\,e^{-(1-0.42)\times(38.921\,\mathrm{V^{-1}})\times(0.105\,\mathrm{V})} = \boxed{1.6\,\mathrm{mA\,cm^{-2}}}\end{aligned}$$

E19D.3(b) If the anodic process is dominant, the current density is given by [19D.5a–*850*], $j = j_0 e^{(1-\alpha)f\eta}$, where $f = F/RT$. At 298.15 K, $f = 38.921\,\mathrm{V^{-1}}$. Taking the ratio of two expressions for j for different overpotentials gives

$$\begin{aligned}j_2/j_1 &= j_0 e^{(1-\alpha)f\eta_2}/j_0 e^{(1-\alpha)f\eta_1}\\ \text{hence } j_2 &= j_1 e^{(1-\alpha)f(\eta_2-\eta_1)}\\ &= (1.22\,\mathrm{mA\,cm^{-2}})\,e^{(1-0.5)\times(38.921\,\mathrm{V^{-1}})\times[(0.60-0.50)\,\mathrm{V})]} = \boxed{8.5\,\mathrm{mA\,cm^{-2}}}\end{aligned}$$

E19D.4(b) (i) The Butler–Volmer equation is [19D.2–*848*], $j = j_0(e^{(1-\alpha)f\eta} - e^{-\alpha f\eta})$. For $\mathrm{Fe^{3+}}$ on Pt $j_0 = 2.5\times10^{-3}\,\mathrm{A\,cm^{-2}}$ and $\alpha = 0.58$; at 298.15 K, $f = 38.921\,\mathrm{V^{-1}}$. For an overpotential of +0.30 V the current density is

$$\begin{aligned}j &= (2.5\times10^{-3}\,\mathrm{A\,cm^{-2}})\\ &\quad\times\left(e^{(1-0.58)\times(38.921\,\mathrm{V^{-1}})\times(0.30\,\mathrm{V})} - e^{-0.58\times(38.921\,\mathrm{V^{-1}})\times(0.30\,\mathrm{V})}\right)\\ &= \boxed{0.34\,\mathrm{A\,cm^{-2}}}\end{aligned}$$

(ii) If the current is entirely anodic, only the first term is needed

$$\begin{aligned} j &= (2.5\times10^{-3}\ \mathrm{A\ cm^{-2}})\times \mathrm{e}^{(1-0.58)\times(38.921\ \mathrm{V^{-1}})\times(0.30\ \mathrm{V})}\\ &= \boxed{0.34\ \mathrm{A\ cm^{-2}}} \end{aligned}$$

The result confirms that the current is indeed dominated by the anodic term, which is the term for which the power of the exponential is positive.

E19D.5(b) The Butler–Volmer equation is [19D.2–*848*], $j = j_0(\mathrm{e}^{(1-\alpha)f\eta} - \mathrm{e}^{-\alpha f\eta})$. The overpotential is equal to the applied potential E minus the potential developed by the electrode which, assuming standard conditions, is +0.77 V: $\eta = E - (0.77\ \mathrm{V})$. With the given value for j_0, and assuming $\alpha = 0.5$

$$j = (2.5\ \mathrm{mA\ cm^{-2}})\times(\mathrm{e}^{(1-0.5)\times f\times[E-(0.77\ \mathrm{V})]} - \mathrm{e}^{-0.5\times f\times[E-(0.77\ \mathrm{V})]})$$

$$\boxed{j = (2.5\ \mathrm{mA\ cm^{-2}})\times(\mathrm{e}^{0.5f[E-(0.77\ \mathrm{V})]} - \mathrm{e}^{-0.5f[E-(0.77\ \mathrm{V})]})}$$

E19D.6(b) At equilibrium, only the exchange current flows, therefore for an electrode with area A the current is j_0A, and thus the charge passing in time t is (current × time): $q = j_0At$. If each species passing through the double layer carries one fundamental change, the number of charges is $N = q/e = j_0At/e$. Thus the number per second through an area of 1.0 $\mathrm{cm^2}$ is, for $\mathrm{H^+/Cu}$,

$$\begin{aligned} N/t = j_0A/e &= (1.0\times10^{-6}\ \mathrm{A\ cm^{-2}})\times(1\ \mathrm{cm^2})/(1.6022\times10^{-19}\ \mathrm{C})\\ &= 6.24...\times10^{12}\ \mathrm{s^{-1}} = \boxed{6.2\times10^{12}\ \mathrm{s^{-1}}} \end{aligned}$$

A similar calculation for $\mathrm{Ce^{4+}/Pt}$ gives $\boxed{2.5\times10^{14}\ \mathrm{s^{-1}}}$.

