Part 1: Equilibrium

1 The properties of gases

Solutions to exercises

Discussion questions

E1.1(b) The partial pressure of a gas in a mixture of gases is the pressure the gas would exert if it occupied alone the same container as the mixture at the same temperature. It is a limiting law because it holds exactly only under conditions where the gases have no effect upon each other. This can only be true in the limit of zero pressure where the molecules of the gas are very far apart. Hence, Dalton's law holds exactly only for a mixture of perfect gases; for real gases, the law is only an approximation.

E1.2(b) The critical constants represent the state of a system at which the distinction between the liquid and vapour phases disappears. We usually describe this situation by saying that above the critical temperature the liquid phase cannot be produced by the application of pressure alone. The liquid and vapour phases can no longer coexist, though fluids in the so-called supercritical region have both liquid and vapour characteristics. (See Box 6.1 for a more thorough discussion of the supercritical state.)

E1.3(b) The van der Waals equation is a cubic equation in the volume, V. Any cubic equation has certain properties, one of which is that there are some values of the coefficients of the variable where the number of real roots passes from three to one. In fact, any equation of state of odd degree higher than 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(odd) to 1. That is, the multiple values of V converge from n to 1 as $T \rightarrow T_c$. 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.

Numerical exercises

E1.4(b) Boyle's law applies.

$$pV = \text{constant} \quad \text{so} \quad p_f V_f = p_i V_i$$

$$p_f = \frac{p_i V_i}{V_f} = \frac{(104\,\text{kPa}) \times (2000\,\text{cm}^3)}{(250\,\text{cm}^3)} = \boxed{832\,\text{kPa}}$$

E1.5(b) **(a)** The perfect gas law is

$$pV = nRT$$

implying that the pressure would be

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

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

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

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

not 2.0 bar.

(b) The van der Waals equation is

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

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

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

E1.6(b) **(a)** Boyle's law applies.

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

$$\text{and } p_\mathrm{i} = \frac{p_\mathrm{f} V_\mathrm{f}}{V_\mathrm{i}} = \frac{(1.48 \times 10^3\,\mathrm{Torr}) \times (2.14\,\mathrm{dm^3})}{(2.14 + 1.80)\,\mathrm{dm^3}} = \boxed{8.04 \times 10^2\,\mathrm{Torr}}$$

(b) The original pressure in bar is

$$p_\mathrm{i} = (8.04 \times 10^2\,\mathrm{Torr}) \times \left(\frac{1\,\mathrm{atm}}{760\,\mathrm{Torr}}\right) \times \left(\frac{1.013\,\mathrm{bar}}{1\,\mathrm{atm}}\right) = \boxed{1.07\,\mathrm{bar}}$$

E1.7(b) Charles's law applies.

$$V \propto T \quad \text{so} \quad \frac{V_\mathrm{i}}{T_\mathrm{i}} = \frac{V_\mathrm{f}}{T_\mathrm{f}}$$

$$\text{and } T_\mathrm{f} = \frac{V_\mathrm{f} T_\mathrm{i}}{V_\mathrm{i}} = \frac{(150\,\mathrm{cm^3}) \times (35 + 273)\,\mathrm{K}}{500\,\mathrm{cm^3}} = \boxed{92.4\,\mathrm{K}}$$

E1.8(b) The relation between pressure and temperature at constant volume can be derived from the perfect gas law

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

The final pressure, then, ought to be

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

E1.9(b) According to the perfect gas law, one can compute the amount of gas from pressure, temperature, and volume. Once this is done, the mass of the gas can be computed from the amount and the molar mass using

$$pV = nRT$$

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

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

E1.10(b) All gases are perfect in the limit of zero pressure. Therefore the extrapolated value of pV_m/T will give the best value of R.

The molar mass is obtained from $pV = nRT = \frac{m}{M}RT$

which upon rearrangement gives $M = \frac{m}{V}\frac{RT}{p} = \rho\frac{RT}{p}$

The best value of M is obtained from an extrapolation of ρ/p versus p to $p = 0$; the intercept is M/RT.

Draw up the following table

p/atm	$(pV_m/T)/(\mathrm{L\,atm\,K^{-1}\,mol^{-1}})$	$(\rho/p)/(\mathrm{g\,L^{-1}\,atm^{-1}})$
0.750 000	0.082 0014	1.428 59
0.500 000	0.082 0227	1.428 22
0.250 000	0.082 0414	1.427 90

From Fig. 1.1(a), $\left(\frac{pV_m}{T}\right)_{p=0} = \boxed{0.082\,061\,5\ \mathrm{L\,atm\,K^{-1}\,mol^{-1}}}$

From Fig. 1.1(b), $\left(\frac{\rho}{p}\right)_{p=0} = 1.42755\ \mathrm{g\,L^{-1}\,atm^{-1}}$

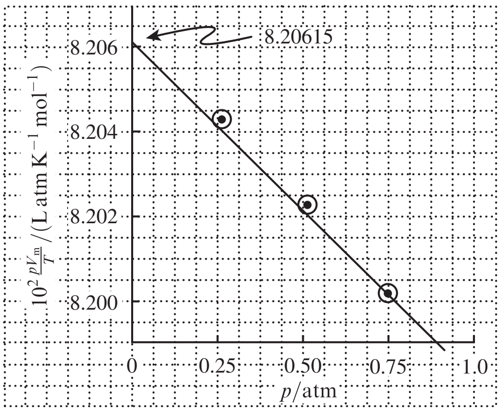


Figure 1.1(a)

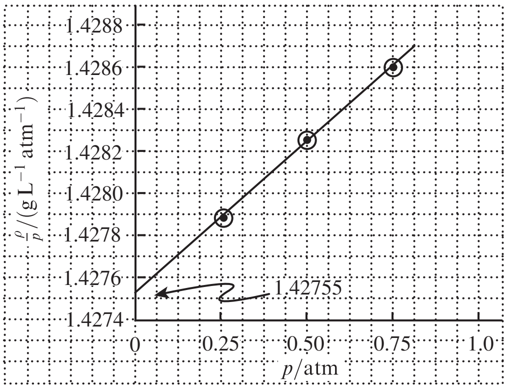


Figure 1.1(b)

$$M = RT\left(\frac{\rho}{p}\right)_{p=0} = (0.082\,061\,5\,\mathrm{L\,atm\,mol^{-1}\,K^{-1}}) \times (273.15\,\mathrm{K}) \times (1.42755\,\mathrm{g\,L^{-1}\,atm^{-1}})$$

$$= \boxed{31.9987\,\mathrm{g\,mol^{-1}}}$$

The value obtained for R deviates from the accepted value by 0.005 per cent. The error results from the fact that only three data points are available and that a linear extrapolation was employed. The molar mass, however, agrees exactly with the accepted value, probably because of compensating plotting errors.

E1.11(b) The mass density ρ is related to the molar volume V_m by

$$V_m = \frac{M}{\rho}$$

where M is the molar mass. Putting this relation into the perfect gas law yields

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

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

$$M = \frac{RT\rho}{p} = \frac{(62.364\,\mathrm{L\,Torr\,K^{-1}\,mol^{-1}}) \times [(100 + 273)\,\mathrm{K}] \times (0.6388\,\mathrm{g\,L^{-1}})}{120\,\mathrm{Torr}} = 124\,\mathrm{g\,mol^{-1}}.$$

The number of atoms per molecule is

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

suggesting a formula of $\boxed{P_4}$

E1.12(b) Use the perfect gas equation to compute the amount; then convert to mass.

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

We need the partial pressure of water, which is 53 per cent of the equilibrium vapour pressure at the given temperature and standard pressure.

$$p = (0.53) \times (2.69 \times 10^3\,\mathrm{Pa}) = 1.4\bar{3} \times 10^3\,\mathrm{Pa}$$

$$\text{so } n = \frac{(1.4\bar{3} \times 10^3\,\mathrm{Pa}) \times (250\,\mathrm{m^3})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (23 + 273)\,\mathrm{K}} = 1.4\bar{5} \times 10^2\,\mathrm{mol}$$

$$\text{or } m = (1.4\bar{5} \times 10^2\,\mathrm{mol}) \times (18.0\,\mathrm{g\,mol^{-1}}) = 2.6\bar{1} \times 10^3\,\mathrm{g} = \boxed{2.6\bar{1}\,\mathrm{kg}}$$

E1.13(b) **(a)** The volume occupied by each gas is the same, since each completely fills the container. Thus solving for V from eqn 14 we have (assuming a perfect gas)

$$V = \frac{n_J RT}{p_J} \qquad n_{\mathrm{Ne}} = \frac{0.225\,\mathrm{g}}{20.18\,\mathrm{g\,mol^{-1}}}$$

$$= 1.11\bar{5} \times 10^{-2}\,\mathrm{mol}, \qquad p_{\mathrm{Ne}} = 66.5\,\mathrm{Torr}, \qquad T = 300\,\mathrm{K}$$

$$V = \frac{(1.11\bar{5} \times 10^{-2}\,\mathrm{mol}) \times (62.36\,\mathrm{L\,Torr\,K^{-1}\,mol^{-1}}) \times (300\,\mathrm{K})}{66.5\,\mathrm{Torr}} = 3.13\bar{7}\,\mathrm{L} = \boxed{3.14\,\mathrm{L}}$$

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

$$n_{\mathrm{CH_4}} = \frac{0.320\,\mathrm{g}}{16.04\,\mathrm{g\,mol^{-1}}} = 1.99\overline{5} \times 10^{-2}\,\mathrm{mol} \quad n_{\mathrm{Ar}} = \frac{0.175\,\mathrm{g}}{39.95\,\mathrm{g\,mol^{-1}}} = 4.38 \times 10^{-3}\,\mathrm{mol}$$

$$n = (1.99\overline{5} + 0.438 + 1.11\overline{5}) \times 10^{-2}\,\mathrm{mol} = 3.54\overline{8} \times 10^{-2}\,\mathrm{mol}$$

$$p = \frac{nRT}{V}[1] = \frac{(3.54\overline{8} \times 10^{-2}\,\mathrm{mol}) \times (62.36\,\mathrm{L\,Torr\,K^{-1}\,mol^{-1}}) \times (300\,\mathrm{K})}{3.13\overline{7}\,\mathrm{L}}$$

$$= \boxed{212\,\mathrm{Torr}}$$

E1.14(b) This is similar to Exercise 1.14(a) with the exception that the density is first calculated.

$$M = \rho\frac{RT}{p} \text{ [Exercise 1.11(a)]}$$

$$\rho = \frac{33.5\,\mathrm{mg}}{250\,\mathrm{mL}} = 0.134\overline{0}\,\mathrm{g\,L^{-1}}, \qquad p = 152\,\mathrm{Torr}, \qquad T = 298\,\mathrm{K}$$

$$M = \frac{(0.134\overline{0}\,\mathrm{g\,L^{-1}}) \times (62.36\,\mathrm{L\,Torr\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})}{152\,\mathrm{Torr}} = \boxed{16.4\,\mathrm{g\,mol^{-1}}}$$

E1.15(b) This exercise is similar to Exercise 1.15(a) in that it uses the definition of absolute zero as that temperature at which the volume of a sample of gas would become zero if the substance remained a gas at low temperatures. The solution uses the experimental fact that the volume is a linear function of the Celsius temperature.

Thus $V = V_0 + \alpha V_0\theta = V_0 + b\theta,\ b = \alpha V_0$

At absolute zero, $V = 0$, or $0 = 20.00\,\mathrm{L} + 0.0741\,\mathrm{L{}^\circ C^{-1}} \times \theta(\text{abs. zero})$

$$\theta(\text{abs. zero}) = -\frac{20.00\,\mathrm{L}}{0.0741\,\mathrm{L{}^\circ C^{-1}}} = \boxed{-270^\circ\mathrm{C}}$$

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

E1.16(b) **(a)** $p = \dfrac{nRT}{V}$

$n = 1.0\,\mathrm{mol}$

$T = $ (i) $273.15\,\mathrm{K}$; (ii) $500\,\mathrm{K}$

$V = $ (i) $22.414\,\mathrm{L}$; (ii) $150\,\mathrm{cm^3}$

(i) $$p = \frac{(1.0\,\mathrm{mol}) \times (8.206 \times 10^{-2}\,\mathrm{L\,atm\,K^{-1}\,mol^{-1}}) \times (273.15\,\mathrm{K})}{22.414\,\mathrm{L}}$$
$$= \boxed{1.0\,\mathrm{atm}}$$

(ii) $$p = \frac{(1.0\,\mathrm{mol}) \times (8.206 \times 10^{-2}\,\mathrm{L\,atm\,K^{-1}\,mol^{-1}}) \times (500\,\mathrm{K})}{0.150\,\mathrm{L}}$$
$$= \boxed{270\,\mathrm{atm}} \text{ (2 significant figures)}$$

(b) From Table (1.6) for H_2S

$a = 4.484\,\mathrm{L^2\,atm\,mol^{-1}} \qquad b = 4.34 \times 10^{-2}\,\mathrm{L\,mol^{-1}}$

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

$$\text{(i)}\quad p = \frac{(1.0\,\text{mol}) \times (8.206 \times 10^{-2}\,\text{L atm K}^{-1}\,\text{mol}^{-1}) \times (273.15\,\text{K})}{22.414\,\text{L} - (1.0\,\text{mol}) \times (4.34 \times 10^{-2}\,\text{L mol}^{-1})} - \frac{(4.484\,\text{L}^2\,\text{atm mol}^{-1}) \times (1.0\,\text{mol})^2}{(22.414\,\text{L})^2}$$

$$= \boxed{0.99\,\text{atm}}$$

$$\text{(ii)}\quad p = \frac{(1.0\,\text{mol}) \times (8.206 \times 10^{-2}\,\text{L atm K}^{-1}\,\text{mol}^{-1}) \times (500\,\text{K})}{0.150\,\text{L} - (1.0\,\text{mol}) \times (4.34 \times 10^{-2}\,\text{L mol}^{-1})} - \frac{(4.484\,\text{L}^2\text{atm mol}^{-1}) \times (1.0\,\text{mol})^2}{(0.150\,\text{L})^2}$$

$$= 18\overline{5.6}\,\text{atm} \approx \boxed{190\,\text{atm}}\ \text{(2 significant figures).}$$

E1.17(b) The critical constants of a van der Waals gas are

$$V_c = 3b = 3(0.0436\,\text{L mol}^{-1}) = \boxed{0.131\,\text{L mol}^{-1}}$$

$$p_c = \frac{a}{27b^2} = \frac{1.32\,\text{atm L}^2\,\text{mol}^{-2}}{27(0.0436\,\text{L mol}^{-1})^2} = \boxed{25.7\,\text{atm}}$$

$$\text{and } T_c = \frac{8a}{27Rb} = \frac{8(1.32\,\text{atm L}^2\,\text{mol}^{-2})}{27(0.08206\,\text{L atm K}^{-1}\,\text{mol}^{-1}) \times (0.0436\,\text{L mol}^{-1})} = \boxed{109\,\text{K}}$$

E1.18(b) The compression factor is

$$Z = \frac{pV_m}{RT} = \frac{V_m}{V_{m,\text{perfect}}}$$

(a) Because $V_m = V_{m,\text{perfect}} + 0.12\,V_{m,\text{perfect}} = (1.12)V_{m,\text{perfect}}$, we have $Z = \boxed{1.12}$ $\boxed{\text{Repulsive}}$ forces dominate.

(b) The molar volume is

$$V = (1.12)V_{m,\text{perfect}} = (1.12) \times \left(\frac{RT}{p}\right)$$

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

E1.19(b) **(a)**

$$V_m^{\circ} = \frac{RT}{p} = \frac{(8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298.15\,\text{K})}{(200\,\text{bar}) \times (10^5\,\text{Pa bar}^{-1})}$$

$$= 1.24 \times 10^{-4}\,\text{m}^3\,\text{mol}^{-1} = \boxed{0.124\,\text{L mol}^{-1}}$$

(b) The van der Waals equation is a cubic equation in V_m. The most direct way of obtaining the molar volume would be to solve the cubic analytically. However, this approach is cumbersome, so we proceed as in Example 1.6. The van der Waals equation is rearranged to the cubic form

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

with $x = V_m/(\text{L mol}^{-1})$.

The coefficients in the equation are evaluated as

$$b + \frac{RT}{p} = (3.183 \times 10^{-2}\,\mathrm{L\,mol^{-1}}) + \frac{(8.206 \times 10^{-2}\,\mathrm{L\,atm\,K^{-1}\,mol^{-1}}) \times (298.15\,\mathrm{K})}{(200\,\mathrm{bar}) \times (1.013\,\mathrm{atm\,bar^{-1}})}$$

$$= (3.183 \times 10^{-2} + 0.120\overline{8})\,\mathrm{L\,mol^{-1}} = 0.152\overline{6}\,\mathrm{L\,mol^{-1}}$$

$$\frac{a}{p} = \frac{1.360\,\mathrm{L^2\,atm\,mol^{-2}}}{(200\,\mathrm{bar}) \times (1.013\,\mathrm{atm\,bar^{-1}})} = 6.71 \times 10^{-3}(\mathrm{L\,mol^{-1}})^2$$

$$\frac{ab}{p} = \frac{(1.360\,\mathrm{L^2\,atm\,mol^{-2}}) \times (3.183 \times 10^{-2}\,\mathrm{L\,mol^{-1}})}{(200\,\mathrm{bar}) \times (1.013\,\mathrm{atm\,bar^{-1}})} = 2.13\overline{7} \times 10^{-4}(\mathrm{L\,mol^{-1}})^3$$

Thus, the equation to be solved is $x^3 - 0.152\overline{6}x^2 + (6.71 \times 10^{-3})x - (2.13\overline{7} \times 10^{-4}) = 0$.

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

$$x = 0.112 \quad \text{or} \quad V_\mathrm{m} = \boxed{0.112\,\mathrm{L\,mol^{-1}}}$$

The difference is about 15 per cent.

E1.20(b) **(a)** $V_\mathrm{m} = \dfrac{M}{\rho} = \dfrac{18.015\,\mathrm{g\,mol^{-1}}}{0.5678\,\mathrm{g\,L^{-1}}} = \boxed{31.72\overline{8}\,\mathrm{L\,mol^{-1}}}$

$$Z = \frac{pV_\mathrm{m}}{RT} = \frac{(1.00\,\mathrm{bar}) \times (31.72\overline{8}\,\mathrm{L\,mol^{-1}})}{(0.083\,145\,\mathrm{L\,bar\,K^{-1}\,mol^{-1}}) \times (383\,\mathrm{K})} = \boxed{0.996\overline{3}}$$

(b) Using $p = \dfrac{RT}{V_\mathrm{m} - b} - \dfrac{a}{V_\mathrm{m}^2}$ and substituting into the expression for Z above we get

$$\begin{aligned} Z &= \frac{V_\mathrm{m}}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}RT} \\ &= \frac{31.72\overline{8}\,\mathrm{L\,mol^{-1}}}{31.72\overline{8}\,\mathrm{L\,mol^{-1}} - 0.030\,49\,\mathrm{L\,mol^{-1}}} \\ &\quad - \frac{5.464\,\mathrm{L^2\,atm\,mol^{-2}}}{(31.72\overline{8}\,\mathrm{L\,mol^{-1}}) \times (0.082\,06\,\mathrm{L\,atm\,K^{-1}\,mol^{-1}}) \times (383\,\mathrm{K})} \\ &= \boxed{0.995\overline{4}} \end{aligned}$$

Comment. Both values of Z are very close to the perfect gas value of 1.000, indicating that water vapour is essentially perfect at 1.00 bar pressure.

E1.21(b) The molar volume is obtained by solving $Z = \dfrac{pV_\mathrm{m}}{RT}$ [1.20*b*], for V_m, which yields

$$V_\mathrm{m} = \frac{ZRT}{p} = \frac{(0.86) \times (0.08206\,\mathrm{L\,atm\,K^{-1}\,mol^{-1}}) \times (300\,\mathrm{K})}{20\,\mathrm{atm}} = 1.0\overline{59}\,\mathrm{L\,mol^{-1}}$$

(a) Then, $V = nV_\mathrm{m} = (8.2 \times 10^{-3}\,\mathrm{mol}) \times (1.0\overline{59}\,\mathrm{L\,mol^{-1}}) = 8.7 \times 10^{-3}\,\mathrm{L} = \boxed{8.7\,\mathrm{mL}}$

(b) An approximate value of B can be obtained from eqn 1.22 by truncation of the series expansion after the second term, B/V_m, in the series. Then,

$$B = V_m\left(\frac{pV_m}{RT} - 1\right) = V_m \times (Z-1)$$

$$= (1.0\overline{59}\,\mathrm{L\,mol^{-1}}) \times (0.86-1) = \boxed{-0.15\,\mathrm{L\,mol^{-1}}}$$

E1.22(b) **(a)** Mole fractions are

$$x_N = \frac{n_N}{n_{\text{total}}} = \frac{2.5\,\mathrm{mol}}{(2.5+1.5)\,\mathrm{mol}} = \boxed{0.63}$$

Similarly, $x_H = \boxed{0.37}$

(c) According to the perfect gas law

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

$$\text{so } p_{\text{total}} = \frac{n_{\text{total}}RT}{V}$$

$$= \frac{(4.0\,\mathrm{mol}) \times (0.08206\,\mathrm{L\,atm\,mol^{-1}\,K^{-1}}) \times (273.15\,\mathrm{K})}{22.4\,\mathrm{L}} = \boxed{4.0\,\mathrm{atm}}$$

(b) The partial pressures are

$$p_N = x_N p_{\text{tot}} = (0.63) \times (4.0\,\mathrm{atm}) = \boxed{2.5\,\mathrm{atm}}$$

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

E1.23(b) The critical volume of a van der Waals gas is

$$V_c = 3b$$

$$\text{so } b = \tfrac{1}{3}V_c = \tfrac{1}{3}(148\,\mathrm{cm^3\,mol^{-1}}) = 49.3\,\mathrm{cm^3\,mol^{-1}} = \boxed{0.0493\,\mathrm{L\,mol^{-1}}}$$

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

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

$$r = \frac{1}{2}\left(\frac{3(49.3\,\mathrm{cm^3\,mol^{-1}})}{4\pi(6.022\times10^{23}\,\mathrm{mol^{-1}})}\right)^{1/3} = 1.94\times10^{-8}\,\mathrm{cm} = \boxed{1.94\times10^{-10}\,\mathrm{m}}$$

The critical pressure is

$$p_c = \frac{a}{27b^2}$$

$$\text{so } a = 27p_cb^2 = 27(48.20\,\mathrm{atm}) \times (0.0493\,\mathrm{L\,mol^{-1}})^2 = \boxed{3.16\,\mathrm{L^2\,atm\,mol^{-2}}}$$

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

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

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

$$T_c = \frac{8(3.16\,\mathrm{L^2\,atm\,mol^{-2}})}{27(0.08206\,\mathrm{L\,atm\,K^{-1}\,mol^{-1}}) \times (0.0493\,\mathrm{L\,mol^{-1}})} = 231\,\mathrm{K}$$

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

E1.24(b) **(a)** The Boyle temperature is the temperature at which $\lim_{V_m\to\infty} \frac{dZ}{d(1/V_m)}$ vanishes. According to the van der Waals equation

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

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

In the limit of large molar volume, we have

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

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

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

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

$$r = \frac{1}{2}\left(\frac{3(0.0434\,\mathrm{dm^3\,mol^{-1}})}{4\pi(6.022\times10^{23}\,\mathrm{mol^{-1}})}\right)^{1/3} = 1.286\times10^{-9}\,\mathrm{dm} = 1.29\times10^{-10}\,\mathrm{m} = \boxed{0.129\,\mathrm{nm}}$$

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

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

The corresponding states are

(a) For H_2S

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

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

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

(b) For CO_2

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

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

(c) For Ar

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

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

E1.26(b) The van der Waals equation is

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

which can be solved for b

$$b = V_m - \frac{RT}{p + \frac{a}{V_m^2}} = 4.00 \times 10^{-4}\,\text{m}^3\,\text{mol}^{-1} - \frac{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (288\,\text{K})}{4.0 \times 10^6\,\text{Pa} + \left(\frac{0.76\,\text{m}^6\,\text{Pa mol}^{-2}}{(4.00 \times 10^{-4}\,\text{m}^3\,\text{mol}^{-1})^2}\right)}$$

$$= \boxed{1.3 \times 10^{-4}\,\text{m}^3\,\text{mol}^{-1}}$$

The compression factor is

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

Solutions to problems

Solutions to numerical problems

P1.2 Identifying p_{ex} in the equation $p = p_{ex} + \rho g h$ [1.4] as the pressure at the top of the straw and p as the atmospheric pressure on the liquid, the pressure difference is

$$p - p_{ex} = \rho g h = (1.0 \times 10^3\,\text{kg m}^{-3}) \times (9.81\,\text{m s}^{-2}) \times (0.15\,\text{m})$$

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

P1.4 $pV = nRT$ [1.12] implies that, with n constant, $\dfrac{p_f V_f}{T_f} = \dfrac{p_i V_i}{T_i}$

Solving for p_f, the pressure at its maximum altitude, yields $p_f = \dfrac{V_i}{V_f} \times \dfrac{T_f}{T_i} \times p_i$

Substituting $V_\mathrm{i} = \frac{4}{3}\pi r_\mathrm{i}^3$ and $V_\mathrm{f} = \frac{4}{3}\pi r_\mathrm{f}^3$

$$p_\mathrm{f} = \left(\frac{(4/3)\pi r_\mathrm{i}^3}{(4/3)\pi r_\mathrm{f}^3}\right) \times \frac{T_\mathrm{f}}{T_\mathrm{i}} \times p_\mathrm{i} = \left(\frac{r_\mathrm{i}}{r_\mathrm{f}}\right)^3 \times \frac{T_\mathrm{f}}{T_\mathrm{i}} \times p_\mathrm{i}$$

$$= \left(\frac{1.0\,\mathrm{m}}{3.0\,\mathrm{m}}\right)^3 \times \left(\frac{253\,\mathrm{K}}{293\,\mathrm{K}}\right) \times (1.0\,\mathrm{atm}) = \boxed{3.2 \times 10^{-2}\,\mathrm{atm}}$$

P1.6 The value of absolute zero can be expressed in terms of α by using the requirement that the volume of a perfect gas becomes zero at the absolute zero of temperature. Hence

$$0 = V_0[1 + \alpha\theta(\text{abs. zero})]$$

Then $\theta(\text{abs. zero}) = -\dfrac{1}{\alpha}$

All gases become perfect in the limit of zero pressure, so the best value of α and, hence, θ(abs. zero) is obtained by extrapolating α to zero pressure. This is done in Fig. 1.2. Using the extrapolated value, $\alpha = 3.6637 \times 10^{-3}\,{}^\circ\mathrm{C}^{-1}$, or

$$\theta(\text{abs. zero}) = -\frac{1}{3.6637 \times 10^{-3}\,{}^\circ\mathrm{C}^{-1}} = \boxed{-272.95^\circ\mathrm{C}}$$

which is close to the accepted value of −273.15°C.

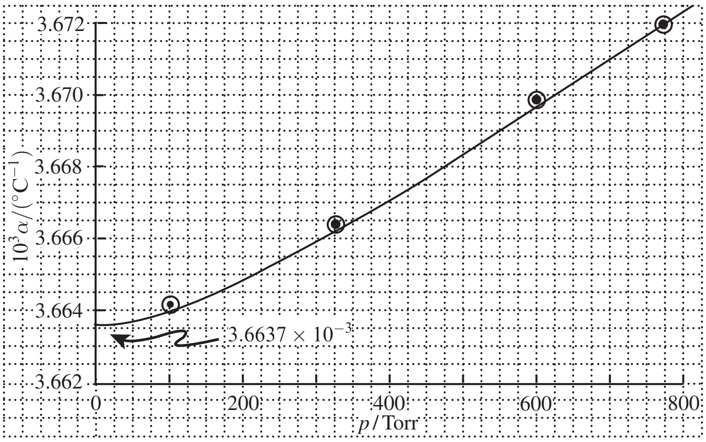


Figure 1.2

P1.7 The mass of displaced gas is ρV, where V is the volume of the bulb and ρ is the density of the gas. The balance condition for the two gases is $m(\text{bulb}) = \rho V(\text{bulb})$, $m(\text{bulb}) = \rho' V(\text{bulb})$

which implies that $\rho = \rho'$. Because [Problem 1.5] $\rho = \dfrac{pM}{RT}$

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

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

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

In experiment 1, $p = 423.22\,\text{Torr}$, $p' = 327.10\,\text{Torr}$; hence

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

In experiment 2, $p = 427.22\,\text{Torr}$, $p' = 293.22\,\text{Torr}$; hence

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

In a proper series of experiments one should reduce the pressure (e.g. by adjusting the balanced weight). Experiment 2 is closer to zero pressure than experiment 1; it may be safe to conclude that $\boxed{M \approx 102\,\text{g mol}^{-1}}$. The molecules $\boxed{\text{CH}_2\text{FCF}_3}$ or $\boxed{\text{CHF}_2\text{CHF}_2}$ have $M \approx 102\,\text{g mol}^{-1}$.

P1.9 We assume that no H_2 remains after the reaction has gone to completion. The balanced equation is

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

We can draw up the following table

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

$$p = \frac{nRT}{V} = (1.66\,\text{mol}) \times \left(\frac{(8.206 \times 10^{-2}\,\text{L atm K}^{-1}\,\text{mol}^{-1}) \times (273.15\,\text{K})}{22.4\,\text{L}}\right) = \boxed{1.66\,\text{atm}}$$

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

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

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

P1.10 **(a)** $$V_\text{m} = \frac{RT}{p} = \frac{(8.206 \times 10^{-2}\,\text{L atm K}^{-1}\,\text{mol}^{-1}) \times (350\,\text{K})}{2.30\,\text{atm}} = \boxed{12.5\,\text{L mol}^{-1}}$$

(b) From $p = \dfrac{RT}{V_\text{m} - b} - \dfrac{a}{V_\text{m}^2}$ [1.25*b*], we obtain $V_\text{m} = \dfrac{RT}{\left(p + \frac{a}{V_\text{m}^2}\right)} + b$ [rearrange 1.25*b*]

Then, with a and b from Table 1.6

$$V_\text{m} \approx \frac{(8.206 \times 10^{-2}\,\text{L atm K}^{-1}\,\text{mol}^{-1}) \times (350\,\text{K})}{(2.30\,\text{atm}) + \left(\frac{6.260\,\text{L}^2\,\text{atm mol}^{-2}}{(12.5\,\text{L mol}^{-1})^2}\right)} + (5.42 \times 10^{-2}\,\text{L mol}^{-1})$$

$$\approx \frac{28.7\overline{2}\,\text{L mol}^{-1}}{2.34} + (5.42 \times 10^{-2}\,\text{L mol}^{-1}) \approx \boxed{12.3\,\text{L mol}^{-1}}.$$

Substitution of $12.3\,\text{L mol}^{-1}$ into the denominator of the first expression again results in $V_\text{m} = 12.3\,\text{L mol}^{-1}$, so the cycle of approximation may be terminated.

P1.13 **(a)** Since $B'(T_{\mathrm{B}}) = 0$ at the Boyle temperature (section 1.3b): $B'(T_{\mathrm{B}}) = a + b\,\mathrm{e}^{-c/T_{\mathrm{B}}^{2}} = 0$

$$\text{Solving for } T_{\mathrm{B}}:\ T_{\mathrm{B}} = \sqrt{\frac{-c}{\ln\left(\frac{-a}{b}\right)}} = \sqrt{\frac{-(1131\,\mathrm{K}^2)}{\ln\left[\frac{-(-0.1993\,\mathrm{bar}^{-1})}{(0.2002\,\mathrm{bar}^{-1})}\right]}} = 501.0\,\mathrm{K}$$

(b) Perfect Gas Equation: $V_{\mathrm{m}}(p,T) = \dfrac{RT}{p}$

$$V_{\mathrm{m}}(50\,\mathrm{bar}, 298.15\,\mathrm{K}) = \frac{0.083145\,\mathrm{L\ bar\ K^{-1}\ mol^{-1}}\ (298.15\,\mathrm{K})}{50\,\mathrm{bar}} = 0.496\,\mathrm{L\ mol^{-1}}$$

$$V_{\mathrm{m}}(50\,\mathrm{bar}, 373.15\,\mathrm{K}) = \frac{0.083145\,\mathrm{L\ bar\ K^{-1}\ mol^{-1}}\ (373.15\,\mathrm{K})}{50\,\mathrm{bar}} = 0.621\,\mathrm{L\ mol^{-1}}$$

Virial Equation (eqn 1.21 to first order): $V_{\mathrm{m}}(p,T) = \dfrac{RT}{p}\,(1+B'(T)\,p) = V_{\text{perfect}}(1+B'(T)\,p)$

$$B'(T) = a + b\,\mathrm{e}^{-\frac{c}{T_{\mathrm{B}}^{2}}}$$

$$B'(298.15\,\mathrm{K}) = -0.1993\,\mathrm{bar}^{-1} + 0.2002\,\mathrm{bar}^{-1}\,\mathrm{e}^{-\frac{1131\,\mathrm{K}^2}{(298.15\,\mathrm{K})^2}} = -0.00163\,\mathrm{bar}^{-1}$$

$$B'(373.15\,\mathrm{K}) = -0.1993\,\mathrm{bar}^{-1} + 0.2002\,\mathrm{bar}^{-1}\,\mathrm{e}^{-\frac{1131\,\mathrm{K}^2}{(373.15\,\mathrm{K})^2}} = -0.000720\,\mathrm{bar}^{-1}$$

$$V_{\mathrm{m}}(50\,\mathrm{bar}, 298.15\,\mathrm{K}) = 0.496\,\mathrm{L\,mol^{-1}}\,\left(1 - 0.00163\,\mathrm{bar}^{-1}\,50\,\mathrm{bar}\right) = 0.456\,\mathrm{L\,mol^{-1}}$$

$$V_{\mathrm{m}}(50\,\mathrm{bar}, 373.15\,\mathrm{K}) = 0.621\,\mathrm{L\,mol^{-1}}\,\left(1 - 0.000720\,\mathrm{bar}^{-1}\,50\,\mathrm{bar}\right) = 0.599\,\mathrm{L\,mol^{-1}}$$

The perfect gas law predicts a molar volume that is 9% too large at 298 K and 4% too large at 373 K. The negative value of the second virial coefficient at both temperatures indicates the dominance of very weak intermolecular attractive forces over repulsive forces.

P1.15 From Table 1.6 $T_{\mathrm{c}} = \left(\dfrac{2}{3}\right) \times \left(\dfrac{2a}{3bR}\right)^{1/2}$, $p_{\mathrm{c}} = \left(\dfrac{1}{12}\right) \times \left(\dfrac{2aR}{3b^3}\right)^{1/2}$

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

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

$$= \left(\frac{8}{3}\right) \times \left(\frac{(40\,\mathrm{atm}) \times (160 \times 10^{-3}\,\mathrm{L\,mol^{-1}})}{8.206 \times 10^{-2}\,\mathrm{L\,atm\,K^{-1}\,mol^{-1}}}\right) = \boxed{2\bar{1}0\,\mathrm{K}}$$

$$v_{\mathrm{mol}} = \frac{b}{N_{\mathrm{A}}} = \left(\frac{1}{3}\right) \times \left(\frac{V_{\mathrm{c}}}{N_{\mathrm{A}}}\right) = \frac{160 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}}{(3) \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}})} = 8.86 \times 10^{-29}\,\mathrm{m^3}$$

$$v_{\mathrm{mol}} = \frac{4\pi}{3}r^3$$

$$r = \left(\frac{3}{4\pi} \times (8.86 \times 10^{-29}\,\mathrm{m^3})\right)^{1/3} = \boxed{0.28\,\mathrm{nm}}$$

P1.16 $V_c = 2b, \qquad T_c = \dfrac{a}{4bR}$ [Table 1.6]

Hence, with V_c and T_c from Table 1.5, $b = \frac{1}{2}V_c = \frac{1}{2} \times (118.8\,\text{cm}^3\,\text{mol}^{-1}) = \boxed{59.4\,\text{cm}^3\,\text{mol}^{-1}}$

$$\begin{aligned} a &= 4bRT_c = 2RT_cV_c \\ &= (2) \times (8.206 \times 10^{-2}\,\text{L atm K}^{-1}\,\text{mol}^{-1}) \times (289.75\,\text{K}) \times (118.8 \times 10^{-3}\,\text{L mol}^{-1}) \\ &= \boxed{5.649\,\text{L}^2\,\text{atm mol}^{-2}} \end{aligned}$$

Hence

$$\begin{aligned} p &= \frac{RT}{V_m - b}\mathrm{e}^{-a/RTV_m} = \frac{nRT}{V - nb}\mathrm{e}^{-na/RTV} \\ &= \frac{(1.0\,\text{mol}) \times (8.206 \times 10^{-2}\,\text{L atm K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})}{(1.0\,\text{L}) - (1.0\,\text{mol}) \times (59.4 \times 10^{-3}\,\text{L mol}^{-1})} \\ &\quad \times \exp\left(\frac{-(1.0\,\text{mol}) \times (5.649\,\text{L}^2\,\text{atm mol}^{-2})}{(8.206 \times 10^{-2}\,\text{L atm K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K}) \times (1.0\,\text{L}^2\,\text{atm mol}^{-1})}\right) \\ &= 26.\bar{0}\,\text{atm} \times \mathrm{e}^{-0.23\bar{1}} = \boxed{21\,\text{atm}} \end{aligned}$$

Solutions to theoretical problems

P1.18 This expansion has already been given in the solutions to Exercise 1.24(**a**) and Problem 1.17; the result is

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

Compare this expansion with $p = \dfrac{RT}{V_m}\left(1 + \dfrac{B}{V_m} + \dfrac{C}{V_{m^2}} + \cdots\right)$ [1.22]

and hence find $\boxed{B = b - \dfrac{a}{RT}}$ and $\boxed{C = b^2}$

Since $C = 1200\,\text{cm}^6\,\text{mol}^{-2}$, $b = C^{1/2} = \boxed{34.6\,\text{cm}^3\,\text{mol}^{-1}}$

$$\begin{aligned} a &= RT(b - B) = (8.206 \times 10^{-2}) \times (273\,\text{L atm mol}^{-1}) \times (34.6 + 21.7)\,\text{cm}^3\,\text{mol}^{-1} \\ &= (22.4\bar{0}\,\text{L atm mol}^{-1}) \times (56.3 \times 10^{-3}\,\text{L mol}^{-1}) = \boxed{1.26\,\text{L}^2\,\text{atm mol}^{-2}} \end{aligned}$$

P1.22 For a real gas we may use the virial expansion in terms of p [1.21]

$$p = \frac{nRT}{V}(1 + B'p + \cdots) = \rho\frac{RT}{M}(1 + B'p + \cdots)$$

which rearranges to $\dfrac{p}{\rho} = \dfrac{RT}{M} + \dfrac{RTB'}{M}p + \cdots$

Therefore, the limiting slope of a plot of $\dfrac{p}{\rho}$ against p is $\dfrac{B'RT}{M}$. From Fig. 1.2 in the *Student's Solutions Manual*, the limiting slope is

$$\frac{B'RT}{M} = \frac{(4.41 - 5.27) \times 10^4\,\text{m}^2\,\text{s}^{-2}}{(10.132 - 1.223) \times 10^4\,\text{Pa}} = -9.7 \times 10^{-2}\,\text{kg}^{-1}\,\text{m}^3$$

From Fig. 1.2, $\dfrac{RT}{M} = 5.39 \times 10^4\,\text{m}^2\,\text{s}^{-2}$; hence

$$B' = -\frac{9.7 \times 10^{-2}\,\text{kg}^{-1}\,\text{m}^3}{5.39 \times 10^4\,\text{m}^2\,\text{s}^{-2}} = -1.8\bar{0} \times 10^{-6}\,\text{Pa}^{-1}$$

$$B' = (-1.8\bar{0} \times 10^{-6}\,\text{Pa}^{-1}) \times (1.0133 \times 10^5\,\text{Pa atm}^{-1}) = \boxed{-0.18\bar{2}\,\text{atm}^{-1}}$$

$$\begin{aligned} B &= RTB' \text{ [Problem 1.21]} \\ &= (8.206 \times 10^{-2}\,\text{L atm K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K}) \times (-0.18\bar{2}\,\text{atm}^{-1}) \\ &= \boxed{-4.4\,\text{L mol}^{-1}} \end{aligned}$$

P1.23 Write $V_\text{m} = f(T, p)$; then $\text{d}V_\text{m} = \left(\dfrac{\partial V_\text{m}}{\partial T}\right)_p \text{d}T + \left(\dfrac{\partial V_\text{m}}{\partial p}\right)_T \text{d}p$

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

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

From the equation of state

$$\left(\frac{\partial p}{\partial V_\text{m}}\right)_T = -\frac{RT}{V_\text{m}^2} - 2(a + bT)V_\text{m}^{-3} \qquad \left(\frac{\partial p}{\partial T}\right)_{V_\text{m}} = \frac{R}{V_\text{m}} + \frac{b}{V_\text{m}^2}$$

Substituting

$$\left(\frac{\partial V_\text{m}}{\partial T}\right)_P = -\frac{\left(\frac{R}{V_\text{m}} + \frac{b}{V_{\text{m}^2}}\right)}{\left(-\frac{RT}{V_\text{m}^2} - \frac{2(a+bT)}{V_\text{m}^3}\right)} = +\frac{\left(R + \left(\frac{b}{V_\text{m}}\right)\right)}{\left(\frac{RT}{V_\text{m}} + \frac{2(a+bT)}{V_\text{m}^2}\right)}$$

From the equation of state $\dfrac{(a + bT)}{V_\text{m}^2} = p - \dfrac{RT}{V_\text{m}}$

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

P1.25 $Z = \dfrac{V_\text{m}}{V_\text{m}^\text{o}}$, where V_m^o = the molar volume of a perfect gas

From the given equation of state

$$V_\text{m} = b + \frac{RT}{p} = b + V_\text{m}^\text{o} \quad \text{then} \quad Z = \frac{b + V_\text{m}^\text{o}}{V_\text{m}^\text{o}} = 1 + \frac{b}{V_\text{m}^\text{o}}$$

For $V_\text{m} = 10b$, $10b = b + V_\text{m}^\text{o}$ or $V_\text{m}^\text{o} = 9b$

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

P1.27 The two masses represent the same volume of gas under identical conditions, and therefore, the same number of molecules (Avogadro's principle) and moles, n. Thus, the masses can be expressed as

$$nM_{\mathrm{N}} = 2.2990\,\mathrm{g}$$

for 'chemical nitrogen' and

$$n_{\mathrm{Ar}}M_{\mathrm{Ar}} + n_{\mathrm{N}}M_{\mathrm{N}} = n[x_{\mathrm{Ar}}M_{\mathrm{Ar}} + (1 - x_{\mathrm{Ar}})M_{\mathrm{N}}] = 2.3102\,\mathrm{g}$$

for 'atmospheric nitrogen'. Dividing the latter expression by the former yields

$$\frac{x_{\mathrm{Ar}}M_{\mathrm{Ar}}}{M_{\mathrm{N}}} + (1 - x_{\mathrm{Ar}}) = \frac{2.3102}{2.2990} \quad \text{so} \quad x_{\mathrm{Ar}}\left(\frac{M_{\mathrm{Ar}}}{M_{\mathrm{N}}} - 1\right) = \frac{2.3102}{2.2990} - 1$$

and $x_{\mathrm{Ar}} = \dfrac{\frac{2.3102}{2.2990} - 1}{\frac{M_{\mathrm{Ar}}}{M_{\mathrm{N}}} - 1} = \dfrac{\frac{2.3102}{2.2990} - 1}{\frac{39.95\,\mathrm{g\,mol^{-1}}}{28.013\,\mathrm{g\,mol^{-1}}} - 1} = \boxed{0.011}$

Comment. This value for the mole fraction of argon in air is close to the modern value.