The number of atoms covering 1 $\mathrm{cm^2}$ of electrode is $(10^{-4}\ \mathrm{m^2})/(260\times10^{-12}\ \mathrm{m})^2 = 1.47...\times10^{15}$. Therefore for $\mathrm{H^+/Cu}$ the number of times per second that each atom is involved in a electron transfer event is (number of such events)/(number of atoms) = $(6.24...\times10^{15}\ \mathrm{s^{-1}})/(1.47...\times10^{15}) = \boxed{4.2\times10^{-3}\ \mathrm{s^{-1}}}$. A similar calculation for $\mathrm{Ce^{4+}/Pt}$ gives $\boxed{0.17\ \mathrm{s^{-1}}}$.

E19D.7(b) In the linear region the current density and overpotential are related by [19D.4–*849*], $\eta = RTj/Fj_0$, therefore the current density is $j = \eta Fj_0/RT$. For an electrode of area A the current is $I = jA$, and therefore the resistance is

$$r = \frac{\eta}{I} = \frac{\eta}{\eta Fj_0A/RT} = \frac{RT}{Fj_0A}$$

For $\mathrm{H^+/Pb}$

$$r = \frac{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(298\ \mathrm{K})}{(96485\ \mathrm{C\ mol^{-1}})\times(5.0\times10^{-12}\ \mathrm{A\ cm^{-2}})\times(1.0\ \mathrm{cm^2})} = \boxed{5.1\times10^{9}\ \Omega}$$

The units are resolved by using (from inside the front cover) $1\ \mathrm{V} = 1\ \mathrm{J\ C^{-1}}$ and $1\ \Omega = 1\ \mathrm{V\ A^{-1}}$. A similar calculation for $\mathrm{Fe^{3+}/Pt}$ gives $\boxed{10\ \Omega}$.

E19D.8(b) Because the standard potential of Zn^{2+}/Zn is -0.76 V, under standard conditions Zn metal will only be deposited when the applied potential is more negative than -0.76 V. The current density is given by [19D.2–*848*], $j = j_0(e^{(1-\alpha)f\eta} - e^{-\alpha f\eta})$, but under these conditions only the second term (the cathodic current) is significant. Using the data given for H^+, assuming $\alpha = 0.5$, and recalling that, at 298.15 K, $f = 38.921\ \text{V}^{-1}$

$$\begin{aligned} j_{H^+} &= -j_0 e^{-\alpha f\eta} \\ &= -(0.79 \times 10^{-3}\ \text{A cm}^{-2})\, e^{-0.5\times(38.921\ \text{V}^{-1})\times(-0.76\ \text{V})} \\ &= -2.1 \times 10^{3}\ \text{A cm}^{-2} \end{aligned}$$

It is usually considered that the metal can be deposited if the current density for discharge of H^+ is less than about 1 mA cm^{-2}. In this case, the current density for discharge of H^+ is vastly in excess of this criterion, which means that zinc metal will not be deposited, and all that will happen is the evolution of H_2.

Solutions to problems

P19D.2 Simultaneous deposition is expected if the two potentials are the same, and this is acheived by altering the ratio of the concentrations of Pb^{2+} and Sn^{2+}. Using the Nernst equation [6C.4–*221*], the potentials of the two half cells are

$$\begin{aligned} E(Pb^{2+}/Pb) &= E(Pb^{2+}/Pb)^{\ominus} + \frac{RT}{2F}\ln a_{Pb^{2+}} \\ E(Sn^{2+}/Sn) &= E(Sn^{2+}/Sn)^{\ominus} + \frac{RT}{2F}\ln a_{Sn^{2+}} \end{aligned}$$

These will be equal when

$$E(Pb^{2+}/Pb)^{\ominus} + \frac{RT}{2F}\ln a_{Pb^{2+}} = E(Sn^{2+}/Sn)^{\ominus} + \frac{RT}{2F}\ln a_{Sn^{2+}}$$

From which it follows that

$$\begin{aligned} \ln(a_{Sn^{2+}}/a_{Pb^{2+}}) &= \frac{2F}{RT}\left[E(Pb^{2+}/Pb)^{\ominus} - E(Sn^{2+}/Sn)^{\ominus}\right] \\ &= \frac{2\times(96485\,\text{C mol}^{-1})}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(298\ \text{K})}\left[(-0.126\ \text{V}) - (-0.136\ \text{V})\right] \\ &= 0.778... \end{aligned}$$

Therefore $a_{Sn^{2+}}/a_{Pb^{2+}} = e^{0.778...} = \boxed{2.18}$. By making the concentration of Sn^{2+} a bit over twice that of Pb^{2+}, simultaneous deposition can be achieved.