P1.29

$$Z = \frac{pV_{\mathrm{m}}}{RT} = \left(\frac{T_{\mathrm{c}}}{T}\right) \times \left(\frac{p}{p_{\mathrm{c}}}\right) \times \left(\frac{p_{\mathrm{c}}V_{\mathrm{m}}}{RT_{\mathrm{c}}}\right) = \frac{p_{\mathrm{r}}V_{\mathrm{r}}'}{T_{\mathrm{r}}} \text{ [1.20}b\text{, 1.28]}$$

$$= \frac{V_{\mathrm{r}}'}{T_{\mathrm{r}}}\left\{\frac{8T_{\mathrm{r}}}{3V_{\mathrm{r}} - 1} - \frac{3}{V_{\mathrm{r}}^2}\right\} \text{ [1.29]}$$

But $V_{\mathrm{r}} = \dfrac{V}{V_{\mathrm{c}}} = \dfrac{RT_{\mathrm{c}}}{p_{\mathrm{c}}V_{\mathrm{c}}} \times \left(\dfrac{p_{\mathrm{c}}V}{RT_{\mathrm{c}}}\right) = \dfrac{8}{3}\dfrac{p_{\mathrm{c}}V}{RT_{\mathrm{c}}}\text{[1.27]} = \dfrac{8}{3}V_{\mathrm{r}}'$

Therefore $Z = \dfrac{V_{\mathrm{r}}'}{T_{\mathrm{r}}}\left\{\dfrac{8T_{\mathrm{r}}}{3\left(\frac{8V_{\mathrm{r}}'}{3}\right) - 1} - \dfrac{3}{\left(\frac{8V_{\mathrm{r}}'}{3}\right)^2}\right\}$

$$= \frac{V_{\mathrm{r}}'}{T_{\mathrm{r}}}\left\{\frac{T_{\mathrm{r}}}{V_{\mathrm{r}}' - 1/8} - \frac{27}{64(V_{\mathrm{r}}')^2}\right\}$$

$$= V_{\mathrm{r}}'\left\{\frac{1}{V_{\mathrm{r}}' - 1/8} - \frac{27}{64T_{\mathrm{r}}(V_{\mathrm{r}}')^2}\right\}$$

$$\boxed{Z = \frac{V_{\mathrm{r}}'}{V_{\mathrm{r}}' - 1/8} - \frac{27}{64T_{\mathrm{r}}V_{\mathrm{r}}'}} \qquad (2)$$

To derive the alternative form, solve eqn 1 for V_{r}', substitute the result into eqn 2, and simplify into polynomial form.

$$V_{\mathrm{r}}' = \frac{ZT_{\mathrm{r}}}{p_{\mathrm{r}}}$$

$$Z = \frac{ZT_{\mathrm{r}}/p_{\mathrm{r}}}{\frac{ZT_{\mathrm{r}}}{p_{\mathrm{r}}} - \frac{1}{8}} - \frac{27}{64T_{\mathrm{r}}}\left(\frac{p_{\mathrm{r}}}{ZT_{\mathrm{r}}}\right)$$

$$= \frac{8ZT_{\mathrm{r}}}{8ZT_{\mathrm{r}} - p_{\mathrm{r}}} - \frac{27p_{\mathrm{r}}}{64ZT_{\mathrm{r}}^2}$$

$$= \frac{512T_{\mathrm{r}}^3Z^2 - 27p_{\mathrm{r}} \times (8T_{\mathrm{r}}Z - p_{\mathrm{r}})}{64T_{\mathrm{r}}^2 \times (8ZT_{\mathrm{r}} - p_{\mathrm{r}})Z}$$

$$64T_{\mathrm{r}}^2(8ZT_{\mathrm{r}} - p_{\mathrm{r}})Z^2 = 512T_{\mathrm{r}}^3Z^2 - 216T_{\mathrm{r}}p_{\mathrm{r}}Z + 27p_{\mathrm{r}}^2$$

$$512T_{\mathrm{r}}^3Z^3 - \left(64T_{\mathrm{r}}^2p_{\mathrm{r}} + 512T_{\mathrm{r}}^3\right)Z^2 + 216T_{\mathrm{r}}p_{\mathrm{r}}Z - 27p_{\mathrm{r}}^2 = 0$$

$$\boxed{Z^3 - \left(\frac{p_\mathrm{r}}{8T_\mathrm{r}} + 1\right) Z^2 + \frac{27p_\mathrm{r}}{64T_\mathrm{r}^2} Z - \frac{27p_\mathrm{r}^2}{512T_\mathrm{r}^3} = 0} \tag{3}$$

At $T_\mathrm{r} = 1.2$ and $p_\mathrm{r} = 3$ eqn 3 predicts that Z is the root of

$$Z^3 - \left(\frac{3}{8(1.2)} + 1\right) Z^3 + \frac{27(3)}{64(1.2)^2} Z - \frac{27(3)^2}{512(1.2)^3} = 0$$

$$Z^3 - 1.3125Z^2 + 0.8789Z - 0.2747 = 0$$

The real root is $\boxed{Z = 0.611}$ and this prediction is independent of the specific gas. Figure 1.27 indicates that the experimental result for the listed gases is closer to 0.55.

Solutions to applications

P1.31 Refer to Fig. 1.3.

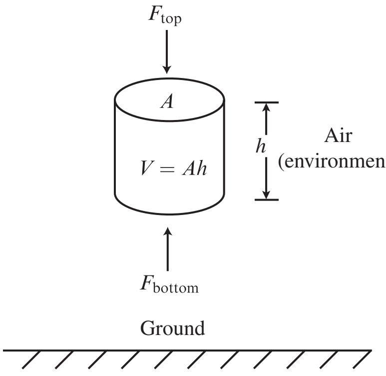


Figure 1.3

The buoyant force on the cylinder is

$$\begin{aligned} F_\text{buoy} &= F_\text{bottom} - F_\text{top} \\ &= A(p_\text{bottom} - p_\text{top}) \end{aligned}$$

according to the barometric formula.

$$p_\text{top} = p_\text{bottom} \mathrm{e}^{-Mgh/RT}$$

where M is the molar mass of the environment (air). Since h is small, the exponential can be expanded in a Taylor series around $h = 0$ $\left(\mathrm{e}^{-x} = 1 - x + \frac{1}{2!}x^2 + \cdots\right)$. Keeping the first-order term only yields

$$p_\text{top} = p_\text{bottom}\left(1 - \frac{Mgh}{RT}\right)$$

The buoyant force becomes

$$\begin{aligned} F_{\text{buoy}} &= Ap_{\text{bottom}}\left(1 - 1 + \frac{Mgh}{RT}\right) = Ah\left(\frac{p_{\text{bottom}}M}{RT}\right)g \\ &= \left(\frac{p_{\text{bottom}}VM}{RT}\right)g = nMg \quad \left[n = \frac{p_{\text{bottom}}V}{RT}\right] \end{aligned}$$

n is the number of moles of the environment (air) displaced by the balloon, and $nM = m$, the mass of the displaced environment. Thus $F_{\text{buoy}} = mg$. The net force is the difference between the buoyant force and the weight of the balloon. Thus

$$F_{\text{net}} = mg - m_{\text{balloon}}g = (m - m_{\text{balloon}})g$$

This is Archimedes' principle.

2 The First Law: the concepts

Solutions to exercises

Discussion questions

E2.1(b) Work is a transfer of energy that results in orderly motion of the atoms and molecules in a system; heat is a transfer of energy that results in disorderly motion. See Molecular Interpretation 2.1 for a more detailed discussion.

E2.2(b) Rewrite the two expressions as follows:

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

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

E2.3(b) Standard reaction enthalpies can be calculated from a knowledge of the standard enthalpies of formation of all the substances (reactants and products) participating in the reaction. This is an exact method which involves no approximations. The only disadvantage is that standard enthalpies of formation are not known for all substances.

Approximate values can be obtained from mean bond enthalpies. See almost any general chemistry text, for example, *Chemical Principles*, by Atkins and Jones, Section 6.21, for an illustration of the method of calculation. This method is often quite inaccurate, though, because the average values of the bond enthalpies used may not be close to the actual values in the compounds of interest.

Another somewhat more reliable approximate method is based on thermochemical groups which mimic more closely the bonding situations in the compounds of interest. See Example 2.6 for an illustration of this kind of calculation. Though better, this method suffers from the same kind of defects as the average bond enthalpy approach, since the group values used are also averages.

Computer aided molecular modeling is now the method of choice for estimating standard reaction enthalpies, especially for large molecules with complex three-dimensional structures, but accurate numerical values are still difficult to obtain.

Numerical exercises

E2.4(b) Work done against a uniform gravitational field is

$$w = mgh$$

(a) $w = (5.0\,\mathrm{kg}) \times (100\,\mathrm{m}) \times (9.81\,\mathrm{m\,s^{-2}}) = \boxed{4.9 \times 10^{3}\,\mathrm{J}}$

(b) $w = (5.0\,\mathrm{kg}) \times (100\,\mathrm{m}) \times (3.73\,\mathrm{m\,s^{-2}}) = \boxed{1.9 \times 10^{3}\,\mathrm{J}}$

E2.5(b) Work done against a uniform gravitational field is

$$w = mgh = (120 \times 10^{-3}\,\mathrm{kg}) \times (50\,\mathrm{m}) \times (9.81\,\mathrm{m\,s^{-2}}) = \boxed{59\,\mathrm{J}}$$

E2.6(b) Work done *by* a system expanding against a constant external pressure is

$$w = -p_{\mathrm{ex}}\Delta V = -(121 \times 10^{3}\,\mathrm{Pa}) \times \left(\frac{(15\,\mathrm{cm}) \times (50\,\mathrm{cm^{2}})}{(100\,\mathrm{cm\,m^{-1}})^{3}}\right) = \boxed{-91\,\mathrm{J}}$$

E2.7(b) For a perfect gas at constant temperature

$$\Delta U = \boxed{0} \quad \text{so} \quad q = -w$$

For a perfect gas at constant temperature, ΔH is also $\boxed{\text{zero}}$

$$\mathrm{d}H = \mathrm{d}(U + pV)$$

we have already noted that U does not change at constant temperature; nor does pV if the gas obeys Boyle's law. These apply to all three cases below.

(a) Isothermal reversible expansion

$$\begin{aligned} w &= -nRT \ln \frac{V_\mathrm{f}}{V_\mathrm{i}} \\ &= -(2.00\,\mathrm{mol}) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (22 + 273)\,\mathrm{K} \times \ln \frac{31.7\,\mathrm{L}}{22.8\,\mathrm{L}} = \boxed{-1.62 \times 10^3\,\mathrm{J}} \\ q &= -w = \boxed{1.62 \times 10^3\,\mathrm{J}} \end{aligned}$$

(b) Expansion against a constant external pressure

$$w = -p_\mathrm{ex}\Delta V$$

where p_ex in this case can be computed from the perfect gas law

$$pV = nRT$$

$$\text{so } p = \frac{(2.00\,\mathrm{mol}) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (22 + 273)\,\mathrm{K}}{31.7\,\mathrm{L}} \times (1000\,\mathrm{L\,m^{-3}}) = 1.55 \times 10^5\,\mathrm{Pa}$$

$$\text{and } w = \frac{-(1.55 \times 10^5\,\mathrm{Pa}) \times (31.7 - 22.8)\,\mathrm{L}}{1000\,\mathrm{L\,m^{-3}}} = \boxed{-1.38 \times 10^3\,\mathrm{J}}$$

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

(c) Free expansion is expansion against no force, so $w = \boxed{0}$, and $q = -w = \boxed{0}$ as well.

E2.8(b) The perfect gas law leads to

$$\frac{p_1 V}{p_2 V} = \frac{nRT_1}{nRT_2} \quad \text{or} \quad p_2 = \frac{p_1 T_2}{T_1} = \frac{(111\,\mathrm{kPa}) \times (356\,\mathrm{K})}{277\,\mathrm{K}} = \boxed{143\,\mathrm{kPa}}$$

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

$$\begin{aligned} q &= \int C_\mathrm{V}\,\mathrm{d}T \approx C_\mathrm{V}\Delta T = (2.5) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (2.00\,\mathrm{mol}) \times (356 - 277)\,\mathrm{K} \\ &= \boxed{3.28 \times 10^3\,\mathrm{J}} \end{aligned}$$

$$\Delta U = q + w = \boxed{3.28 \times 10^3\,\mathrm{J}}$$

E2.9(b) **(a)** $w = -p_{\text{ex}}\Delta V = \dfrac{-(7.7\times10^{3}\,\text{Pa})\times(2.5\,\text{L})}{1000\,\text{L m}^{-3}} = \boxed{-19\,\text{J}}$

(b) $$w = -nRT\ln\frac{V_\text{f}}{V_\text{i}}$$
$$= -\left(\frac{6.56\,\text{g}}{39.95\,\text{g mol}^{-1}}\right)\times(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(305\,\text{K})\times\ln\frac{(2.5+18.5)\,\text{L}}{18.5\,\text{L}}$$
$$= \boxed{-52.8\,\text{J}}$$

E2.10(b) Isothermal reversible work is

$$w = -nRT\ln\frac{V_\text{f}}{V_\text{i}} = -(1.77\times10^{-3}\,\text{mol})\times(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(273\,\text{K})\times\ln 0.224$$
$$= \boxed{+6.01\,\text{J}}$$

E2.11(b) $q = \Delta H = n(-\Delta_{\text{vap}}H^{\ominus}) = (2.00\,\text{mol})\times(-35.3\,\text{kJ mol}^{-1}) = \boxed{-70.6\,\text{kJ}}$

Because the condensation also occurs at constant pressure, the work is

$$w = -\int p_{\text{ex}}\,\text{d}V = -p\Delta V$$

The change in volume from a gas to a condensed phase is approximately equal in magnitude to the volume of the gas

$$w \approx -p(-V_{\text{vapor}}) = nRT = (2.00\,\text{mol})\times(8.3145\,\text{kJ K}^{-1}\,\text{mol}^{-1})\times(64+273)\,\text{K}$$
$$= \boxed{5.60\times10^{3}\,\text{J}}$$
$$\Delta U = q + w = (-70.6+5.60)\,\text{kJ} = \boxed{-65.0\,\text{kJ}}$$

E2.12(b) The reaction is

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

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

$$w = -p\Delta V = -pV_{\text{gas}} = -nRT = -\left(\frac{5.0\,\text{g}}{65.4\,\text{g mol}^{-1}}\right)$$
$$\times(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(23+273)\,\text{K}$$
$$= \boxed{-188\,\text{J}}$$

E2.13(b) $q = n\Delta_{\text{fus}}H^{\ominus} = \left(\dfrac{500\,\text{kg}}{39.1\times10^{-3}\,\text{kg mol}^{-1}}\right)\times(2.35\,\text{kJ mol}^{-1}) = \boxed{3.01\times10^{4}\,\text{kJ}}$

E2.14(b) **(a)** At constant pressure

$$q = \int C_\text{p}\,\text{d}T = \int_{0+273\,\text{K}}^{100+273\,\text{K}}[20.17 + (0.4001)T/\text{K}]\,\text{d}T\,\text{J K}^{-1}$$
$$= [(20.17)T + \tfrac{1}{2}(0.4001)\times(T^2/\text{K})]\,\text{J K}^{-1}\Big|_{273\,\text{K}}^{373\,\text{K}}$$
$$= [(20.17)\times(373-273) + \tfrac{1}{2}(0.4001)\times(373^2-273^2)]\,\text{J} = \boxed{14.9\times10^{3}\,\text{J}} = \Delta H$$

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

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

(b) ΔU and ΔH depend only on temperature in perfect gases. Thus, $\Delta H = \boxed{14.9\,\text{kJ}}$ and $\Delta U = \boxed{14.1\,\text{kJ}}$ as above. At constant volume, $w = \boxed{0}$ and $\Delta U = q$, so $q = \boxed{+14.1\,\text{kJ}}$

E2.15(b) For reversible adiabatic expansion

$$V_\text{f}T_\text{f}^c = V_\text{i}T_\text{i}^c \quad \text{so} \quad T_\text{f} = T_\text{i}\left(\frac{V_\text{i}}{V_\text{f}}\right)^{1/c}$$

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

So the final temperature is

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

E2.16(b) Reversible adiabatic work is

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

where the temperatures are related by [solution to Exercise 2.15b]

$$T_\text{f} = T_\text{i}\left(\frac{V_\text{i}}{V_\text{f}}\right)^{1/c}$$

where $c = \dfrac{C_{V,\text{m}}}{R} = \dfrac{C_{p,\text{m}} - R}{R} = \dfrac{(29.125 - 8.3145)\,\text{J K}^{-1}\,\text{mol}^{-1}}{8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}} = 2.503$

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

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

E2.17(b) For reversible adiabatic expansion

$$p_\text{f}V_\text{f}^\gamma = p_\text{i}V_\text{i}^\gamma \quad \text{so}$$

$$p_\text{f} = p_\text{i}\left(\frac{V_\text{i}}{V_\text{f}}\right)^\gamma = (87.3\,\text{Torr}) \times \left(\frac{500 \times 10^{-3}\,\text{L}}{3.0\,\text{L}}\right)^{1.3}$$

$$= \boxed{8.5\,\text{Torr}}$$

E2.18(b) For reversible adiabatic expansion

$$p_\text{f}V_\text{f}^\gamma = p_\text{i}V_\text{i}^\gamma \quad \text{so} \quad p_\text{f} = p_\text{i}\left(\frac{V_\text{i}}{V_\text{f}}\right)^\gamma$$

We need p_i, which we can obtain from the perfect gas law

$$pV = nRT \quad \text{so} \quad p = \frac{nRT}{V}$$

$$p_\mathrm{i} = \frac{\left(\frac{1.4\,\mathrm{g}}{18\,\mathrm{g\,mol^{-1}}}\right) \times (0.08206\,\mathrm{L\,atm\,K^{-1}\,mol^{-1}}) \times (300\,\mathrm{K})}{1.0\,\mathrm{L}} = \boxed{1.9\,\mathrm{atm}}$$

$$p_\mathrm{f} = (1.9\,\mathrm{atm}) \times \left(\frac{1.0\,\mathrm{L}}{3.0\,\mathrm{L}}\right)^{1.3} = \boxed{0.46\,\mathrm{atm}}$$

E2.19(b) The reaction is

$$n\text{-}\mathrm{C_6H_{14}} + \tfrac{19}{2}\mathrm{O_2} \rightarrow 6\mathrm{CO_2} + 7\mathrm{H_2O}$$

$$\Delta H^{\ominus} = \Delta_\mathrm{c} H^{\ominus}$$
$$= 6\Delta_\mathrm{f} H^{\ominus}(\mathrm{CO_2}) + 7\Delta_\mathrm{f} H^{\ominus}(\mathrm{H_2O}) - \Delta_\mathrm{f} H^{\ominus}(n\text{-}\mathrm{C_6H_{14}}) - \tfrac{19}{2}\Delta_\mathrm{f} H^{\ominus}(\mathrm{O_2})$$

so $\Delta_\mathrm{f} H^{\ominus}(n\text{-}\mathrm{C_6H_{14}}) = 6\Delta_\mathrm{f} H^{\ominus}(\mathrm{CO_2}) + 7\Delta_\mathrm{f} H^{\ominus}(\mathrm{H_2O}) - \Delta_\mathrm{c} H^{\ominus} - \tfrac{19}{2}\Delta_\mathrm{f} H^{\ominus}(\mathrm{O_2})$

$$\Delta_\mathrm{f} H^{\ominus}(n\text{-}\mathrm{C_6H_{14}}) = [6 \times (-393.51) + 7 \times (-285.83) + 4163 - (0)]\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta_\mathrm{f} H^{\ominus}(n\text{-}\mathrm{C_6H_{14}}) = \boxed{-199\,\mathrm{kJ\,mol^{-1}}}$$

E2.20(b) $q_p = nC_{p,\mathrm{m}}\Delta T$

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

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

E2.21(b) $\Delta H = q_p = \boxed{-2.3\,\mathrm{kJ}}$, the energy extracted from the sample.

$$q_p = C\Delta T \quad \text{so} \quad C = \frac{q_p}{\Delta T} = \frac{-2.3\,\mathrm{kJ}}{(275 - 288)\,\mathrm{K}} = \boxed{0.18\,\mathrm{kJ\,K^{-1}}}$$

E2.22(b) $\Delta H = q_p = C_p\Delta T = nC_{p,\mathrm{m}}\Delta T = (2.0\,\mathrm{mol}) \times (37.11\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (277 - 250)\,\mathrm{K}$

$$= \boxed{2.0 \times 10^3\,\mathrm{J\,mol^{-1}}}$$

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

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

$$= \boxed{1.6 \times 10^3\,\mathrm{J\,mol^{-1}}}$$

E2.23(b) In an adiabatic process, $q = \boxed{0}$. Work against a constant external pressure is

$$w = -p_\mathrm{ex}\Delta V = \frac{-(78.5 \times 10^3\,\mathrm{Pa}) \times (4 \times 15 - 15)\,\mathrm{L}}{1000\,\mathrm{L\,m^{-3}}} = \boxed{-3.5 \times 10^3\,\mathrm{J}}$$

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

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

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

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + nR\Delta T,$$

$$= -3.5 \times 10^3\,\mathrm{J} + (5.0\,\mathrm{mol}) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (-24\,\mathrm{K}) = \boxed{-4.5 \times 10^3\,\mathrm{J}}$$

E2.24(b) For adiabatic compression, $q = \boxed{0}$ and

$$w = C_V\Delta T = (2.5\,\text{mol}) \times (27.6\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (255 - 220)\,\text{K} = \boxed{2.4 \times 10^3\,\text{J}}$$

$$\Delta U = q + w = \boxed{2.4 \times 10^3\,\text{J}}$$

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + nR\Delta T$$

$$= 2.4 \times 10^3\,\text{J} + (2.5\,\text{mol}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (255 - 220)\,\text{K} = \boxed{3.1 \times 10^3\,\text{J}}$$

The initial and final states are related by

$$V_\text{f}T_\text{f}^c = V_\text{i}T_\text{i}^c \quad \text{so} \quad V_\text{f} = V_\text{i}\left(\frac{T_\text{i}}{T_\text{f}}\right)^c$$

where $c = \dfrac{C_{V,\text{m}}}{R} = \dfrac{27.6\,\text{J K}^{-1}\,\text{mol}^{-1}}{8.314\,\text{J K}^{-1}\,\text{mol}^{-1}} = 3.32$

$$V_\text{i} = \frac{nRT_\text{i}}{p_\text{i}} = \frac{2.5\,\text{mol} \times 8.3145\,\text{J K}^{-1}\,\text{mol}^{-1} \times 220\,\text{K}}{200 \times 10^3\,\text{Pa}} = 0.022\bar{9}\,\text{m}^3$$

$$V_\text{f} = (0.022\bar{9}\,\text{m}^3) \times \left(\frac{220\,\text{K}}{255\,\text{K}}\right)^{3.32} = 0.014\,\text{m}^3 = \boxed{14\,\text{L}}$$

$$p_\text{f} = \frac{nRT_\text{f}}{V_\text{f}} = \frac{2.5\,\text{mol} \times 8.3145\,\text{J K}^{-1}\,\text{mol}^{-1} \times 255\,\text{K}}{0.014\,\text{m}^3} = \boxed{3.8 \times 10^5\,\text{Pa}}$$

E2.25(b) For reversible adiabatic expansion

$$p_\text{f}V_\text{f}^\gamma = p_\text{i}V_\text{i}^\gamma \quad \text{so} \quad V_\text{f} = V_\text{i}\left(\frac{p_\text{i}}{p_\text{f}}\right)^{1/\gamma}$$

where $\gamma = \dfrac{C_{p,\text{m}}}{C_{p,\text{m}} - R} = \dfrac{20.8\,\text{J K}^{-1}\,\text{mol}^{-1}}{(20.8 - 8.3145)\,\text{J K}^{-1}\,\text{mol}^{-1}} = 1.67$

and $V_\text{i} = \dfrac{nRT_\text{i}}{p_\text{i}} = \dfrac{(1.5\,\text{mol}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (315\,\text{K})}{230 \times 10^3\,\text{Pa}} = 0.017\bar{1}\,\text{m}^3$

so $V_\text{f} = V_\text{i}\left(\dfrac{p_\text{i}}{p_\text{f}}\right)^{1/\gamma} = (0.017\bar{1}\,\text{m}^3) \times \left(\dfrac{230\,\text{kPa}}{170\,\text{kPa}}\right)^{1/1.67} = \boxed{0.020\bar{1}\,\text{m}^3}$

$$T_\text{f} = \frac{p_\text{f}V_\text{f}}{nR} = \frac{(170 \times 10^3\,\text{Pa}) \times (0.020\bar{1}\,\text{m}^3)}{(1.5\,\text{mol}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})} = \boxed{27\bar{5}\,\text{K}}$$

$$w = C_V\Delta T = (1.5\,\text{mol}) \times (20.8 - 8.3145)\,\text{J K}^{-1}\,\text{mol}^{-1} \times (27\bar{5} - 315\,\text{K}) = \boxed{-7.5 \times 10^2\,\text{J}}$$

E2.26(b) The expansion coefficient is defined as

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial \ln V}{\partial T}\right)_p$$

so for a small change in temperature (see Exercise 2.26a),

$$\Delta V = V_\text{i}\alpha\Delta T = (5.0\,\text{cm}^3) \times (0.354 \times 10^{-4}\,\text{K}^{-1}) \times (10.0\,\text{K}) = \boxed{1.8 \times 10^{-3}\,\text{cm}^3}$$

E2.27(b) In an adiabatic process, $q = \boxed{0}$. Work against a constant external pressure is

$$w = -p_{\text{ex}}\Delta V = -(110 \times 10^3\,\text{Pa}) \times \frac{(15\,\text{cm}) \times (22\,\text{cm}^2)}{(100\,\text{cm m}^{-1})^3} = \boxed{-36\,\text{J}}$$

$$\Delta U = q + w = \boxed{-36\,\text{J}}$$

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

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

$$= \frac{-36\,\text{J}}{(3.0\,\text{mol}) \times (29.355 - 8.3145)\,\text{J K}^{-1}\,\text{mol}^{-1}} = \boxed{-0.57\,\text{K}}$$

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + nR\Delta T$$

$$= -36\,\text{J} + (3.0\,\text{mol}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (-0.57\,\text{K}) = \boxed{-50\,\text{J}}$$

E2.28(b) The amount of N_2 in the sample is

$$n = \frac{15.0\,\text{g}}{28.013\,\text{g mol}^{-1}} = 0.535\,\text{mol}$$

(a) For reversible adiabatic expansion

$$p_\text{f}V_\text{f}^\gamma = p_\text{i}V_\text{i}^\gamma \quad \text{so} \quad V_\text{f} = V_\text{i}\left(\frac{p_\text{i}}{p_\text{f}}\right)^{1/\gamma}$$

where $\gamma = \dfrac{C_{p,\text{m}}}{C_{V,\text{m}}}$ where $C_{V,\text{m}} = (29.125 - 8.3145)\,\text{J K}^{-1}\,\text{mol}^{-1} = 20.811\,\text{J K}^{-1}\,\text{mol}^{-1}$

so $\gamma = \dfrac{29.125\,\text{J K}^{-1}\,\text{mol}^{-1}}{20.811\,\text{J K}^{-1}\,\text{mol}^{-1}} = 1.3995$

and $V_\text{i} = \dfrac{nRT_\text{i}}{p_\text{i}} = \dfrac{(0.535\,\text{mol}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (200\,\text{K})}{220 \times 10^3\,\text{Pa}} = 4.04 \times 10^{-3}\,\text{m}^3$

so $V_\text{f} = V_\text{i}\left(\dfrac{p_\text{i}}{p_\text{f}}\right)^{1/\gamma} = (4.04 \times 10^{-3}\,\text{m}^3) \times \left(\dfrac{220 \times 10^3\,\text{Pa}}{110 \times 10^3\,\text{Pa}}\right)^{1/1.3995} = 6.63 \times 10^{-3}\,\text{m}^3.$

$$T_\text{f} = \frac{p_\text{f}V_\text{f}}{nR} = \frac{(110 \times 10^3\,\text{Pa}) \times (6.63 \times 10^{-3}\,\text{m}^3)}{(0.535\,\text{mol}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})} = \boxed{164\,\text{K}}$$

(b) For adiabatic expansion against a constant external pressure

$$w = -p_{\text{ex}}\Delta V = C_V\Delta T \quad \text{so} \quad -p_{\text{ex}}(V_\text{f} - V_\text{i}) = C_V(T_\text{f} - T_\text{i})$$

In addition, the perfect gas law holds

$$p_\text{f}V_\text{f} = nRT_\text{f}$$

Solve the latter for T_f in terms of V_f, and insert into the previous relationship to solve for V_f

$$T_\text{f} = \frac{p_\text{f}V_\text{f}}{nR} \quad \text{so} \quad -p_{\text{ex}}(V_\text{f} - V_\text{i}) = C_V\left(\frac{p_\text{f}V_\text{f}}{nR} - T_\text{i}\right)$$

Collecting terms gives

$$C_VT_\text{i} + p_{\text{ex}}V_\text{i} = V_\text{f}\left(p_{\text{ex}} + \frac{C_Vp_\text{f}}{nR}\right) \quad \text{so} \quad V_\text{f} = \frac{C_VT_\text{i} + p_{\text{ex}}V_\text{i}}{p_{\text{ex}} + \left(\frac{C_{V,\text{m}}p_\text{f}}{R}\right)}$$

$$V_\mathrm{f} = \frac{(20.811\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (0.535\,\mathrm{mol}) \times (200\,\mathrm{K}) + (110 \times 10^3\,\mathrm{Pa}) \times (4.04 \times 10^{-3}\,\mathrm{m^3})}{110 \times 10^3\,\mathrm{Pa} + \left[\frac{(20.811\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (110 \times 10^3\,\mathrm{Pa})}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\right]}$$

$$V_\mathrm{f} = 6.93 \times 10^{-3}\,\mathrm{m^3}$$

Finally, the temperature is

$$T_\mathrm{f} = \frac{p_\mathrm{f} V_\mathrm{f}}{nR} = \frac{(110 \times 10^3\,\mathrm{Pa}) \times (6.93 \times 10^{-3}\,\mathrm{m^3})}{(0.535\,\mathrm{mol}) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})} = \boxed{171\,\mathrm{K}}$$

E2.29(b) At constant pressure

$$q = \Delta H = n\Delta_\mathrm{vap}H^\ominus = (0.75\,\mathrm{mol}) \times (32.0\,\mathrm{kJ\,mol^{-1}}) = \boxed{24.\bar{0}\,\mathrm{kJ}}$$

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

$$= -1.6 \times 10^3\,\mathrm{J} = \boxed{-1.6\,\mathrm{kJ}}$$

$$\Delta U = w + q = 24.\bar{0} - 1.6\,\mathrm{kJ} = \boxed{22.\bar{4}\,\mathrm{kJ}}$$

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

E2.30(b) The reaction is

$$\mathrm{C_6H_5OH} + 7\mathrm{O_2} \rightarrow 6\mathrm{CO_2} + 3\mathrm{H_2O}$$

$$\begin{aligned}\Delta_\mathrm{c}H^\ominus &= 6\Delta_\mathrm{f}H^\ominus(\mathrm{CO_2}) + 3\Delta_\mathrm{f}H^\ominus(\mathrm{H_2O}) - \Delta_\mathrm{f}H^\ominus(\mathrm{C_6H_5OH}) - 7\Delta_\mathrm{f}H^\ominus(\mathrm{O_2})\\ &= [6(-393.51) + 3(-285.83) - (-165.0) - 7(0)]\,\mathrm{kJ\,mol^{-1}}\\ &= \boxed{-3053.6\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

E2.31(b) The hydrogenation reaction is

$$\mathrm{C_4H_8} + \mathrm{H_2} \rightarrow \mathrm{C_4H_{10}}$$

$$\Delta_\mathrm{hyd}H^\ominus = \Delta_\mathrm{f}H^\ominus(\mathrm{C_4H_{10}}) - \Delta_\mathrm{f}H^\ominus(\mathrm{C_4H_8}) - \Delta_\mathrm{f}H^\ominus(\mathrm{H_2})$$

The enthalpies of formation of all of these compounds are available in Table 2.5. Therefore

$$\Delta_\mathrm{hyd}H^\ominus = [-126.15 - (-0.13)]\,\mathrm{kJ\,mol^{-1}} = -126.02\,\mathrm{kJ\,mol^{-1}}$$

If we had to, we could find $\Delta_\mathrm{f}H^\ominus(\mathrm{C_4H_8})$ from information about another of its reactions

$$\mathrm{C_4H_8} + 6\mathrm{O_2} \rightarrow 4\mathrm{CO_2} + 4\mathrm{H_2O},$$

$$\Delta_\mathrm{c}H^\ominus = 4\Delta_\mathrm{f}H^\ominus(\mathrm{CO_2}) + 4\Delta_\mathrm{f}H^\ominus(\mathrm{H_2O}) - \Delta_\mathrm{f}H^\ominus(\mathrm{C_4H_8}) - 6\Delta_\mathrm{f}H^\ominus(\mathrm{O_2})$$

so $\Delta_\mathrm{f}H^\ominus(\mathrm{C_4H_8}) = 4\Delta_\mathrm{f}H^\ominus(\mathrm{CO_2}) + 4\Delta_\mathrm{f}H^\ominus(\mathrm{H_2O}) - 6\Delta_\mathrm{f}H^\ominus(\mathrm{O_2}) - \Delta_\mathrm{c}H^\ominus$

$$\begin{aligned}&= [4(-393.51) + 4(-285.83) - 6(0) - (-2717)]\,\mathrm{kJ\,mol^{-1}}\\ &= 0.\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

$$\Delta_\mathrm{hyd}H^\ominus = -126.15 - (0.) - (0)\,\mathrm{kJ\,mol^{-1}} = \boxed{-126\,\mathrm{kJ\,mol^{-1}}}$$

This value compares favourably to that calculated above.

E2.32(b) We need $\Delta_f H^\ominus$ for the reaction

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

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

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

$$= \{-2368 + 3 \times (-241.8) - (-1941)\}\,\text{kJ mol}^{-1} = \boxed{-1152\,\text{kJ mol}^{-1}}$$

E2.33(b) The formation reaction is

$$C + 2H_2(g) + \tfrac{1}{2}O_2(g) + N_2(g) \rightarrow CO(NH_2)_2(s)$$

$$\Delta H = \Delta U + \Delta(pV) \approx \Delta U + RT\Delta n_{\text{gas}} \quad \text{so} \quad \Delta_f U^\ominus = \Delta_f H^\ominus - RT\Delta n_{\text{gas}}$$

$$\Delta_f U^\ominus = -333.51\,\text{kJ mol}^{-1} - (8.3145 \times 10^{-3}\,\text{kJ K}^{-1}\,\text{mol}^{-1}) \times (298.15\,\text{K}) \times (-7/2)$$

$$= \boxed{-324.83\,\text{kJ mol}^{-1}}$$

E2.34(b) The energy supplied to the calorimeter equals $C\Delta T$, where C is the calorimeter constant. That energy is

$$E = (2.86\,\text{A}) \times (22.5\,\text{s}) \times (12.0\,\text{V}) = 772\,\text{J}$$

So $C = \dfrac{E}{\Delta T} = \dfrac{772\,\text{J}}{1.712\,\text{K}} = \boxed{451\,\text{J K}^{-1}}$

E2.35(b) For anthracene the reaction is

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

$$\Delta_c U^\ominus = \Delta_c H^\ominus - \Delta n_g RT[26] \quad \Delta n_g = -\frac{5}{2}\,\text{mol}$$

$\Delta_c H^\ominus = -7163\,\text{kJ mol}^{-1}$ (*Handbook of Chemistry and Physics*)

$$\Delta_c U^\ominus = -7163\,\text{kJ mol}^{-1} - (-\tfrac{5}{2} \times 8.3 \times 10^{-3}\,\text{kJ K}^{-1}\,\text{mol}^{-1} \times 298\,\text{K}) \quad (\text{assume } T = 298\,\text{K})$$

$$= -7157\,\text{kJ mol}^{-1}$$

$$|q| = |q_V| = |n\Delta_c U^\ominus| = \left(\frac{2.25 \times 10^{-3}\,\text{g}}{172.23\,\text{g mol}^{-1}}\right) \times (7157\,\text{kJ mol}^{-1})$$

$$= 0.0935\,\text{kJ}$$

$$C = \frac{|q|}{\Delta T} = \frac{0.0935\,\text{kJ}}{1.35\,\text{K}} = 0.0693\,\text{kJ K}^{-1} = \boxed{69.3\,\text{J K}^{-1}}$$

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

$\Delta_c H^\ominus = -3054\,\text{kJ mol}^{-1}$ (Table 2.5)

$$\Delta_c U^\ominus = \Delta_c H^\ominus - \Delta n_g RT, \quad \Delta n_g = -\tfrac{3}{2}\,\text{mol}$$

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

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

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

$$\Delta T = \frac{|q|}{C} = \frac{4.37\bar{5}\,\mathrm{kJ}}{0.0693\,\mathrm{kJ\,K^{-1}}} = \boxed{+63.1\,\mathrm{K}}$$

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

E2.36(b) The reaction is

$$\mathrm{AgBr(s)} \rightarrow \mathrm{Ag^+(aq)} + \mathrm{Br^-(aq)}$$

$$\begin{aligned}\Delta_{\mathrm{sol}} H^\ominus &= \Delta_f H^\ominus(\mathrm{Ag^+}) + \Delta_f H^\ominus(\mathrm{Br^-}) - \Delta_f H^\ominus(\mathrm{AgBr}) \\ &= [105.58 + (-121.55) - (-100.37)]\,\mathrm{kJ\,mol^{-1}} = \boxed{+84.40\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

E2.37(b) The difference of the equations is C(gr) → C(d)

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

E2.38(b) Combustion of liquid butane can be considered as a two-step process: vaporization of the liquid followed by combustion of the butane gas. Hess's law states that the enthalpy of the overall process is the sum of the enthalpies of the steps

(a) $\Delta_c H^\ominus = [21.0 + (-2878)]\,\mathrm{kJ\,mol^{-1}} = \boxed{-2857\,\mathrm{kJ\,mol^{-1}}}$

(b) $\Delta_c H^\ominus = \Delta_c U^\ominus + \Delta(pV) = \Delta_c U^\ominus + RT\Delta n_g$ so $\Delta_c U^\ominus = \Delta_c H^\ominus - RT\Delta n_g$

The reaction is

$$\mathrm{C_4H_{10}(l)} + \tfrac{13}{2}\mathrm{O_2(g)} \rightarrow 4\mathrm{CO_2(g)} + 5\mathrm{H_2O(l)}$$

so $\Delta n_g = -2.5$ and

$$\begin{aligned}\Delta_c U^\ominus &= -2857\,\mathrm{kJ\,mol^{-1}} - (8.3145 \times 10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K}) \times (-2.5) \\ &= \boxed{-2851\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

E2.39(b) **(a)**
$$\begin{aligned}\Delta_r H^\ominus &= \Delta_f H^\ominus(\text{propene, g}) - \Delta_f H^\ominus(\text{cyclopropane, g}) = [(20.42) - (53.30)]\,\mathrm{kJ\,mol^{-1}} \\ &= \boxed{-32.88\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

(b) The net ionic reaction is obtained from

$$\mathrm{H^+(aq)} + \mathrm{Cl^-(aq)} + \mathrm{Na^+(aq)} + \mathrm{OH^-(aq)} \rightarrow \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)} + \mathrm{H_2O(l)}$$

and is $\mathrm{H^+(aq)} + \mathrm{OH^-(aq)} \rightarrow \mathrm{H_2O(l)}$

$$\begin{aligned}\Delta_r H^\ominus &= \Delta_f H^\ominus(\mathrm{H_2O, l}) - \Delta_f H^\ominus(\mathrm{H^+, aq}) - \Delta_f H^\ominus(\mathrm{OH^-, aq}) \\ &= [(-285.83) - (0) - (-229.99)]\,\mathrm{kJ\,mol^{-1}} \\ &= \boxed{-55.84\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

E2.40(b) reaction (3) = reaction (2) − 2(reaction (1))

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

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

(b)
$$\Delta_f H^\ominus(\mathrm{HI}) = \tfrac{1}{2}(52.96\,\mathrm{kJ\,mol^{-1}}) = \boxed{26.48\,\mathrm{kJ\,mol^{-1}}}$$
$$\Delta_f H^\ominus(\mathrm{H_2O}) = -\tfrac{1}{2}(483.64\,\mathrm{kJ\,mol^{-1}}) = \boxed{-241.82\,\mathrm{kJ\,mol^{-1}}}$$

E2.41(b)
$$\begin{aligned}\Delta_r H^\ominus &= \Delta_r U^\ominus + \Delta(pV) = \Delta_r U^\ominus + RT\Delta n_g\\ &= -772.7\,\mathrm{kJ\,mol^{-1}} + (8.3145\times10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})\times(5)\\ &= \boxed{-760.3\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

E2.42(b)

(1) $\tfrac{1}{2}\mathrm{N_2(g)} + \tfrac{1}{2}\mathrm{O_2(g)} + \tfrac{1}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{NOCl(g)} \quad \Delta_f H^\ominus = ?$

(2) $2\mathrm{NOCl(g)} \rightarrow 2\mathrm{NO(g)} + \mathrm{Cl_2(g)} \quad \Delta_r H^\ominus = +75.5\,\mathrm{kJ\,mol^{-1}}$

(3) $\tfrac{1}{2}\mathrm{N_2(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{NO(g)} \quad \Delta_f H^\ominus = 90.25\,\mathrm{kJ\,mol^{-1}}$

(1) = (3) − $\tfrac{1}{2}$(2)

$$\begin{aligned}\Delta_f H^\ominus(\mathrm{NOCl,\ g}) &= \left(90.25\,\mathrm{kJ\,mol^{-1}}\right) - \tfrac{1}{2}(75.5\,\mathrm{kJ\,mol^{-1}})\\ &= \boxed{52.5\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

E2.43(b)
$$\Delta_r H^\ominus(100^\circ\mathrm{C}) - \Delta_r H^\ominus(25^\circ\mathrm{C}) = \int_{25^\circ\mathrm{C}}^{100^\circ\mathrm{C}} \left(\frac{\partial \Delta_r H^\ominus}{\partial T}\right) \mathrm{d}T = \int_{25^\circ\mathrm{C}}^{100^\circ\mathrm{C}} \Delta_r C_{p,\mathrm{m}}\,\mathrm{d}T$$

Because $C_{p,\mathrm{m}}$ can frequently be parametrized as

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

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

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

Combining this expression with our original integral, we have

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

Now for the pieces

$$\Delta_r H^\ominus(25^\circ\mathrm{C}) = 2(-285.83\,\mathrm{kJ\,mol^{-1}}) - 2(0) - 0 = -571.66\,\mathrm{kJ\,mol^{-1}}$$
$$\Delta_r a = [2(75.29) - 2(27.28) - (29.96)]\,\mathrm{J\,K^{-1}\,mol^{-1}} = 0.06606\,\mathrm{kJ\,K^{-1}\,mol^{-1}}$$
$$\Delta_r b = [2(0) - 2(3.29) - (4.18)]\times10^{-3}\,\mathrm{J\,K^{-2}\,mol^{-1}} = -10.76\times10^{-6}\,\mathrm{kJ\,K^{-2}\,mol^{-1}}$$
$$\Delta_r c = [2(0) - 2(0.50)\times(-1.67)]\times10^{5}\,\mathrm{J\,K\,mol^{-1}} = 67\,\mathrm{kJ\,K\,mol^{-1}}$$

$$\Delta_r H^\ominus(100^\circ\mathrm{C}) = \Big[-571.66 + (373 - 298) \times (0.06606) + \tfrac{1}{2}(373^2 - 298^2) \times(-10.76 \times 10^{-6}) - (67) \times \left(\frac{1}{373} - \frac{1}{298}\right)\Big]\ \mathrm{kJ\,mol^{-1}}$$

$$= \boxed{-566.93\,\mathrm{kJ\,mol^{-1}}}$$

E2.44(b) The hydrogenation reaction is

$$(1)\ \mathrm{C_2H_2(g) + H_2(g) \rightarrow C_2\,H_4(g)} \quad \Delta_r H^\ominus(T) = ?$$

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

$$(2)\ \mathrm{H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l)} \quad \Delta_c H^\ominus(2) = -285.83\,\mathrm{kJ\,mol^{-1}}$$

$$(3)\ \mathrm{C_2H_4(g) + 3O_2(g) \rightarrow 2H_2O(l) + 2CO_2(g)} \quad \Delta_c H^\ominus(3) = -1411\,\mathrm{kJ\,mol^{-1}}$$

$$(4)\ \mathrm{C_2H_2(g) + \tfrac{5}{2}O_2(g) \rightarrow H_2O(l) + 2CO_2(g)} \quad \Delta_c H^\ominus(4) = -1300\,\mathrm{kJ\,mol^{-1}}$$

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

Hence,

(a)
$$\Delta_r H^\ominus(T) = \Delta_c H^\ominus(2) - \Delta_c H^\ominus(3) + \Delta_c H^\ominus(4)$$
$$= \{(-285.83) - (-1411) + (-1300)\}\,\mathrm{kJ\,mol^{-1}}$$
$$= \boxed{-175\,\mathrm{kJ\,mol^{-1}}}$$

$$\Delta_r U^\ominus(T) = \Delta_r H^\ominus(T) - \Delta n_g RT\ [26] \quad \Delta n_g = -1$$
$$= (-175\,\mathrm{kJ\,mol^{-1}} + 2.48\,\mathrm{kJ\,mol^{-1}}) = \boxed{-173\,\mathrm{kJ\,mol^{-1}}}$$

(b)
$$\Delta_r H^\ominus(348\,\mathrm{K}) = \Delta_r H^\ominus(298\,\mathrm{K}) + \Delta_r C_p(348\,\mathrm{K} - 298\,\mathrm{K}) \quad [\text{Example 2.7}]$$
$$\Delta_r C_p = \sum_J \nu_J C_{p,\mathrm{m}}(\mathrm{J})\ [47] = C_{p,\mathrm{m}}(\mathrm{C_2H_4, g}) - C_{p,\mathrm{m}}(\mathrm{C_2H_2, g}) - C_{p,\mathrm{m}}(\mathrm{H_2, g})$$
$$= (43.56 - 43.93 - 28.82) \times 10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}} = -29.19 \times 10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}}$$
$$\Delta_r H^\ominus(348\,\mathrm{K}) = (-175\,\mathrm{kJ\,mol^{-1}}) - (29.19 \times 10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}}) \times (50\,\mathrm{K})$$
$$= \boxed{-176\,\mathrm{kJ\,mol^{-1}}}$$

E2.45(b) The cycle is shown in Fig. 2.1.

$$-\Delta_{\mathrm{hyd}} H^\ominus(\mathrm{Ca^{2+}}) = -\Delta_{\mathrm{soln}} H^\ominus(\mathrm{CaBr_2}) - \Delta_f H^\ominus(\mathrm{CaBr_2, s}) + \Delta_{\mathrm{sub}} H^\ominus(\mathrm{Ca})$$
$$+\Delta_{\mathrm{vap}} H^\ominus(\mathrm{Br_2}) + \Delta_{\mathrm{diss}} H^\ominus(\mathrm{Br_2}) + \Delta_{\mathrm{ion}} H^\ominus(\mathrm{Ca})$$
$$+\Delta_{\mathrm{ion}} H^\ominus(\mathrm{Ca^+}) + 2\Delta_{\mathrm{eg}} H^\ominus(\mathrm{Br}) + 2\Delta_{\mathrm{hyd}} H^\ominus(\mathrm{Br^-})$$
$$= [-(-103.1) - (-682.8) + 178.2 + 30.91 + 192.9 + 589.7 + 1145 + 2(-331.0) + 2(-337)]\,\mathrm{kJ\,mol^{-1}}$$
$$= \boxed{1587\,\mathrm{kJ\,mol^{-1}}}$$

and $\Delta_{\mathrm{hyd}} H^\ominus(\mathrm{Ca^{2+}}) = \boxed{-1587\,\mathrm{kJ\,mol^{-1}}}$

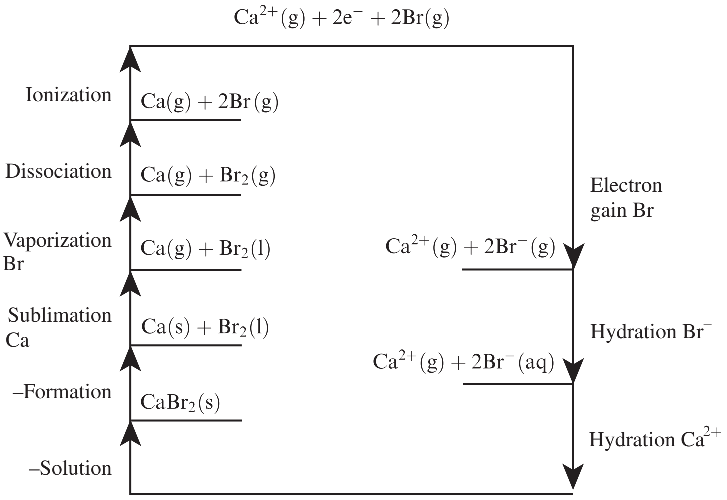


Figure 2.1

E2.46 **(a)** 2,2,4-trimethylpentane has five $C(H)_3(C)$ groups, one $C(H)_2(C)_2$ group, one $C(H)(C)_3$ group, and one $C(C)_4$ group.

(b) 2,2-dimethylpropane has four $C(H_3)(C)$ groups and one $C(C)_4$ group.

Using data from Table 2.7

(a) $[5 \times (-42.17) + 1 \times (-20.7) + 1 \times (-6.91) + 1 \times 8.16]\,\mathrm{kJ\,mol^{-1}} = \boxed{-230.3\,\mathrm{kJ\,mol^{-1}}}$

(b) $[4 \times (-42.17) + 1 \times 8.16]\,\mathrm{kJ\,mol^{-1}} = \boxed{-160.5\,\mathrm{kJ\,mol^{-1}}}$

Solutions to problems

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

Solutions to numerical problems

P2.4 We assume that the solid carbon dioxide has already evaporated and is contained within a closed vessel of $100\,\mathrm{cm^3}$ which is its initial volume. It then expands to a final volume which is determined by the perfect gas equation.

(a) $w = -p_{\mathrm{ex}}\Delta V$

$$V_{\mathrm{i}} = 100\,\mathrm{cm^3} = 1.00 \times 10^{-4}\,\mathrm{m^3}, \quad p = 1.0\,\mathrm{atm} = 1.0\overline{13} \times 10^5\,\mathrm{Pa}$$

$$V_{\mathrm{f}} = \frac{nRT}{p} = \left(\frac{5.0\,\mathrm{g}}{44.01\,\mathrm{g\,mol^{-1}}}\right) \times \left(\frac{(8.206 \times 10^{-2}\,\mathrm{L\,atm\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})}{1.0\,\mathrm{atm}}\right) = 2.7\overline{8}\,\mathrm{L}$$

$$= 2.7\overline{8} \times 10^{-3}\,\mathrm{m^3}$$

Therefore, $w = (-1.0\overline{13} \times 10^5\,\mathrm{Pa}) \times [(2.7\overline{8} \times 10^{-3}) - (1.00 \times 10^{-4})]\,\mathrm{m^3}$

$$= -27\overline{2}\,\mathrm{Pa\,m^3} = \boxed{-0.27\,\mathrm{kJ}}$$

(b) $$w = -nRT \ln \frac{V_\mathrm{f}}{V_\mathrm{i}} \ [2.13]$$
$$= \left(\frac{-5.0\,\mathrm{g}}{44.01\,\mathrm{g\,mol^{-1}}}\right) \times (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K}) \times \ln\left(\frac{2.7\overline{8} \times 10^{-3}\,\mathrm{m^3}}{1.00 \times 10^{-4}\,\mathrm{m^3}}\right)$$
$$= (-28\overline{2}) \times (\ln 27.8) = \boxed{-0.94\,\mathrm{kJ}}$$

P2.5 $$w = -p_\mathrm{ex}\Delta V \ [2.10] \qquad V_\mathrm{f} = \frac{nRT}{p_\mathrm{ex}} \gg V_\mathrm{i}; \quad \text{so} \quad \Delta V \approx V_\mathrm{f}$$

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

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

Even if there is no physical piston, the gas drives back the atmosphere, so the work is also $\boxed{-8.9\,\mathrm{kJ}}$

P2.7 The virial expression for pressure up to the second coefficient is

$$p = \left(\frac{RT}{V_\mathrm{m}}\right)\left(1 + \frac{B}{V_\mathrm{m}}\right) [1.22]$$
$$w = -\int_\mathrm{i}^\mathrm{f} p\,\mathrm{d}V = -n\int_\mathrm{i}^\mathrm{f} \left(\frac{RT}{V_\mathrm{m}}\right) \times \left(1 + \frac{B}{V_\mathrm{m}}\right) \mathrm{d}V_\mathrm{m} = -nRT\ln\left(\frac{V_\mathrm{f}}{V_\mathrm{i}}\right) + nBRT\left(\frac{1}{V_\mathrm{mf}} - \frac{1}{V_\mathrm{mi}}\right)$$

From the data,

$$nRT = (70 \times 10^{-3}\,\mathrm{mol}) \times (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (373\,\mathrm{K}) = 21\overline{7}\,\mathrm{J}$$
$$V_\mathrm{mi} = \frac{5.25\,\mathrm{cm^3}}{70\,\mathrm{mmol}} = 75.\overline{0}\,\mathrm{cm^3\,mol^{-1}}, \quad V_\mathrm{mf} = \frac{6.29\,\mathrm{cm^3}}{70\,\mathrm{mmol}} = 89.\overline{9}\,\mathrm{cm^3\,mol^{-1}}$$

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

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

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

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

$$\Delta H = \Delta U + \Delta(pV) \quad \text{with } pV = nRT\left(1 + \frac{B}{V_\mathrm{m}}\right)$$
$$\Delta(pV) = nRTB\Delta\left(\frac{1}{V_\mathrm{m}}\right) = nRTB\left(\frac{1}{V_\mathrm{mf}} - \frac{1}{V_\mathrm{mi}}\right), \quad \text{as } \Delta T = 0$$
$$= (21\overline{7}\,\mathrm{J}) \times (6.3\overline{4} \times 10^{-2}) = 13.\overline{8}\,\mathrm{J}$$

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

P2.8 $$q_p = \Delta H = n\Delta_\mathrm{vap}H = \boxed{+22.2\,\mathrm{kJ}} \qquad \Delta_\mathrm{vap}H = \frac{q_p}{n} = \left(\frac{18.02\,\mathrm{g\,mol^{-1}}}{10\,\mathrm{g}}\right) \times (22.2\,\mathrm{kJ})$$
$$= \boxed{+40\,\mathrm{kJ\,mol^{-1}}}$$

$$\Delta U = \Delta H - \Delta n_g RT, \quad \Delta n_g = \frac{10\,\text{g}}{18.02\,\text{g mol}^{-1}} = 0.55\bar{5}\,\text{mol}$$

Hence $\Delta U = (22.2\,\text{kJ}) - (0.55\bar{5}\,\text{mol}) \times (8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (373\,\text{K}) = (22.2\,\text{kJ}) - (1.7\bar{2}\,\text{kJ}) = \boxed{+20.5\,\text{kJ}}$

$$w = \Delta U - q \text{ [as } \Delta U = q + w] = (20.5\,\text{kJ} - 22.2\,\text{kJ}) = \boxed{-1.7\,\text{kJ}}$$

P2.11 This is constant-pressure process; hence $q_p(\text{object}) + q_p(\text{methane}) = 0$.

$$q_p(\text{object}) = -32.5\,\text{kJ} \qquad q_p(\text{methane}) = n\Delta_{\text{vap}}H = 32.5\,\text{kJ}$$

$$n = \frac{q_p(\text{methane})}{\Delta_{\text{vap}}H} \qquad \Delta_{\text{vap}}H = 8.18\,\text{kJ mol}^{-1} \text{ (Table 2.3)}$$

The volume occupied by the methane gas at a pressure p is $V = \dfrac{nRT}{p}$; therefore

$$V = \frac{qRT}{p\Delta_{\text{vap}}H} = \frac{(32.5\,\text{kJ}) \times (8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (112\,\text{K})}{(1.013 \times 10^5\,\text{Pa}) \times (8.18\,\text{kJ mol}^{-1})}$$

$$= 3.65 \times 10^{-2}\,\text{m}^3 = \boxed{36.5\,\text{L}}$$

P2.14 $\text{Cr(C}_6\text{H}_6)_2\text{(s)} \rightarrow \text{Cr(s)} + 2\text{C}_6\text{H}_6\text{(g)} \quad \Delta n_g = +2\,\text{mol}$

$$\Delta_r H^\ominus = \Delta_r U^\ominus + 2RT, \text{ from [26]}$$

$$= (8.0\,\text{kJ mol}^{-1}) + (2) \times (8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (583\,\text{K}) = \boxed{+17.7\,\text{kJ mol}^{-1}}$$

In terms of enthalpies of formation

$$\Delta_r H^\ominus = (2) \times \Delta_f H^\ominus(\text{benzene, 583 K}) - \Delta_f H^\ominus(\text{metallocene, 583 K})$$

or $\Delta_r H^\ominus(\text{metallocene, 583 K}) = 2\Delta_f H^\ominus(\text{C}_6\text{H}_6\text{, g, 583 K}) - 17.7\,\text{kJ mol}^{-1}$

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

$$\begin{aligned}\Delta_f H^\ominus(\text{benzene, 583 K}) = {} & \Delta_f H^\ominus(\text{benzene, 298 K}) + (T_b - 298\,\text{K})C_p(\text{l}) + (583\,\text{K} - T_b)C_p(\text{g}) \\ & + \Delta_{\text{vap}}H^\ominus - 6 \times (583\,\text{K} - 298\,\text{K})C_p(\text{graphite}) \\ & - 3 \times (583\,\text{K} - 298\,\text{K})C_p(\text{H}_2,\ \text{g})\end{aligned}$$

where T_b is the boiling temperature of benzene (353 K). We shall assume that the heat capacities of graphite and hydrogen are approximately constant in the range of interest, and use their values from Table 2.6

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

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

P2.17 We must relate the formation of $DyCl_3$ to the three reactions for which we have information

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

This reaction can be seen as a sequence of reaction (2), three times reaction (3), and the reverse of reaction (1), so

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

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

P2.19 **(a)**

$$\Delta_r H^\ominus = \Delta_f H^\ominus(SiH_3OH) - \Delta_f H^\ominus(SiH_4) - \tfrac{1}{2}\Delta_f H^\ominus(O_2) = [-67.5 - 34.3 - \tfrac{1}{2}(0)]\,\text{kJ mol}^{-1} = \boxed{-101.8\,\text{kJ mol}^{-1}}$$

(b)

$$\Delta_r H^\ominus = \Delta_f H^\ominus(SiH_2O) - \Delta_f H^\ominus(H_2O) - \Delta_f H^\ominus(SiH_4) - \Delta_f H^\ominus(O_2) = [-23.5 + (-285.83) - 34.3 - 0]\,\text{kJ mol}^{-1} = \boxed{-344.2\,\text{kJ mol}^{-1}}$$

(c)

$$\Delta_r H^\ominus = \Delta_f H^\ominus(SiH_2O) - \Delta_f H^\ominus(SiH_3OH) - \Delta_f H^\ominus(H_2) = [-23.5 - (-67.5) - 0]\,\text{kJ mol}^{-1} = \boxed{44.0\,\text{kJ mol}^{-1}}$$

P2.21 When necessary we assume perfect gas behaviour, also, the symbols w, V, q, U, etc. will represent molar quantities in all cases.

$$w = -\int p\,\mathrm{d}V = -\int \frac{C}{V^n}\,\mathrm{d}V = -C\int \frac{\mathrm{d}V}{V^n}$$

For $n \neq 1$, this becomes (we treat the case $n = 1$ later)

$$(1)\quad w = \frac{C}{n-1}V^{-n+1}\Big|_{\text{initial state},\,V_i}^{\text{final state},\,V_f} = \frac{C}{n-1}\left\{\frac{1}{V_f^{n-1}} - \frac{1}{V_i^{n-1}}\right\}$$

$$= \frac{p_iV_i^n}{n-1} \times \left\{\frac{1}{V_f^{n-1}} - \frac{1}{V_i^{n-1}}\right\} \quad [\text{because } pV^n = C]$$

$$= \frac{p_iV_iV_i^{n-1}}{n-1} \times \left\{\frac{1}{V_f^{n-1}} - \frac{1}{V_i^{n-1}}\right\}$$

$$(2)\quad w = \frac{p_iV_i}{n-1} \times \left\{\left(\frac{V_i}{V_f}\right)^{n-1} - 1\right\} = \frac{RT_i}{n-1} \times \left\{\left(\frac{V_i}{V_f}\right)^{n-1} - 1\right\}$$

But $pV^n = C$ or $V = \left(\frac{C}{p}\right)^{1/n}$ for $n \neq 0$ (we treat $n = 0$ as a special case below). So,

$$(3)\quad \left(\frac{V_i}{V_f}\right)^{n-1} = \left(\frac{p_f}{p_i}\right)^{\frac{n-1}{n}} \quad n \neq 0$$

Substitution of eqn 3 into eqn 2 and using '1' and '2' to represent the initial and final states, respectively, yields

$$(4)\quad \boxed{w = \frac{RT_1}{n-1} \times \left\{\left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}} - 1\right\}} \text{ for } n \neq 0 \text{ and } n \neq 1$$

In the case for which $n = 0$, eqn 1 gives

$$w = \frac{C}{0-1} \times \left\{ \frac{1}{V_\mathrm{f}^{-1}} - \frac{1}{V_\mathrm{i}^{-1}} \right\} = -C(V_\mathrm{f} - V_\mathrm{i})$$

$$= -(pV^0)_{\text{any state}} \times (V_\mathrm{f} - V_\mathrm{i}) = -(p)_{\text{any state}}(V_\mathrm{f} - V_\mathrm{i})$$

(5) $\boxed{w = -p\Delta V}$ for $n = 0$, isobaric case

In the case for which $n = 1$

$$w = -\int p\,\mathrm{d}V = -\int \frac{C}{V^n}\,\mathrm{d}V = -\int \frac{C}{V}\,\mathrm{d}V = -C\ln\left(\frac{V_\mathrm{f}}{V_\mathrm{i}}\right)$$

$$w = (pV^n)_{\text{any state}} \ln\left(\frac{V_\mathrm{i}}{V_\mathrm{f}}\right) = (pV)_{\text{any state}} \ln\left(\frac{V_\mathrm{i}}{V_\mathrm{f}}\right)$$

$$= (RT)_{\text{any state}} \ln\left(\frac{V_\mathrm{i}}{V_\mathrm{f}}\right)$$

(6) $\boxed{w = RT\ln\left(\frac{V_1}{V_2}\right) = RT\ln\left(\frac{p_2}{p_1}\right)}$ for $n = 1$, isothermal case

To derive the equation for heat, note that, for a perfect gas, $\Delta U = q + w = C_V(T_\mathrm{f} - T_\mathrm{i})$. So

(7)

$$q + w = C_V T_\mathrm{i}\left(\frac{T_\mathrm{f}}{T_\mathrm{i}} - 1\right) = C_V T_\mathrm{i}\left(\frac{p_\mathrm{f} V_\mathrm{f}}{p_\mathrm{i} V_\mathrm{i}} - 1\right)$$

$$= C_V T_\mathrm{i}\left(\frac{V_\mathrm{i}^{n-1}}{V_\mathrm{f}^{n-1}} - 1\right) \quad [\text{because } pV^n = C]$$

$$= C_V T_\mathrm{i}\left(\left(\frac{p_\mathrm{f}}{p_\mathrm{i}}\right)^{\frac{n-1}{n}} - 1\right) \quad [\text{using eqn 3 } (n \neq 0)]$$

$$q = C_V T_\mathrm{i}\left(\left(\frac{p_\mathrm{f}}{p_\mathrm{i}}\right)^{\frac{n-1}{n}} - 1\right) - \frac{RT_\mathrm{i}}{n-1}\left(\left(\frac{p_\mathrm{f}}{p_\mathrm{i}}\right)^{\frac{n-1}{n}} - 1\right) \quad [\text{using eqn 4 } (n \neq 0,\ n \neq 1)]$$

$$= \left(C_V T_\mathrm{i} - \frac{RT_\mathrm{i}}{n-1}\right) \times \left\{\left(\frac{p_\mathrm{f}}{p_\mathrm{i}}\right)^{\frac{n-1}{n}} - 1\right\}$$

$$= \left(\frac{C_V}{R} - \frac{1}{n-1}\right) RT_\mathrm{i}\left\{\left(\frac{p_\mathrm{f}}{p_\mathrm{i}}\right)^{\frac{n-1}{n}} - 1\right\}$$

$$= \left(\frac{C_V}{C_p - C_V} - \frac{1}{n-1}\right) RT_\mathrm{i}\left\{\left(\frac{p_\mathrm{f}}{p_\mathrm{i}}\right)^{\frac{n-1}{n}} - 1\right\} \quad [2.31]$$

$$= \left(\frac{C_V}{C_V\left(\frac{C_p}{C_V} - 1\right)} - \frac{1}{n-1}\right) RT_\mathrm{i}\left\{\left(\frac{p_\mathrm{f}}{p_\mathrm{i}}\right)^{\frac{n-1}{n}} - 1\right\}$$

$$= \left(\frac{1}{\gamma - 1} - \frac{1}{n-1}\right) RT_\mathrm{i}\left\{\left(\frac{p_\mathrm{f}}{p_\mathrm{i}}\right)^{\frac{n-1}{n}} - 1\right\} \quad [2.37]$$

$$= \frac{(n-1) - (\gamma - 1)}{(n-1) \times (\gamma - 1)} RT_\mathrm{i}\left\{\left(\frac{p_\mathrm{f}}{p_\mathrm{i}}\right)^{\frac{n-1}{n}} - 1\right\}$$

$$= \left[\frac{n - \gamma}{(n-1) \times (\gamma - 1)}\right] RT_\mathrm{i}\left\{\left(\frac{p_\mathrm{f}}{p_\mathrm{i}}\right)^{\frac{n-1}{n}} - 1\right\}$$

Using the symbols '1' and '2' this becomes

$$\boxed{q = \left[\frac{n-\gamma}{(n-1)\times(\gamma-1)}\right] RT_1 \left\{\left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}} - 1\right\}} \text{ for } n \neq 0, n \neq 1 \tag{8}$$

In the case for which $n = 1$, (the isothermal case) eqns 7 and 6 yield

$$\boxed{q = -w = RT \ln \frac{V_2}{V_1} = RT \ln \frac{p_1}{p_2}} \text{ for } n = 1, \text{ isothermal case} \tag{9}$$

In the case for which $n = 0$ (the isobaric case) eqns 7 and 5 yield

$$\begin{aligned} q &= \Delta U - w = C_V(T_\mathrm{f} - T_\mathrm{i}) + p(V_\mathrm{f} - V_\mathrm{i}) \\ &= C_V(T_\mathrm{f} - T_\mathrm{i}) + R(T_\mathrm{f} - T_\mathrm{i}) \\ &= (C_V + R) \times (T_\mathrm{f} - T_\mathrm{i}) = C_p(T_\mathrm{f} - T_\mathrm{i}) \end{aligned}$$

$$\boxed{q = C_p \Delta T} \text{ for } n = 0, \text{ isobaric case} \tag{10}$$

A summary of the equations for the process $pV^n = C$ is given below

n	w	q	Process type
0	$-p\Delta V$	$C_p\Delta T$	Isobaric [2.29]
1	$RT \ln\left(\frac{p_2}{p_1}\right)$	$RT \ln\left(\frac{p_1}{p_2}\right)$	Isothermal [2.13]
γ	$C_V\Delta T^*$	0	Adiabatic [2.33]
∞	0	$C_V\Delta T^\dagger$	†Isochoric [2.22]
Any n except $n = 0$ and $n = 1$	$\frac{RT_1}{n-1}\left\{\left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}} - 1\right\}$	$\left[\frac{n-\gamma}{(n-1)(\gamma-1)}\right] RT_1 \left\{\left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}} - 1\right\}$	

* Equation 8 gives this result when $n = \gamma$

$$q = \left[\frac{\gamma-\gamma}{(\gamma-1)\times(\gamma-1)}\right] RT_1 \left\{\left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right\} = 0$$

Therefore, $w = \Delta U - q = \Delta U = C_V\Delta T$.

† Equation 8 gives this result in the limit as $n \to \infty$

$$\begin{aligned} \lim_{n\to\infty} q &= \left(\frac{1}{\gamma-1}\right) RT_1 \left\{\frac{p_2}{p_1} - 1\right\} \\ &= \left(\frac{C_V}{C_p - C_V}\right) RT_1 \left\{\frac{p_2 - p_1}{p_1}\right\} \\ &= \left(\frac{C_V}{C_p - C_V}\right) V_1(p_2 - p_1) \end{aligned}$$

However, $\lim_{n\to\infty} V = \lim_{n\to\infty} \frac{C}{p^{1/n}} = \frac{C}{p^0} = C$. So in this limit an isochoric process is being discussed and $V_2 = V_1 = V$ and

$$\lim_{n\to\infty} q = \frac{C_V}{C_p - C_V}(p_2V_2 - p_1V_1) = \frac{C_V}{R}(RT_2 - RT_1) = C_V\Delta T$$

Solutions to theoretical problems

P2.23 $\mathrm{d}w = -F(x)\,\mathrm{d}x$ [2.6], with $z = x$

Hence to move the mass from x_1 to x_2

$$w = -\int_{x_1}^{x_2} F(x)\,\mathrm{d}x$$

Inserting $F(x) = F\sin\left(\frac{\pi x}{a}\right)$ [F = constant]

$$w = -F\int_{x_1}^{x_2} \sin\left(\frac{\pi x}{a}\right)\mathrm{d}x = \frac{Fa}{\pi}\left(\cos\frac{\pi x_2}{a} - \cos\frac{\pi x_1}{a}\right)$$

(a) $x_2 = a, \quad x_1 = 0, \qquad w = \frac{Fa}{\pi}(\cos\pi - \cos 0) = \boxed{\frac{-2Fa}{\pi}}$

(b) $x_2 = 2a, \quad x_1 = 0, \qquad w = \frac{Fa}{\pi}(\cos 2\pi - \cos 0) = \boxed{0}$

The work done by the machine in the first part of the cycle is regained by the machine in the second part of the cycle, and hence no net work is done by the machine.

P2.25 **(a)** The amount is a constant; therefore, it can be calculated from the data for any state. In state A, $V_A = 10\,\mathrm{L}$, $p_A = 1\,\mathrm{atm}$, $T_A = 313\,\mathrm{K}$. Hence

$$n = \frac{p_A V_A}{RT_A} = \frac{(1.0\,\mathrm{atm})\times(10\,\mathrm{L})}{(0.0821\,\mathrm{L\,atm\,K^{-1}\,mol^{-1}})\times(313\,\mathrm{K})} = \boxed{0.38\bar{9}\,\mathrm{mol}}$$

Since T is a constant along the isotherm, Boyle's law applies

$$p_A V_A = p_B V_B; \quad V_B = \frac{p_A}{p_B}V_A = \left(\frac{1.0\,\mathrm{atm}}{20\,\mathrm{atm}}\right)\times(10\,\mathrm{L}) = \boxed{0.50\,\mathrm{L}} \quad V_C = V_B = \boxed{0.50\,\mathrm{L}}$$

(b) Along ACB, there is work only from A → C; hence

$$w = -p_{\mathrm{ext}}\Delta V[10] = (-1.0\times10^5\,\mathrm{Pa})\times(0.50-10)\,\mathrm{L}\times(10^{-3}\mathrm{m^3\,L^{-1}}) = 9.5\times10^2\,\mathrm{J}$$

Along ADB, there is work only from D → B; hence

$$w = -p_{\mathrm{ext}}\Delta V[10] = (-20\times10^5\,\mathrm{Pa})\times(0.50-10)\,\mathrm{L}\times(10^{-3}\mathrm{m^3\,L^{-1}}) = \boxed{1.9\times10^4\,\mathrm{J}}$$

(c)
$$w = -nRT\ln\frac{V_B}{V_A}[13] = (-0.38\bar{9})\times(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(313\,\mathrm{K})\times\left(\ln\frac{0.5}{10}\right)$$
$$= \boxed{+3.0\times10^3\,\mathrm{J}}$$

The work along each of these three paths is different, illustrating the fact that work is not a state property.

(d) Since the initial and final states of all three paths are the same, ΔU for all three paths is the same. Path AB is isothermal; hence $\boxed{\Delta U = 0}$, since the gas is assumed to be perfect. Therefore, $\boxed{\Delta U = 0}$ for paths ACB and ADB as well and the fact that $C_{V,\mathrm{m}} = \frac{3}{2}R$ is not needed for the solution.

In each case, $q = \Delta U - w = -w$, thus for

path ACB, $q = \boxed{-9.5 \times 10^2\,\mathrm{J}}$; path ADB, $q = \boxed{-1.9 \times 10^4\,\mathrm{J}}$;

path AB, $q = \boxed{-3.0 \times 10^3\,\mathrm{J}}$

The heat is different for all three paths; heat is not a state property.

P2.27 Since ΔU is independent of path $\Delta U(\mathrm{A} \rightarrow \mathrm{B}) = q(\mathrm{ACB}) + w(\mathrm{ACB}) = 80\,\mathrm{J} - 30\,\mathrm{J} = 50\,\mathrm{J}$

(a) $\Delta U = 50\,\mathrm{J} = q(ADB) + w(ADB)$

$q(ADB) = 50\,\mathrm{J} - (-10\,\mathrm{J}) = \boxed{+60\,\mathrm{J}}$

(b) $q(\mathrm{B} \rightarrow \mathrm{A}) = \Delta U(\mathrm{B} \rightarrow \mathrm{A}) - w(\mathrm{B} \rightarrow \mathrm{A}) = -50\,\mathrm{J} - (+20\,\mathrm{J}) = \boxed{-70\,\mathrm{J}}$

The system liberates heat.

(c) $\Delta U(\mathrm{ADB}) = \Delta U(\mathrm{A} \rightarrow \mathrm{D}) + \Delta U(\mathrm{D} \rightarrow \mathrm{B});\quad 50\,\mathrm{J} = 40\,\mathrm{J} + \Delta U(\mathrm{D} \rightarrow \mathrm{B})$

$\Delta U(\mathrm{D} \rightarrow \mathrm{B}) = 10\,\mathrm{J} = q(\mathrm{D} \rightarrow \mathrm{B}) + w(\mathrm{D} \rightarrow \mathrm{B});\quad w(\mathrm{D} \rightarrow \mathrm{B}) = 0,$

hence $q(\mathrm{D} \rightarrow \mathrm{B}) = \boxed{+10\,\mathrm{J}}$

$q(\mathrm{ADB}) = 60\,\mathrm{J}[\text{part a}] = q(\mathrm{A} \rightarrow \mathrm{D}) + q(\mathrm{D} \rightarrow \mathrm{B})$

$60\,\mathrm{J} = q(\mathrm{A} \rightarrow \mathrm{D}) + 10\,\mathrm{J};\quad q(\mathrm{A} \rightarrow \mathrm{D}) = \boxed{+50\,\mathrm{J}}$

P2.29

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

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

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

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

$$T_\mathrm{r} = \frac{T}{T_\mathrm{c}},\quad V_\mathrm{r} = \frac{V}{V_\mathrm{c}},\qquad T_\mathrm{c} = \frac{8a}{27Rb},\quad V_\mathrm{c} = 3nb\quad [\text{Table 1.6}]$$

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

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

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

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

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

Solutions to applications

P2.30 **(a)** $$q = n\Delta_c H^\ominus = \frac{1.5\,\text{g}}{342.3\,\text{g mol}} \times (-5645\,\text{kJ mol}^{-1}) = \boxed{-25\,\text{kJ}}$$

(b) Effective work available is $\approx 25\,\text{kJ} \times 0.25 = 6.2\,\text{kJ}$

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

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

(c) The energy released as heat is

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

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

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

P2.35 **(a)** and **(b)**. The table displays computed enthalpies of formation (semi-empirical, PM3 level, PC Spartan Pro™), enthalpies of combustion based on them (and on experimental enthalpies of formation of H_2O(l) and CO_2(g), -285.83 and $-393.51\,\text{kJ mol}^{-1}$ respectively), experimental enthalpies of combustion from Table 2.5, and the relative error in enthalpy of combustion.

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

The combustion reactions can be expressed as:

$$C_nH_{2n+2}(\text{g}) + \left(\frac{3\text{n}+1}{2}\right) O_2(\text{g}) \to n\,CO_2(\text{g}) + (n+1)\,H_2O(1).$$

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

$$\Delta_c H^\ominus = n\Delta_f H^\ominus(CO_2) + (n+1)\Delta_f H^\ominus(H_2O) - \Delta_f H^\ominus(C_nH_{2n+2}),$$

where we have left out $\Delta_f H^\ominus(O_2) = 0$. The % error is defined as:

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

The agreement is quite good.

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

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

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

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

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

Compound	$M/(\mathrm{g\,mol^{-1}})$	$\Delta_c H^{\ominus}/\mathrm{kJ\,mol^{-1}}$	$\ln M(\mathrm{g\,mol^{-1}})$	$\ln|\Delta_c H^{\ominus}/\mathrm{kJ\,mol^{-1}}|$
$CH_4(g)$	16.04	−890	2.775	6.81
$C_2H_6(g)$	30.07	−1560	3.404	7.358
$C_3H_8(g)$	44.10	−2220	3.786	7.708
$C_4H_{10}(g)$	58.12	−2878	4.063	7.966
$C_5H_{12}(g)$	72.15	−3537	4.279	8.172

The plot is shown below in Fig 2.2.

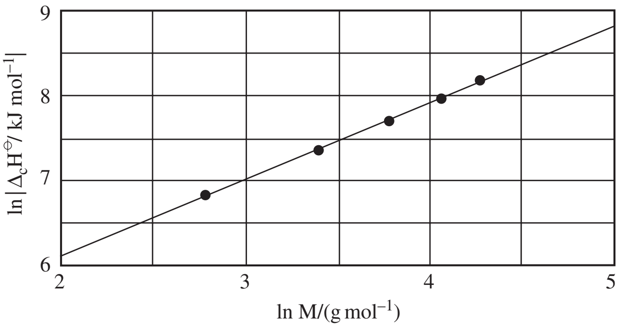


Figure 2.2

The linear least-squares fit equation is:

$$\ln|\Delta_c H^{\ominus}/\mathrm{kJ\,mol^{-1}}| = 4.30 + 0.093\ \ln M/(\mathrm{g\,mol^{-1}})\ r^2 = 1.00$$

These compounds support the proposed relationships, with

$$\boxed{n = 0.903}$$

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

The aggreement of these theoretical values of k and n with the experimental values obtained in P2.34 is rather good.

P2.37 In general, the reaction

$$\mathrm{RH} \rightarrow \mathrm{R} + \mathrm{H}$$

has a standard enthalpy (the bond dissociation enthalpy) of

$$\Delta H^{\ominus}(\mathrm{R{-}H}) = \Delta_f H^{\ominus}(\mathrm{R}) + \Delta_f H^{\ominus}(\mathrm{H}) - \Delta_f H^{\ominus}(\mathrm{RH})$$

so $\Delta_f H^{\ominus}(\mathrm{R}) = \Delta H^{\ominus}(\mathrm{R{-}H}) - \Delta_f H^{\ominus}(\mathrm{H}) + \Delta_f H^{\ominus}(\mathrm{RH})$

Since we are provided with bond dissociation energies, we need

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + RT\Delta n_g$$

So $\Delta_r H^{\ominus}(\mathrm{R{-}H}) = \Delta_r U^{\ominus}(\mathrm{R{-}H}) + RT$

and $\Delta_r H^{\ominus}(\mathrm{R}) = \Delta_r H^{\ominus}(\mathrm{R{-}H}) + RT - \Delta_f H^{\ominus}(\mathrm{H}) + \Delta_f H^{\ominus}(\mathrm{RH})$

Inserting the bond dissociation energies and enthalpies of formation from Tables 2.5 and 2.6, we obtain

$$\Delta_f H^{\ominus}(C_2H_5) = (420.5 + 2.48 - 217.97 - 84.68)\,\mathrm{kJ\,mol^{-1}} = \boxed{120.3\,\mathrm{kJ\,mol^{-1}}}$$

$$\begin{aligned}\Delta_f H^{\ominus}(sec\text{-}C_4H_9) &= (410.5 + 2.48 - 217.97 - 126.15)\,\mathrm{kJ\,mol^{-1}}\\ &= \boxed{68.9\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

$$\Delta_f H^{\ominus}(tert\text{-}C_4H_9) = (398.3 + 2.48 - 217.97 - 134.2)\,\mathrm{kJ\,mol^{-1}} = \boxed{48.1\,\mathrm{kJ\,mol^{-1}}}$$

3 The First Law: the machinery

Solutions to exercises

Discussion questions

E3.1(b) The following list includes only those state functions that we have encountered in the first three chapters. More will be encountered in later chapters.

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

E3.2(b) One can use the general expression for π_T given in *Justification* 3.3 to derive its specific form for a van der Waals gas as given in Exercise 3.14(a), that is, $\pi_T = a/V_m^2$. (The derivation is carried out in Example 5.1.) For an isothermal expansion in a van der Waals gas $dU_m = (a/V_m)^2$. Hence $\Delta U_m = -a(1/V_{m,2} - 1/V_{m,1})$. See this derivation in the solution to Exercise 3.14(a). This formula corresponds to what one would expect for a real gas. As the molecules get closer and closer the molar volume gets smaller and smaller and the energy of attraction gets larger and larger.

E3.3(b) The solution to Problem 3.23 shows that the Joule–Thomson coefficient can be expressed in terms of the parameters representing the attractive and repulsive interactions in a real gas. If the attractive forces predominate then expanding the gas will reduce its energy and hence its temperature. This reduction in temperature could continue until the temperature of the gas falls below its condensation point. This is the principle underlying the liquefaction of gases with the Linde Refrigerator which utilizes the Joule–Thomson effect. See Section 3.4 for a more complete discussion.

Numerical exercises

E3.4(b) A function has an exact differential if its mixed partial derivatives are equal. That is, $f(x, y)$ has an exact differential if

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

(a) $$\frac{\partial f}{\partial x} = 3x^2y^2 \quad \text{and} \quad \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = 6x^2y$$
$$\frac{\partial f}{\partial y} = 2x^3y \quad \text{and} \quad \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = 6x^2y \qquad \text{Therefore, exact.}$$

(b) $$\frac{\partial f}{\partial s} = te^s + 1 \quad \text{and} \quad \frac{\partial}{\partial t}\left(\frac{\partial f}{\partial s}\right) = e^s$$
$$\frac{\partial f}{\partial t} = 2t + e^s \quad \text{and} \quad \frac{\partial}{\partial s}\left(\frac{\partial f}{\partial t}\right) = e^s \qquad \text{Therefore, exact.}$$

E3.5(b) $$dz = \frac{\partial z}{\partial x}dx + \frac{\partial z}{\partial y}dy = \boxed{\frac{dx}{(1+y)^2} - \frac{2x\,dy}{(1+y)^3}}$$

E3.6(b) **(a)** $$dz = \frac{\partial z}{\partial x}dx + \frac{\partial z}{\partial y}dy = \boxed{(3x^2 - 2y^2)\,dx - 4xy\,dy}$$

(b) $$\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial}{\partial y}(3x^2 - 2y^2) = -4y$$

and $$\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial}{\partial x}(-4xy) = -4y$$

E3.7(b)

$$\mathrm{d}z = \frac{\partial z}{\partial x}\,\mathrm{d}x + \frac{\partial z}{\partial y}\,\mathrm{d}y = \boxed{(2xy + y^2)\,\mathrm{d}x + (x^2 + 2xy)\,\mathrm{d}y}$$

$$\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial}{\partial y}(2xy + y^2) = 2x + 2y$$

$$\text{and} \quad \frac{\partial^2 z}{\partial x \partial y} = \frac{\partial}{\partial x}(x^2 + 2xy) = 2x + 2y$$

E3.8(b)

$$\left(\frac{\partial C_p}{\partial p}\right)_T = \left[\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial T}\right)_p\right]_T = \frac{\partial^2 H}{\partial p \partial T}\boxed{\left[\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial p}\right)_T\right]_p}$$

Because $\left(\frac{\partial H}{\partial p}\right)_T = 0$ for a perfect gas, its temperature derivative also equals zero; thus $\left(\frac{\partial C_p}{\partial p}\right)_T = 0$.