P19D.4 The overpotential is $\eta = E' - E$, where E is the equilibrium potential; in this case $\eta = E' + (0.388\ \text{V})$. The data given correspond to positive overpotentials, so the anodic current will dominate and hence $\ln j = \ln j_0 + (1-\alpha)f\eta$. For the In^{3+}/In electrode three electrons are transferred, therefore the relationship needs to be modified to $\ln j = \ln j_0 + 3(1-\alpha)f\eta$. A plot of $\ln j$ against η will have slope $3(1-\alpha)f$ and intercept $\ln j_0$. Such a plot is shown in Fig. 19.7.

E'/V	η/V	$j/(\mathrm{A\,m^{-2}})$	$\ln[j/(\mathrm{A\,m^{-2}})]$
−0.365	0.023	0.590	−0.528
−0.350	0.038	1.438	0.363
−0.335	0.053	3.507	1.255

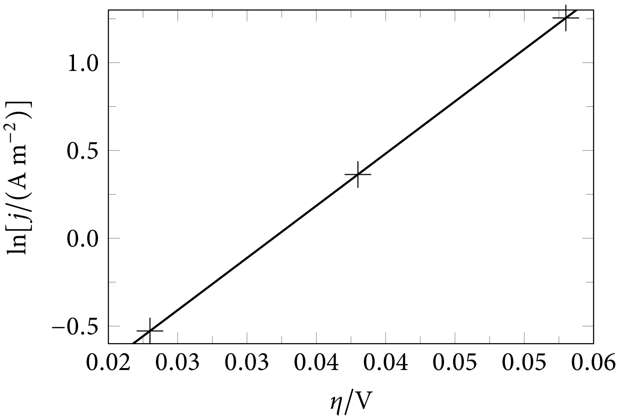


Figure 19.7

The data fall on a good straight line with equation

$$\ln[j/(\mathrm{A\,m^{-2}})] = 59.41 \times (\eta/\mathrm{V}) - 1.894$$

From the slope it follows that $3 \times (1-\alpha) \times (38.921\,\mathrm{V^{-1}}) = 59.41\ \mathrm{V^{-1}}$ hence $\boxed{\alpha = 0.49}$. The exchange current density is computed from the intercept as $\boxed{j_0 = 0.150\ \mathrm{A\,m^{-2}}}$.

Note that there is an error in the problem: the cathodic current should be computed for $E' = -0.365$ V. The cathodic current is $j_\mathrm{c} = -j_0 e^{-3\alpha f\eta}$, thus with the data already determined

$$j_\mathrm{c} = -(0.150\ \mathrm{A\,m^{-2}})\,e^{-3(0.49)\times(38.921\,\mathrm{V^{-1}})\times[(-0.365+0.388)\ \mathrm{V}]} = \boxed{-0.0402\ \mathrm{A\,m^{-2}}}$$

P19D.6 (a) The Butler–Volmer equation, [19D.2–*848*], $j = j_0(e^{(1-\alpha)f\eta} - e^{-\alpha f\eta})$ is expanded to second order in $f\eta$

$$\begin{aligned} j &= j_0\left[1 + (1-\alpha)f\eta + \tfrac{1}{2}(1-\alpha)^2 f^2\eta^2 - 1 + \alpha f\eta - \tfrac{1}{2}\alpha^2 f^2\eta^2\right] \\ &= j_0\left[f\eta + \tfrac{1}{2}f^2\eta^2(1-2\alpha)\right] = \underbrace{j_0 f\eta}_{\text{term 1}} + \underbrace{j_0\beta f^2\eta^2}_{\text{term 2}} \end{aligned}$$

where $\beta = \frac{1}{2}(1-2\alpha)$ is used.

The current density is integrated over a complete period with $\eta = \eta_0 \cos\omega t$; the period is $2\pi/\omega$ and the result of the integration is the total charge passing over this time. Term 1 integrates to zero because the integral of a cosine wave over a complete period is zero. The integral of term 2 is

$$j_0\beta f^2\eta_0^2\int_0^{2\pi/\omega}\cos^2\omega t\,\mathrm{d}t = \tfrac{1}{2}j_0\beta f^2\eta_0^2\int_0^{2\pi/\omega}\mathrm{d}t + \underbrace{\tfrac{1}{2}j_0\beta f^2\eta_0^2\int_0^{2\pi/\omega}\cos 2\omega t\,\mathrm{d}t}_{\text{term 3}}$$

where the identity $\cos^2 A = \frac{1}{2}(1+\cos 2A)$ is used. Term 3 is zero as it is the integral of a cosine wave over two complete periods. The other integral evaluates to $2\pi/\omega$ and therefore the charge passing over the complete period is

$$\tfrac{1}{2}j_0\beta f^2\eta_0^2\frac{2\pi}{\omega}$$

The *mean* current over the complete period is found by dividing the charge passing by the time, which is the period $2\pi/\omega$. Therefore

$$j_{\text{av}} = \tfrac{1}{2}j_0\beta f^2\eta_0^2 = \boxed{j_0 f^2\eta_0^2\tfrac{1}{2}(\tfrac{1}{2}-\alpha)}$$

As required, the mean current goes to zero when $\alpha = \frac{1}{2}$.