E3.9(b)

$$\left(\frac{\partial H}{\partial U}\right)_p = \frac{(\partial H/\partial V)_p}{(\partial U/\partial V)_p} = \frac{\left(\frac{\partial (U+pV)}{\partial V}\right)_p}{(\partial U/\partial V)_p} = \frac{(\partial U/\partial V)_p + p}{(\partial U/\partial V)_p} = \boxed{1 + \frac{p}{(\partial U/\partial V)_p}}$$

E3.10(b)

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

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

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

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

We express $\left(\frac{\partial p}{\partial T}\right)_V$ in terms of κ_T and the expansion coefficient $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

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

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

E3.11(b)

$$U = \left(\frac{3}{2}\right)nRT \quad \text{so} \quad \left(\frac{\partial U}{\partial p}\right)_T = \boxed{0} \quad \text{by direct differentiation}$$

$$H = U + pV = \left(\tfrac{3}{2}\right)nRT + nRT = \left(\tfrac{5}{2}\right)nRT,$$

$$\text{so} \left(\frac{\partial H}{\partial p}\right)_T = \boxed{0} \quad \text{by direct differentiation}$$

E3.12(b)

$$\alpha = \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_p \qquad V = \frac{nRT}{p} \qquad \left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p} = \frac{V}{T}$$

$$\alpha = \left(\frac{1}{V}\right) \times \left(\frac{V}{T}\right) = \boxed{\frac{1}{T}}$$

$$\kappa_T = -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial p}\right)_T \qquad \left(\frac{\partial V}{\partial p}\right)_T = -\frac{nRT}{p^2}$$

$$\kappa_T = -\left(\frac{1}{V}\right)\times\left(-\frac{nRT}{p^2}\right) = \boxed{\frac{1}{p}}$$

E3.13(b) The Joule–Thomson coefficient μ is the ratio of temperature change to pressure change under conditions of isenthalpic expansion. So

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

E3.14(b) $U_\mathrm{m} = U_\mathrm{m}(T, V_\mathrm{m}) \qquad \mathrm{d}U_\mathrm{m} = \left(\frac{\mathrm{d}U_\mathrm{m}}{\partial T}\right)_{V_\mathrm{m}}\mathrm{d}T + \left(\frac{\partial U_\mathrm{m}}{\partial V_\mathrm{m}}\right)\mathrm{d}V_\mathrm{m}$

$\mathrm{d}T = 0$ in an isothermal process, so

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

$$\Delta U_\mathrm{m} = \int_{V_\mathrm{m1}}^{V_\mathrm{m2}} \mathrm{d}U_\mathrm{m} = \int_{V_\mathrm{m1}}^{V_\mathrm{m2}} \frac{a}{V_\mathrm{m}^2}\,\mathrm{d}V_\mathrm{m} = a\int_{1.00\,\mathrm{L\,mol^{-1}}}^{22.1\,\mathrm{L\,mol^{-1}}} \frac{\mathrm{d}V_\mathrm{m}}{V_\mathrm{m}^2} = -\left.\frac{a}{V_\mathrm{m}}\right|_{1.00\,\mathrm{L\,mol^{-1}}}^{22.1\,\mathrm{L\,mol^{-1}}}$$

$$= -\frac{a}{22.1\,\mathrm{L\,mol^{-1}}} + \frac{a}{1.00\,\mathrm{L\,mol^{-1}}} = \frac{21.1a}{22.1\,\mathrm{L\,mol^{-1}}} = 0.954\overline{75}a\,\mathrm{L^{-1}\,mol}$$

$$a = 1.337\,\mathrm{atm\,L^2\,mol^{-2}}$$

$$\Delta U_\mathrm{m} = (0.95475\,\mathrm{mol\,L^{-1}}) \times (1.337\,\mathrm{atm\,L^2\,mol^{-2}})$$

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

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

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

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

Thus

$$q = +\int_{1.00\,\mathrm{L\,mol^{-1}}}^{22.1\,\mathrm{L\,mol^{-1}}}\left(\frac{RT}{V_\mathrm{m}-b}\right)\mathrm{d}V_\mathrm{m} = +RT\ln(V_\mathrm{m}-b)\Big|_{1.00\,\mathrm{L\,mol^{-1}}}^{22.1\,\mathrm{L\,mol^{-1}}}$$

$$= +(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})$$

$$\times \ln\left\{\frac{22.1 - 3.20\times 10^{-2}}{1.00 - 3.20\times 10^{-2}}\right\}$$

$$= \boxed{+7.74\overline{65}\,\mathrm{kJ\,mol^{-1}}}$$

$$w = -774\bar{7}\,\mathrm{J\,mol^{-1}} + 129\,\mathrm{J\,mol^{-1}} = \boxed{-761\bar{8}\,\mathrm{J\,mol^{-1}}} = \boxed{-7.62\,\mathrm{kJ\,mol^{-1}}}$$

E3.15(b) The expansion coefficient is

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

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

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

E3.16(b) Isothermal compressibility is

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

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

$$\Delta p = \frac{0.0008}{2.21\times10^{-6}\,\mathrm{atm}^{-1}} = \boxed{3.\underline{6}\times10^{2}\,\mathrm{atm}}$$

E3.17(b) The isothermal Joule–Thomson coefficient is

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

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

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

$$\Delta H = -(41.2\,\mathrm{J\,atm}^{-1}\,\mathrm{mol}^{-1})\times(12.0\,\mathrm{mol})\times(-55\,\mathrm{atm}) = \boxed{27.\bar{2}\times10^{3}\,\mathrm{J}}$$

E3.18(b) The Joule–Thomson coefficient is

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H \approx \frac{\Delta T}{\Delta p} \quad \text{so} \quad \Delta p = \frac{\Delta T}{\mu} = \frac{-4.5\,\mathrm{K}}{13.3\times10^{-3}\,\mathrm{K\,kPa}^{-1}} = \boxed{-3.4\times10^{2}\,\mathrm{kPa}}$$

Solutions to problems

Assume that all gases are perfect and that all data refer to 298 K unless stated otherwise.

Solutions to numerical problems

P3.1

$$\kappa_T = (2.21\times10^{-6}\,\mathrm{atm}^{-1})\times\left(\frac{1\,\mathrm{atm}}{1.013\times10^{5}\,\mathrm{Pa}}\right) = \boxed{2.18\times10^{-11}\,\mathrm{Pa}^{-1}}$$

For the change of volume with pressure, we use

$$\mathrm{d}V = \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p[\text{constant temperature}] = -\kappa_T V\,\mathrm{d}p \quad \left[\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T\right]$$

$$\Delta V = -\kappa_T V\Delta p \quad [\text{If change in } V \text{ is small compared to } V]$$

$$\Delta p = (1.03\times10^{3}\,\mathrm{kg\,m}^{-3})\times(9.81\,\mathrm{m\,s}^{-2})\times(1000\,\mathrm{m}) = 1.01\bar{0}\times10^{7}\,\mathrm{Pa}.$$

Consequently, since $V = 1000\,\text{cm}^3 = 1.0 \times 10^{-3}\,\text{m}^3$,

$$\Delta V \approx (-2.18 \times 10^{-11}\,\text{Pa}^{-1}) \times (1.0 \times 10^{-3}\,\text{m}^3) \times (1.01\bar{0} \times 10^{7}\,\text{Pa})$$

$$= -2.2 \times 10^{-7}\,\text{m}^3, \quad \text{or} \quad \boxed{-0.220\,\text{cm}^3}.$$

For the change of volume with temperature, we use

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T\,[\text{constant pressure}] = \alpha V\,\mathrm{d}T \qquad \left[\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p\right]$$

$$\Delta V = \alpha V \Delta T \quad [\text{if change in } V \text{ is small compared to } V]$$

$$\approx (8.61 \times 10^{-5}\,\text{K}^{-1}) \times (1.0 \times 10^{-3}\,\text{m}^3) \times (-30\,\text{K})$$

$$\approx -2.6 \times 10^{-6}\,\text{m}^3, \quad \text{or} \quad -2.6\,\text{cm}^3$$

Overall, $\Delta V \approx -2.8\,\text{cm}^3$ $\boxed{V = 997.2\,\text{cm}^3}$

Comment. A more exact calculation of the change of volume as a result of simultaneous pressure and temperature changes would be based on the relationship

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

This would require information not given in the problem statement.

P3.5 Use the formula derived in Problem 3.25.

$$C_{p,\text{m}} - C_{V,\text{m}} = \lambda R \qquad \frac{1}{\lambda} = 1 - \frac{(3V_\text{r} - 1)^2}{4V_\text{r}^3 T_\text{r}}$$

which gives $\gamma = \dfrac{C_{p,\text{m}}}{C_{V,\text{m}}} = \dfrac{C_{V,\text{m}} + \lambda R}{C_{V,\text{m}}} = 1 + \dfrac{\lambda R}{C_{V,\text{m}}}$

In conjunction with $C_{V,\text{m}} = \frac{3}{2}R$ for a monatomic, perfect gas, this gives

$$\gamma = 1 + \tfrac{2}{3}\lambda$$

For a van der Waals gas $V_\text{r} = \dfrac{V_\text{m}}{V_\text{c}} = \dfrac{V_\text{m}}{3b}$, $T_\text{r} = \dfrac{T}{T_\text{c}} = \dfrac{27RbT}{8a}$ (Table 1.6) with $a = 4.137\,\text{L}^2\,\text{atm}\,\text{mol}^{-2}$ and $b = 5.16 \times 10^{-2}\,\text{L}\,\text{mol}^{-1}$ (Table 1.6). Hence, at 100°C and 1.00 atm, where $V_\text{m} \approx \dfrac{RT}{p} = 30.6\,\text{L}\,\text{mol}^{-1}$

$$V_\text{r} \approx \frac{30.6\,\text{L}\,\text{mol}^{-1}}{(3) \times (5.16 \times 10^{-2}\,\text{L}\,\text{mol}^{-1})} = 198$$

$$T_\text{r} \approx \frac{(27) \times (8.206 \times 10^{-2}\,\text{L}\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (5.16 \times 10^{-2}\,\text{L}\,\text{mol}^{-1}) \times (373\,\text{K})}{(8) \times (4.317\,\text{L}^2\,\text{atm}\,\text{mol}^{-2})} \approx 1.29$$

Hence

$$\frac{1}{\lambda} = 1 - \frac{[(3) \times (198) - (1)]^2}{(4) \times (198)^3 \times (1.29)} = 1 - 0.0088 = 0.9912, \qquad \lambda = 1.009$$

$$\gamma \approx (1) + \left(\frac{2}{3}\right) \times (1.009) = \boxed{1.67}$$

Comment. At 100°C and 1.00 atm xenon is expected to be close to perfect, so it is not surprising that γ differs only slightly from the perfect gas value of $\frac{5}{3}$.

P3.7 See the solution to Problem 3.6. It does not matter whether the piston between chambers 2 and 3 is diathermic or adiabatic as long as the piston between chambers 1 and 2 is adiabatic. The answers are the same as for Problem 3.6. However, if both pistons are diathermic, the result is different. The solution for both pistons being diathermic follows.

See Fig. 3.1.

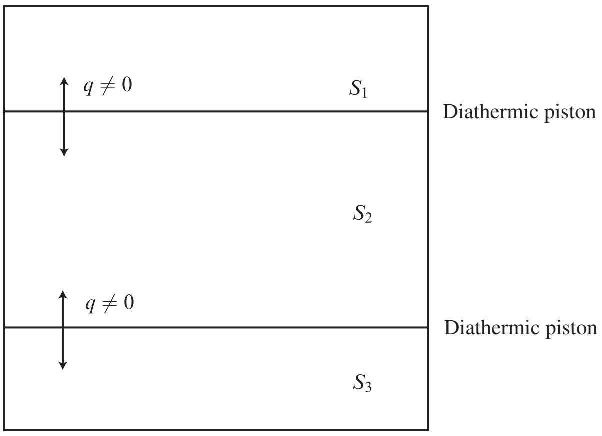


Figure 3.1

Initial equilibrium state.

$n = 1.00\,\text{mol}$ diatomic gas in each section

$p_i = 1.00\,\text{bar}$

$T_i = 298\,\text{K}$

For each section

$$V_i = \frac{nRT_i}{p_i} = \frac{(1\,\text{mol}) \times (0.083\,145\,\text{L bar K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})}{1.00\,\text{bar}}$$

$$= 24.8\,\text{L}$$

$V_{\text{total}} = 3V_i = 74.3\,\text{L} = \text{constant}$

Final equilibrium state. The diathermic walls allow the passage of heat. Consequently, at equlibrium all chambers will have the same temperature $T_1 = T_2 = T_3 = 348\,\text{K}$. The chambers will also be at mechanical equlibrium so

$$p_1 = p_2 = p_3 = \frac{(n_1 + n_2 + n_3)RT_1}{V_{\text{total}}}$$

$$= \frac{(3\,\text{mol}) \times (0.083\,145\,\text{L bar K}^{-1}\,\text{mol}^{-1}) \times (348\,\text{K})}{74.3\,\text{L}}$$

$$= 1.17\,\text{bar} = p_2 = p_3$$

The chambers will have equal volume.

$$V_1 = \frac{V_{\text{total}}}{3} = V_{\text{i}} = \boxed{24.8\,\text{L} = V_1 = V_2 = V_3}$$

$$\Delta U_1 = n_1 C_V \Delta T_1 = n_1\left(\tfrac{5}{2}R\right)\Delta T_1$$

$$= (1\,\text{mol}) \times \left(\tfrac{5}{2}\right) \times (8.314\,51\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (348\,\text{K} - 298\,\text{K})$$

$$\Delta U_1 = 1.04\,\text{kJ} = \Delta U_2 = \Delta U_3$$

$$\Delta U_{\text{total}} = 3\Delta U_1 = 3.12\,\text{kJ} = \Delta U_{\text{total}}$$

Solutions to theoretical problems

P3.11

$$\mathrm{d}w = \left(\frac{\partial w}{\partial x}\right)_{y,z}\mathrm{d}x + \left(\frac{\partial w}{\partial y}\right)_{x,z}\mathrm{d}y + \left(\frac{\partial w}{\partial z}\right)_{x,y}\mathrm{d}z$$

$$\mathrm{d}w = \boxed{(y+z)\,\mathrm{d}x + (x+z)\,\mathrm{d}y + (x+y)\,\mathrm{d}z}$$

This is the total differential of the function w, and a total differential is necessarily exact, but here we will demonstrate its exactness showing that its integral is independent of path.

Path a

$$\mathrm{d}w = 2x\,\mathrm{d}x + 2y\,\mathrm{d}y + 2z\,\mathrm{d}z = 6x\,\mathrm{d}x$$

$$\int_{(0,0,0)}^{(1,1,1)} \mathrm{d}w = \int_0^1 6x\,\mathrm{d}x = 3$$

Path b

$$\mathrm{d}w = 2x^2\,\mathrm{d}x + (y^{1/2} + y)\,\mathrm{d}y + (z^{1/2} + z)\,\mathrm{d}z = (2x^2 + 2x + 2x^{1/2})\,\mathrm{d}x$$

$$\int_{(0,0,0)}^{(1,1,1)} \mathrm{d}w = \int_0^1 (2x^2 + 2x + 2x^{1/2})\,\mathrm{d}x = \frac{2}{3} + 1 + \frac{4}{3} = 3$$

Therefore, $\mathrm{d}w$ is exact.

P3.12

$$U = U(T, V)$$

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V = C_V\,\mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V$$

For U = constant, $\mathrm{d}U = 0$, and

$$C_V\,\mathrm{d}T = -\left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V \quad \text{or} \quad C_V = -\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_U = -\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_U$$

This relationship is essentially the permuter [Relation 3, *Further information* 1.7].

P3.13

$$H = H(T, p)$$

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p = C_p\,\mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p$$

For H = constant, $\mathrm{d}H = 0$, and

$$\left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p = -C_p\,\mathrm{d}T$$

$$\left(\frac{\partial H}{\partial p}\right)_T = -C_p\left(\frac{\mathrm{d}T}{\mathrm{d}p}\right)_H = -C_p\left(\frac{\partial T}{\partial p}\right)_H = -C_p\mu = \boxed{-\mu C_p}$$

This relationship is essentially the permuter [Relation 3, *Further information* 1.7].

P3.16 The reasoning here is that an exact differential is always exact. If the differential of heat can be shown to be inexact in one instance, then its differential is in general inexact, and heat is not a state function. Consider the cycle shown in Fig. 3.2.

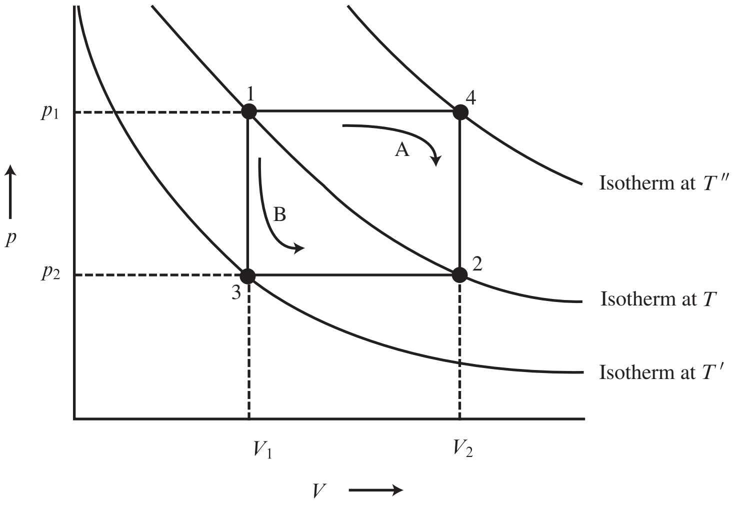


Figure 3.2

The following perfect gas relations apply at points labelled 1, 2, 3 and 4 in Fig. 3.2.

$$(1)\ p_1V_1 = p_2V_2 = nRT, \quad (2)\ p_2V_1 = nRT', \quad (3)\ p_1V_2 = nRT''$$

Define $\Delta T' = T - T'$, $\Delta T'' = T'' - T$

Subtract (2) from (1)

$$-nRT' + nRT = -p_2V_1 + p_1V_1$$

giving $\Delta T' = \dfrac{V_1(p_1 - p_2)}{RT}$

Subtracting (1) from (3) we obtain

$$\Delta T'' = \frac{V_2(p_1 - p_2)}{RT}$$

Since $V_1 \neq V_2$, $\Delta T' \neq \Delta T''$

$$q_A = C_p\Delta T'' - C_V\Delta T'' = (C_p - C_V)\Delta T''$$
$$q_B = -C_V\Delta T' + C_p\Delta T' = (C_p - C_V)\Delta T'$$

giving $q_A \neq q_B$ and $q(\text{cycle}) = q_A - q_B \neq 0$.

Therefore $\oint \mathrm{d}q \neq 0$ and $\mathrm{d}q$ is not exact.

P3.18

$$p = p(T, V) = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

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

In what follows adopt the notation $V_{\mathrm{m}} = V$.

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V-b}; \qquad \left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$

then, $\mathrm{d}p = \boxed{\left(\frac{R}{V-b}\right)\mathrm{d}T + \left\{\frac{2a}{V^3} - \frac{RT}{(V-b)^2}\right\}\mathrm{d}V}$

Because the van der Waals equation is a cubic in V, $\left(\frac{\partial V}{\partial T}\right)_p$ is more readily evaluated with the use of the permuter.

$$\left(\frac{\partial V}{\partial T}\right)_p = -\frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} = -\frac{\frac{R}{V-b}}{\left(-\frac{RT}{(V-b)^2} + \frac{2a}{V^3}\right)} = \boxed{\frac{RV^3(V-b)}{RTV^3 - 2a(V-b)^2}}$$

For path a

$$\begin{aligned}\int_{T_1,V_1}^{T_2,V_2} \mathrm{d}p &= \int_{T_1}^{T_2} \frac{R}{V_1-b}\,\mathrm{d}T + \int_{V_1}^{V_2}\left[-\frac{RT_2}{(V-b)^2} + \frac{2a}{V^3}\right]\mathrm{d}V \\ &= \frac{R}{V_1-b}(T_2-T_1) + \frac{RT_2}{(V_2-b)} - \frac{RT_2}{(V_1-b)} - a\left(\frac{1}{V_2^2} - \frac{1}{V_1^2}\right) \\ &= -\frac{RT_1}{V_1-b} + \frac{RT_2}{V_2-b} - a\left(\frac{1}{V_2^2} - \frac{1}{V_1^2}\right)\end{aligned}$$

For path b

$$\begin{aligned}\int_{T_1,V_1}^{T_2,V_2} \mathrm{d}p &= \int_{V_1}^{V_2}\left[-\frac{RT_1}{(V-b)^2} + \frac{2a}{V^3}\right]\mathrm{d}V + \int_{T_1}^{T_2} \frac{R}{V_2-b}\,\mathrm{d}T \\ &= \frac{RT_1}{V_2-b} - \frac{RT_1}{V_1-b} - a\left(\frac{1}{V_2^2} - \frac{1}{V_1^2}\right) + \frac{R}{V_2-b}(T_2-T_1) \\ &= -\frac{RT_1}{V_1-b} + \frac{RT_2}{V_2-b} - a\left(\frac{1}{V_2^2} - \frac{1}{V_1^2}\right)\end{aligned}$$

Thus, they are the same and $\mathrm{d}p$ satisfies the condition of an exact differential, namely, that its integral between limits is independent of path.

P3.20 $p = p(V,T)$

Therefore,

$$\mathrm{d}p = \left(\frac{\partial p}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}T \quad \text{with } p = \frac{nRT}{V-nb} - \frac{n^2a}{V^2} \text{ [Table 1.6]}$$

$$\left(\frac{\partial p}{\partial V}\right)_T = \frac{-nRT}{(V-nb)^2} + \frac{2n^2a}{V^3} = \frac{-p}{V-nb} + \left(\frac{n^2a}{V^3}\right) \times \left(\frac{V-2nb}{V-nb}\right)$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V-nb} = \frac{p}{T} + \frac{n^2a}{TV^2}$$

Therefore, upon substitution

$$\begin{aligned}\mathrm{d}p &= \left(\frac{-p\,\mathrm{d}V}{V-nb}\right)+\left(\frac{n^2a}{V^3}\right)\times(V-2nb)\times\left(\frac{\mathrm{d}V}{V-nb}\right)+\left(\frac{p\,\mathrm{d}T}{T}\right)+\left(\frac{n^2a}{V^2}\right)\times\left(\frac{\mathrm{d}T}{T}\right)\\ &= \left(\frac{(n^2a)\times(V-nb)/V^3-p}{V-nb}\right)\mathrm{d}V+\left(\frac{p+n^2a/V^2}{T}\right)\mathrm{d}T\\ &= \boxed{\left(\frac{a(V_\mathrm{m}-b)/V_\mathrm{m}^3-p}{V_\mathrm{m}-b}\right)\mathrm{d}V_\mathrm{m}+\left(\frac{p+a/V_\mathrm{m}^2}{T}\right)\mathrm{d}T}\end{aligned}$$

Comment. This result may be compared to the expression for $\mathrm{d}p$ obtained in Problem 3.18.

P3.21 $p=\dfrac{nRT}{V-nb}-\dfrac{n^2a}{V^2}$ (Table 1.6)

Hence $\boxed{T=\left(\dfrac{p}{nR}\right)\times(V-nb)+\left(\dfrac{na}{RV^2}\right)\times(V-nb)}$

$$\boxed{\left(\frac{\partial T}{\partial p}\right)_V=\frac{V-nb}{nR}}=\frac{V_\mathrm{m}-b}{R}=\frac{1}{\left(\frac{\partial p}{\partial T}\right)_V}$$

For Euler's chain relation, we need to show that $\left(\dfrac{\partial T}{\partial p}\right)_V\left(\dfrac{\partial p}{\partial V}\right)_T\left(\dfrac{\partial V}{\partial T}\right)_p=-1$

Hence, in addition to $\left(\dfrac{\partial T}{\partial p}\right)_V$ and $\left(\dfrac{\partial p}{\partial V}\right)_T$ [Problem 3.20] we need $\left(\dfrac{\partial V}{\partial T}\right)_p=\dfrac{1}{\left(\frac{\partial T}{\partial V}\right)_p}$

which can be found from $\left(\dfrac{\partial T}{\partial V}\right)_p=\left(\dfrac{p}{nR}\right)+\left(\dfrac{na}{RV^2}\right)-\left(\dfrac{2na}{RV^3}\right)\times(V-nb)$

$$=\left(\frac{T}{V-nb}\right)-\left(\frac{2na}{RV^3}\right)\times(V-nb)$$

Therefore,

$$\begin{aligned}\left(\frac{\partial T}{\partial p}\right)_V\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p &= \frac{\left(\frac{\partial T}{\partial p}\right)_V\left(\frac{\partial p}{\partial V}\right)_T}{\left(\frac{\partial T}{\partial V}\right)_p}\\ &= \frac{\left(\frac{V-nb}{nR}\right)\times\left(\frac{-nRT}{(V-nb)^2}+\frac{2n^2a}{V^3}\right)}{\left(\frac{T}{V-nb}\right)-\left(\frac{2na}{RV^3}\right)\times(V-nb)}=\frac{\left(\frac{-T}{V-nb}\right)+\left(\frac{2na}{RV^3}\right)\times(V-nb)}{\left(\frac{T}{V-nb}\right)-\left(\frac{2na}{RV^3}\right)\times(V-nb)}\\ &= -1\end{aligned}$$

P3.23 $\mu C_p=T\left(\dfrac{\partial V}{\partial T}\right)_p-V=\dfrac{T}{\left(\frac{\partial T}{\partial V}\right)_p}-V$ [Relation 2, *Further information* 1.7]

$$\left(\frac{\partial T}{\partial V}\right)_p=\frac{T}{V-nb}-\frac{2na}{RV^3}(V-nb)\text{ [Problem 3.21]}$$

Introduction of this expression followed by rearrangement leads to

$$\mu C_p = \frac{(2na) \times (V - nb)^2 - nbRTV^2}{RTV^3 - 2na(V - nb)^2} \times V$$

Then, introducing $\zeta = \dfrac{RTV^3}{2na(V - nb)^2}$ to simplify the appearance of the expression

$$\boxed{\mu C_p = \left(\frac{1 - \frac{nb\zeta}{V}}{\zeta - 1}\right) V} = \left(\frac{1 - \frac{b\zeta}{V_m}}{\zeta - 1}\right) V$$

For xenon, $V_m = 24.6\,\mathrm{L\,mol^{-1}}$, $T = 298\,\mathrm{K}$, $a = 4.137\,\mathrm{L^2\,atm\,mol^{-2}}$, $b = 5.16 \times 10^{-2}\,\mathrm{L\,mol^{-1}}$,

$$\frac{nb}{V} = \frac{b}{V_m} = \frac{5.16 \times 10^{-2}\,\mathrm{L\,mol^{-1}}}{24.6\,\mathrm{L\,mol^{-1}}} = 2.09 \times 10^{-3}$$

$$\zeta = \frac{(8.206 \times 10^{-2}\,\mathrm{L\,atm\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K}) \times (24.6\,\mathrm{L\,mol^{-1}})^3}{(2) \times (4.137\,\mathrm{L^2\,atm\,mol^{-2}}) \times (24.6\,\mathrm{L\,mol^{-1}} - 5.16 \times 10^{-2}\,\mathrm{L\,mol^{-1}})^2} = 73.0$$

Therefore, $\mu C_p = \dfrac{1 - (73.0) \times (2.09 \times 10^{-3})}{72.0} \times (24.6\,\mathrm{L\,mol^{-1}}) = 0.290\,\mathrm{L\,mol^{-1}}$

$C_p = 20.79\,\mathrm{J\,K^{-1}\,mol^{-1}}$[Table 2.6], so

$$\begin{aligned}\mu &= \frac{0.290\,\mathrm{L\,mol^{-1}}}{20.79\,\mathrm{J\,K^{-1}\,mol^{-1}}} = \frac{0.290 \times 10^{-3}\,\mathrm{m^3\,mol^{-1}}}{20.79\,\mathrm{J\,K^{-1}\,mol^{-1}}}\\ &= 1.39\bar{3} \times 10^{-5}\,\mathrm{K\,m^3\,J^{-1}} = 1.39\bar{3} \times 10^{-5}\,\mathrm{K\,Pa^{-1}}\\ &= (1.39\bar{3} \times 10^{-5}) \times (1.013 \times 10^5\,\mathrm{K\,atm^{-1}}) = \boxed{1.41\,\mathrm{K\,atm^{-1}}}\end{aligned}$$

The value of μ changes at $T = T_1$ and when the sign of the numerator $1 - \dfrac{nb\zeta}{V}$ changes sign ($\zeta - 1$ is positive). Hence

$$\frac{b\zeta}{V_m} = 1 \text{ at } T = T_1 \quad \text{or} \quad \frac{RT_1bV^3}{2na(V - nb)^2V_m} = 1 \quad \text{implying that } T_1 = \frac{2a(V_m - b)^2}{RbV_m^2}$$

that is, $T_1 = \left(\dfrac{2a}{Rb}\right) \times \left(1 - \dfrac{b}{V_m}\right)^2 = \boxed{\dfrac{27}{4}T_c\left(1 - \dfrac{b}{V_m}\right)^2}$

For xenon, $\dfrac{2a}{Rb} = \dfrac{(2) \times (4.137\,\mathrm{L^2\,atm\,mol^{-2}})}{(8.206 \times 10^{-2}\,\mathrm{L\,atm\,K^{-1}\,mol^{-1}}) \times (5.16 \times 10^{-2}\,\mathrm{L\,mol^{-1}})} = 1954\,\mathrm{K}$

and so $T_1 = (1954\,\mathrm{K}) \times \left(1 - \dfrac{5.16 \times 10^{-2}}{24.6}\right)^2 = \boxed{1946\,\mathrm{K}}$

Question. An approximate relationship for μ of a van der Waals gas was obtained in Problem 3.17. Use it to obtain an expression for the inversion temperature, calculate it for xenon, and compare to the result above.

P3.25 $$C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = \frac{\alpha^2 TV}{\kappa_T}\ [3.21] = \alpha TV\left(\frac{\partial p}{\partial T}\right)_V\ [\textit{Justification}\ 3.3]$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V-nb}\ [\text{Problem 3.20}]$$

$$\alpha V = \left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{\left(\frac{\partial T}{\partial V}\right)_p}$$

Substituting,

$$C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = \frac{T\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial T}{\partial V}\right)_p} \quad \text{so} \quad \left(\frac{\partial T}{\partial V}\right)_p = \frac{T}{V-nb} - \frac{2na}{RV^3}(V-nb)\ [\text{Problem 3.21}]$$

Substituting,

$$C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = \frac{\frac{nRT}{(V-nb)}}{\frac{T}{(V-nb)} - \left(\frac{2na}{RV^3}\right)\times(V-nb)} = n\lambda R \quad \text{with } \lambda = \frac{1}{1-\left(\frac{2na}{RTV^3}\right)\times(V-nb)^2}$$

For molar quantities,

$$C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = \lambda R \quad \text{with } \frac{1}{\lambda} = 1 - \frac{2a(V_\mathrm{m}-b)^2}{RTV_\mathrm{m}^3}$$

Now introduce the reduced variables and use $T_\mathrm{c} = \dfrac{8a}{27Rb}$, $V_\mathrm{c} = 3b$.

After rearrangement,

$$\boxed{\frac{1}{\lambda} = 1 - \frac{(3V_\mathrm{r}-1)^2}{4T_\mathrm{r}V_\mathrm{r}^3}}$$

For xenon, $V_\mathrm{c} = 118.1\ \mathrm{cm^3\ mol^{-1}}$, $T_\mathrm{c} = 289.8\ \mathrm{K}$. The perfect gas value for V_m may be used as any error introduced by this approximation occurs only in the correction term for $\dfrac{1}{\lambda}$.

Hence, $V_\mathrm{m} \approx 2.45\ \mathrm{L\ mol^{-1}}$, $V_\mathrm{c} = 118.8\ \mathrm{cm^3\ mol^{-1}}$, $T_\mathrm{c} = 289.8\ \mathrm{K}$, and $V_\mathrm{r} = 20.6$ and $T_\mathrm{r} = 1.03$; therefore

$$\frac{1}{\lambda} = 1 - \frac{(61.8-1)^2}{(4)\times(1.03)\times(20.6)^3} = 0.90, \quad \text{giving } \lambda \approx 1.1$$

and

$$C_{p,\mathrm{m}} - C_{V,\mathrm{m}} \approx 1.1R = \boxed{9.2\ \mathrm{J\ K^{-1}\ mol^{-1}}}$$

P3.27 (**a**) $$\mu = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T = \frac{1}{C_p}\left\{T\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p - V_\mathrm{m}\right\}\ [\textit{Justification}\ 3.1 \text{ and Problem 3.24}]$$

$$V_\mathrm{m} = \frac{RT}{p} + aT^2$$

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

$$\mu = \frac{1}{C_p}\left\{\frac{RT}{p} + 2aT^2 - \frac{RT}{p} - aT^2\right\}$$

$$\boxed{\mu = \frac{aT^2}{C_p}}$$

(b) $$C_V = C_p - \alpha T V_{\mathrm{m}}\left(\frac{\partial p}{\partial T}\right)_V$$

$$= C_p - T\left(\frac{\partial V_{\mathrm{m}}}{\partial T}\right)_p\left(\frac{\partial p}{\partial T}\right)_V$$

But, $p = \dfrac{RT}{V_{\mathrm{m}} - aT^2}$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V_{\mathrm{m}} - aT^2} - \frac{RT(-2aT)}{(V_{\mathrm{m}} - aT^2)^2}$$

$$= \frac{R}{(RT/p)} + \frac{2aRT^2}{(RT/p)^2}$$

$$= \frac{p}{T} + \frac{2ap^2}{R}$$

Therefore

$$C_V = C_p - T\left(\frac{R}{p} + 2aT\right) \times \left(\frac{p}{T} + \frac{2ap^2}{R}\right)$$

$$= C_p - \frac{RT}{p}\left(1 + \frac{2apT}{R}\right) \times \left(1 + \frac{2apT}{R}\right) \times \left(\frac{p}{T}\right)$$

$$\boxed{C_V = C_p - R\left(1 + \frac{2apT}{R}\right)^2}$$

Solutions to additional problems

P3.29 **(a)** The Joule–Thomson coefficient is related to the given data by

$$\mu = -(1/C_p)(\partial H/\partial p)_T = -(-3.29 \times 10^3\,\mathrm{J\,mol^{-1}\,MPa^{-1}})/(110.0\,\mathrm{J\,K^{-1}\,mol^{-1}})$$

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

(b) The Joule–Thomson coefficient is defined as

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

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

$$\Delta T = \mu\Delta p = (29.9\,\mathrm{K\,MPa^{-1}}) \times [(0.5 - 1.5) \times 10^{-1}\,\mathrm{MPa}] = \boxed{-2.99\,\mathrm{K}}$$

4 The Second Law: the concepts

Solutions to exercises

Discussion questions

E4.1(b) Trouton's rule is that the ratio of the enthalpy of vaporization of a liquid to its boiling point is a constant. Energy in the form of heat (enthalpy) supplied to a liquid manifests itself as turbulent motion (kinetic energy) of the molecules. When the kinetic energy of the molecules is sufficient to overcome the attractive energy that holds them together the liquid vaporizes. The enthalpy of vaporization is the heat energy (enthalpy) required to accomplish this at constant pressure. It seems reasonable that the greater the enthalpy of vaporization, the greater the kinetic energy required, and the greater the temperature needed to achieve this kinetic energy. Hence, we expect that $\Delta_{\text{vap}}H \propto T_{\text{b}}$, which implies that their ratio is a constant.

E4.2(b) The device proposed uses geothermal heat (energy) and appears to be similar to devices currently in existence for heating and lighting homes. As long as the amount of heat extracted from the hot source (the ground) is not less than the sum of the amount of heat discarded to the surroundings (by heating the home and operating the steam engine) and of the amount of work done by the engine to operate the heat pump, this device is possible; at least, it does not violate the first law of thermodynamics. However, the feasability of the device needs to be tested from the point of view of the second law as well. There are various equivalent versions of the second law, some are more directly useful in this case than others. Upon first analysis, it might seem that the net result of the operation of this device is the complete conversion of heat into the work done by the heat pump. This work is the difference between the heat absorbed from the surroundings and the heat discharged to the surroundings, and all of that difference has been converted to work. We might, then, conclude that this device violates the second law in the form stated in the introduction to Chapter 4; and therefore, that it cannot operate as described. However, we must carefully examine the exact wording of the second law. The key words are "sole result." Another slightly different, though equivalent, wording of Kelvin's statement is the following: "It is impossible by a cyclic process to take heat from a reservoir and convert it into work without at the same time transferring heat from a hot to a cold reservoir." So as long as some heat is discharged to surroundings colder than the geothermal source during its operation, there is no reason why this device should not work. A detailed analysis of the entropy changes associated with this device follows.

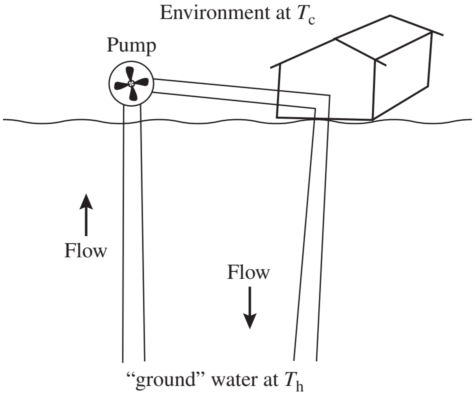


Figure 4.1 C_V and C_p are the temperature dependent heat capacities of water

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

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

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

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

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

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

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

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

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

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

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

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

This expression satisfies the second law ($\Delta S_{\text{tot}} > 0$) only when $T_{\text{h}} > T_{\text{c}}$. We can conclude that, if the proposal involves collecting heat from environmentally cool ground water and using the energy to heat a home or to perform work, the proposal cannot succeed no matter what level of sophisticated technology is applied. Should the "ground" water be collected from deep within the Earth so that $T_{\text{h}} > T_{\text{c}}$, the resultant geothermal pump is feasible. However, the efficiency, given by eqn 4.11, must be high to compete with fossil fuels because high installation costs must be recovered during the lifetime of the apparatus.

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

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

E4.3(b) See the solution to exercises 4.3 (a).

Numerical exercises

E4.4(b)

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

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

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

E4.5(b) At 250 K, the entropy is equal to its entropy at 298 K plus ΔS where

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

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

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

E4.6(b)

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

$$\Delta S = (1.00\,\mathrm{mol}) \times \left(\frac{5}{2} + 1\right) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\frac{(100 + 273)\,\mathrm{K}}{273\,\mathrm{K}} = \boxed{9.08\,\mathrm{J\,K^{-1}}}$$

E4.7(b) However the change occurred, ΔS has the same value as if the change happened by reversible heating at constant pressure (step 1) followed by reversible isothermal compression (step 2)

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

For the first step

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

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

and for the second

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

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

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

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

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

E4.8(b)

$$q = q_{\mathrm{rev}} = \boxed{0} \text{ (adiabatic reversible process)}$$

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

$$\begin{aligned}\Delta U = nC_{V,\mathrm{m}}\Delta T &= (2.00\,\mathrm{mol}) \times (27.5\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (300 - 250)\,\mathrm{K} \\ &= 2750\,\mathrm{J} = \boxed{+2.75\,\mathrm{kJ}}\end{aligned}$$

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

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

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

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

E4.9(b) However the change occurred, ΔS has the same value as if the change happened by reversible heating at constant volume (step 1) followed by reversible isothermal expansion (step 2)

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

For the first step

$$\begin{aligned}\Delta S_1 &= \int \frac{\mathrm{d}q_{\mathrm{rev}}}{T} = \int \frac{C_{V,\mathrm{m}}\,\mathrm{d}T}{T} = C_{V,\mathrm{m}} \ln \frac{T_\mathrm{f}}{T_\mathrm{i}} \quad \left[C_{V,\mathrm{m}} = C_{p,\mathrm{m}} - R\right] \\ &= (3.50\,\mathrm{mol}) \times \left(\frac{3}{2}\right) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln \frac{700\,\mathrm{K}}{250\,\mathrm{K}} = 44.9\,\mathrm{J\,K^{-1}}\end{aligned}$$

and for the second

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

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

so $\Delta S_2 = nR \ln \frac{p_\mathrm{i}}{p_\mathrm{f}} = (3.50\,\mathrm{mol}) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln \frac{60.0\,\mathrm{L}}{20.0\,\mathrm{L}} = 32.0\,\mathrm{J\,K^{-1}}$

$$\Delta S = 44.9 + 32.0\,\mathrm{J\,K^{-1}} = \boxed{76.9\,\mathrm{J\,K^{-1}}}$$

E4.10(b) $\Delta S = \frac{q_{\mathrm{rev}}}{T}$ If reversible $q = q_{\mathrm{rev}}$

$$\begin{aligned} q_{\mathrm{rev}} &= T\Delta S = (5.51\,\mathrm{J\,K^{-1}}) \times (350\,\mathrm{K}) \\ &= 192\overline{8.5}\,\mathrm{J} \end{aligned}$$

$$q = 1.50\,\mathrm{kJ} \neq 19.3\,\mathrm{kJ} = q_{\mathrm{rev}}$$

$q \neq q_{\mathrm{rev}}$; therefore the process is $\boxed{\text{not reversible}}$

E4.11(b) **(a)** The heat flow is

$$\begin{aligned} q &= C_p \Delta T = nC_{p,\mathrm{m}}\Delta T \\ &= \left(\frac{2.75\,\mathrm{kg}}{63.54 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}}\right) \times (24.44\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (275 - 330)\,\mathrm{K} \\ &= \boxed{-58.2 \times 10^3\,\mathrm{J}} \end{aligned}$$

(b)

$$\begin{aligned}\Delta S &= \int \frac{\mathrm{d}q_{\mathrm{rev}}}{T} = \int \frac{C_p\,\mathrm{d}T}{T} = nC_{p,\mathrm{m}} \ln \frac{T_\mathrm{f}}{T_\mathrm{i}} \\ &= \left(\frac{2.75\,\mathrm{kg}}{63.54 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}}\right) \times (24.44\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln \frac{275\,\mathrm{K}}{330\,\mathrm{K}} = \boxed{-193\,\mathrm{J\,K^{-1}}}\end{aligned}$$

E4.12(b) $\Delta S = \int \frac{\mathrm{d}q_{\mathrm{rev}}}{T} = \frac{q_{\mathrm{rev}}}{T}$ where $q_{\mathrm{rev}} = -w = nRT \ln \frac{V_\mathrm{f}}{V_\mathrm{i}} = nRT \ln \frac{p_\mathrm{i}}{p_\mathrm{f}}$

so $\Delta S = nR \ln \frac{p_\mathrm{i}}{p_\mathrm{f}} = \left(\frac{35\,\mathrm{g}}{28.013\,\mathrm{g\,mol^{-1}}}\right) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln \frac{21.1\,\mathrm{atm}}{4.3\,\mathrm{atm}} = \boxed{17\,\mathrm{J\,K^{-1}}}$

E4.13(b) $\Delta S = \displaystyle\int \frac{\mathrm{d}q_{\text{rev}}}{T} = \frac{q_{\text{rev}}}{T} \quad \text{where } q_{\text{rev}} = -w = nRT \ln \frac{V_{\text{f}}}{V_{\text{i}}}$

so $\Delta S = nR \ln \dfrac{V_{\text{f}}}{V_{\text{i}}}$ and $V_{\text{f}} = V_{\text{i}} \exp\left(\dfrac{\Delta S}{nR}\right)$

We need to compute the amount of gas from the perfect gas law

$$pV = nRT \quad \text{so} \quad n = \frac{pV}{RT} = \frac{(1.20\,\text{atm}) \times (11.0\,\text{L})}{(0.08206\,\text{L atm K}^{-1}\,\text{mol}^{-1}) \times (270\,\text{K})} = 0.596\,\text{mol}$$

$$\text{So } V_{\text{f}} = (11.0\,\text{L}) \exp\left(\frac{-3.0\,\text{J K}^{-1}}{(0.596\,\text{mol}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})}\right) = \boxed{6.00\,\text{L}}$$

E4.14(b) Find the final temperature by equating the heat lost by the hot sample to the heat gained by the cold sample.

$$-n_1 C_{p,\text{m}}\,(T_{\text{f}} - T_{\text{i}1}) = n_2 C_{p,\text{m}}\,(T_{\text{f}} - T_{\text{i}2})$$

$$\begin{aligned} T_{\text{f}} &= \frac{n_1 T_{\text{i}1} + n_2 T_{\text{i}2}}{n_1 + n_2} = \frac{\frac{1}{M}(m_1 T_{\text{i}1} + m_2 T_{\text{i}2})}{\frac{1}{M}(m_1 + m_2)} \\ &= \frac{m_1 T_{\text{i}1} + m_2 T_{\text{i}2}}{m_1 + m_2} \\ &= \frac{(25\,\text{g}) \times (323\,\text{K}) + (70\,\text{g}) \times (293\,\text{K})}{25\,\text{g} + 70\,\text{g}} = 300.9\,\text{K} \end{aligned}$$

$$\begin{aligned} \Delta S = \Delta S_1 + \Delta S_2 &= n_1 C_{p,\text{m}} \ln\left(\frac{T_{\text{f}}}{T_{\text{i}1}}\right) + n_2 C_{p,\text{m}} \ln\left(\frac{T_{\text{f}}}{T_{\text{i}2}}\right) \\ &= \left\{\left(\frac{25\,\text{g}}{46.07\,\text{g mol}^{-1}}\right)\ln\left(\frac{30\overline{0.9}}{323}\right) + \left(\frac{70\,\text{g}}{46.07\,\text{g mol}^{-1}}\right) \times \ln\left(\frac{30\overline{0.9}}{293}\right)\right\} C_{p,\text{m}} \\ &= \left\{-3.8\overline{46} \times 10^{-2} + 4.0\overline{43} \times 10^{-2}\right\} C_{p,\text{m}} \\ &= (0.1\overline{96} \times 10^{-2}\,\text{mol}) \times (111.5\,\text{J K}^{-1}\,\text{mol}^{-1}) \\ &= \boxed{0.2\,\text{J K}^{-1}} \end{aligned}$$

E4.15(b) $\boxed{\Delta H_{\text{total}} = 0}$ in an isolated container.