(b) For H^+/Pt $j_0 = 7.9\times10^{-4}$ A cm^{-2}; with the data given

$$j_{\text{av}} = (7.9\times10^{-4}\ \text{A cm}^{-2})\times(38.921\ \text{V}^{-1})^2\times(0.010\ \text{V})^2\times\tfrac{1}{2}(0.5-0.38)$$
$$= \boxed{7.2\ \mu\text{A cm}^{-2}}$$

P19D.8 (a) This voltammogram is that expected for a reversible process, as described in Section 19D.3 on page 850, and characteristic of a process with a 'large' exchange current density. Only a small overpotential is required to achieve a significant current.

(b) The first part of the voltammogram shows two successive reductions, at different potentials. Both of these reductions appear to be reversible as the current changes direction on the reverse sweep, with two features which complement those in the first part of the sweep.

(c) This voltammogram is that expected for a irreversible process, as described in Section 19D.3 on page 850, and characteristic of a process with a 'small' exchange current density. In this case a larger overpotential is needed to generate a significant current and the cathodic process dominates.

(d) The first part of the voltammogram shows two successive reductions, at different potentials. The second of these appears to be reversible as the current changes direction for the first part of the reverse sweep, but the second reduction appears to be irreversible as there is no negative-going current associated with it.

Answers to integrated activities

I19.2 The relativistic correction term is

$$\frac{e\Delta\phi}{2m_ec^2} = \frac{(1.6022\times10^{-19}\ \text{C})\times(50\times10^3\ \text{V})}{2\times(9.1094\times10^{-31}\ \text{kg})\times(2.9979\times10^8\ \text{m s}^{-1})^2} = 0.0489...$$

The non-relativistic wavelength is

$$\begin{aligned}\lambda_{\text{non-rel}} &= \frac{h}{(2m_e e\Delta\phi)^{1/2}}\\ &= \frac{6.6261\times10^{-34}\,\text{J s}}{[2\times(9.1094\times10^{-31}\,\text{kg})\times(1.6022\times10^{-19}\,\text{C})\times(50\times10^{3}\,\text{V})]^{1/2}}\\ &= 5.48\ \text{pm}\end{aligned}$$

With the relativistic correction

$$\begin{aligned}\lambda_{\text{rel}} &= \frac{6.6261\times10^{-34}\,\text{J s}}{[2\times(9.1094\times10^{-31}\,\text{kg})\times(1.6022\times10^{-19}\,\text{C})\times(50\times10^{3}\,\text{V})]^{1/2}}\\ &\quad\times\frac{1}{(1+0.0489...)^{1/2}} = 5.36\ \text{pm}\end{aligned}$$

There is a significant difference of about 2%. Whether or not this will affect any particular measurement depends on whether it is necessary to know the wavelength to high precision.

I19.4 The tunneling of a particle through a rectangular barrier is described in Section 7D.4 on page 268. The decay of the wavefunction in the barrier depends on the parameter κ given by $\kappa = [2m(V_0-E)]^{1/2}/\hbar$, where E is the energy and V_0 is the height of the barrier. In this case $(V_0-E) = 2.0$ eV and so

$$\begin{aligned}\kappa &= [2\times(9.1094\times10^{-31}\,\text{kg})\times(2.0\times1.6022\times10^{-19}\,\text{J})]^{1/2}/(1.0546\times10^{-34}\,\text{J s})\\ &= 7.24...\times10^{9}\ \text{m}^{-1}\end{aligned}$$

Assuming that $\kappa L \gg 1$ for the distances L considered in this calculation, the transmission probability T is approximated by [7D.20b–*270*], $T = 16\varepsilon(1-\varepsilon)\,\text{e}^{-2\kappa L}$, where $\varepsilon = E/V_0$. When the distance increases from L_1 to L_2 the ratio of the transmission probabilities is

$$\begin{aligned}T_2/T_1 &= \text{e}^{-2\kappa(L_2-L_1)}\\ &= \text{e}^{-2\times(7.24...\times10^{9}\ \text{m}^{-1})\times[(0.60-0.50)\times10^{-9}\ \text{m}]} = 0.235\end{aligned}$$

Assuming that the current is proportional to the transmission probability, this ratio would also be the ratio of the currents.