Since the masses are equal and the heat capacity is assumed constant, the final temperature will be the average of the two initial temperatures

$$T_{\text{f}} = \tfrac{1}{2}(200^\circ\text{C} + 25^\circ\text{C}) = 112.\bar{5}^\circ\text{C}$$

$nC_m = mC_{\text{s}}$ where C_{s} is the specific heat capacity

$$\Delta S = mC_{\text{s}} \ln\left(\frac{T_{\text{f}}}{T_{\text{i}}}\right) \qquad 200^\circ\text{C} = 473.2\,\text{K};\ 25^\circ\text{C} = 298.2\,\text{K};\ 112.\bar{5}^\circ\text{C} = 385.\bar{7}\,\text{K}$$

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

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

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

E4.16(b) **(a)** $\boxed{q = 0}$ [adiabatic]

(b) $$w = -p_{\text{ex}}\Delta V = -(1.5\,\text{atm}) \times \left(\frac{1.01 \times 10^5\,\text{Pa}}{\text{atm}}\right) \times (100.0\,\text{cm}^2) \times (15\,\text{cm}) \times \left(\frac{1\,\text{m}^3}{10^6\,\text{cm}^3}\right)$$
$$= -22\overline{7.2}\,\text{J} = \boxed{-230\,\text{J}}$$

(c) $\Delta U = q + w = 0 - 230\,\text{J} = \boxed{-230\,\text{J}}$

(d) $\Delta U = nC_{V,\text{m}}\Delta T$

$$\Delta T = \frac{\Delta U}{nC_{V,\text{m}}} = \frac{-22\overline{7.2}\,\text{J}}{(1.5\,\text{mol}) \times (28.8\,\text{J K}^{-1}\,\text{mol}^{-1})}$$
$$= \boxed{-5.3\,\text{K}}$$

(e) $$\Delta S = nC_{V,\text{m}} \ln\left(\frac{T_\text{f}}{T_\text{i}}\right) + nR\ln\left(\frac{V_\text{f}}{V_\text{i}}\right)$$
$$T_\text{f} = 288.\overline{15}\,\text{K} - 5.26\,\text{K} = 282.\overline{9}\,\text{K}$$
$$V_\text{i} = \frac{nRT}{p_\text{i}} = \frac{(1.5\,\text{mol}) \times (8.206 \times 10^{-2}\,\text{L atm K}^{-1}\,\text{mol}^{-1}) \times (288.\bar{2}\,\text{K})}{9.0\,\text{atm}}$$
$$= 3.9\overline{42}\,\text{L}$$

$$V_\text{f} = 3.9\overline{42}\,\text{L} + (100\,\text{cm}^2) \times (15\,\text{cm}) \times \left(\frac{1\,\text{L}}{1000\,\text{cm}^3}\right)$$
$$= 3.9\overline{42}\,\text{L} + 1.5\,\text{L} = 5.4\bar{4}\,\text{L}$$
$$\Delta S = (1.5\,\text{mol}) \times \left\{(28.8\,\text{J K}^{-1}\,\text{mol}^{-1}) \times \ln\left(\frac{282.\bar{9}}{288.\bar{2}}\right) + (8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times \ln\left(\frac{5.4\bar{4}}{3.9\overline{42}}\right)\right\}$$
$$= 1.5\,\text{mol}(-0.534\bar{6}\,\text{J K}^{-1}\,\text{mol}^{-1} + 2.67\bar{8}\,\text{J K}^{-1}\,\text{mol}^{-1}) = \boxed{3.2\,\text{J K}^{-1}}$$

E4.17(b) **(a)** $$\Delta_\text{vap}S^\ominus = \frac{\Delta_\text{vap}H^\ominus}{T_\text{b}} = \frac{35.27 \times 10^3\,\text{J mol}^{-1}}{(64.1 + 273.15)\,\text{K}} = +104.5\bar{8}\,\text{J K}^{-1} = \boxed{104.6\,\text{J K}^{-1}}$$

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

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

E4.18(b) **(a)** $$\Delta_\text{r}S^\ominus = S_\text{m}^\ominus(\text{Zn}^{2+}, \text{aq}) + S_\text{m}^\ominus(\text{Cu, s}) - S_\text{m}^\ominus(\text{Zn, s}) - S_\text{m}^\ominus(\text{Cu}^{2+}, \text{aq})$$
$$= [-112.1 + 33.15 - 41.63 + 99.6]\,\text{J K}^{-1}\text{mol}^{-1} = \boxed{-21.0\,\text{J K}^{-1}\text{mol}^{-1}}$$

(b) $$\Delta_\text{r}S^\ominus = 12S_\text{m}^\ominus(\text{CO}_2, \text{g}) + 11S_\text{m}^\ominus(\text{H}_2\text{O, l}) - S_\text{m}^\ominus(\text{C}_{12}\text{H}_{22}\text{O}_{11}, \text{s}) - 12S_\text{m}^\ominus(\text{O}_2, \text{g})$$
$$= [(12 \times 213.74) + (11 \times 69.91) - 360.2 - (12 \times 205.14)]\,\text{J K}^{-1}\,\text{mol}^{-1}$$
$$= \boxed{+512.0\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

E4.19(b) **(a)** $$\Delta_\text{r}H^\ominus = \Delta_\text{f}H^\ominus(\text{Zn}^{2+}, \text{aq}) - \Delta_\text{f}H^\ominus(\text{Cu}^{2+}, \text{aq})$$
$$= -153.89 - 64.77\,\text{kJ mol}^{-1} = -218.66\,\text{kJ mol}^{-1}$$

$$\Delta_\text{r}G^\ominus = -218.66\,\text{kJ mol}^{-1} - (298.15\,\text{K}) \times (-21.0\,\text{J K}^{-1}\,\text{mol}^{-1}) = \boxed{-212.40\,\text{kJ mol}^{-1}}$$

(b) $\Delta_r H^{\ominus} = \Delta_c H^{\ominus} = -5645\,\text{kJ mol}^{-1}$

$$\Delta_r G^{\ominus} = -5645\,\text{kJ mol}^{-1} - (298.15\,\text{K}) \times (512.0\,\text{J K}^{-1}\,\text{mol}^{-1}) = \boxed{-5798\,\text{kJ mol}^{-1}}$$

E4.20(b) **(a)** $\Delta_r G^{\ominus} = \Delta_f G^{\ominus}(\text{Zn}^{2+}, \text{aq}) - \Delta_f G^{\ominus}(\text{Cu}^{2+}, \text{aq})$

$$= -147.06 - 65.49\,\text{kJ mol}^{-1} = \boxed{-212.55\,\text{kJ mol}^{-1}}$$

(b) $\Delta_r G^{\ominus} = 12\Delta_f G^{\ominus}(\text{CO}_2, \text{g}) + 11\Delta_f G^{\ominus}(\text{H}_2\text{O}, \text{l}) - \Delta_f G^{\ominus}(\text{C}_{12}\text{H}_{22}\text{O}_{11}, \text{s})$

$$= [12 \times (-394.36) + 11 \times (-237.13) - (-1543)]\ \text{kJ mol}^{-1} = \boxed{-5798\,\text{kJ mol}^{-1}}$$

Comment. In each case these values of $\Delta_r G^{\ominus}$ agree closely with the calculated values in Exercise 4.19(b).

E4.21(b) $\text{CO(g)} + \text{CH}_3\text{OH(l)} \rightarrow \text{CH}_3\text{COOH(l)}$

$$\begin{aligned}
\Delta_r H^{\ominus} &= \sum \nu_J \Delta_f H^{\ominus}(\text{J}) \\
&= -484.5\,\text{kJ mol}^{-1} - (-238.66\,\text{kJ mol}^{-1}) - (-110.53\,\text{kJ mol}^{-1}) \\
&= -135.3\bar{1}\,\text{kJ mol}^{-1} \\
\Delta_r S^{\ominus} &= \sum \nu_J S^{\ominus}(\text{J}) \\
&= 159.8\,\text{J K}^{-1}\,\text{mol}^{-1} - 126.8\,\text{J K}^{-1}\,\text{mol}^{-1} - 197.67\,\text{J K}^{-1}\,\text{mol}^{-1} \\
&= -164.6\bar{7}\,\text{J K}^{-1}\,\text{mol}^{-1} \\
\Delta_r G^{\ominus} &= \Delta_r H^{\ominus} - T\Delta_r S^{\ominus} \\
&= -135.3\bar{1}\,\text{kJ mol}^{-1} - (298\,\text{K}) \times (-164.6\bar{7}\,\text{J K}^{-1}\,\text{mol}^{-1}) \\
&= -135.3\bar{1}\,\text{kJ mol}^{-1} + 49.07\bar{2}\,\text{kJ mol}^{-1} = \boxed{-86.2\,\text{kJ mol}^{-1}}
\end{aligned}$$

E4.22(b) The formation reaction of urea is

$$\text{C(gr)} + \tfrac{1}{2}\text{O}_2\text{(g)} + \text{N}_2\text{(g)} + 2\text{H}_2\text{(g)} \rightarrow \text{CO(NH}_2)_2\text{(s)}$$

The combustion reaction is

$$\text{CO(NH}_2)_2\text{(s)} + \tfrac{3}{2}\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)} + \text{N}_2\text{(g)}$$

$$\Delta_c H = \Delta_f H^{\ominus}(\text{CO}_2, \text{g}) + 2\Delta_f H^{\ominus}(\text{H}_2\text{O}, \text{l}) - \Delta_f H^{\ominus}(\text{CO(NH}_2)_2, \text{s})$$

$$\begin{aligned}
\Delta_f H^{\ominus}(\text{CO(NH}_2)_2, \text{s}) &= \Delta_f H^{\ominus}(\text{CO}_2, \text{g}) + 2\Delta_f H^{\ominus}(\text{H}_2\text{O}, \text{l}) - \Delta_c H(\text{CO(NH}_2)_2, \text{s}) \\
&= -393.51\,\text{kJ mol}^{-1} + (2) \times (-285.83\,\text{kJ mol}^{-1}) - (-632\,\text{kJ mol}^{-1}) \\
&= -333.1\bar{7}\,\text{kJ mol}^{-1}
\end{aligned}$$

$$\begin{aligned}
\Delta_f S^{\ominus} &= S_m^{\ominus}(\text{CO(NH}_2)_2, \text{s}) - S_m^{\ominus}(\text{C, gr}) - \tfrac{1}{2}S_m^{\ominus}(\text{O}_2, \text{g}) - S_m^{\ominus}(\text{N}_2, \text{g}) - 2S_m^{\ominus}(\text{H}_2, \text{g}) \\
&= 104.60\,\text{J K}^{-1}\,\text{mol}^{-1} - 5.740\,\text{J K}^{-1}\,\text{mol}^{-1} - \tfrac{1}{2}(205.138\,\text{J K}^{-1}\,\text{mol}^{-1}) \\
&\quad - 191.61\,\text{J K}^{-1}\,\text{mol}^{-1} - 2(130.684\,\text{J K}^{-1}\,\text{mol}^{-1}) \\
&= -456.68\bar{7}\,\text{J K}^{-1}\,\text{mol}^{-1}
\end{aligned}$$

$$\begin{aligned}
\Delta_f G^{\ominus} &= \Delta_f H^{\ominus} - T\Delta_f S^{\ominus} \\
&= -333.1\bar{7}\,\text{kJ mol}^{-1} - (298\,\text{K}) \times (-456.68\bar{7}\,\text{J K}^{-1}\,\text{mol}^{-1}) \\
&= -333.1\bar{7}\,\text{kJ mol}^{-1} + 136.\overline{093}\,\text{kJ mol}^{-1} \\
&= \boxed{-197\,\text{kJ mol}^{-1}}
\end{aligned}$$

E4.23(b) **(a)**

$$\Delta S(\text{gas}) = nR\ln\left(\frac{V_\text{f}}{V_\text{i}}\right) = \left(\frac{21\,\text{g}}{39.95\,\text{g mol}^{-1}}\right) \times (8.314\,\text{J K}^{-1}\,\text{mol}^{-1})\ln 2$$

$$= 3.0\overline{29}\,\text{J K}^{-1} = \boxed{3.0\,\text{J K}^{-1}}$$

$$\Delta S(\text{surroundings}) = -\Delta S(\text{gas}) = \boxed{-3.0\,\text{J K}^{-1}} \text{ [reversible]}$$

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

(b) (Free expansion)

$$\Delta S(\text{gas}) = \boxed{+3.0\,\text{J K}^{-1}} \quad [S \text{ is a state function}]$$

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

$$\Delta S(\text{total}) = \boxed{+3.0\,\text{J K}^{-1}}$$

(c)

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

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

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

E4.24(b) Because entropy is a state function, we can choose any convenient path between the initial and final states.

Choose isothermal compression followed by constant-volume heating

$$\Delta S = nR\ln\left(\frac{V_\text{f}}{V_\text{i}}\right) + nC_{V,\text{m}}\ln\left(\frac{T_\text{f}}{T_\text{i}}\right)$$

$$= -nR\ln 3 + nC_{V,\text{m}}\ln 3$$

$$= n(C_{V,\text{m}} - R)\ln 3 \quad C_{V,\text{m}} = \tfrac{5}{2}R \text{ for a diatomic perfect gas}$$

$$\boxed{\Delta S = \tfrac{3}{2}nR\ln 3}$$

E4.25(b)

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$$

$$\Delta_\text{r}G^\ominus = 3\Delta_\text{f}G^\ominus(CO_2, g) + 4\Delta_\text{f}G^\ominus(H_2O, l) - \Delta_\text{f}G^\ominus(C_3H_8, g) - 0$$

$$= 3(-394.36\,\text{kJ mol}^{-1}) + 4(-237.13\,\text{kJ mol}^{-1}) - 1(-23.49\,\text{kJ mol}^{-1})$$

$$= -2108.11\,\text{kJ mol}^{-1}$$

The maximum non-expansion work is $\boxed{2108.11\,\text{kJ mol}^{-1}}$ since $|w_\text{e}| = |\Delta_\text{r}G|$

E4.26(b) **(a)**

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

$$= 1 - \frac{500\,\text{K}}{1000\,\text{K}} = \boxed{0.500}$$

(b) Maximum work $= \varepsilon|q_\text{h}| = (0.500) \times (1.0\,\text{kJ}) = \boxed{0.50\,\text{kJ}}$

(c)

$$\varepsilon_\text{max} = \varepsilon_\text{rev} \quad \text{and} \quad |w_\text{max}| = |q_\text{h}| - |q_\text{c,min}|$$

$$|q_\text{c,min}| = |q_\text{h}| - |w_\text{max}|$$

$$= 1.0\,\text{kJ} - 0.50\,\text{kJ}$$

$$= \boxed{0.5\,\text{kJ}}$$

Solutions to problems

Assume that all gases are perfect and that data refer to 298 K unless otherwise stated.

Solutions to numerical problems

P4.1 **(a)** Because entropy is a state function $\Delta_{\mathrm{trs}}S(\mathrm{l} \rightarrow \mathrm{s}, -5°\mathrm{C})$ may be determined indirectly from the following cycle

$$\begin{tikzcd}
\mathrm{H_2O(l, 0°C)} \arrow[r, "\Delta_{\mathrm{trs}}S(\mathrm{l}\rightarrow\mathrm{s}, 0°\mathrm{C})"] & \mathrm{H_2O(s, 0°C)} \arrow[d, "\Delta S_{\mathrm{s}}"] \\
\mathrm{H_2O(l, -5°C)} \arrow[u, "\Delta S_{\mathrm{l}}"] \arrow[r, "\Delta_{\mathrm{trs}}S(\mathrm{l}\rightarrow\mathrm{s}, -5°\mathrm{C})"] & \mathrm{H_2O(s, -5°C)}
\end{tikzcd}$$

$$\Delta_{\mathrm{trs}}S(\mathrm{l} \rightarrow \mathrm{s},\ -5°\mathrm{C}) = \Delta S_{\mathrm{l}} + \Delta_{\mathrm{trs}}S(\mathrm{l} \rightarrow \mathrm{s},\ 0°\mathrm{C}) + \Delta S_{\mathrm{s}}$$

$$\Delta S_{\mathrm{l}} = C_{p,\mathrm{m}}(\mathrm{l}) \ln \frac{T_{\mathrm{f}}}{T} \quad [\theta_{\mathrm{f}} = 0°\mathrm{C},\ \theta = -5°\mathrm{C}]$$

$$\Delta S_{\mathrm{s}} = C_{p,\mathrm{m}}(\mathrm{s}) \ln \frac{T}{T_{\mathrm{f}}}$$

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

$$\Delta_{\mathrm{trs}}S(\mathrm{l} \rightarrow \mathrm{s},\ T_{\mathrm{f}}) = \frac{-\Delta_{\mathrm{fus}}H}{T_{\mathrm{f}}}$$

$$\begin{aligned}
\text{Thus, } \Delta_{\mathrm{trs}}S(\mathrm{l} \rightarrow \mathrm{s},\ T) &= \frac{-\Delta_{\mathrm{fus}}H}{T_{\mathrm{f}}} - \Delta C_p \ln \frac{T}{T_{\mathrm{f}}} \\
&= \frac{-6.01 \times 10^3\,\mathrm{J\,mol^{-1}}}{273\,\mathrm{K}} - (37.3\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln \frac{268}{273} \\
&= \boxed{-21.3\,\mathrm{J\,K^{-1}\,mol^{-1}}}
\end{aligned}$$

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

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

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

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

$$\begin{aligned}
\text{Thus, } \Delta S_{\mathrm{sur}} &= \frac{\Delta_{\mathrm{fus}}H(T)}{T} = \frac{\Delta_{\mathrm{fus}}H(T_{\mathrm{f}})}{T} + \Delta C_p \frac{(T - T_{\mathrm{f}})}{T} \\
&= \frac{6.01\,\mathrm{kJ\,mol^{-1}}}{268\,\mathrm{K}} + (37.3\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \left(\frac{268 - 273}{268}\right) \\
&= \boxed{+21.7\,\mathrm{J\,K^{-1}\,mol^{-1}}}
\end{aligned}$$

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

Since $\Delta S_{\mathrm{total}} > 0$, the transition $\mathrm{l} \rightarrow \mathrm{s}$ is spontaneous at $-5°\mathrm{C}$

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

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

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

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

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

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

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

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

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

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

P4.2

$$\Delta S_{\text{m}} = \int_{T_1}^{T_2} \frac{C_{p,\text{m}}\,\text{d}T}{T}[19] = \int_{T_1}^{T_2} \left(\frac{a + bT}{T}\right)\text{d}T = a\ln\left(\frac{T_2}{T_1}\right) + b(T_2 - T_1)$$

$$a = 91.47\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}, \qquad b = 7.5 \times 10^{-2}\,\text{J}\,\text{K}^{-2}\,\text{mol}^{-1}$$

$$\Delta S_{\text{m}} = (91.47\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) \times \ln\left(\frac{300\,\text{K}}{273\,\text{K}}\right) + (0.075\,\text{J}\,\text{K}^{-2}\,\text{mol}^{-1}) \times (27\,\text{K})$$

$$= 10.\bar{7}\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$$

Therefore, for 1.00 mol, $\boxed{\Delta S = +11\,\text{J}\,\text{K}^{-1}}$

P4.8

	ΔS	ΔS_{sur}	ΔH	ΔT	ΔA	ΔG
Process (a)	$+5.8\,\text{J}\,\text{K}^{-1}$	$-5.8\,\text{J}\,\text{K}^{-1}$	0	0	$-1.7\,\text{kJ}$	$-1.7\,\text{kJ}$
Process (b)	$+5.8\,\text{J}\,\text{K}^{-1}$	$-1.7\,\text{J}\,\text{K}^{-1}$	0	0	$-1.7\,\text{kJ}$	$-1.7\,\text{kJ}$
Process (c)	$+3.9\,\text{J}\,\text{K}^{-1}$	0	$-8.4 \times 10^2\,\text{J}$	$-41\,\text{K}$	?	?

Process (a)

$\boxed{\Delta H = \Delta T = 0}$ [isothermal process in a perfect gas]

$$\Delta S_{\text{tot}} = 0 = \Delta S + \Delta S_{\text{surr}}$$

$$\Delta S = nR\ln\left(\frac{V_{\text{f}}}{V_{\text{i}}}\right)[4.17] = (1.00\,\text{mol}) \times (8.314\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) \times \ln\left(\frac{20\,\text{L}}{10\,\text{L}}\right) = \boxed{+5.8\,\text{J}\,\text{K}^{-1}}$$

$$\Delta S_{\text{surr}} = -\Delta S = \boxed{-5.8\,\text{J}\,\text{K}^{-1}}$$

$\Delta A = \Delta U - T\Delta S$ [36] $\quad \Delta U = 0$ [isothermal process in perfect gas]

$$\Delta A = 0 - (298\,\text{K}) \times (5.7\bar{6}\,\text{J}\,\text{K}^{-1}) = \boxed{-1.7 \times 10^3\,\text{J}}$$

$$\Delta G = \Delta H - T\Delta S = 0 - T\Delta S = \boxed{-1.7 \times 10^3\,\text{J}}$$

Process (*b*)

$$\boxed{\Delta H = \Delta T = 0} \quad \text{[isothermal process in perfect gas]}$$

$$\Delta S = \boxed{+5.8\,\mathrm{J\,K^{-1}}} \quad \text{[Same as process (a); } S \text{ is a state function]}$$

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T_{\text{surr}}} \quad q_{\text{surr}} = -q = -(-w) = w \ \ \text{[First Law with } \Delta U = 0\text{]}$$

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

$$= -(0.50\,\mathrm{atm}) \times (1.01 \times 10^5\,\mathrm{Pa\,atm^{-1}}) \times (20\,\mathrm{L} - 10\,\mathrm{L}) \times \left(\frac{10^{-3}\,\mathrm{m^3}}{\mathrm{L}}\right) = -5.0\bar{5} \times 10^2\,\mathrm{J}$$

$$= q_{\text{surr}}$$

$$\Delta S_{\text{surr}} = \frac{-5.0\bar{5} \times 10^2\,\mathrm{J}}{298\,\mathrm{K}} = \boxed{-1.7\,\mathrm{J\,K^{-1}}}$$

$$\Delta A = \boxed{-1.7 \times 10^3\,\mathrm{J}}$$

$$\Delta G = \boxed{-1.7 \times 10^3\,\mathrm{J}} \quad \text{[same as process (a); } A \text{ and } G \text{ are state functions]}$$

Process (*c*)

$$\Delta U = w \quad \text{[adiabatic process]}$$

$$w = -p_{\text{ex}}\Delta V = -5.0\bar{5} \times 10^2\,\mathrm{J} \quad \text{[same as process (b)]}$$

$$\Delta U = nC_{V,\text{m}}\Delta T \quad \Delta T = \frac{\Delta U}{nC_{V,\text{m}}} = \frac{-5.0\bar{5} \times 10^2\,\mathrm{J}}{(1.00\,\mathrm{mol}) \times \left(\frac{3}{2}\right) \times \left(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}\right)} = \boxed{-40.\bar{6}\,\mathrm{K}}$$

$$T_{\text{f}} = T_{\text{i}} - 40.\bar{6}\,\mathrm{K} = 298\,\mathrm{K} - 40.\bar{6}\,\mathrm{K} = 257\,\mathrm{K}$$

$$\Delta S = nC_{V,\text{m}} \ln\left(\frac{T_{\text{f}}}{T_{\text{i}}}\right) [20] + nR\ln\left(\frac{V_{\text{f}}}{V_{\text{i}}}\right) \ [17]$$

$$= (1.00\,\mathrm{mol}) \times \left(\frac{3}{2}\right) \times (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{257\,\mathrm{K}}{298\,\mathrm{K}}\right) + (1.00\,\mathrm{mol})$$

$$\times (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{20\,\mathrm{L}}{10\,\mathrm{L}}\right) = \boxed{+3.9\,\mathrm{J\,K^{-1}}}$$

$$\Delta S_{\text{surr}} = \boxed{0} \quad \text{[adiabatic process]}$$

ΔA and ΔG cannot be determined from the information provided without use of additional relations developed in Chapters 5 and 19.

$$\Delta H = nC_{p,\text{m}}\Delta T \quad C_{p,\text{m}} = C_{V,\text{m}} + R = \tfrac{5}{2}R$$

$$= (1.00\,\mathrm{mol}) \times \left(\tfrac{5}{2}\right) \times (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (-40.\bar{6}\,\mathrm{K}) = \boxed{-8.4 \times 10^2\,\mathrm{J}}$$

P4.9 $S_{\text{m}}^{\ominus}(T) = S_{\text{m}}^{\ominus}(298\,\mathrm{K}) + \Delta S$

$$\Delta S = \int_{T_1}^{T_2} C_{p,\text{m}} \frac{\mathrm{d}T}{T} = \int_{T_1}^{T_2} \left(\frac{a}{T} + b + \frac{c}{T^3}\right) \mathrm{d}T = a\ln\frac{T_2}{T_1} + b(T_2 - T_1) - \frac{1}{2}c\left(\frac{1}{T_2^2} - \frac{1}{T_1^2}\right)$$

$$\textbf{(a)}\quad S_m^\ominus(373\,\mathrm{K}) = (192.45\,\mathrm{J\,K^{-1}\,mol^{-1}}) + (29.75\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{373}{298}\right)$$
$$+ (25.10 \times 10^{-3}\,\mathrm{J\,K^{-2}\,mol^{-1}}) \times (75.0\,\mathrm{K})$$
$$+ \left(\tfrac{1}{2}\right) \times (1.55 \times 10^5\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \left(\tfrac{1}{(373.15)^2} - \tfrac{1}{(298.15)^2}\right)$$
$$= \boxed{200.7\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

$$\textbf{(b)}\quad S_m^\ominus(773\,\mathrm{K}) = (192.45\,\mathrm{J\,K^{-1}\,mol^{-1}}) + (29.75\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{773}{298}\right)$$
$$+ (25.10 \times 10^{-3}\,\mathrm{J\,K^{-2}\,mol^{-1}}) \times (475\,\mathrm{K})$$
$$+ \left(\tfrac{1}{2}\right) \times (1.55 \times 10^5\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \left(\tfrac{1}{773^2} - \tfrac{1}{298^2}\right)$$
$$= \boxed{232.0\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

P4.10 ΔS depends on only the initial and final states, so we can use $\Delta S = nC_{p,\mathrm{m}} \ln \frac{T_\mathrm{f}}{T_\mathrm{i}}$ [4.20]

Since $q = nC_{p,\mathrm{m}}(T_\mathrm{f} - T_\mathrm{i}),\ T_\mathrm{f} = T_\mathrm{i} + \frac{q}{nC_{p,\mathrm{m}}} = T_\mathrm{i} + \frac{I^2Rt}{nC_{p,\mathrm{m}}}$ $(q = ItV = I^2Rt)$

That is, $\Delta S = nC_{p,\mathrm{m}} \ln\left(1 + \frac{I^2Rt}{nC_{p,\mathrm{m}}T_\mathrm{i}}\right)$

Since $n = \frac{500\,\mathrm{g}}{63.5\,\mathrm{g\,mol^{-1}}} = 7.87\,\mathrm{mol}$

$$\Delta S = (7.87\,\mathrm{mol}) \times (24.4\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(1 + \frac{(1.00\,\mathrm{A})^2 \times (1000\,\Omega) \times (15.0\,\mathrm{s})}{(7.87) \times (24.4\,\mathrm{J\,K^{-1}}) \times (293\,\mathrm{K})}\right)$$
$$= (192\,\mathrm{J\,K^{-1}}) \times (\ln 1.27) = \boxed{+45.4\,\mathrm{J\,K^{-1}}}$$

For the second experiment, no change in state occurs for the copper; hence, $\Delta S(\text{copper}) = 0$. However, for the water, considered as a large heat sink

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

P4.12 **(a)** Calculate the final temperature as in Exercise 4.14(a)

$$T_\mathrm{f} = \frac{n_1T_{\mathrm{i}1} + n_2T_{\mathrm{i}2}}{n_1 + n_2} = \frac{1}{2}(T_{\mathrm{i}1} + T_{\mathrm{i}2}) = 318\,\mathrm{K} \quad [n_1 = n_2]$$
$$\Delta S = n_1C_{p,\mathrm{m}} \ln \frac{T_\mathrm{f}}{T_{\mathrm{i}1}} + n_2C_{p,\mathrm{m}} \ln \frac{T_\mathrm{f}}{T_{\mathrm{i}2}} = n_1C_{p,\mathrm{m}} \ln \frac{T_\mathrm{f}^2}{T_{\mathrm{i}1}T_{\mathrm{i}2}} \quad [n_1 = n_2]$$
$$= \left(\frac{200\,\mathrm{g}}{18.02\,\mathrm{g\,mol^{-1}}}\right) \times (75.3\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{318^2}{273 \times 363}\right) = \boxed{+17.0\,\mathrm{J\,K^{-1}}}$$

(b) Heat required for melting is

$$n_1\Delta_{\text{fus}}H = (11.1\,\text{mol}) \times (6.01\,\text{kJ mol}^{-1}) = 66.7\,\text{kJ}$$

The decrease in temperature of the hot water as a result of heat transfer to the ice is

$$\Delta T = \frac{q}{nC_{p,\text{m}}} = \frac{66.7\,\text{kJ}}{(11.1\,\text{mol}) \times (75.3\,\text{J K}^{-1}\,\text{mol}^{-1})} = 79.8\,\text{K}$$

At this stage the system consists of 200 g water at 0°C and 200 g water at (90°C − 79.8°C) = 10°C (283 K). The entropy change so far is therefore

$$\begin{aligned}\Delta S &= \frac{n\Delta H_{\text{fus}}}{T_{\text{f}}} + nC_{p,\text{m}}\ln\frac{283\,\text{K}}{363\,\text{K}}\\ &= \left(\frac{(11.1\,\text{mol}) \times (6.01\,\text{kJ mol}^{-1})}{273\,\text{K}}\right) + (11.1\,\text{mol}) \times (75.3\,\text{J K}^{-1}\,\text{mol}^{-1}) \times \ln\left(\frac{283\,\text{K}}{363\,\text{K}}\right)\\ &= 244\,\text{J K}^{-1} - 208.\bar{1}\,\text{J K}^{-1} = +35.\bar{3}\,\text{J K}^{-1}\end{aligned}$$

The final temperature is $T_{\text{f}} = \frac{1}{2}(273\,\text{K} + 283\,\text{K}) = 278\,\text{K}$, and the entropy change in this step is

$$\Delta S = nC_{p,\text{m}}\ln\frac{T_{\text{f}}^2}{T_{\text{i1}}T_{\text{i2}}} = (11.1) \times (75.3\,\text{J K}^{-1}) \times \ln\left(\frac{278^2}{273 \times 283}\right) = +0.27\,\text{J K}^{-1}$$

Therefore, overall, $\Delta S = 35.\bar{3}\,\text{J K}^{-1} + 0.27\,\text{J K}^{-1} = \boxed{+36\,\text{J K}^{-1}}$

P4.15

$$\Delta_{\text{r}}H^{\ominus} = \sum_{\text{J}} \nu_{\text{J}}\Delta_{\text{f}}H^{\ominus}(\text{J})\ [2.41]$$

$$\begin{aligned}\Delta_{\text{r}}H^{\ominus}(298\,\text{K}) &= 1 \times \Delta_{\text{f}}H^{\ominus}(\text{CO, g}) + 1 \times \Delta_{\text{f}}H^{\ominus}(\text{H}_2\text{O, g}) - 1 \times \Delta_{\text{f}}H^{\ominus}(\text{CO}_2\text{, g})\\ &= \{-110.53 - 241.82 - (-393.51)\}\ \text{kJ mol}^{-1} = \boxed{+41.16\,\text{kJ mol}^{-1}}\end{aligned}$$

$$\Delta_{\text{r}}S^{\ominus} = \sum_{\text{J}} \nu_{\text{J}}S_{\text{m}}^{\ominus}(\text{J})\ [4.22]$$

$$\begin{aligned}\Delta_{\text{r}}S^{\ominus}(298\,\text{K}) &= 1 \times S_{\text{m}}^{\ominus}(\text{CO, g}) + 1 \times S_{\text{m}}^{\ominus}(\text{H}_2\text{O, g}) - 1 \times S_{\text{m}}^{\ominus}(\text{CO}_2\text{, g}) - 1 \times S_{\text{m}}^{\ominus}(\text{H}_2\text{, g})\\ &= (197.67 + 188.83 - 213.74 - 130.684)\ \text{kJ mol}^{-1} = \boxed{+42.08\,\text{J K}^{-1}\,\text{mol}^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta_{\text{r}}H^{\ominus}(398\,\text{K}) &= \Delta_{\text{r}}H^{\ominus}(298\,\text{K}) + \int_{298\,\text{K}}^{398\,\text{K}} \Delta_{\text{r}}C_p\,\text{d}T\ [2.44]\\ &= \Delta_{\text{r}}H^{\ominus}(298\,\text{K}) + \Delta_{\text{r}}C_p\Delta T \quad [\text{heat capacities constant}]\end{aligned}$$

$$\begin{aligned}\Delta_{\text{r}}C_p &= 1 \times C_{p,\text{m}}(\text{CO, g}) + 1 \times C_{p,\text{m}}(\text{H}_2\text{O, g}) - 1 \times C_{p,\text{m}}(\text{CO}_2\text{, g}) - 1 \times C_{p,\text{m}}(\text{H}_2\text{, g})\\ &= (29.14 + 33.58 - 37.11 - 28.824)\,\text{J K}^{-1}\,\text{mol}^{-1} = -3.21\,\text{J K}^{-1}\,\text{mol}^{-1}\end{aligned}$$

$$\Delta_{\text{r}}H^{\ominus}(398\,\text{K}) = (41.16\,\text{kJ mol}^{-1}) + (-3.21\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (100\,\text{K}) = \boxed{+40.84\,\text{kJ mol}^{-1}}$$

For each substance in the reaction

$$\Delta S = C_{p,\text{m}}\ln\left(\frac{T_{\text{f}}}{T_{\text{i}}}\right) = C_{p,\text{m}}\ln\left(\frac{398\,\text{K}}{298\,\text{K}}\right)\ [4.20]$$

Thus

$$\begin{aligned}
\Delta_r S^\ominus(398\,\mathrm{K}) &= \Delta_r S^\ominus(298\,\mathrm{K}) + \sum_J \nu_J C_{p,m}(\mathrm{J}) \ln\left(\frac{T_f}{T_i}\right) \\
&= \Delta_r S^\ominus(298\,\mathrm{K}) + \Delta_r C_p \ln\left(\frac{398\,\mathrm{K}}{298\,\mathrm{K}}\right) \\
&= (42.01\,\mathrm{J\,K^{-1}\,mol^{-1}}) + (-3.21\,\mathrm{J\,K^{-1}\,mol^{-1}}) = (42.01 - 0.93)\,\mathrm{J\,K^{-1}\,mol^{-1}} \\
&= \boxed{+41.08\,\mathrm{J\,K^{-1}\,mol^{-1}}}
\end{aligned}$$

Comment. Both $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ changed little over 100 K for this reaction. This is not an uncommon result.

P4.17 $$S_m(T) = S_m(0) + \int_0^T \frac{C_{p,m}\,dT}{T} \quad [4.19]$$

Perform a graphical integration by plotting $C_{p,m}/T$ against T and determining the area under the curve.

Draw up the following table

T/K	10	20	30	40	50	60	70	80
$(C_{p,m}/T)/(\mathrm{J\,K^{-1}\,mol^{-1}})$	0.209	0.722	1.215	1.564	1.741	1.850	1.877	1.868

T/K	90	100	110	120	130	140	150	160
$(C_{p,m}/T)/(\mathrm{J\,K^{-1}\,mol^{-1}})$	1.837	1.796	1.753	1.708	1.665	1.624	1.584	1.546

T/K	170	180	190	200
$(C_{p,m}/T)/(\mathrm{J\,K^{-1}\,mol^{-1}})$	1.508	1.473	1.437	1.403

Plot $C_{p,m}/T$ against T (Fig. 4.2(a)). Extrapolate to $T = 0$ using $C_{p,m} = aT^3$ fitted to the point at $T = 10\,\mathrm{K}$, which gives $a = 2.09\,\mathrm{mJ\,K^{-2}\,mol^{-1}}$. Determine the area under the graph up to each T and plot S_m against T (Fig. 4.2(b)).

T/K	25	50	75	100	125	150	175	200
$\{S_m^\ominus - S_m^\ominus(0)\}/(\mathrm{J\,K^{-1}\,mol^{-1}})$	9.25	43.50	88.50	135.00	178.25	219.0	257.3	293.5

The molar enthalpy is determined in a similar manner from a plot of $C_{p,m}$ against T by determining the area under the curve (Fig. 4.3)

$$H_m^\ominus(200\,\mathrm{K}) - H_m^\ominus(0) = \int_0^{200\,\mathrm{K}} C_{p,m}\,dT = \boxed{32.00\,\mathrm{kJ\,mol^{-1}}}$$

Solutions to theoretical problems

P4.20 Refer to Fig. 4.5 of the text for a description of the Carnot cycle and the heat terms accompanying each step of the cycle. Labelling the steps (a), (b), (c), and (d) going clockwise around the cycle starting from state A, the four episodes of heat transfer are

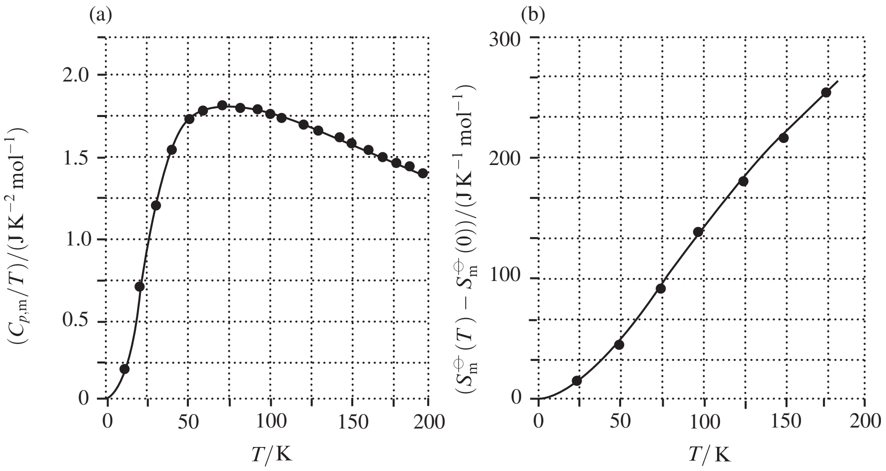


Figure 4.2

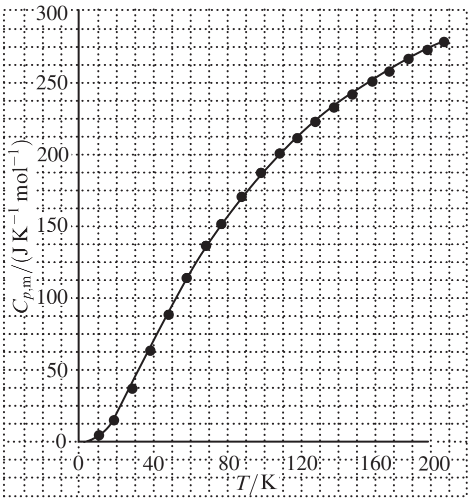


Figure 4.3

(a) $q_\mathrm{h} = nRT_\mathrm{h} \ln \dfrac{V_\mathrm{B}}{V_\mathrm{A}} \qquad \dfrac{q_\mathrm{h}}{T_\mathrm{h}} = nR \ln \dfrac{V_\mathrm{B}}{V_\mathrm{A}}$

(b) 0 [adiabatic]

(c) $q_\mathrm{c} = nRT_\mathrm{c} \ln \dfrac{V_\mathrm{D}}{V_\mathrm{C}} \qquad \dfrac{q_\mathrm{c}}{T_\mathrm{c}} = nR \ln \dfrac{V_\mathrm{D}}{V_\mathrm{C}}$

(d) 0 [adiabatic]

Therefore $\displaystyle\oint \frac{\mathrm{d}q}{T} = \frac{q_\mathrm{h}}{T_\mathrm{h}} + \frac{q_\mathrm{c}}{T_\mathrm{c}} = nR \ln \frac{V_\mathrm{B} V_\mathrm{D}}{V_\mathrm{A} V_\mathrm{C}}$

However, $\displaystyle\frac{V_\mathrm{B} V_\mathrm{D}}{V_\mathrm{A} V_\mathrm{C}} = \frac{V_\mathrm{B} V_\mathrm{D}}{V_\mathrm{C} V_\mathrm{A}} = \left(\frac{T_\mathrm{c}}{T_\mathrm{h}}\right)^c \times \left(\frac{T_\mathrm{h}}{T_\mathrm{c}}\right)^c$ [2.34 of Section 2.6] $= 1$

Therefore $\displaystyle\oint \frac{\mathrm{d}q}{T} = 0$

If the first stage is replaced by isothermal, irreversible expansion against a constant external pressure, $q = -w = p_\mathrm{ex}(V_\mathrm{B} - V_\mathrm{A})$ ($\Delta U = 0$, since this is an isothermal process in a perfect gas)

Therefore, $\dfrac{q_\mathrm{h}}{T_\mathrm{h}} = \left(\dfrac{p_\mathrm{ex}}{T_\mathrm{h}}\right) \times (V_\mathrm{B} - V_\mathrm{A})$

However, $p_\mathrm{ex}(V_\mathrm{B} - V_\mathrm{A}) < nRT_\mathrm{h} \ln \dfrac{V_\mathrm{B}}{V_\mathrm{A}}$ because less work is done in the irreversible expansion, so

$$\oint \frac{\mathrm{d}q}{T} < nR \ln \frac{V_\mathrm{B}}{V_\mathrm{A}} + nR \ln \frac{V_\mathrm{D}}{V_\mathrm{C}} = 0. \quad \text{That is,} \quad \oint \frac{\mathrm{d}q}{T} < 0$$

Comment. Whenever an irreversible step is included in the cycle the above result will be obtained.

Question. Can you provide a general proof of this result?

P4.22 The isotherms correspond to T = constant, and the reversibly traversed adiabats correspond to S = constant. Thus we can represent the cycle as in Fig. 4.4.

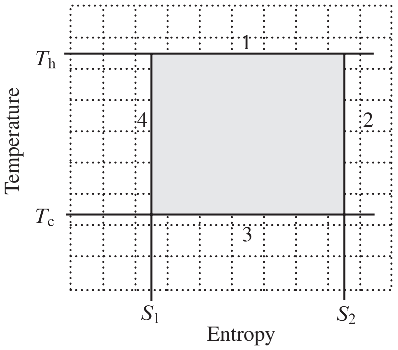


Figure 4.4

In this figure, paths 1, 2, 3, and 4 correspond to the four stages of the Carnot cycle listed in the text following eqn 4.7

The area within the rectangle is

$$\text{Area} = \oint T\,\mathrm{d}S = (T_\mathrm{h} - T_\mathrm{c}) \times (S_2 - S_1) = (T_\mathrm{h} - T_\mathrm{c})\Delta S = (T_\mathrm{h} - T_\mathrm{c})nR \ln \frac{V_\mathrm{B}}{V_\mathrm{A}}$$

(isothermal expansion from V_A to V_B, stage 1)

But, $w(\text{cycle}) = \varepsilon q_\mathrm{h} = \left(\dfrac{T_\mathrm{h} - T_\mathrm{c}}{T_\mathrm{h}}\right) nRT_\mathrm{h} \ln \dfrac{V_\mathrm{B}}{V_\mathrm{A}}$ [Fig. 4.5] $= nR(T_\mathrm{h} - T_\mathrm{c}) \ln \dfrac{V_\mathrm{B}}{V_\mathrm{A}}$

Therefore, the area is equal to the net work done in the cycle.

P4.23 $\Delta S = \boxed{nC_{p,\mathrm{m}} \ln \dfrac{T_\mathrm{f}}{T_\mathrm{h}} + nC_{p,\mathrm{m}} \ln \dfrac{T_\mathrm{f}}{T_\mathrm{c}}}$ [4.20] [T_f is the final temperature, $T_\mathrm{f} = \frac{1}{2}(T_\mathrm{h} + T_\mathrm{c})$]

In the present case, $T_\mathrm{f} = \frac{1}{2}(500\,\mathrm{K} + 250\,\mathrm{K}) = 375\,\mathrm{K}$

$$\Delta S = nC_{p,\mathrm{m}} \ln \frac{T_\mathrm{f}^2}{T_\mathrm{h}T_\mathrm{c}} = nC_{p,\mathrm{m}} \ln \frac{(T_\mathrm{h} + T_\mathrm{c})^2}{4T_\mathrm{h}T_\mathrm{c}} = \left(\frac{500\,\mathrm{g}}{63.54\,\mathrm{g\,mL^{-1}}}\right) \times (24.4\,\mathrm{J\,K^{-1}\,mol^{-1}})$$

$$\times \ln\left(\frac{375^2}{500 \times 250}\right) = \boxed{+22.6\,\mathrm{J\,K^{-1}}}$$

P4.26 $g = f + yz$

$\mathrm{d}g = \mathrm{d}f + y\,\mathrm{d}z + z\,\mathrm{d}y = a\,\mathrm{d}x - z\,\mathrm{d}y + y\,\mathrm{d}z + z\,\mathrm{d}y = a\,\mathrm{d}x + y\,\mathrm{d}z$

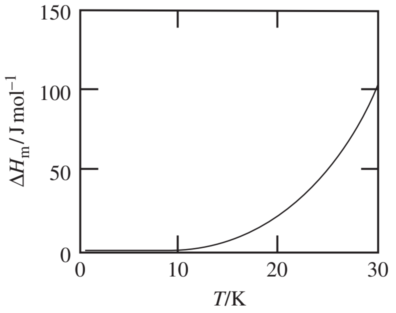
Comment. This procedure is referred to as a Legendre transformation and is essentially the method used in Chapter 5 to express the differentials of H, G, and A in terms of the differential of U.

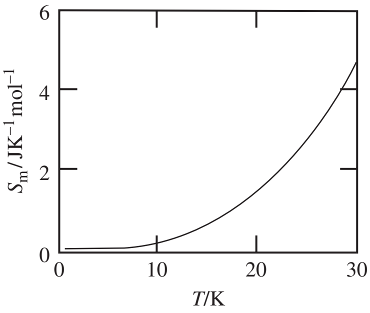
P4.27 **(a)** According to eqns 2.43, 4.19, and 4.39:

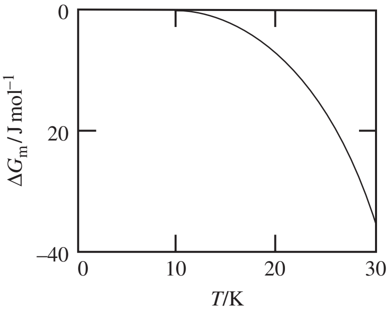
$$\Delta H_{\mathrm{m}}(T) = H_{\mathrm{m}}(T) - H_{\mathrm{m}}(0) = \int_{0\,\mathrm{K}}^{30\,\mathrm{K}} C_p(T)\,\mathrm{d}T \quad \text{where } C_p(T) = aT^3\left(1 - \mathrm{e}^{-\beta/T^2}\right)$$

$$S_{\mathrm{m}}(T) = \int_{0\,\mathrm{K}}^{30\,\mathrm{K}} \frac{C_p(T)}{T}\,\mathrm{d}T \quad \text{and} \quad \Delta G_{\mathrm{m}}(T) = G_{\mathrm{m}}(T) - G_{\mathrm{m}}(0) = \Delta H_{\mathrm{m}}(T) - TS_{\mathrm{m}}(T)$$

The integral computations are easily performed with the built-in numerical integration capabilities of a scientific calculator or computer software spreadsheet. Computations at ten or more equally spaced temperatures between 0 K and 30 K will produce smooth-looking plots.







(b) According to the law of Dulong and Petit the constant pressure heat capacity of $\mathrm{Ce_2Si_2O_7}$ (11 moles of atoms per mole of compound) is approximately equal to $11 \times 3 \times R = 274\,\mathrm{J\,K^{-1}\,mol^{-1}}$. The experimental value at 900 K equals $287\mathrm{J\,K^{-1}\,mol^{-1}}$. The law of Dulong and Petit gives a reasonable estimate of the heat capacity at very high temperature.

Solutions to applications

P4.29 **(a)** $\Delta_{\mathrm{r}}G^{\ominus} = \Delta_{\mathrm{r}}H^{\ominus} - T\Delta_{\mathrm{r}}S^{\ominus}$

$$\Delta_{\mathrm{r}}H^{\ominus} = \Delta_{\mathrm{f}}H^{\ominus}(sec\text{-}\mathrm{C_4H_9}) - \Delta_{\mathrm{f}}H^{\ominus}(tert\text{-}\mathrm{C_4H_9})$$

$$= (67.5 - 51.3)\,\mathrm{kJ\,mol^{-1}} = 16.2\,\mathrm{kJ\,mol^{-1}}$$

$$\begin{aligned}
\Delta_r S^\ominus &= S_m^\ominus(sec\text{-}C_4H_9) - S_m^\ominus(tert\text{-}C_4H_9) \\
&= (336.6 - 314.6)\,\mathrm{J\,K^{-1}\,mol^{-1}} = 22.0\,\mathrm{J\,K^{-1}\,mol^{-1}} \\
\Delta_r G^\ominus &= 16.2\,\mathrm{kJ\,mol^{-1}} - (700\,\mathrm{K}) \times (22.0 \times 10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}}) \\
&= \boxed{0.8\,\mathrm{kJ\,mol^{-1}}}
\end{aligned}$$

(b)

$$\begin{aligned}
\Delta_r H^\ominus &= \Delta_f H^\ominus(C_3H_6) + \Delta_f H^\ominus(CH_3) - \Delta_f H^\ominus(tert\text{-}C_4H_9) \\
\Delta_r H^\ominus &= (20.42 + 145.49 - 51.3)\,\mathrm{kJ\,mol^{-1}} = 114.6\,\mathrm{kJ\,mol^{-1}} \\
\Delta_r S^\ominus &= (267.05 + 194.2 - 314.6)\,\mathrm{J\,K^{-1}\,mol^{-1}} = 146.7\,\mathrm{J\,K^{-1}\,mol^{-1}} \\
\Delta_r G^\ominus &= 114.6\,\mathrm{kJ\,mol^{-1}} - (700\,\mathrm{K}) \times (0.1467\,\mathrm{kJ\,K^{-1}\,mol^{-1}}) \\
&= \boxed{11.9\,\mathrm{kJ\,mol^{-1}}}
\end{aligned}$$

(c)

$$\begin{aligned}
\Delta_r H^\ominus &= \Delta_f H^\ominus(C_2H_4) + \Delta_f H^\ominus(C_2H_5) - \Delta_f H^\ominus(tert\text{-}C_4H_9) \\
\Delta_r H^\ominus &= (52.26 + 121.0 - 51.3)\,\mathrm{kJ\,mol^{-1}} = 122.0\,\mathrm{kJ\,mol^{-1}} \\
\Delta_r S^\ominus &= (219.56 + 247.8 - 314.6)\,\mathrm{J\,K^{-1}\,mol^{-1}} = 152.8\,\mathrm{J\,K^{-1}\,mol^{-1}} \\
\Delta_r G^\ominus &= 122.0\,\mathrm{kJ\,mol^{-1}} - (700\,\mathrm{K}) \times (0.1528\,\mathrm{kJ\,K^{-1}\,mol^{-1}}) \\
&= \boxed{15.0\,\mathrm{kJ\,mol^{-1}}}
\end{aligned}$$

P4.32 The minimum power output that is needed to maintain the temperature difference $T_h - T_c$ occurs when $\mathrm{d}p/\mathrm{d}T_c = 0$

$$\begin{aligned}
p &= \frac{\mathrm{d}|w|}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}(|q_h| - |q_c|)\ [9\text{–}11] \\
&= \frac{\mathrm{d}}{\mathrm{d}t}\left(|q_c|\left\{\frac{|q_h|}{|q_c|} - 1\right\}\right) = \frac{\mathrm{d}}{\mathrm{d}t}\left(|q_c|\left\{\frac{T_h}{T_c} - 1\right\}\right) \\
&= \left(\frac{T_h}{T_c} - 1\right)\frac{\mathrm{d}|q_c|}{\mathrm{d}t} = \left(\frac{T_h}{T_c} - 1\right)kAT_c^4
\end{aligned}$$

At constant T_h

$$\frac{\mathrm{d}p}{\mathrm{d}T_c} = \left(-\frac{T_h}{T_c^2}\right)\left(kAT_c^4\right) + 4kAT_c^3\left(\frac{T_h}{T_c} - 1\right)$$

This is a minimum when equal to zero. Simplifying yields

$$-\frac{T_h}{T_c} + 4\left(\frac{T_h}{T_c} - 1\right) = 0$$

$$\frac{T_h}{T_c} = \boxed{\frac{4}{3}}$$

5 The Second Law: the machinery

Solutions to exercises

Discussion questions

E5.1(b) See the solution to Exercise 3.14(a) and Example 5.1, where it is demonstrated that $\pi_T = a/V_\mathrm{m}^2$ for a van der Waals gas. Therefore, there is no dependence on b for a van der Waals gas. The internal pressure results from attractive interactions alone. For van der Waals gases and liquids with strong attractive forces (large a) at small volumes, the internal pressure can be very large.

E5.2(b) The relation $(\partial G/\partial T)_p = -S$ shows that the Gibbs function of a system decreases with T at constant p in proportion to the magnitude of its entropy. This makes good sense when one considers the definition of G, which is $G = U + pV - TS$. Hence, G is expected to decrease with T in proportion to S when p is constant. Furthermore, an increase in temperature causes entropy to increase according to

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

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

E5.3(b) The fugacity coefficient, ϕ, can be expressed in terms of an integral involving the compression factor, specifically an integral of $Z - 1$ (see eqn 5.20). Therefore, we expect that the variation with pressure of the fugacity coefficient should be similar, in a very qualitative sense, to the variation with pressure of the compression factor itself. Comparison of figures 1.27 and 5.8 of the text shows this to be roughly the case, though the detailed shapes of the curves are necessarily different because ϕ is an integral function of $Z - 1$ over a range of pressures. So we expect no simple proportionality between ϕ and Z. But we find $\phi < 1$ in pressure regions where attractive forces are expected to predominate and $\phi > 1$ when repulsive forces predominate, which in behavior is similar to that of Z. See Section 5.5(b) for a more complete discussion.

Numerical exercises

E5.4(b)

$$\alpha = \frac{1}{V} \times \left(\frac{\partial V}{\partial T}\right)_p \qquad \kappa_\mathrm{T} = -\left(\frac{1}{V}\right) \times \left(\frac{\partial V}{\partial p}\right)_T$$

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

E5.5(b)

$$\Delta G = nRT \ln\left(\frac{p_\mathrm{f}}{p_\mathrm{i}}\right) \quad \text{at constant temperature, } \frac{p_\mathrm{f}}{p_\mathrm{i}} = \frac{V_\mathrm{i}}{V_\mathrm{f}}$$

$$= nRT \ln\left(\frac{V_\mathrm{i}}{V_\mathrm{f}}\right)$$

$$= (2.5 \times 10^{-3}\,\mathrm{mol}) \times (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K}) \times \ln\left(\frac{72}{100}\right)$$

$$= -2.0\overline{35} = \boxed{-2.0\,\mathrm{J}}$$

E5.6(b)

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad \left(\frac{\partial G_\mathrm{f}}{\partial T}\right)_p = -S_\mathrm{f} \quad \text{and} \quad \left(\frac{\partial G_\mathrm{i}}{\partial T}\right)_p = -S_\mathrm{i}$$

$$\begin{aligned}\Delta S = S_\mathrm{f} - S_\mathrm{i} &= -\left(\frac{\partial G_\mathrm{f}}{\partial T}\right)_p + \left(\frac{\partial G_\mathrm{i}}{\partial T}\right)_p \\ &= -\left\{\frac{\partial(G_\mathrm{f} - G_\mathrm{i})}{\partial T}\right\}_p = -\left(\frac{\partial \Delta G}{\partial T}\right)_p \\ &= -\frac{\partial}{\partial T}\{-73.1 + 42.8\,T/\mathrm{K}\}\ \mathrm{J} \\ &= \boxed{-42.8\,\mathrm{J\,K^{-1}}}\end{aligned}$$

E5.7(b) See the solution to Exercise 5.7(a). Without knowledge of the compressibility of methanol we can only assume that $V = V_1(1 - \kappa_T p) \approx V_1$. Then

$$\Delta G = V\Delta p$$

$$\rho = \frac{m}{V} \quad \text{so} \quad V = \frac{m}{\rho} = \frac{25\,\mathrm{g}}{0.791\,\mathrm{g\,cm^{-3}}} = 31.\overline{61}\,\mathrm{cm^3}$$

$$\Delta G = (31.\overline{61}\,\mathrm{cm^3}) \times \left(\frac{1\,\mathrm{m^3}}{10^6\,\mathrm{cm^3}}\right) \times (99.9 \times 10^6\,\mathrm{Pa})$$

$$= \boxed{+3.2\,\mathrm{kJ}}$$

E5.8(b) **(a)** $\Delta S = nR\ln\left(\frac{V_\mathrm{f}}{V_\mathrm{i}}\right) = nR\ln\left(\frac{p_\mathrm{i}}{p_\mathrm{f}}\right)$ [Boyle's Law]

Taking inverse logarithms

$$\begin{aligned}p_\mathrm{f} = p_\mathrm{i}\mathrm{e}^{-\Delta S/nR} &= (150\,\mathrm{kPa})\exp - \left(\frac{-(-15.0\,\mathrm{J\,K^{-1}})}{(3.00\,\mathrm{mol}) \times (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}})}\right) \\ &= \boxed{274\,\mathrm{kPa}}\end{aligned}$$

(b) $\Delta G = nRT\ln\left(\frac{p_\mathrm{f}}{p_\mathrm{i}}\right) = -T\Delta S$ [$\Delta H = 0$, constant temperature, perfect gas]

$$= -(230\,\mathrm{K}) \times (-15.0\,\mathrm{J\,K^{-1}})$$

$$= +3450\,\mathrm{J} = \boxed{3.45\,\mathrm{kJ}}$$

E5.9(b)

$$\begin{aligned}\Delta\mu = \mu_\mathrm{f} - \mu_\mathrm{i} &= RT\ln\left(\frac{p_\mathrm{f}}{p_\mathrm{i}}\right) \\ &= (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (323\,\mathrm{K}) \times \ln\left(\frac{252.0}{92.0}\right) \\ &= \boxed{2.71\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

E5.10(b)

$$\mu^0 = \mu^\ominus + RT\ln\left(\frac{p}{p^\ominus}\right)$$

$$\mu = \mu^\ominus + RT\ln\left(\frac{f}{p^\ominus}\right)$$

$$\mu - \mu^0 = RT\ln\left(\frac{f}{p}\right) \quad \left[\frac{f}{p} \equiv \phi\right]$$

$$\begin{aligned}\mu - \mu^0 &= RT\ln\phi \\ &= (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (290\,\mathrm{K}) \times \ln(0.68) \\ &= -92\overline{9.8}\,\mathrm{J\,mol^{-1}} \\ &= -930\,\mathrm{J\,mol^{-1}} \quad \text{or} \quad \boxed{-0.93\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

E5.11(b)

$$B' = \frac{B}{RT} = -\frac{(160.0\,\mathrm{cm^3\,mol^{-1}}) \times \left(\frac{1\,\mathrm{m^3}}{10^6\,\mathrm{cm^3}}\right)}{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (100\,\mathrm{K})}$$

$$= \boxed{-1.92\overline{4} \times 10^{-7}\,\mathrm{Pa^{-1}}}$$

$$\begin{aligned}\phi &= \mathrm{e}^{B'p+\cdots} \\ &\approx \mathrm{e}^{-(1.92\overline{4}\times10^{-7}\,\mathrm{Pa^{-1}})\times(62\times10^6\,\mathrm{Pa})} \\ &\approx \mathrm{e}^{-11.\overline{93}} \\ &= \overline{7} \times 10^{-6} \quad \text{or} \quad \text{of the order of } \boxed{10^{-6}}\end{aligned}$$

E5.12(b)

$$\begin{aligned}\Delta G = nV_\mathrm{m}\Delta p &= V\Delta p \\ &= (1.0\,\mathrm{L}) \times \left(\frac{1\,\mathrm{m^3}}{10^3\,\mathrm{L}}\right) \times (200 \times 10^3\,\mathrm{Pa}) \\ &= 200\,\mathrm{Pa\,m^3} = \boxed{200\,\mathrm{J}}\end{aligned}$$

E5.13(b)

$$\begin{aligned}\Delta G_\mathrm{m} &= RT\ln\left(\frac{p_\mathrm{f}}{p_\mathrm{i}}\right) \\ &= (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (500\,\mathrm{K}) \times \ln\left(\frac{100.0\,\mathrm{kPa}}{50.0\,\mathrm{kPa}}\right) \\ &= \boxed{+2.88\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

E5.14(b)

$$V = \left(\frac{\partial G}{\partial p}\right)_T [5.10] = \boxed{\frac{RT}{p} + B' + C'p + D'p^2}$$

which is the virial equation of state.

E5.15(b)

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

For a Dieterici gas

$$p = \frac{RT\mathrm{e}^{-a/RTV_\mathrm{m}}}{V_\mathrm{m} - b}$$

$$\left(\frac{\partial p}{\partial T}\right)_{V_\mathrm{m}} = \boxed{\frac{R\left(1 + \frac{a}{RV_\mathrm{m}T}\right)\mathrm{e}^{-a/RV_\mathrm{m}T}}{V_\mathrm{m} - b}}$$

$$\mathrm{d}S = \left(\frac{\partial S}{\partial V_\mathrm{m}}\right)_T \mathrm{d}V_\mathrm{m} = \left(\frac{\partial p}{\partial T}\right)_{V_\mathrm{m}} \mathrm{d}V_\mathrm{m}$$

$$\Delta S = \int_{V_{\mathrm{m,i}}}^{V_{\mathrm{m,f}}} \mathrm{d}S = \boxed{R\left(1+\frac{a}{RV_{\mathrm{m}}T}\right)\mathrm{e}^{-a/RV_{\mathrm{m}}T}\left(\frac{V_{\mathrm{m,f}}-b}{V_{\mathrm{m,i}}-b}\right)}$$

For a perfect gas $\Delta S = R \ln\left(\dfrac{V_{\mathrm{m,f}}}{V_{\mathrm{m,i}}}\right)$

ΔS for a Dieterici gas may be greater or lesser than ΔS for a perfect gas depending on T and the magnitudes of a and b. At very high T, ΔS is greater. At very low T, ΔS is less.

Solutions to problems

Solutions to numerical problem

P5.2 For the reaction

$$\mathrm{N_2(g)} + 3\mathrm{H_2(g)} \rightarrow 2\mathrm{NH_3(g)} \quad \Delta_{\mathrm{r}}G^{\ominus} = 2\Delta_{\mathrm{f}}G^{\ominus}(\mathrm{NH_3,\ g})$$

(a)

$$\begin{aligned}\Delta_{\mathrm{r}}G^{\ominus}(500\,\mathrm{K}) &= \tau\Delta_{\mathrm{r}}G^{\ominus}(T_{\mathrm{c}}) + (1-\tau)\Delta_{\mathrm{r}}H^{\ominus}(T_{\mathrm{c}}) \quad \left[\text{Problem 5.1, } \tau = \frac{T}{T_{\mathrm{c}}}\right]\\ &= \left(\frac{500\,\mathrm{K}}{298.15\,\mathrm{K}}\right)\times(2)\times(-16.45\,\mathrm{kJ\,mol^{-1}})\\ &\quad + \left(1-\frac{500\,\mathrm{K}}{298.15\,\mathrm{K}}\right)\times(2)\times(-46.11\,\mathrm{kJ\,mol^{-1}})\\ &= -55.\overline{17} + 62.\overline{43}\,\mathrm{kJ\,mol^{-1}} = \boxed{+7\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

(b)

$$\begin{aligned}\Delta_{\mathrm{r}}G^{\ominus}(1000\,\mathrm{K}) &= \left(\frac{1000\,\mathrm{K}}{298.15\,\mathrm{K}}\right)\times(2)\times(-16.45\,\mathrm{kJ\,mol^{-1}})\\ &\quad + \left(1-\frac{1000\,\mathrm{K}}{298.15\,\mathrm{K}}\right)\times(2)\times(-46.11\,\mathrm{kJ\,mol^{-1}})\\ &= (-110.\overline{35} + 217.\overline{09})\,\mathrm{kJ\,mol^{-1}} = \boxed{+107\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

Solutions to theoretical problems

P5.5 We start from the fundamental relation

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V \ [2]$$

But, since $U = U(S, V)$, we may also write

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V$$

Comparing the two expressions, we see that

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

These relations are true in general and hence hold for the perfect gas. We can demonstrate this more explicitly for the perfect gas as follows. For the perfect gas at constant volume

$$\mathrm{d}U = C_V\,\mathrm{d}T$$

and

$$dS = \frac{dq_{\text{rev}}}{T} = \frac{C_V\,dT}{T}$$

Then $\left(\frac{dU}{dS}\right)_V = \left(\frac{\partial U}{\partial S}\right)_V = \frac{C_V\,dT}{\left(\frac{C_V\,dT}{T}\right)} = T$

For a reversible adiabatic (constant-entropy) change in a perfect gas

$$dU = dw = -p\,dV$$

Therefore, $\left(\frac{\partial U}{\partial V}\right)_S = -p$

P5.8 $$\left(\frac{\partial p}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S \text{ [Maxwell relation]}$$

$$= \frac{1}{\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial V}{\partial S}\right)_T}\text{[chain relation]} = \frac{\left(\frac{\partial S}{\partial V}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_V} \text{ [inversion]}$$

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

$$= \frac{-\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial U}{\partial S}\right)_V}{\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial U}{\partial T}\right)_V}\text{[inversion twice]} = \boxed{\frac{\alpha T}{\kappa_T C_V}} \quad \left[\left(\frac{\partial U}{\partial S}\right)_V = T\right]$$

P5.10 $$\left(\frac{\partial H}{\partial p}\right)_T = \left(\frac{\partial H}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_T + \left(\frac{\partial H}{\partial p}\right)_S \text{ [Relation 1, \textit{Further information} 1.7]}$$

$$\left.\begin{array}{l} dH = T\,dS + V\,dp \text{ [Problem 5.6]} \\ dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp \quad (H = H(p, S)) \end{array}\right\} \text{compare}$$

Thus, $\left(\frac{\partial H}{\partial S}\right)_p = T,\ \left(\frac{\partial H}{\partial p}\right)_S = V$ [dH exact]

Substitution yields, $\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V = \boxed{-T\left(\frac{\partial V}{\partial T}\right)_p + V}$ [Maxwell relation]

(a) For $pV = nRT$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p}, \quad \text{hence} \quad \left(\frac{\partial H}{\partial p}\right)_T = \frac{-nRT}{p} + V = \boxed{0}$$

(b) For $p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$ [Table 1.6]

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

$$\left(\frac{\partial T}{\partial V}\right)_p = \frac{p}{nR} + \frac{na}{RV^2} - \frac{2na(V-nb)}{RV^3}$$

Therefore, $\left(\frac{\partial H}{\partial p}\right)_T = \frac{-T}{\left(\frac{\partial T}{\partial V}\right)_p} + V[\text{inversion}] = \frac{-T}{\frac{p}{nR} + \frac{na}{RV^2} - \frac{2na(V-nb)}{RV^3}} + V$

which yields after algebraic manipulation

$$\left(\frac{\partial H}{\partial p}\right)_T = \boxed{\frac{nb - \left(\frac{2na}{RT}\right)\lambda^2}{1 - \left(\frac{2na}{RTV}\right)\lambda^2}, \quad \lambda = 1 - \frac{nb}{V}}$$

When $\frac{b}{V_\mathrm{m}} \ll 1$, $\lambda \approx 1$ and

$$\frac{2na}{RTV} = \frac{2na}{RT} \times \frac{1}{V} \approx \frac{2na}{RT} \times \frac{p}{nRT} = \frac{2pa}{R^2T^2}$$

Therefore, $\left(\frac{\partial H}{\partial p}\right)_T \approx \frac{nb - \left(\frac{2na}{RT}\right)}{1 - \left(\frac{2pa}{R^2T^2}\right)}$

For argon, $a = 1.337\,\mathrm{L^2\,atm\,mol^{-2}}$, $b = 3.20 \times 10^{-2}\,\mathrm{L\,mol^{-1}}$,

$$\frac{2na}{RT} = \frac{(2) \times (1.0\,\mathrm{mol}) \times (1.337\,\mathrm{L^2\,atm\,mol^{-2}})}{(8.206 \times 10^{-2}\,\mathrm{L\,atm\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})} = 0.11\,\mathrm{L}$$

$$\frac{2pa}{R^2T^2} = \frac{(2) \times (10.0\,\mathrm{atm}) \times (1.337\,\mathrm{L^2\,atm\,mol^{-2}})}{\left[(8.206 \times 10^{-2}\,\mathrm{L\,atm\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})\right]^2} = 0.045$$

Hence, $\left(\frac{\partial H}{\partial p}\right)_T \approx \frac{\{(3.20 \times 10^{-2}) - (0.11)\}\,\mathrm{L}}{1 - 0.045} = -0.0817\,\mathrm{L} = \boxed{-8.3\,\mathrm{J\,atm^{-1}}}$

$$\Delta H \approx \left(\frac{\partial H}{\partial p}\right)_T \Delta p \approx (-8.3\,\mathrm{J\,atm^{-1}}) \times (1\,\mathrm{atm}) = \boxed{-8\,\mathrm{J}}$$

P5.12 $\pi_T = T\left(\frac{\partial p}{\partial T}\right)_V - p\ [5.8]$

$p = \frac{RT}{V_\mathrm{m}} + \frac{BRT}{V_\mathrm{m}^2}$ [The virial expansion, Table 1.6, truncated after the term in B]

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

Hence, $\pi_T = \frac{RT^2}{V_\mathrm{m}^2}\left(\frac{\partial B}{\partial T}\right)_V \approx \frac{RT^2\Delta B}{V_\mathrm{m}^2\Delta T}$

Since π_T represents a (usually) small deviation from perfect gas behaviour, we may approximate V_m.

$$V_\mathrm{m} \approx \frac{RT}{p} \qquad \boxed{\pi_T \approx \frac{p^2}{R} \times \frac{\Delta B}{\Delta T}}$$

From the data $\Delta B = ((-15.6) - (-28.0))\ \text{cm}^3\,\text{mol}^{-1} = +12.4\,\text{cm}^3\,\text{mol}^{-1}$

Hence,

(a) $$\pi_T = \frac{(1.0\,\text{atm})^2 \times (12.4 \times 10^{-3}\,\text{L}\,\text{mol}^{-1})}{(8.206 \times 10^{-2}\,\text{L}\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (50\,\text{K})} = \boxed{3.0 \times 10^{-3}\,\text{atm}}$$

(b) $\pi_T \propto p^2$; so at $p = 10.0\,\text{atm}$, $\pi_T = \boxed{0.30\,\text{atm}}$

Comment. In **(a)** π_T is 0.3 per cent of p; in **(b)** it is 3 per cent. Hence at these pressures the approximation for V_m is justified. At 100 atm it would not be.

Question. How would you obtain a reliable estimate of π_T for argon at 100 atm?

P5.13 $$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \text{and} \quad C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

(a) $$\left(\frac{\partial C_V}{\partial V}\right)_T = \frac{\partial^2 U}{\partial V \partial T} = \frac{\partial^2 U}{\partial T \partial V} = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V = 0 \quad [\pi_T = 0]$$

$$\left(\frac{\partial C_V}{\partial p}\right)_T = \frac{\partial^2 U}{\partial p \partial T} = \frac{\partial^2 U}{\partial T \partial p} = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial p}\right)_T\right)_V$$

$$= \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T\right)_V = 0 \quad (\pi_T = 0)$$

Since $C_p = C_V + R$, $\left(\frac{\partial C_p}{\partial x}\right)_T = \left(\frac{\partial C_V}{\partial x}\right)_T$ for $x = p$ or V

C_V and C_p may depend on temperature. Since $\frac{\mathrm{d}C_V}{\mathrm{d}T} = \frac{\mathrm{d}^2 U}{\mathrm{d}T^2}$, $\frac{\mathrm{d}C_V}{\mathrm{d}T}$ is nonzero if U depends on T through a nonlinear relation. See Chapter 20 for further discussion of this point. However, for a perfect monatomic gas, U is a linear function of T; hence C_V is independent of T. A similar argument applies to C_p.

(b) This equation of state is the same as that of Problem 5.12.

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \frac{\partial^2 U}{\partial T \partial V} = \left(\frac{\partial \pi_T}{\partial T}\right)_V \quad \text{[Part (a)]}$$

$$= \left(\frac{\partial}{\partial T}\frac{RT^2}{V_\text{m}^2}\left(\frac{\partial B}{\partial T}\right)_V\right)_V \quad \text{[Problem 5.12]}$$

$$= \frac{2RT}{V_\text{m}^2}\left(\frac{\partial B}{\partial T}\right)_V + \frac{RT^2}{V_\text{m}^2}\left(\frac{\partial^2 B}{\partial T^2}\right)_V$$

$$= \boxed{\frac{RT}{V_\text{m}^2}\left(\frac{\partial^2 (BT)}{\partial T^2}\right)_V}$$

P5.15 $$\pi_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \ [5.8]$$

$$p = \frac{nRT}{V - nb} \times \mathrm{e}^{-an/RTV} \ \text{[Table 1.6]}$$

$$T\left(\frac{\partial p}{\partial T}\right)_V = \frac{nRT}{V - nb} \times \mathrm{e}^{-an/RTV} + \frac{na}{RTV} \times \frac{nRT}{V - nb} \times \mathrm{e}^{-an/RTV} = p + \frac{nap}{RTV}$$

Hence, $\boxed{\pi_T = \dfrac{nap}{RTV}}$

$\pi_T \to 0$ as $p \to 0,\ V \to \infty,\ a \to 0$, and $T \to \infty$. The fact that $\pi_T > 0$ (because $a > 0$) is consistent with a representing attractive contributions, since it implies that $\left(\dfrac{\partial U}{\partial V}\right)_T > 0$ and the internal energy rises as the gas expands (so decreasing the average attractive interactions).

P5.17 $\mathrm{d}G = \left(\dfrac{\partial G}{\partial p}\right)_T \mathrm{d}p = V\,\mathrm{d}p$

$$G(p_\mathrm{f}) - G(p_\mathrm{i}) = \int_{p_\mathrm{i}}^{p_\mathrm{f}} V\,\mathrm{d}p$$

In order to complete the integration, V as a function of p is required.

$$\left(\frac{\partial V}{\partial p}\right)_T = -\kappa_T V \text{ (given)}, \quad \text{so} \quad \mathrm{d}\ln V = -\kappa\,\mathrm{d}p$$

Hence, the volume varies with pressure as

$$\int_{V_0}^{V} \mathrm{d}\ln V = -\kappa_T \int_{p_\mathrm{i}}^{p} \mathrm{d}p$$

or $V = V_0 \mathrm{e}^{-\kappa_T(p-p_\mathrm{i})}$ ($V = V_0$ when $p = p_\mathrm{i}$)

Hence, $\displaystyle\int_{p_\mathrm{i}}^{p_\mathrm{f}} \mathrm{d}G = \int V\,\mathrm{d}p = V_0 \int_{p_\mathrm{i}}^{p_\mathrm{f}} \mathrm{e}^{-\kappa_T(p-p_i)}\,\mathrm{d}p$

$$G(p_\mathrm{f}) = G(p_\mathrm{i}) + (V_0) \times \left(\frac{1-\mathrm{e}^{-\kappa_T(p_\mathrm{f}-p_\mathrm{i})}}{\kappa_T}\right) = G(p_\mathrm{i}) + (V_0) \times \left(\frac{1-\mathrm{e}^{-\kappa_T\Delta p}}{\kappa_T}\right)$$

If $\kappa_T\Delta p \ll 1,\ 1-\mathrm{e}^{-\kappa_T\Delta p} \approx 1 - \left(1 - \kappa_T\Delta p + \frac{1}{2}\kappa_T^2\Delta p^2\right) = \kappa_T\Delta p - \frac{1}{2}\kappa_T^2\Delta p^2$

Hence, $\boxed{G' = G + V_0\Delta p\left(1 - \dfrac{1}{2}\kappa_T\Delta p\right)}$

For the compression of copper, the change in molar Gibbs function is

$$\begin{aligned}\Delta G_\mathrm{m} &= V_\mathrm{m}\Delta p\left(1 - \frac{1}{2}\kappa_T\Delta p\right) = \left(\frac{M\Delta p}{\rho}\right) \times \left(1 - \frac{1}{2}\kappa_T\Delta p\right)\\ &= \left(\frac{63.54\,\mathrm{g\,mol^{-1}}}{8.93\times10^6\,\mathrm{g\,m^{-3}}}\right) \times (500) \times (1.013\times10^5\,\mathrm{Pa}) \times \left(1 - \frac{1}{2}\kappa_T\Delta p\right)\\ &= (360.\bar{4}\,\mathrm{J}) \times \left(1 - \tfrac{1}{2}\kappa_T\Delta p\right)\end{aligned}$$

If we take $\kappa_T = 0$ (incompressible), $\Delta G_\mathrm{m} = +360\,\mathrm{J}$. For its actual value

$$\tfrac{1}{2}\kappa_T\Delta p = \left(\tfrac{1}{2}\right) \times (0.8\times10^{-6}\,\mathrm{atm^{-1}}) \times (500\,\mathrm{atm}) = 2\times10^{-4}$$

$$1 - \tfrac{1}{2}\kappa_T\Delta p = 0.9998$$

Hence, ΔG_m differs from the simpler version by only 2 parts in 10^4 $\boxed{\text{(0.02 per cent)}}$

P5.19 $$\kappa_S = -\left(\frac{1}{V}\right) \times \left(\frac{\partial V}{\partial p}\right)_S = -\frac{1}{V\left(\frac{\partial p}{\partial V}\right)_S}$$

The only constant-entropy changes of state for a perfect gas are reversible adiabatic changes, for which

$$pV^{\gamma} = \text{const}$$

Then, $\left(\frac{\partial p}{\partial V}\right)_S = \left(\frac{\partial}{\partial V}\frac{\text{const}}{V^{\gamma}}\right)_S = -\gamma \times \left(\frac{\text{const}}{V^{\gamma+1}}\right) = \frac{-\gamma p}{V}$

Therefore, $\kappa_S = \frac{-1}{V\left(\frac{-\gamma p}{V}\right)} = \frac{+1}{\gamma p}$

Hence, $\boxed{p\gamma\kappa_S = +1}$

P5.21 $$S = S(T, p)$$

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial S}{\partial p}\right)_T \mathrm{d}p$$

$$T\,\mathrm{d}S = T\left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T + T\left(\frac{\partial S}{\partial p}\right)_T \mathrm{d}p$$

Use $\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial S}{\partial H}\right)_p\left(\frac{\partial H}{\partial T}\right)_p = \frac{1}{T} \times C_p \quad \left[\left(\frac{\partial H}{\partial S}\right)_p = T, \text{ Problem 5.6}\right]$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad \text{[Maxwell relation]}$$

Hence, $T\,\mathrm{d}S = C_p\,\mathrm{d}T - T\left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p = \boxed{C_p\,\mathrm{d}T - \alpha TV\,\mathrm{d}p}$

For reversible, isothermal compression, $T\,\mathrm{d}S = \mathrm{d}q_{\text{rev}},\ \mathrm{d}T = 0$; hence

$$\mathrm{d}q_{\text{rev}} = -\alpha TV\,\mathrm{d}p$$

$$q_{\text{rev}} = \int_{p_\text{i}}^{p_\text{f}} -\alpha TV\,\mathrm{d}p = \boxed{-\alpha TV\Delta p} \quad [\alpha \text{ and } V \text{ assumed constant}]$$

For mercury

$$q_{\text{rev}} = (-1.82 \times 10^{-4}\,\mathrm{K}^{-1}) \times (273\,\mathrm{K}) \times (1.00 \times 10^{-4}\,\mathrm{m}^{-3}) \times (1.0 \times 10^{8}\,\mathrm{Pa}) = \boxed{-0.50\,\mathrm{kJ}}$$

P5.25 When we neglect b in the van der Waals equation we have

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

and hence

$$Z = 1 - \frac{a}{RTV_\text{m}}$$

Then substituting into eqn 5.20 we get

$$\ln\phi = \int_o^p \left(\frac{Z-1}{p}\right)\mathrm{d}p = \int_o^p \frac{-a}{p^{RTV_\text{m}}}\mathrm{d}p$$

In order to perform this integration we must eliminate the variable V_m by solving for it in terms of p. Rewriting the expression for p in the form of a quadratic we have

$$V_\mathrm{m}^2 - \frac{RT}{p}V_\mathrm{m} + \frac{a}{p} = 0$$

The solution is

$$V_\mathrm{m} = \frac{1}{2}\left(RT/p \pm \frac{1}{p}\sqrt{(RT)^2 - 4ap}\right)$$

applying the approximation $(RT)^2 \gg 4ap$ we obtain

$$V_\mathrm{m} = \frac{1}{2}\left(\frac{RT}{p} \pm \frac{RT}{p}\right)$$

Choosing the $+$ sign we get

$$V_\mathrm{m} = \frac{RT}{p} \text{ which is the perfect volume}$$

Then

$$\ln\phi = \int_0^p -\frac{a}{RT^2}\,\mathrm{d}p = \boxed{-\frac{ap}{(RT)^2}}$$

For ammonia $a = 4.169\,\mathrm{atm\,L^2\,mol^{-2}}$

$$\begin{aligned}\ln\phi &= -\frac{4.169\,\mathrm{atm\,L^2\,mol^{-2}} \times 10.00\,\mathrm{atm}}{(0.08206\,\mathrm{L\,atm\,K^{-1}mol^{-1}} \times 298.15\,\mathrm{K})^2}\\ &= -0.06965\\ \phi &= 0.9237 = \frac{f}{p}\end{aligned}$$

$$f = \phi p = 0.9237 \times 10.00\,\mathrm{atm} = \boxed{9.237\,\mathrm{atm}}$$

P5.27 The equation of state $\frac{pV_\mathrm{m}}{RT} = 1 + \frac{qT}{V_\mathrm{m}}$ is solved for $V_\mathrm{m} = \left(\frac{RT}{2p}\right)\left[1 + \left(1 + \frac{4pq}{R}\right)^{1/2}\right]$ so

$$\frac{Z-1}{p} = \frac{\frac{pV_\mathrm{m}}{RT} - 1}{p} = \frac{qT}{pV_\mathrm{m}} = \frac{\frac{2q}{R}}{1 + \left(1 + \frac{4pq}{R}\right)^{1/2}}$$

$$\ln\phi = \int_0^p \left(\frac{Z-1}{p}\right)\mathrm{d}p[24] = \frac{2q}{R}\int_0^p \frac{\mathrm{d}p}{1 + \left(1 + \frac{4pq}{R}\right)^{1/2}}$$

Defining, $a \equiv 1 + \left(1 + \frac{4pq}{R}\right)^{1/2}$, $\mathrm{d}p = \frac{R(a-1)}{2q}\,\mathrm{d}a$, gives

$$\begin{aligned}\ln\phi &= \int_2^a \left(\frac{a-1}{a}\right)\mathrm{d}a \quad [a = 2,\ \text{when } p = 0]\\ &= a - 2 - \ln\frac{1}{2}a = \left(1 + \frac{4pq}{R}\right)^{1/2} - 1 - \ln\left\{\frac{1}{2}\left(1 + \frac{4pq}{R}\right)^{1/2} + \frac{1}{2}\right\}\end{aligned}$$

Hence, $\boxed{\phi = \frac{2\mathrm{e}^{\{(1+4pq/R)^{1/2}-1\}}}{1 + \left(1 + \frac{4pq}{R}\right)^{1/2}}}$

This function is plotted in Fig. 5.1(a) when $\dfrac{4pq}{R} \ll 1$, and using the approximations

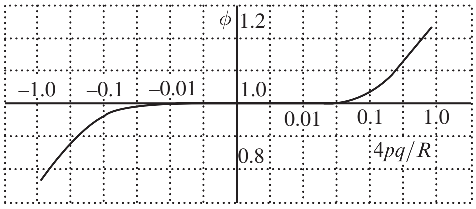


Figure 5.1(a)

$$e^x \approx 1 + x,\ (1+x)^{1/2} \approx 1 + \frac{1}{2}x, \quad \text{and} \quad (1+x)^{-1} \approx 1 - x \quad [x \ll 1]$$

$$\phi \approx 1 + \frac{pq}{R}$$

When ϕ is plotted against $x = 4pq/R$ on a linear rather than exponential scale, the apparent curvature seen in Fig. 5.1(a) is diminished and the curve seems almost linear. See Fig. 5.1(b).

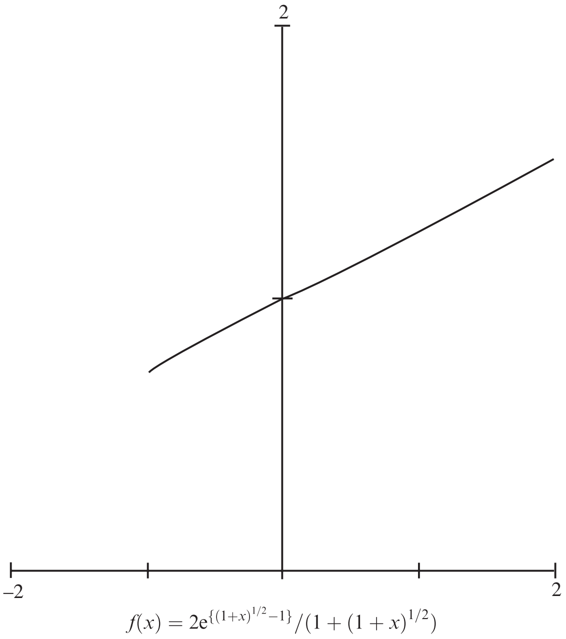


Figure 5.1(b)

Solution to applications

P5.28 $w_{\text{add,max}} = \Delta_r G$ [4.38]

$$\Delta_r G^{\ominus}(37^\circ\text{C}) = \tau \Delta_r G^{\ominus}(T_c) + (1-\tau)\Delta_r H^{\ominus}(T_c) \quad \left[\text{Problem 5.1, } \tau = \frac{T}{T_c}\right]$$

$$= \left(\frac{310\,\text{K}}{298.15\,\text{K}}\right) \times (-6333\,\text{kJ mol}^{-1}) + \left(1 - \frac{310\,\text{K}}{298.15\,\text{K}}\right) \times (-5797\,\text{kJ mol}^{-1})$$

$$= -6354\,\text{kJ mol}^{-1}$$

The difference is $\Delta_r G^{\ominus}(37^\circ\text{C}) - \Delta_r G^{\ominus}(T_c) = \{-6354 - (-6333)\}\ \text{kJ mol}^{-1} = \boxed{-21\,\text{kJ mol}^{-1}}$
Therefore, an additional 21 kJ mol^{-1} of non-expansion work may be done at the higher temperature.

Comment. As shown by Problem 5.1, increasing the temperature does not necessarily increase the maximum non-expansion work. The relative magnitude of $\Delta_r G^\ominus$ and $\Delta_r H^\ominus$ is the determining factor.

P5.31 The Gibbs–Helmholtz equation is

$$\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right) = -\frac{\Delta H}{T^2}$$

so for a small temperature change

$$\Delta\left(\frac{\Delta_r G^\ominus}{T}\right) = \frac{\Delta_r H^\ominus}{T^2}\Delta T \quad \text{and} \quad \frac{\Delta_r G_2^\ominus}{T_2} = \frac{\Delta_r G_1^\ominus}{T_1} - \frac{\Delta_r H^\ominus}{T^2 \Delta T}$$

$$\text{so} \int \mathrm{d}\frac{\Delta_r G^\ominus}{T} = -\int \frac{\Delta_r H^\ominus \,\mathrm{d}T}{T^2} \quad \text{and} \quad \frac{\Delta_r G_{190}^\ominus}{T_{190}} = \frac{\Delta_r G_{220}^\ominus}{T_{220}} + \Delta_r H^\ominus\left(\frac{1}{T_{190}} - \frac{1}{T_{220}}\right)$$

$$\Delta_r G_{190}^\ominus = \Delta_r G_{220}^\ominus \frac{T_{190}}{T_{220}} + \Delta_r H^\ominus\left(1 - \frac{T_{190}}{T_{220}}\right)$$

For the monohydrate

$$\Delta_r G_{190}^\ominus = (46.2\,\mathrm{kJ\,mol^{-1}}) \times \left(\frac{190\,\mathrm{K}}{220\,\mathrm{K}}\right) + (127\,\mathrm{kJ\,mol^{-1}}) \times \left(1 - \frac{190\,\mathrm{K}}{220\,\mathrm{K}}\right),$$

$$\Delta_r G_{190}^\ominus = \boxed{57.2\,\mathrm{kJ\,mol^{-1}}}$$

For the dihydrate

$$\Delta_r G_{190}^\ominus = (69.4\,\mathrm{kJ\,mol^{-1}}) \times \left(\frac{190\,\mathrm{K}}{220\,\mathrm{K}}\right) + (188\,\mathrm{kJ\,mol^{-1}}) \times \left(1 - \frac{190\,\mathrm{K}}{220\,\mathrm{K}}\right),$$

$$\Delta_r G_{190}^\ominus = \boxed{85.6\,\mathrm{kJ\,mol^{-1}}}$$

For the monohydrate

$$\Delta_r G_{190}^\ominus = (93.2\,\mathrm{kJ\,mol^{-1}}) \times \left(\frac{190\,\mathrm{K}}{220\,\mathrm{K}}\right) + (237\,\mathrm{kJ\,mol^{-1}}) \times \left(1 - \frac{190\,\mathrm{K}}{220\,\mathrm{K}}\right),$$

$$\Delta_r G_{190}^\ominus = \boxed{112.8\,\mathrm{kJ\,mol^{-1}}}$$

P5.32 The change in the Helmholtz energy equals the maximum work associated with stretching the polymer. Then

$$\mathrm{d}w_{\max} = \mathrm{d}A = -f\,\mathrm{d}l$$

For stretching at constant T

$$f = -\left(\frac{\partial A}{\partial l}\right)_T = -\left(\frac{\partial U}{\partial l}\right)_T + T\left(\frac{\partial S}{\partial l}\right)_T$$

assuming that $(\partial U/\partial l)_T = 0$ (valid for rubbers)

$$\begin{aligned} f &= T\left(\frac{\partial S}{\partial l}\right)_T = T\left(\frac{\partial}{\partial l}\right)_T\left\{-\frac{3k_B l^2}{2Na^2} + C\right\} \\ &= T\left\{-\frac{3k_B l}{Na^2}\right\} = -\left(\frac{3k_B T}{Na^2}\right) l \end{aligned}$$

This tensile force has the Hooke's law form $f = -k_H l$ with $k_H = 3k_B T/Na^2$.

6 Physical transformations of pure substances

Solutions to exercises

Discussion questions

E6.1(b) Refer to Fig. 6.8. The white lines represent the regions of superheating and supercooling. The chemical potentials along these lines are higher than the chemical potentials of the stable phases represented by the colored lines. Though thermodynamically unstable, these so-called metastable phases may persist for a long time if the system remains undisturbed, but will eventually transform into the thermodynamically stable phase having the lower chemical potential. Transformation to the condensed phases usually requires nucleation centers. In the absence of such centers, the metastable regions are said to be kinetically stable.

E6.2(b) At 298 K and 1.0 atm, the sample of carbon dioxide is a gas. (a) After heating to 320 K at constant pressure, the system is still gaseous. (b) Isothermal compression at 320 K to 100 atm pressure brings the sample into the supercritical region. The sample is now not much different in appearance from ordinary carbon dioxide, but some of its properties are (see Box 6.1). (c) After cooling the sample to 210 K at constant pressure, the carbon dioxide sample solidifies. (d) Upon reducing the pressure to 1.0 atm at 210 K, the sample vapourizes (sublimes); and finally (e) upon heating to 298 K at 1.0 atm, the system has resumed its initial conditions in the gaseous state. Note the lack of a sharp gas to liquid transition in steps (b) and (c). This process illustrates the continuity of the gaseous and liquid states.

E6.3(b) First-order phase transitions show discontinuities in the first derivative of the Gibbs energy with respect to temperature. They are recognized by finite discontinuities in plots of H, U, S, and V against temperature and by an infinite discontinuity in C_p. Second-order phase transitions show discontinuities in the second derivatives of the Gibbs energy with respect to temperature, but the first derivatives are continuous. The second-order transitions are recognized by kinks in plots of H, U, S, and V against temperature, but most easily by a finite discontinuity in a plot of C_p against temperature. A λ-transition shows characteristics of both first and second-order transitions and, hence, is difficult to classify by the Ehrenfest scheme. It resembles a first-order transition in a plot of C_p against T, but appears to be a higher-order transition with respect to other properties. See the book by H. E. Stanley listed under Further reading for more details.

Numerical exercises

E6.4(b) Assume vapour is a perfect gas and $\Delta_{\text{vap}}H$ is independent of temperature

$$\ln\frac{p^*}{p} = +\frac{\Delta_{\text{vap}}H}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)$$

$$\frac{1}{T} = \frac{1}{T^*} + \frac{R}{\Delta_{\text{vap}}H}\ln\frac{p^*}{p}$$

$$= \frac{1}{293.2\,\text{K}} + \frac{8.314\,\text{J K}^{-1}\,\text{mol}^{-1}}{32.7\times 10^{3}\,\text{J mol}^{-1}}\times\ln\left(\frac{58.0}{66.0}\right)$$

$$= 3.378\times 10^{-3}\,\text{K}^{-1}$$

$$T = \frac{1}{3.37\overline{8}\times 10^{-3}\,\text{K}^{-1}} = 296\,\text{K} = \boxed{23^{\circ}\text{C}}$$

E6.5(b)

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta S_\mathrm{m}}{\Delta V_\mathrm{m}}$$

$$\Delta_\mathrm{fus} S = \Delta V_\mathrm{m}\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right) \approx \Delta V_\mathrm{m}\frac{\Delta p}{\Delta T}$$

assuming $\Delta_\mathrm{fus} S$ and ΔV_m independent of temperature.

$$\Delta_\mathrm{fus} S = (152.6\,\mathrm{cm^3\,mol^{-1}} - 142.0\,\mathrm{cm^3\,mol^{-1}}) \times \frac{(1.2\times 10^6\,\mathrm{Pa}) - (1.01\times 10^5\,\mathrm{Pa})}{429.26\,\mathrm{K} - 427.15\,\mathrm{K}}$$

$$= (10.6\,\mathrm{cm^3\,mol^{-1}}) \times \left(\frac{1\,\mathrm{m^3}}{10^6\,\mathrm{cm^3}}\right) \times (5.21\times 10^5\,\mathrm{Pa\,K^{-1}})$$

$$= 5.52\,\mathrm{Pa\,m^3\,K^{-1}\,mol^{-1}} = \boxed{5.5\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

$$\Delta_\mathrm{fus} H = T_\mathrm{f}\Delta S = (427.15\,\mathrm{K}) \times (5.5\overline{2}\,\mathrm{J\,K^{-1}\,mol^{-1}})$$

$$= \boxed{2.4\,\mathrm{kJ\,mol^{-1}}}$$

E6.6(b) Use $\displaystyle\int \mathrm{d}\ln p = \int \frac{\Delta_\mathrm{vap} H}{RT^2}\,\mathrm{d}T$

$$\ln p = \text{constant} - \frac{\Delta_\mathrm{vap} H}{RT}$$

Terms with $\dfrac{1}{T}$ dependence must be equal, so

$$-\frac{3036.8\,\mathrm{K}}{T/\mathrm{K}} = -\frac{\Delta_\mathrm{vap} H}{RT}$$

$$\Delta_\mathrm{vap} H = (3036.8\,\mathrm{K})R = (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (3036.8\,\mathrm{K})$$

$$= \boxed{25.25\,\mathrm{kJ\,mol^{-1}}}$$

E6.7(b) (**a**) $\log p = \text{constant} - \dfrac{\Delta_\mathrm{vap} H}{RT(2.303)}$

Thus

$$\Delta_\mathrm{vap} H = (1625\,\mathrm{K}) \times (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (2.303)$$

$$= \boxed{31.11\,\mathrm{kJ\,mol^{-1}}}$$

(**b**) Normal boiling point corresponds to $p = 1.000\,\mathrm{atm} = 760\,\mathrm{Torr}$

$$\log(760) = 8.750 - \frac{1625}{T/\mathrm{K}}$$

$$\frac{1625}{T/\mathrm{K}} = 8.750 - \log(760)$$

$$T/\mathrm{K} = \frac{1625}{8.750 - \log(760)} = 276.8\overline{7}$$

$$T_\mathrm{b} = \boxed{276.9\,\mathrm{K}}$$

E6.8(b)

$$\Delta T = \frac{\Delta_{\mathrm{fus}}V}{\Delta_{\mathrm{fus}}S}\times \Delta p = \frac{T_{\mathrm{f}}\Delta_{\mathrm{fus}}V}{\Delta_{\mathrm{fus}}H}\times \Delta p = \frac{T_{\mathrm{f}}\Delta p M}{\Delta_{\mathrm{fus}}H}\times \Delta\left(\frac{1}{\rho}\right)$$

$$[T_{\mathrm{f}} = -3.65 + 273.15 = 269.50\,\mathrm{K}]$$

$$\Delta T = \frac{(269.50\,\mathrm{K})\times(99.9\,\mathrm{MPa})M}{8.68\,\mathrm{kJ\,mol^{-1}}}\times\left(\frac{1}{0.789\,\mathrm{g\,cm^{-3}}} - \frac{1}{0.801\,\mathrm{g\,cm^{-3}}}\right)$$

$$= (3.10\overline{17}\times 10^{6}\,\mathrm{K\,Pa\,J^{-1}\,mol})\times(M)\times(+.01\overline{899}\,\mathrm{cm^{3}/g})\times\left(\frac{\mathrm{m^{3}}}{10^{6}\,\mathrm{cm^{3}}}\right)$$

$$= (+5.\overline{889}\times 10^{-2}\,\mathrm{K\,Pa\,m^{3}\,J^{-1}\,g^{-1}\,mol})M = (+5.\overline{889}\times 10^{-2}\,\mathrm{K\,g^{-1}\,mol})M$$

$$\Delta T = (46.07\,\mathrm{g\,mol^{-1}})\times(+5.\overline{889}\times 10^{-2}\,\mathrm{K\,g^{-1}\,mol})$$

$$= +2.\overline{71}\,\mathrm{K}$$

$$T_{\mathrm{f}} = 269.50\,\mathrm{K} + 2.\overline{71}\,\mathrm{K} = \boxed{272\,\mathrm{K}}$$

E6.9(b)

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{\mathrm{d}n}{\mathrm{d}t}\times M_{\mathrm{H_2O}} \quad \text{where } n = \frac{q}{\Delta_{\mathrm{vap}}H}$$

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{\mathrm{d}q/\mathrm{d}t}{\Delta_{\mathrm{vap}}H} = \frac{(0.87\times 10^{3}\,\mathrm{W\,m^{-2}})\times(10^{4}\,\mathrm{m^{2}})}{44.0\times 10^{3}\,\mathrm{J\,mol^{-1}}}$$

$$= 19\overline{7.7}\,\mathrm{J\,s^{-1}\,J^{-1}\,mol}$$

$$= 20\bar{0}\,\mathrm{mol\,s^{-1}}$$

$$\frac{\mathrm{d}m}{\mathrm{d}t} = (19\overline{7.7}\,\mathrm{mol\,s^{-1}})\times(18.02\,\mathrm{g\,mol^{-1}})$$

$$= \boxed{3.6\,\mathrm{kg\,s^{-1}}}$$

E6.10(b) The vapour pressure of ice at −5°C is 3.9×10^{-3} atm, or 3 Torr. Therefore, the frost will sublime. A partial pressure of 3 Torr or more will ensure that the frost remains.

E6.11(b) **(a)** According to Trouton's rule (Section 4.3, eqn 4.16)

$$\Delta_{\mathrm{vap}}H = (85\,\mathrm{J\,K^{-1}\,mol^{-1}})\times T_{\mathrm{b}} = (85\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(342.2\,\mathrm{K}) = \boxed{29.\bar{1}\,\mathrm{kJ\,mol^{-1}}}$$

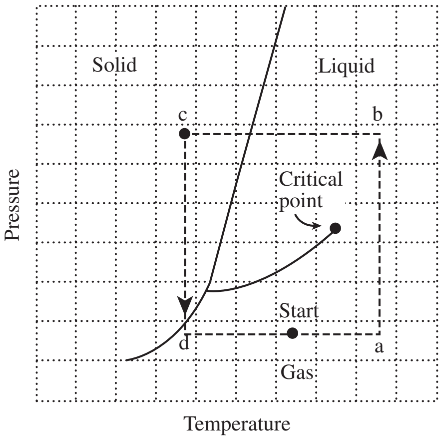


Figure 6.1

(b) Use the Clausius–Clapeyron equation [Exercise 6.11(a)]

$$\ln\left(\frac{p_2}{p_1}\right)=\frac{\Delta_{\text{vap}}H}{R}\times\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

At $T_2 = 342.2\,\text{K}$, $p_2 = 1.000\,\text{atm}$; thus at 25°C

$$\ln p_1=-\left(\frac{29.\overline{1}\times 10^3\,\text{J mol}^{-1}}{8.314\,\text{J K}^{-1}\,\text{mol}^{-1}}\right)\times\left(\frac{1}{298.2\,\text{K}}-\frac{1}{342.2\,\text{K}}\right)=-1.50\overline{9}$$

$$p_1=\boxed{0.22\,\text{atm}}=16\overline{8}\,\text{Torr}$$

At 60°C,

$$\ln p_1=-\left(\frac{29.\overline{1}\times 10^3\,\text{J mol}^{-1}}{8.314\,\text{J K}^{-1}\,\text{mol}^{-1}}\right)\times\left(\frac{1}{333.2\,\text{K}}-\frac{1}{342.2\,\text{K}}\right)=-0.27\overline{6}$$

$$p_1=\boxed{0.76\,\text{atm}}=57\overline{6}\,\text{Torr}$$

E6.12(b) $\Delta T = T_{\text{f}}(10\,\text{MPa}) - T_{\text{f}}(0.1\,\text{MPa}) = \dfrac{T_{\text{f}}\Delta pM}{\Delta_{\text{fus}}H}\Delta\left(\dfrac{1}{\rho}\right)$

$\Delta_{\text{fus}}H = 6.01\,\text{kJ mol}^{-1}$

$$\begin{aligned}\Delta T &= \left\{\frac{(273.15\,\text{K})\times(9.9\times 10^6\,\text{Pa})\times(18\times 10^{-3}\,\text{kg mol}^{-1})}{6.01\times 10^3\,\text{J mol}^{-1}}\right\}\\ &\quad\times\left\{\frac{1}{9.98\times 10^2\,\text{kg m}^{-3}}-\frac{1}{9.15\times 10^2\,\text{kg m}^{-3}}\right\}\\ &= -0.74\,\text{K}\end{aligned}$$

$T_{\text{f}}(10\,\text{MPa}) = 273.15\,\text{K} - 0.74\,\text{K} = \boxed{272.41\,\text{K}}$

E6.13(b) $\Delta_{\text{vap}}H = \Delta_{\text{vap}}U + \Delta_{\text{vap}}(pV)$

$\Delta_{\text{vap}}H = 43.5\,\text{kJ mol}^{-1}$

$\Delta_{\text{vap}}(pV) = p\Delta_{\text{vap}}V = p(V_{\text{gas}} - V_{\text{liq}}) = pV_{\text{gas}} = RT$ [per mole, perfect gas]

$\Delta_{\text{vap}}(pV) = (8.314\,\text{J K}^{-1}\,\text{mol}^{-1})\times(352\,\text{K}) = 292\overline{7}\,\text{J mol}^{-1}$

$$\begin{aligned}\text{Fraction} &= \frac{\Delta_{\text{vap}}(pV)}{\Delta_{\text{vap}}H}=\frac{2.92\overline{7}\,\text{kJ mol}^{-1}}{43.5\,\text{kJ mol}^{-1}}\\ &= \boxed{6.73\times 10^{-2}}=6.73\,\text{per cent}\end{aligned}$$

E6.14(b) $V_{\text{m}} = \dfrac{M}{\rho} = \dfrac{18.02\,\text{g mol}^{-1}}{999.4\times 10^3\,\text{g m}^{-3}} = 1.803\times 10^{-5}\,\text{m}^3\,\text{mol}^{-1}$

$$\begin{aligned}\frac{2\gamma V_{\text{m}}}{rRT} &= \frac{2(7.275\times 10^{-2}\,\text{N m}^{-1})\times(1.803\times 10^{-5}\,\text{m}^3\,\text{mol}^{-1})}{(20.0\times 10^{-9}\,\text{m})\times(8.314\,\text{J K}^{-1}\,\text{mol}^{-1})\times(308.2\,\text{K})}\\ &= 5.11\overline{9}\times 10^{-2}\end{aligned}$$

$p = (5.623\,\text{kPa})\text{e}^{0.0511\overline{9}} = \boxed{5.92\,\text{kPa}}$

E6.15(b)

$$\gamma = \tfrac{1}{2}\rho g h r = \tfrac{1}{2}(0.9956\,\mathrm{g\,cm^{-3}}) \times (9.807\,\mathrm{m\,s^{-2}}) \times (9.11 \times 10^{-2}\,\mathrm{m})$$

$$\times\ (0.16 \times 10^{-3}\,\mathrm{m}) \times \left(\frac{1000\,\mathrm{kg\,m^{-3}}}{\mathrm{g\,cm^{-3}}}\right)$$

$$= \boxed{7.12 \times 10^{-2}\,\mathrm{N\,m^{-1}}}$$

E6.16(b)

$$p_{\mathrm{in}} - p_{\mathrm{out}} = \frac{2\gamma}{r} = \frac{2(22.39 \times 10^{-3}\,\mathrm{N\,m^{-1}})}{(220 \times 10^{-9}\,\mathrm{m})}$$

$$= 2.04 \times 10^{5}\,\mathrm{N\,m^{-2}} = \boxed{2.04 \times 10^{5}\,\mathrm{Pa}}$$

Solutions to problems

Solutions to numerical problems

P6.3 **(a)**

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}}S}{\Delta_{\mathrm{vap}}V} = \frac{\Delta_{\mathrm{vap}}H}{T_{\mathrm{b}}\Delta_{\mathrm{vap}}V}\ \text{[6.6, Clapeyron equation]}$$

$$= \frac{14.4 \times 10^{3}\,\mathrm{J\,mol^{-1}}}{(180\,\mathrm{K}) \times (14.5 \times 10^{-3} - 1.15 \times 10^{-4})\,\mathrm{m^{3}\,mol^{-1}}} = \boxed{+5.56\,\mathrm{kPa\,K^{-1}}}$$

(b)

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}}H}{RT^{2}} \times p\ \left[11,\ \text{with}\ \mathrm{d}\ln p = \frac{\mathrm{d}p}{p}\right]$$

$$= \frac{(14.4 \times 10^{3}\,\mathrm{J\,mol^{-1}}) \times (1.013 \times 10^{5}\,\mathrm{Pa})}{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (180\,\mathrm{K})^{2}} = +5.42\,\mathrm{kPa\,K^{-1}}$$

The percentage error is $\boxed{2.5\ \text{per cent}}$

P6.5 **(a)**

$$\left(\frac{\partial\mu(\mathrm{l})}{\partial p}\right)_{T} - \left(\frac{\partial\mu(\mathrm{s})}{\partial p}\right)_{T} = V_{\mathrm{m}}(\mathrm{l}) - V_{\mathrm{m}}(\mathrm{s})[6.13] = M\Delta\left(\frac{1}{\rho}\right)$$

$$= (18.02\,\mathrm{g\,mol^{-1}}) \times \left(\frac{1}{1.000\,\mathrm{g\,cm^{-3}}} - \frac{1}{0.917\,\mathrm{g\,cm^{-3}}}\right)$$

$$= \boxed{-1.63\,\mathrm{cm^{3}\,mol^{-1}}}$$

(b)

$$\left(\frac{\partial\mu(\mathrm{g})}{\partial p}\right)_{T} - \left(\frac{\partial\mu(\mathrm{l})}{\partial p}\right)_{T} = V_{\mathrm{m}}(\mathrm{g}) - V_{\mathrm{m}}(\mathrm{l})$$

$$= (18.02\,\mathrm{g\,mol^{-1}}) \times \left(\frac{1}{0.598\,\mathrm{g\,L^{-1}}} - \frac{1}{0.958 \times 10^{3}\,\mathrm{g\,L^{-1}}}\right)$$

$$= \boxed{+30.1\,\mathrm{L\,mol^{-1}}}$$

At $1.\bar{0}$ atm and 100°C, $\mu(\mathrm{l}) = \mu(\mathrm{g})$; therefore, at 1.2 atm and 100°C $\mu(\mathrm{g}) - \mu(\mathrm{l}) \approx \Delta V_{\mathrm{vap}}\Delta p =$ (as in Problem 6.4)

$$(30.1 \times 10^{-3}\,\mathrm{m^{3}\,mol^{-1}}) \times (0.2) \times (1.013 \times 10^{5}\,\mathrm{Pa}) \approx \boxed{+0.6\,\mathrm{kJ\,mol^{-1}}}$$

Since $\mu(\mathrm{g}) > \mu(\mathrm{l})$, the gas tends to condense into a liquid.

P6.7 The amount (moles) of water evaporated is $n_{\mathrm{g}} = \dfrac{p_{\mathrm{H_2O}}V}{RT}$

The heat leaving the water is $q = n\Delta_{\mathrm{vap}}H$

The temperature change of the water is $\Delta T = \dfrac{-q}{nC_{p,\mathrm{m}}}$, $n =$ amount of liquid water

$$\text{Therefore, } \Delta T = \frac{-p_{\mathrm{H_2O}} V \Delta_{\mathrm{vap}} H}{RTnC_{p,\mathrm{m}}}$$

$$= \frac{-(23.8\,\mathrm{Torr}) \times (50.0\,\mathrm{L}) \times (44.0 \times 10^3\,\mathrm{J\,mol^{-1}})}{(62.364\,\mathrm{L\,Torr\,K^{-1}\,mol^{-1}}) \times (298.15\,\mathrm{K}) \times (75.5\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \left(\frac{250\,\mathrm{g}}{18.02\,\mathrm{g\,mol^{-1}}}\right)}$$

$$= -2.7\,\mathrm{K}$$

The final temperature will be about $\boxed{22°\mathrm{C}}$

P6.9 **(a)** Follow the procedure in Problem 6.8, but note that $T_b = \boxed{227.5°\mathrm{C}}$ is obvious from the data.

(b) Draw up the following table

$\theta/°\mathrm{C}$	57.4	100.4	133.0	157.3	203.5	227.5
T/K	330.6	373.6	406.2	430.5	476.7	500.7
$1000\,\mathrm{K}/T$	3.02	2.68	2.46	2.32	2.10	2.00
$\ln p/\mathrm{Torr}$	0.00	2.30	3.69	4.61	5.99	6.63

The points are plotted in Fig. 6.2. The slope is $-6.4 \times 10^3\,\mathrm{K}$, so $\dfrac{-\Delta_{\mathrm{vap}}H}{R} = -6.4 \times 10^3\,\mathrm{K}$, implying that $\Delta_{\mathrm{vap}}H = \boxed{+53\,\mathrm{kJ\,mol^{-1}}}$

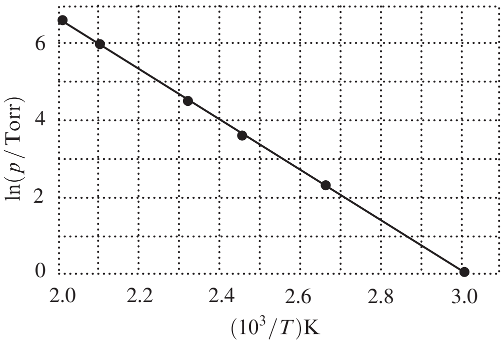


Figure 6.2

P6.11 **(a)** The phase diagram is shown in Fig. 6.3.

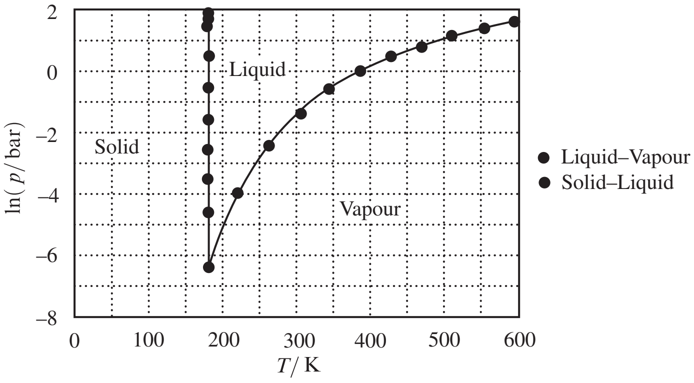


Figure 6.3

(b) The standard melting point is the temperature at which solid and liquid are in equilibrium at 1 bar. That temperature can be found by solving the equation of the solid–liquid coexistence curve for the temperature

$$1 = p_3/\mathrm{bar} + 1000(5.60 + 11.727x)x,$$

So $11\,727x^2 + 5600x + (4.362 \times 10^{-7} - 1) = 0$

The quadratic formula yields

$$x = \frac{-5600 \pm \{(5600)^2 - 4(11\,727) \times (-1)\}^{1/2}}{2(11\,727)} = \frac{-1 \pm \left\{1 + \frac{4(11\,727)}{5600^2}\right\}^{1/2}}{2\left(\frac{11727}{5600}\right)}$$

The square root is rewritten to make it clear that the square root is of the form $\{1 + a\}^{1/2}$, with $a \ll 1$; thus the numerator is approximately $-1 + (1 + \frac{1}{2}a) = \frac{1}{2}a$, and the whole expression reduces to

$$x \approx 1/5600 = 1.79 \times 10^{-4}$$

Thus, the melting point is

$$T = (1 + x)T_3 = (1.000179) \times (178.15\,\mathrm{K}) = \boxed{178.18\,\mathrm{K}}$$

(c) The standard boiling point is the temperature at which the liquid and vapour are in equilibrium at 1 bar. That temperature can be found by solving the equation of the liquid–vapour coexistence curve for the temperature. This equation is too complicated to solve analytically, but not difficult to solve numerically with a spreadsheet. The calculated answer is $\boxed{T = 383.6\,\mathrm{K}}$

(d) The slope of the liquid–vapour coexistence curve is given by

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}}H}{T\Delta_{\mathrm{vap}}V^{\ominus}} \quad \text{so} \quad \Delta_{\mathrm{vap}}H^{\ominus} = T\Delta_{\mathrm{vap}}V^{\ominus}\frac{\mathrm{d}p}{\mathrm{d}T}$$

The slope can be obtained by differentiating the equation for the coexistence curve.

$$\frac{\mathrm{d}p}{\mathrm{d}T} = p\frac{\mathrm{d}\ln p}{\mathrm{d}T} = p\frac{\mathrm{d}\ln p}{\mathrm{d}y}\frac{\mathrm{d}y}{\mathrm{d}T}$$

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \left(\frac{10.418}{y^2} - 15.996 + 2(14.015)y - 3(5.0120)y^2 - (1.70) \times (4.7224) \times (1 - y)^{0.70}\right) \times \left(\frac{p}{T_\mathrm{c}}\right)$$

At the boiling point, $y = 0.6458$, so

$$\frac{\mathrm{d}p}{\mathrm{d}T} = 2.851 \times 10^{-2}\,\mathrm{bar\,K^{-1}} = 2.851\,\mathrm{kPa\,K^{-1}}$$

and $\Delta_{\mathrm{vap}}H^{\ominus} = (383.6\,\mathrm{K}) \times \left(\frac{(30.3 - 0.12)\,\mathrm{L\,mol^{-1}}}{1000\,\mathrm{L\,m^{-3}}}\right) \times (2.851\,\mathrm{kPa\,K^{-1}}) = \boxed{33.0\,\mathrm{kJ\,mol^{-1}}}$

P6.12 The slope of the solid–vapour coexistence curve is given by

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{sub}}H^{\ominus}}{T\Delta_{\mathrm{sub}}V^{\ominus}} \quad \text{so} \quad \Delta_{\mathrm{sub}}H^{\ominus} = T\Delta_{\mathrm{sub}}V^{\ominus}\frac{\mathrm{d}p}{\mathrm{d}T}$$

The slope can be obtained by differentiating the coexistence curve graphically (Fig. 6.4).

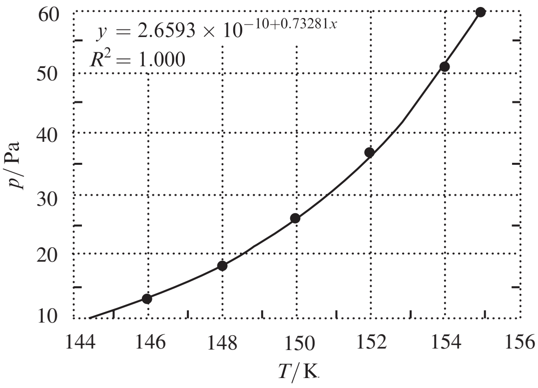


Figure 6.4

$$\frac{dp}{dT} = 4.41\,\text{Pa}\,\text{K}^{-1}$$

according to the exponential best fit of the data. The change in volume is the volume of the vapour

$$V_\text{m} = \frac{RT}{p} = \frac{(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (150\,\text{K})}{26.1\,\text{Pa}} = 47.8\,\text{m}^3$$

So

$$\Delta_\text{sub}H^\ominus = (150\,\text{K}) \times (47.8\,\text{m}^3) \times (4.41\,\text{Pa}\,\text{K}^{-1}) = 3.16 \times 10^4\,\text{J}\,\text{mol}^{-1} = \boxed{31.6\,\text{kJ}\,\text{mol}^{-1}}$$

Solutions to theoretical problems

P6.14

$$\left(\frac{\partial \Delta G}{\partial p}\right)_T = \left(\frac{\partial G_\beta}{\partial p}\right)_T - \left(\frac{\partial G_\alpha}{\partial p}\right)_T = V_\beta - V_\alpha$$

Therefore, if $V_\beta = V_\alpha$, ΔG is independent of pressure. In general, $V_\beta \neq V_\alpha$, so that ΔG is nonzero, though small, since $V_\beta - V_\alpha$ is small.

P6.16

Amount of gas bubbled through liquid $= \dfrac{pV}{RT}$

(p = initial pressure of gas and emerging gaseous mixture)

Amount of vapour carried away $= \dfrac{m}{M}$

Mole fraction of vapour in gaseous mixture $= \dfrac{\frac{m}{M}}{\frac{m}{M} + \frac{pV}{RT}}$

$$\text{Partial pressure of vapour} = p = \frac{\frac{m}{M}}{\frac{m}{M} + \frac{pV}{RT}} \times p = \frac{p\left(\frac{mRT}{PVM}\right)}{\left(\frac{mRT}{PVM}\right) + 1} = \frac{mPA}{mA + 1}, \quad A = \frac{RT}{PVM}$$

For geraniol, $M = 154.2\,\text{g}\,\text{mol}^{-1}$, $T = 383\,\text{K}$, $V = 5.00\,\text{L}$, $p = 1.00\,\text{atm}$, and $m = 0.32\,\text{g}$, so

$$A = \frac{(8.206 \times 10^{-2}\,\text{L}\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (383\,\text{K})}{(1.00\,\text{atm}) \times (5.00\,\text{L}) \times (154.2 \times 10^{-3}\,\text{kg}\,\text{mol}^{-1})} = 40.7\bar{6}\,\text{kg}^{-1}$$

Therefore

$$p = \frac{(0.32 \times 10^{-3}\,\text{kg}) \times (760\,\text{Torr}) \times (40.7\bar{6}\,\text{kg}^{-1})}{(0.32 \times 10^{-3}\,\text{kg}) \times (40.76\,\text{kg}^{-1}) + 1} = \boxed{9.8\,\text{Torr}}$$

P6.17

$$p = p_0 e^{-Mgh/RT} \text{ [Box 1.1]}$$

$$p = p^* e^{-\chi} \quad \chi = \frac{\Delta_{\text{vap}}H}{R} \times \left(\frac{1}{T} - \frac{1}{T^*}\right) \text{ [6.12]}$$

Let $T^* = T_{\text{b}}$ the normal boiling point; then $p^* = 1\,\text{atm}$. Let $T = T_{\text{h}}$, the boiling point at the altitude h. Take $p_0 = 1\,\text{atm}$. Boiling occurs when the vapour (p) is equal to the ambient pressure, that is, when $p(T) = p(h)$, and when this is so, $T = T_{\text{h}}$. Therefore, since $p_0 = p^*$, $p(T) = p(h)$ implies that

$$e^{-Mgh/RT} = \exp\left\{-\frac{\Delta_{\text{vap}}H}{R} \times \left(\frac{1}{T_{\text{h}}} - \frac{1}{T_{\text{b}}}\right)\right\}$$

It follows that $\boxed{\dfrac{1}{T_{\text{h}}} = \dfrac{1}{T_{\text{b}}} + \dfrac{Mgh}{T\,\Delta_{\text{vap}}H}}$

where T is the ambient temperature and M the molar mass of the air. For water at 3000 m, using $M = 29\,\text{g mol}^{-1}$

$$\frac{1}{T_{\text{h}}} = \frac{1}{373\,\text{K}} + \frac{(29 \times 10^{-3}\,\text{kg mol}^{-1}) \times (9.81\,\text{m s}^{-2}) \times (3.000 \times 10^3\,\text{m})}{(293\,\text{K}) \times (40.7 \times 10^3\,\text{J mol}^{-1})}$$

$$= \frac{1}{373\,\text{K}} + \frac{1}{1.397 \times 10^4\,\text{K}}$$

Hence, $T_{\text{h}} = \boxed{363\,\text{K}}$ (90°C)

P6.20

$$S_{\text{m}} = S_{\text{m}}(T, p)$$

$$\text{d}S_{\text{m}} = \left(\frac{\partial S_{\text{m}}}{\partial T}\right)_p \text{d}T + \left(\frac{\partial S_{\text{m}}}{\partial p}\right)_T \text{d}p$$

$$\left(\frac{\partial S_{\text{m}}}{\partial T}\right)_p = \frac{C_{p,\text{m}}}{T} \text{ [Problem 5.7]} \qquad \left(\frac{\partial S_{\text{m}}}{\partial p}\right)_T = -\left(\frac{\partial V_{\text{m}}}{\partial T}\right)_p \text{ [Maxwell relation]}$$

$$\text{d}q_{\text{rev}} = T\,\text{d}S_{\text{m}} = C_{p,\text{m}}\,\text{d}T - T\left(\frac{\partial V_{\text{m}}}{\partial T}\right)_p \text{d}p$$

$$C_S = \left(\frac{\partial q}{\partial T}\right)_s = C_{p,\text{m}} - TV_{\text{m}}\alpha\left(\frac{\partial p}{\partial T}\right)_s = C_{p,\text{m}} - \alpha V_{\text{m}} \times \frac{\Delta H_{\text{m}}}{\Delta V_{\text{m}}} \text{ [6.7]}$$

P6.22

$$\text{C(graphite)} \rightleftharpoons \text{C(diamond)} \quad \Delta_{\text{r}}G^{\ominus} = 2.8678\,\text{kJ mol}^{-1} \text{ at } \mathcal{T}.$$

We want the pressure at which $\Delta_{\text{r}}G = 0$; above that pressure the reaction will be spontaneous. Equation 5.10 determines the rate of change of $\Delta_{\text{r}}G$ with p at constant T.

(1) $$\left(\frac{\partial \Delta_{\text{r}}G}{\partial p}\right)_T = \Delta_{\text{r}}V = (V_{\text{D}} - V_{\text{G}})M$$

where M is the molar mas of carbon; V_{D} and V_{G} are the specific volumes of diamond and graphite, respectively.

$\Delta_{\text{r}}G(\mathcal{T}, p)$ may be expanded in a Taylor series around the pressure $p^{\ominus} = 100\,\text{kPa}$ at $\mathcal{T}$.

(2) $$\Delta_{\text{r}}G(\mathcal{T}, p) = \Delta_{\text{r}}G^{\ominus}(\mathcal{T}, p^{\ominus}) + \left(\frac{\partial \Delta_{\text{r}}G^{\ominus}(\mathcal{T}, p^{\ominus})}{\partial p}\right)_T (p - p^{\ominus}) + \frac{1}{2}\left(\frac{\partial^2 \Delta_{\text{r}}G^{\ominus}(\mathcal{T}, p^{\ominus})}{\partial p^2}\right)_T (p - p^{\ominus})^2 + \theta(p - p^{\ominus})^3$$

We will neglect the third and higher-order terms; the derivative of the first-order term can be calculated with eqn 1. An expression for the derivative of the second-order term can be derived with eqn 1.

$$\left(\frac{\partial^2 \Delta_r G}{\partial p^2}\right)_T = \left\{\left(\frac{\partial V_D}{\partial p}\right)_T - \left(\frac{\partial V_G}{\partial p}\right)_T\right\} M = \{V_G\kappa_T(\mathrm{G}) - V_D\kappa_T(\mathrm{D})\}M \ [3.13] \tag{3}$$

Calculating the derivatives of eqns 1 and 2 at $\mathfrak{T}$ and $p^\ominus$

$$\left(\frac{\partial \Delta_r G(\mathfrak{T},\ p^\ominus)}{\partial p}\right)_T = (0.284 - 0.444) \times \left(\frac{\mathrm{cm}^3}{\mathrm{g}}\right) \times \left(\frac{12.01\ \mathrm{g}}{\mathrm{mol}}\right) = -1.92\ \mathrm{cm}^3\ \mathrm{mol}^{-1} \tag{4}$$

$$\begin{aligned}\left(\frac{\partial^2 \Delta_r G(\mathfrak{T},\ p^\ominus)}{\partial p^2}\right)_T &= \{0.444(3.04 \times 10^{-8}) - 0.284(0.187 \times 10^{-8})\} \\ &\quad \times \left(\frac{\mathrm{cm}^3\ \mathrm{kPa}^{-1}}{\mathrm{g}}\right) \times \left(\frac{12.01\ \mathrm{g}}{\mathrm{mol}}\right) \\ &= 1.56 \times 10^{-7}\ \mathrm{cm}^3\ (\mathrm{kPa})^{-1}\ \mathrm{mol}^{-1}\end{aligned} \tag{5}$$

It is convenient to convert the value of $\Delta_r G^\ominus$ to the units $\mathrm{cm}^3\ \mathrm{kPa\ mol}^{-1}$

$$\Delta_r G^\ominus = 2.8678\ \mathrm{kJ\ mol}^{-1} \left(\frac{8.315 \times 10^{-2}\ \mathrm{L\ bar\ K}^{-1}\ \mathrm{mol}^{-1}}{8.315\ \mathrm{J\ K}^{-1}\ \mathrm{mol}^{-1}}\right) \times \left(\frac{10^3\ \mathrm{cm}^3}{\mathrm{L}}\right) \times \left(\frac{10^5\ \mathrm{Pa}}{\mathrm{bar}}\right)$$

$$\Delta_r G^\ominus = 2.8678 \times 10^6\ \mathrm{cm}^3\ \mathrm{kPa\ mol}^{-1} \tag{6}$$

Setting $\chi = p - p^\ominus$, eqns 2 and 3–6 give

$$2.8678 \times 10^6\ \mathrm{cm}^3\ \mathrm{kPa\ mol}^{-1} - (1.92\ \mathrm{cm}^3\ \mathrm{mol}^{-1})\chi + (7.80 \times 10^{-8}\ \mathrm{cm}^3\ \mathrm{kPa}^{-1}\ \mathrm{mol}^{-1})\chi^2 = 0$$

when $\Delta_r G(\mathfrak{T},\ p) = 0$. One real root of this equation is

$$\begin{aligned}\chi &= 1.60 \times 10^6\ \mathrm{kPa} = p - p^\ominus \text{ or} \\ p &= 1.60 \times 10^6\ \mathrm{kPa} - 10^2\ \mathrm{kPa} \\ &= 1.60 \times 10^6\ \mathrm{kPa} = \boxed{1.60 \times 10^4\ \mathrm{bar}}\end{aligned}$$

Above this pressure the reaction is spontaneous. The other real root is much higher: 2.3×10^7 kPa.

Question. What interpretation might you give to the other real root?

7 Simple mixtures

Solutions to exercises

Discussion questions

E7.1(b) For a component in an ideal solution, Raoult's law is: $p = xp^*$. For real solutions, the activity, a, replaces the mole fraction, x, and Raoult's law becomes $p = ap^*$.

E7.2(b) All the colligative properties are a result of the lowering of the chemical potential of the solvent due to the presence of the solute. This reduction takes the form $\mu_A = \mu_A{}^* + RT \ln x_A$ or $\mu_A = \mu_A{}^* + RT \ln a_A$, depending on whether or not the solution can be considered ideal. The lowering of the chemical potential results in a freezing point depression and a boiling point elevation as illustrated in Fig. 7.20 of the text. Both of these effects can be explained by the lowering of the vapour pressure of the solvent in solution due to the presence of the solute. The solute molecules get in the way of the solvent molecules, reducing their escaping tendency.

E7.3(b) The activity of a solute is that property which determines how the chemical potential of the solute varies from its value in a specified reference state. This is seen from the relation $\mu = \mu^{\ominus} + RT \ln a$, where $\mu^{\ominus}$ is the value of the chemical potential in the reference state. The reference state is either the hypothetical state where the pure solute obeys Henry's law (if the solute is volatile) or the hypothetical state where the solute at unit molality obeys Henry's law (if the solute is involatile). The activity of the solute can then be defined as that physical property which makes the above relation true. It can be interpreted as an effective concentration.

Numerical exercises

E7.4(b) Total volume $V = n_A V_A + n_B V_B = n(x_A V_A + x_B V_B)$

Total mass $m = n_A M_A + n_B M_B$

$$= n(x_A M_A + (1 - x_A)M_B) \quad \text{where } n = n_A + n_B$$

$$\frac{m}{x_A M_A + (1 - x_A)M_B} = n$$

$$n = \frac{1.000\,\text{kg}(10^3\,\text{g/kg})}{(0.3713) \times (241.1\,\text{g/mol}) + (1 - 0.3713) \times (198.2\,\text{g/mol})} = 4.670\bar{1}\,\text{mol}$$

$$V = n(x_A V_A + x_B V_B)$$

$$= (4.670\bar{1}\,\text{mol}) \times [(0.3713) \times (188.2\,\text{cm}^3\,\text{mol}^{-1}) + (1 - 0.3713) \times (176.14\,\text{cm}^3\,\text{mol}^{-1})]$$

$$= \boxed{843.5\,\text{cm}^3}$$

E7.5(b) Let A denote water and B ethanol. The total volume of the solution is $V = n_A V_A + n_B V_B$

We know V_B; we need to determine n_A and n_B in order to solve for V_A.

Assume we have $100\,\text{cm}^3$ of solution; then the mass is

$$m = \rho V = (0.9687\,\text{g cm}^{-3}) \times (100\,\text{cm}^3) = 96.87\,\text{g}$$

of which $(0.20) \times (96.87\,\text{g}) = 19.3\overline{74}\,\text{g}$ is ethanol and $(0.80) \times (96.87\,\text{g}) = 77.\overline{496}\,\text{g}$ is water.

$$n_A = \frac{77.\overline{496}\,\text{g}}{18.02\,\text{g mol}^{-1}} = 4.3\bar{0}\,\text{mol H}_2\text{O}$$

$$n_B = \frac{19.374\,\text{g}}{46.07\,\text{g mol}^{-1}} = 0.42\overline{05}\,\text{mol ethanol}$$

$$\frac{V - n_{\mathrm{B}}V_{\mathrm{B}}}{n_{\mathrm{A}}} = V_{\mathrm{A}} = \frac{100\,\mathrm{cm}^3 - (0.42\overline{05}\,\mathrm{mol}) \times (52.2\,\mathrm{cm}^3\,\mathrm{mol}^{-1})}{4.3\bar{0}\,\mathrm{mol}} = 18.\overline{15}\,\mathrm{cm}^3$$

$$= \boxed{18\,\mathrm{cm}^3}$$

E7.6(b) Check that $p_{\mathrm{B}}/x_{\mathrm{B}}$ = a constant (K_{B})

x_{B}	0.010	0.015	0.020
$(p_{\mathrm{B}}/x_{\mathrm{B}})/\mathrm{kPa}$	8.2×10^3	8.1×10^3	8.3×10^3

$K_{\mathrm{B}} = p/x$, average value is $\boxed{8.2 \times 10^3\,\mathrm{kPa}}$

E7.7(b) In exercise 7.6(b), the Henry's law constant was determined for concentrations expressed in mole fractions. Thus the concentration in molality must be converted to mole fraction.

$m(\mathrm{A}) = 1000\,\mathrm{g}$, corresponding to

$$n(\mathrm{A}) = \frac{1000\,\mathrm{g}}{74.1\,\mathrm{g\,mol}^{-1}} = 13.5\bar{0}\,\mathrm{mol} \qquad n(\mathrm{B}) = 0.25\,\mathrm{mol}$$

Therefore,

$$x_{\mathrm{B}} = \frac{0.25\,\mathrm{mol}}{0.25\,\mathrm{mol} + 13.5\bar{0}\,\mathrm{mol}} = 0.018\bar{2}$$

using $K_{\mathrm{B}} = 8.2 \times 10^3\,\mathrm{kPa}$ [exercise 7.6(b)]

$$p = 0.018\bar{2} \times 8.2 \times 10^3\,\mathrm{kPa} = \boxed{1.5 \times 10^2\,\mathrm{kPa}}$$

E7.8(b)

$$K_{\mathrm{f}} = \frac{RT^{*2}M}{\Delta_{\mathrm{fus}}H} = \frac{8.314\,\mathrm{J\,K^{-1}\,mol^{-1}} \times (354\,\mathrm{K})^2 \times 0.12818\,\mathrm{kg\,mol^{-1}}}{18.80 \times 10^3\,\mathrm{J\,mol^{-1}}}$$

$$= \boxed{7.1\,\mathrm{K\,kg\,mol^{-1}}}$$

$$K_{\mathrm{b}} = \frac{RT^{*2}M}{\Delta_{\mathrm{vap}}H} = \frac{8.314\,\mathrm{J\,K^{-1}\,mol^{-1}} \times (490.9\,\mathrm{K})^2 \times 0.12818\,\mathrm{kg\,mol^{-1}}}{51.51 \times 10^3\,\mathrm{J\,mol^{-1}}}$$

$$= \boxed{4.99\,\mathrm{K\,kg\,mol^{-1}}}$$

E7.9(b) We assume that the solvent, 2-propanol, is ideal and obeys Raoult's law.

$$x_{\mathrm{A}}(\text{solvent}) = p/p^* = \frac{49.62}{50.00} = 0.9924$$

$$M_{\mathrm{A}}(\mathrm{C_3H_8O}) = 60.096\,\mathrm{g\,mol^{-1}}$$

$$n_{\mathrm{A}} = \frac{250\,\mathrm{g}}{60.096\,\mathrm{g\,mol^{-1}}} = 4.16\overline{00}\,\mathrm{mol}$$

$$x_{\mathrm{A}} = \frac{n_{\mathrm{A}}}{n_{\mathrm{A}} + n_{\mathrm{B}}} \qquad n_{\mathrm{A}} + n_{\mathrm{B}} = \frac{n_{\mathrm{A}}}{x_{\mathrm{A}}}$$

$$n_{\mathrm{B}} = n_{\mathrm{A}}\left(\frac{1}{x_{\mathrm{A}}} - 1\right)$$

$$= 4.16\overline{00}\,\mathrm{mol}\left(\frac{1}{0.9924} - 1\right) = 3.1\overline{86} \times 10^{-2}\,\mathrm{mol}$$

$$M_{\mathrm{B}} = \frac{8.69\,\mathrm{g}}{3.186 \times 10^{-2}\,\mathrm{mol}} = 27\bar{3}\,\mathrm{g\,mol^{-1}} = \boxed{270\,\mathrm{g\,mol^{-1}}}$$

E7.10(b) $K_{\mathrm{f}} = 6.94$ for naphthalene

$$M_{\mathrm{B}} = \frac{\text{mass of B}}{n_{\mathrm{B}}}$$

$n_{\mathrm{B}} = \text{mass of naphthalene} \cdot b_{\mathrm{B}}$

$$b_{\mathrm{B}} = \frac{\Delta T}{K_{\mathrm{f}}} \quad \text{so} \quad M_{\mathrm{B}} = \frac{(\text{mass of B}) \times K_{\mathrm{f}}}{(\text{mass of naphthalene}) \times \Delta T}$$

$$M_{\mathrm{B}} = \frac{(5.00\,\mathrm{g}) \times (6.94\,\mathrm{K\,kg\,mol^{-1}})}{(0.250\,\mathrm{kg}) \times (0.780\,\mathrm{K})} = \boxed{178\,\mathrm{g\,mol^{-1}}}$$

E7.11(b) $\Delta T = K_{\mathrm{f}} b_{\mathrm{B}}$ and $b_{\mathrm{B}} = \dfrac{n_{\mathrm{B}}}{\text{mass of water}} = \dfrac{n_{\mathrm{B}}}{V\rho}$

$\rho = 10^3\,\mathrm{kg\,m^{-3}}$ (density of solution $\approx$ density of water)

$$n_{\mathrm{B}} = \frac{\Pi V}{RT} \qquad \Delta T = K_{\mathrm{f}}\frac{\Pi}{RT\rho} \qquad K_{\mathrm{f}} = 1.86\,\mathrm{K\,mol^{-1}\,kg}$$

$$\Delta T = \frac{(1.86\,\mathrm{K\,kg\,mol^{-1}}) \times (99 \times 10^3\,\mathrm{Pa})}{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (288\,\mathrm{K}) \times (10^3\,\mathrm{kg\,m^{-3}})} = 7.7 \times 10^{-2}\,\mathrm{K}$$

$$T_{\mathrm{f}} = \boxed{-0.077^{\circ}\mathrm{C}}$$

E7.12(b) $\Delta_{\mathrm{mix}}G = nRT(x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}})$

$$n_{\mathrm{Ar}} = n_{\mathrm{Ne}}, \qquad x_{\mathrm{Ar}} = x_{\mathrm{Ne}} = 0.5, \qquad n = n_{\mathrm{Ar}} + n_{\mathrm{Ne}} = \frac{pV}{RT}$$

$$\Delta_{\mathrm{mix}}G = pV\left(\tfrac{1}{2}\ln\tfrac{1}{2} + \tfrac{1}{2}\ln\tfrac{1}{2}\right) = -pV\ln 2$$

$$= -(100 \times 10^3\,\mathrm{Pa}) \times (0.250\,\mathrm{L})\left(\frac{1\,\mathrm{m}^3}{10^3\,\mathrm{L}}\right)\ln 2$$

$$= -17.3\,\mathrm{Pa\,m^3} = -17.3\,\mathrm{J} \qquad \Delta_{\mathrm{mix}}S = \frac{-\Delta_{\mathrm{mix}}G}{T} = \frac{17.3\,\mathrm{J}}{273\,\mathrm{K}} = \boxed{6.34 \times 10^{-2}\,\mathrm{J\,K^{-1}}}$$

E7.13(b) $\Delta_{\mathrm{mix}}G = nRT\sum_{\mathrm{J}} x_{\mathrm{J}} \ln x_{\mathrm{J}}$ [7.18] $\qquad \Delta_{\mathrm{mix}}S = -nR\sum_{\mathrm{J}} x_{\mathrm{J}} \ln x_{\mathrm{J}}$ [7.19] $= \dfrac{-\Delta_{\mathrm{mix}}G}{T}$

$n = 1.00\,\mathrm{mol} + 1.00\,\mathrm{mol} = 2.00\,\mathrm{mol}$

$x(\mathrm{Hex}) = x(\mathrm{Hep}) = 0.500$

Therefore,

$$\Delta_{\mathrm{mix}}G = (2.00\,\mathrm{mol}) \times (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K}) \times (0.500\ln 0.500 + 0.500\ln 0.500)$$

$$= \boxed{-3.43\,\mathrm{kJ}}$$

$$\Delta_{\text{mix}}S = \frac{+3.43\,\text{kJ}}{298\,\text{K}} = \boxed{+11.5\,\text{J}\,\text{K}^{-1}}$$

$\Delta_{\text{mix}}H$ for an ideal solution is zero as it is for a solution of perfect gases [7.20]. It can be demonstrated from

$$\Delta_{\text{mix}}H = \Delta_{\text{mix}}G + T\Delta_{\text{mix}}S = (-3.43\times10^3\,\text{J}) + (298\,\text{K})\times(11.5\,\text{J}\,\text{K}^{-1}) = \boxed{0}$$

E7.14(b) Benzene and ethylbenzene form nearly ideal solutions, so

$$\Delta_{\text{mix}}S = -nR(x_\text{A}\ln x_\text{A} + x_\text{B}\ln x_\text{B})$$

To find maximum $\Delta_{\text{mix}}S$, differentiate with respect to x_A and find value of x_A at which the derivative is zero.

Note that $x_\text{B} = 1 - x_\text{A}$ so

$$\Delta_{\text{mix}}S = -nR(x_\text{A}\ln x_\text{A} + (1-x_\text{A})\ln(1-x_\text{A}))$$

use $\dfrac{\text{d}\ln x}{\text{d}x} = \dfrac{1}{x}$

$$\frac{\text{d}}{\text{d}x}(\Delta_{\text{mix}}S) = -nR(\ln x_\text{A} + 1 - \ln(1-x_\text{A}) - 1) = -nR\ln\frac{x_\text{A}}{1-x_\text{A}}$$

$$= 0 \quad \text{when } x_\text{A} = \tfrac{1}{2}$$

Thus the maximum entropy of mixing is attained by mixing equal molar amounts of two components.

$$\frac{n_\text{B}}{n_\text{E}} = \boxed{1} = \frac{m_\text{B}/M_\text{B}}{m_\text{E}/M_\text{E}} \qquad \frac{m_\text{E}}{m_\text{B}} = \frac{M_\text{E}}{M_\text{B}} = \frac{106.169}{78.115} = 1.3591$$

$$\frac{m_\text{B}}{m_\text{E}} = \boxed{0.7358}$$

E7.15(b) Assume Henry's law [7.26] applies; therefore, with $K(\text{N}_2) = 6.51\times10^7$ Torr and $K(\text{O}_2) = 3.30\times10^7$ Torr, as in Exercise 7.14, the amount of dissolved gas in 1 kg of water is

$$n(\text{N}_2) = \left(\frac{10^3\,\text{g}}{18.02\,\text{g}\,\text{mol}^{-1}}\right)\times\left(\frac{p(\text{N}_2)}{6.51\times10^7\,\text{Torr}}\right) = (8.52\times10^{-7}\,\text{mol})\times(p/\text{Torr})$$

For $p(\text{N}_2) = xp$ and $p = 760\,\text{Torr}$

$$n(\text{N}_2) = (8.52\times10^{-7}\,\text{mol})\times(x)\times(760) = x(6.48\times10^{-4}\,\text{mol})$$

and, with $x = 0.78$

$$n(\text{N}_2) = (0.78)\times(6.48\times10^{-4}\,\text{mol}) = 5.1\times10^{-4}\,\text{mol} = 0.51\,\text{mmol}$$

The molality of the solution is therefore approximately $\boxed{0.51\,\text{mmol}\,\text{kg}^{-1}}$ in N_2. Similarly, for oxygen,

$$n(\text{O}_2) = \left(\frac{10^3\,\text{g}}{18.02\,\text{g}\,\text{mol}^{-1}}\right)\times\left(\frac{p(\text{O}_2)}{3.30\times10^7\,\text{Torr}}\right) = (1.68\times10^{-6}\,\text{mol})\times(p/\text{Torr})$$

For $p(\text{O}_2) = xp$ and $p = 760\,\text{Torr}$

$$n(\text{O}_2) = (1.68\times10^{-6}\,\text{mol})\times(x)\times(760) = x(1.28\,\text{mmol})$$

and when $x = 0.21$, $n(\text{O}_2) \approx 0.27\,\text{mmol}$. Hence the solution will be $\boxed{0.27\,\text{mmol}\,\text{kg}^{-1}}$ in O_2.

E7.16(b) Use $n(\mathrm{CO_2}) = (4.4 \times 10^{-5}\,\mathrm{mol}) \times (p/\mathrm{Torr}),\ \ p = 2.0(760\,\mathrm{Torr}) = 1520\,\mathrm{Torr}$

$$n(\mathrm{CO_2}) = (4.4 \times 10^{-5}\,\mathrm{mol}) \times (1520) = 0.067\,\mathrm{mol}$$

The molality will be about $0.067\,\mathrm{mol\,kg^{-1}}$ and, since molalities and molar concentration for dilute aqueous solutions are approximately equal, the molar concentration is about $\boxed{0.067\,\mathrm{mol\,L^{-1}}}$

E7.17(b) $M(\text{glucose}) = 180.16\,\mathrm{g\,mol^{-1}}$

$\Delta T = K_f b_B \quad K_f = 1.86\,\mathrm{K\,kg\,mol^{-1}}$

$$\Delta T = (1.86\,\mathrm{K\,kg\,mol^{-1}}) \times \left(\frac{10\,\mathrm{g}/180.16\,\mathrm{g\,mol^{-1}}}{0.200\,\mathrm{kg}}\right) = 0.52\,\mathrm{K}$$

Freezing point will be 0°C − 0.52°C = −0.52°C

E7.18(b) The procedure here is identical to Exercise 7.18(a).

$$\ln x_B = \frac{\Delta_{\mathrm{fus}}H}{R} \times \left(\frac{1}{T^*} - \frac{1}{T}\right) \text{ [7.39; B, the solute, is lead]}$$

$$= \left(\frac{5.2 \times 10^3\,\mathrm{J\,mol^{-1}}}{8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}}\right) \times \left(\frac{1}{600\,\mathrm{K}} - \frac{1}{553\,\mathrm{K}}\right)$$

$$= -0.088\bar{6}, \quad \text{implying that } x_B = 0.92$$

$$x_B = \frac{n(\mathrm{Pb})}{n(\mathrm{Pb}) + n(\mathrm{Bi})}, \quad \text{implying that } n(\mathrm{Pb}) = \frac{x_B n(\mathrm{Bi})}{1 - x_B}$$

For 1 kg of bismuth, $n(\mathrm{Bi}) = \dfrac{1000\,\mathrm{g}}{208.98\,\mathrm{g\,mol^{-1}}} = 4.785\,\mathrm{mol}$

Hence, the amount of lead that dissolves in 1 kg of bismuth is

$$n(\mathrm{Pb}) = \frac{(0.92) \times (4.785\,\mathrm{mol})}{1 - 0.92} = 55\,\mathrm{mol}, \quad \text{or} \quad \boxed{11\,\mathrm{kg}}$$

Comment. It is highly unlikely that a solution of 11 kg of lead and 1 kg of bismuth could in any sense be considered ideal. The assumptions upon which eqn 7.39 is based are not likely to apply. The answer above must then be considered an order of magnitude result only.

E7.19(b) Proceed as in Exercise 7.19(a). The data are plotted in Fig. 7.1, and the slope of the line is $1.78\,\mathrm{cm}/(\mathrm{mg\,cm^{-3}}) = 1.78\,\mathrm{cm}/(\mathrm{g\,L^{-1}}) = 1.78 \times 10^{-2}\,\mathrm{m^4\,kg^{-1}}$.

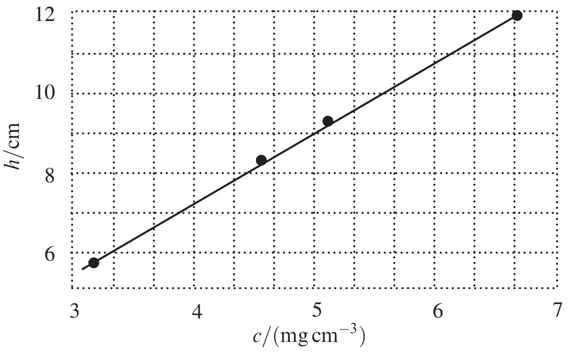


Figure 7.1

Therefore,

$$M = \frac{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (293.15\,\mathrm{K})}{(1.000 \times 10^3\,\mathrm{kg\,m^{-3}}) \times (9.81\,\mathrm{m\,s^{-2}}) \times (1.78 \times 10^{-2}\,\mathrm{m^4\,kg^{-1}})} = \boxed{14.0\,\mathrm{kg\,mol^{-1}}}$$

E7.20(b) Let A = water and B = solute.

$$a_\mathrm{A} = \frac{p_\mathrm{A}}{p_\mathrm{A}^*}\ [42] = \frac{0.02239\,\mathrm{atm}}{0.02308\,\mathrm{atm}} = \boxed{0.9701}$$

$$\gamma_\mathrm{A} = \frac{a_\mathrm{A}}{x_\mathrm{A}} \quad \text{and} \quad x_\mathrm{A} = \frac{n_\mathrm{A}}{n_\mathrm{A} + n_\mathrm{B}}$$

$$n_\mathrm{A} = \frac{0.920\,\mathrm{kg}}{0.01802\,\mathrm{kg\,mol^{-1}}} = 51.0\bar{5}\,\mathrm{mol} \qquad n_\mathrm{B} = \frac{0.122\,\mathrm{kg}}{0.241\,\mathrm{kg\,mol^{-1}}} = 0.506\,\mathrm{mol}$$

$$x_\mathrm{A} = \frac{51.0\bar{5}}{51.05 + 0.506} = 0.990 \qquad \gamma_\mathrm{A} = \frac{0.9701}{0.990} = \boxed{0.980}$$

E7.21(b) B = Benzene $\quad \mu_\mathrm{B}(\mathrm{l}) = \mu_\mathrm{B}^*(\mathrm{l}) + RT \ln x_\mathrm{B}$ [7.50, ideal solution]

$$RT \ln x_\mathrm{B} = (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (353.3\,\mathrm{K}) \times (\ln 0.30) = \boxed{-353\bar{6}\,\mathrm{J\,mol^{-1}}}$$

Thus, its chemical potential is lowered by this amount.

$$p_\mathrm{B} = a_\mathrm{B} p_\mathrm{B}^*[42] = \gamma_\mathrm{B} x_\mathrm{B} p_\mathrm{B}^* = (0.93) \times (0.30) \times (760\,\mathrm{Torr}) = \boxed{212\,\mathrm{Torr}}$$

Question. What is the lowering of the chemical potential in the nonideal solution with $\gamma = 0.93$?

E7.22(b)

$$y_\mathrm{A} = \frac{p_\mathrm{A}}{p_\mathrm{A} + p_\mathrm{B}} = \frac{p_\mathrm{A}}{760\,\mathrm{Torr}} = 0.314$$

$$p_\mathrm{A} = (760\,\mathrm{Torr}) \times (0.314) = 238.\overline{64}\,\mathrm{Torr}$$

$$p_\mathrm{B} = 760\,\mathrm{Torr} - 238.\overline{64}\,\mathrm{Torr} = 521.\overline{36}\,\mathrm{Torr}$$

$$a_\mathrm{A} = \frac{p_\mathrm{A}}{p_\mathrm{A}^*} = \frac{238.64\,\mathrm{Torr}}{(73.0 \times 10^3\,\mathrm{Pa}) \times \left(\frac{1\,\mathrm{atm}}{101\,325\,\mathrm{Pa}}\right) \times \left(\frac{760\,\mathrm{Torr}}{\mathrm{atm}}\right)} = \boxed{0.436}$$

$$a_\mathrm{B} = \frac{p_\mathrm{B}}{p_\mathrm{B}^*} = \frac{521.\overline{36}\,\mathrm{Torr}}{(92.1 \times 10^3\,\mathrm{Pa}) \times \left(\frac{1\,\mathrm{atm}}{101\,325\,\mathrm{Pa}}\right) \times \left(\frac{760\,\mathrm{Torr}}{\mathrm{atm}}\right)} = \boxed{0.755}$$

$$\gamma_\mathrm{A} = \frac{a_\mathrm{A}}{x_\mathrm{A}} = \frac{0.436}{0.220} = \boxed{1.98}$$

$$\gamma_\mathrm{B} = \frac{a_\mathrm{B}}{x_\mathrm{B}} = \frac{0.755}{0.780} = \boxed{0.968}$$

Solutions to problems

Solutions to numerical problems

P7.3

$$V_\mathrm{salt} = \left(\frac{\partial V}{\partial b}\right)_{\mathrm{H_2O}} \mathrm{mol^{-1}}\ \text{[Problem 7.2]}$$

$$= 69.38(b - 0.070)\,\mathrm{cm^3\,mol^{-1}} \quad \text{with } b \equiv b/(\mathrm{mol\,kg^{-1}})$$

Therefore, at $b = 0.050\,\mathrm{mol\,kg^{-1}}$, $V_\mathrm{salt} = \boxed{-1.4\,\mathrm{cm^3\,mol^{-1}}}$

The total volume at this molality is

$$V = (1001.21) + (34.69) \times (0.02)^2\,\mathrm{cm^3} = 1001.22\,\mathrm{cm^3}$$

Hence, as in Problem 7.2,

$$V(\mathrm{H_2O}) = \frac{(1001.22\,\mathrm{cm^3}) - (0.050\,\mathrm{mol}) \times (-1.4\,\mathrm{cm^3\,mol^{-1}})}{55.49\,\mathrm{mol}} = \boxed{18.04\,\mathrm{cm^3\,mol^{-1}}}$$

Question. What meaning can be ascribed to a negative partial molar volume?

P7.5 Let E denote ethanol and W denote water; then

$$V = n_\mathrm{E}V_\mathrm{E} + n_\mathrm{W}V_\mathrm{W}\ [7.3]$$

For a 50 per cent mixture by mass, $m_\mathrm{E} = m_\mathrm{W}$, implying that

$$n_\mathrm{E}M_\mathrm{E} = n_\mathrm{W}M_\mathrm{W}, \quad \text{or} \quad n_\mathrm{W} = \frac{n_\mathrm{E}M_\mathrm{E}}{M_\mathrm{W}}$$

Hence, $V = n_\mathrm{E}V_\mathrm{E} + \dfrac{n_\mathrm{E}M_\mathrm{E}V_\mathrm{W}}{M_\mathrm{W}}$

which solves to $n_\mathrm{E} = \dfrac{V}{V_\mathrm{E} + \frac{M_\mathrm{E}V_\mathrm{W}}{M_\mathrm{W}}}$, $n_\mathrm{W} = \dfrac{M_\mathrm{E}V}{V_\mathrm{E}M_\mathrm{W} + M_\mathrm{E}V_\mathrm{W}}$

Furthermore, $x_\mathrm{E} = \dfrac{n_\mathrm{E}}{n_\mathrm{E} + n_\mathrm{W}} = \dfrac{1}{1 + \frac{M_\mathrm{E}}{M_\mathrm{W}}}$

Since $M_\mathrm{E} = 46.07\,\mathrm{g\,mol^{-1}}$ and $M_\mathrm{W} = 18.02\,\mathrm{g\,mol^{-1}}$, $\dfrac{M_\mathrm{E}}{M_\mathrm{W}} = 2.557$. Therefore

$$x_\mathrm{E} = 0.2811, \qquad x_\mathrm{W} = 1 - x_\mathrm{E} = 0.7189$$

At this composition

$$V_\mathrm{E} = 56.0\,\mathrm{cm^3\,mol^{-1}} \qquad V_\mathrm{W} = 17.5\,\mathrm{cm^3\,mol^{-1}}\ [\text{Fig.7.1 of the text}]$$

Therefore, $n_\mathrm{E} = \dfrac{100\,\mathrm{cm^3}}{(56.0\,\mathrm{cm^3\,mol^{-1}}) + (2.557) \times (17.5\,\mathrm{cm^3\,mol^{-1}})} = 0.993\,\mathrm{mol}$

$$n_\mathrm{W} = (2.557) \times (0.993\,\mathrm{mol}) = 2.54\,\mathrm{mol}$$

The fact that these amounts correspond to a mixture containing 50 per cent by mass of both components is easily checked as follows

$$m_\mathrm{E} = n_\mathrm{E}M_\mathrm{E} = (0.993\,\mathrm{mol}) \times (46.07\,\mathrm{g\,mol^{-1}}) = 45.7\,\mathrm{g\ ethanol}$$
$$m_\mathrm{W} = n_\mathrm{W}M_\mathrm{W} = (2.54\,\mathrm{mol}) \times (18.02\,\mathrm{g\,mol^{-1}}) = 45.7\,\mathrm{g\ water}$$

At 20°C the densities of ethanol and water are, $\rho_\mathrm{E} = 0.789\,\mathrm{g\,cm^{-3}}$, $\rho_\mathrm{W} = 0.997\,\mathrm{g\,cm^{-3}}$. Hence,

$$V_\mathrm{E} = \frac{m_\mathrm{E}}{\rho_\mathrm{E}} = \frac{45.7\,\mathrm{g}}{0.789\,\mathrm{g\,cm^{-3}}} = \boxed{57.9\,\mathrm{cm^3}}\ \text{of ethanol}$$

$$V_\mathrm{W} = \frac{m_\mathrm{W}}{\rho_\mathrm{W}} = \frac{45.7\,\mathrm{g}}{0.997\,\mathrm{g\,cm^{-3}}} = \boxed{45.8\,\mathrm{cm^3}}\ \text{of water}$$

The change in volume upon adding a small amount of ethanol can be approximated by

$$\Delta V = \int \mathrm{d}V \approx \int V_{\mathrm{E}}\,\mathrm{d}n_{\mathrm{E}} \approx V_{\mathrm{E}}\,\Delta n_{\mathrm{E}}$$

where we have assumed that both V_{E} and V_{W} are constant over this small range of n_{E}. Hence

$$\Delta V \approx (56.0\,\mathrm{cm^3\,mol^{-1}}) \times \left(\frac{(1.00\,\mathrm{cm^3}) \times (0.789\,\mathrm{g\,cm^{-3}})}{(46.07\,\mathrm{g\,mol^{-1}})}\right) = \boxed{+0.96\,\mathrm{cm^3}}$$

P7.7

$$m_{\mathrm{B}} = \frac{\Delta T}{K_{\mathrm{f}}} = \frac{0.0703\,K}{1.86\,K/(\mathrm{mol\,kg^{-1}})} = 0.0378\,\mathrm{mol\,kg^{-1}}$$

Since the solution molality is nominally $0.0096\,\mathrm{mol\,kg^{-1}}$ in $\mathrm{Th(NO_3)_4}$, each formula unit supplies $\frac{0.0378}{0.0096} \approx \boxed{4 \text{ ions.}}$ (More careful data, as described in the original reference gives $\nu \approx 5$ to 6.)

P7.9 The data are plotted in Figure 7.2. The regions where the vapor pressure curves show approximate straight lines are denoted R for Raoult and H for Henry. A and B denote acetic acid and benzene respectively.

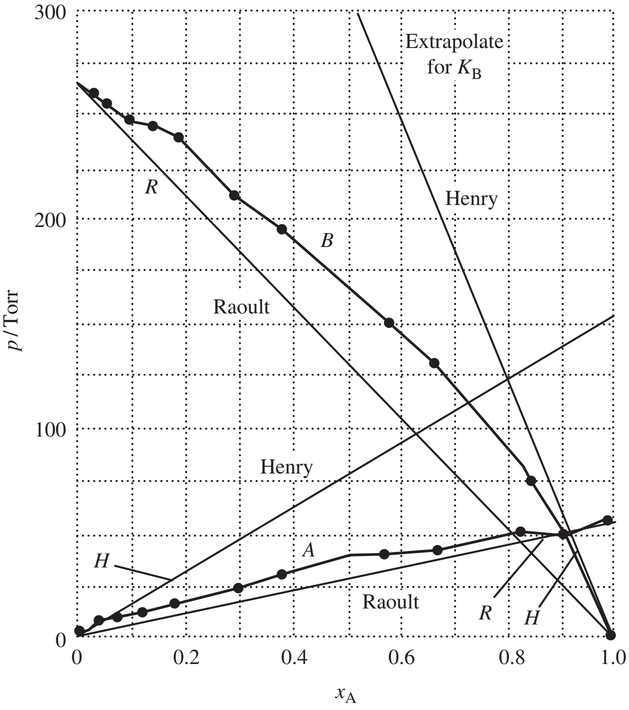


Figure 7.2

As in Problem 7.8, we need to form $\gamma_{\mathrm{A}} = \frac{p_{\mathrm{A}}}{x_{\mathrm{A}}p_{\mathrm{A}}^*}$ and $\gamma_{\mathrm{B}} = \frac{p_{\mathrm{B}}}{x_{\mathrm{B}}p_{\mathrm{B}}^*}$ for the Raoult's law activity coefficients and $\gamma_{\mathrm{B}} = \frac{p_{\mathrm{B}}}{x_{\mathrm{B}}K}$ for the activity coefficient of benzene on a Henry's law basis, with K determined by extrapolation. We use $p_A^* = 55\,\mathrm{Torr}$, $p_B^* = 264\,\mathrm{Torr}$ and $K_B^* = 600\,\mathrm{Torr}$ to draw up the following table:

x_A	0	0.2	0.4	0.6	0.8	1.0
p_A/Torr	0	20	30	38	50	55
p_B/Torr	264	228	190	150	93	0
a_A(R)	0	0.36	0.55	0.69	0.91	1.00[p_A/p_A^*]
a_B(R)	1.00	0.86	0.72	0.57	0.35	0[p_B/p_B^*]
γ_A(R)	—	1.82	1.36	1.15	1.14	1.00[$p_A/x_A p_A^*$]
γ_B(R)	1.00	1.08	1.20	1.42	1.76	—[$p_B/x_B p_B^*$]
a_B(H)	0.44	0.38	0.32	0.25	0.16	0[p_B/K_B]
γ_B(H)	0.44	0.48	0.53	0.63	0.78	1.00[$p_B/x_B K_B$]

G^E is defined as [Section 7.4]:

$$G^E = \Delta_{\text{mix}}G(\text{actual}) - \Delta_{\text{mix}}G(\text{ideal}) = nRT(x_A \ln a_A + x_B \ln a_B) - nRT(x_A \ln x_A + x_B \ln x_B)$$

and with $a = \gamma x$

$$G^E = nRT(x_A \ln \gamma_A + x_A \ln \gamma_B).$$

For $n = 1$, we can draw up the following table from the information above and $RT = 2.69\ \text{kJ mol}^{-1}$:

x_A	0	0.2	0.4	0.6	0.8	1.0
$x_A \ln \gamma_A$	0	0.12	0.12	0.08	0.10	0
$x_B \ln \gamma_B$	0	0.06	0.11	0.14	0.11	0
$G^E/(\text{kJ mol}^{-1})$	0	0.48	0.62	0.59	0.56	0

P7.11 **(a)** The volume of an ideal mixture is

$$V_{\text{ideal}} = n_1 V_{\text{m},1} + n_2 V_{\text{m},2}$$

so the volume of a real mixture is

$$V = V_{\text{ideal}} + V^E$$

We have an expression for excess molar volume in terms of mole fractions. To compute partial molar volumes, we need an expression for the actual excess volume as a function of moles

$$V^E = (n_1 + n_2)V_\text{m}^E = \frac{n_1 n_2}{n_1 + n_2}\left(a_0 + \frac{a_1(n_1 - n_2)}{n_1 + n_2}\right)$$

so $V = n_1 V_{\text{m},1} + n_2 V_{\text{m},2} + \dfrac{n_1 n_2}{n_1 + n_2}\left(a_0 + \dfrac{a_1(n_1 - n_2)}{n_1 + n_2}\right)$

The partial molar volume of propionic acid is

$$V_1 = \left(\frac{\partial V}{\partial n_1}\right)_{p,T,n_2} = V_{\text{m},1} + \frac{a_0 n_2^2}{(n_1 + n_2)^2} + \frac{a_1(3n_1 - n_2)n_2^2}{(n_1 + n_2)^3}$$

$$\boxed{V_1 = V_{\text{m},1} + a_0 x_2^2 + a_1(3x_1 - x_2)x_2^2}$$

That of oxane is

$$\boxed{V_2 = V_{\text{m},2} + a_0 x_1^2 + a_1(x_1 - 3x_2)x_1^2}$$

(b) We need the molar volumes of the pure liquids

$$V_{\mathrm{m},1} = \frac{M_1}{\rho_1} = \frac{74.08\,\mathrm{g\,mol^{-1}}}{0.97174\,\mathrm{g\,cm^{-3}}} = 76.23\,\mathrm{cm^3\,mol^{-1}}$$

and $V_{\mathrm{m},2} = \dfrac{86.13\,\mathrm{g\,mol^{-1}}}{0.86398\,\mathrm{g\,cm^{-3}}} = 99.69\,\mathrm{cm^3\,mol^{-1}}$

In an equimolar mixture, the partial molar volume of propionic acid is

$$V_1 = 76.23 + (-2.4697) \times (0.500)^2 + (0.0608) \times [3(0.5) - 0.5] \times (0.5)^2\,\mathrm{cm^3\,mol^{-1}}$$
$$= \boxed{75.63\,\mathrm{cm^3\,mol^{-1}}}$$

and that of oxane is

$$V_2 = 99.69 + (-2.4697) \times (0.500)^2 + (0.0608) \times [0.5 - 3(0.5)] \times (0.5)^2\,\mathrm{cm^3\,mol^{-1}}$$
$$= \boxed{99.06\,\mathrm{cm^3\,mol^{-1}}}$$

P7.13 Henry's law constant is the slope of a plot of p_{B} versus x_{B} in the limit of zero x_{B} (Fig. 7.3). The partial pressures of CO_2 are almost but not quite equal to the total pressures reported above

$$p_{\mathrm{CO_2}} = p y_{\mathrm{CO_2}} = p(1 - y_{\mathrm{cyc}})$$

Linear regression of the low-pressure points gives $K_{\mathrm{H}} = \boxed{371\,\mathrm{bar}}$

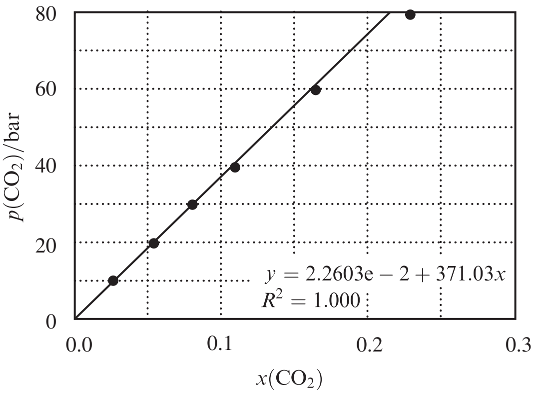


Figure 7.3

The activity of a solute is

$$a_{\mathrm{B}} = \frac{p_{\mathrm{B}}}{K_{\mathrm{H}}} = x_{\mathrm{B}}\gamma_{\mathrm{B}}$$

so the activity coefficient is

$$\gamma_{\mathrm{B}} = \frac{p_{\mathrm{B}}}{x_{\mathrm{B}}K_{\mathrm{H}}} = \frac{y_{\mathrm{B}}p}{x_{\mathrm{B}}K_{\mathrm{H}}}$$

where the last equality applies Dalton's law of partial pressures to the vapour phase. A spreadsheet applied this equation to the above data to yield

p/bar	y_cyc	x_cyc	γ_{CO_2}
10.0	0.0267	0.9741	1.01
20.0	0.0149	0.9464	0.99
30.0	0.0112	0.9204	1.00
40.0	0.009 47	0.892	0.99
60.0	0.008 35	0.836	0.98
80.0	0.009 21	0.773	0.94

P7.16 $G^\text{E} = RTx(1-x)\{0.4857 - 0.1077(2x-1) + 0.0191(2x-1)^2\}$

with $x = 0.25$ gives $G^\text{E} = 0.1021RT$. Therefore, since

$$\Delta_\text{mix}G(\text{actual}) = \Delta_\text{mix}G(\text{ideal}) + nG^\text{E}$$

$$\Delta_\text{mix}G = nRT(x_\text{A}\ln x_\text{A} + x_\text{B}\ln x_\text{B}) + nG^\text{E} = nRT(0.25\ln 0.25 + 0.75\ln 0.75) + nG^\text{E}$$

$$= -0.562nRT + 0.1021nRT = -0.460nRT$$

Since $n = 4\,\text{mol}$ and $RT = (8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (303.15\,\text{K}) = 2.52\,\text{kJ mol}^{-1}$,

$$\Delta_\text{mix}G = (-0.460) \times (4\,\text{mol}) \times (2.52\,\text{kJ mol}^{-1}) = \boxed{-4.6\,\text{kJ}}$$

Solutions to theoretical problems

P7.18 $x_\text{A}\,\text{d}\mu_\text{A} + x_\text{B}\,\text{d}\mu_\text{B} = 0$ [7.11, Gibbs–Duhem equation]

Therefore, after dividing through by $\text{d}x_\text{A}$

$$x_\text{A}\left(\frac{\partial\mu_\text{A}}{\partial x_\text{A}}\right)_{p,T} + x_\text{B}\left(\frac{\partial\mu_\text{B}}{\partial x_\text{A}}\right)_{p,T} = 0$$

or, since $\text{d}x_\text{B} = -\text{d}x_\text{A}$, as $x_\text{A} + x_\text{B} = 1$

$$x_\text{A}\left(\frac{\partial\mu_\text{A}}{\partial x_\text{A}}\right)_{p,T} - x_\text{B}\left(\frac{\partial\mu_\text{B}}{\partial x_\text{B}}\right)_{p,T} = 0$$

or, $\left(\frac{\partial\mu_\text{A}}{\partial\ln x_\text{A}}\right)_{p,T} = \left(\frac{\partial\mu_\text{B}}{\partial\ln x_\text{B}}\right)_{p,T}$ $\left[\text{d}\ln x = \frac{\text{d}x}{x}\right]$

Then, since $\mu = \mu^\ominus + RT\ln\frac{f}{p^\ominus}$, $\left(\frac{\partial\ln f_\text{A}}{\partial\ln x_\text{A}}\right)_{p,T} = \left(\frac{\partial\ln f_\text{B}}{\partial\ln x_\text{B}}\right)_{p,T}$

On replacing f by p, $\left(\frac{\partial\ln p_\text{A}}{\partial\ln x_\text{A}}\right)_{p,T} = \left(\frac{\partial\ln p_\text{B}}{\partial\ln x_\text{B}}\right)_{p,T}$

If A satisfies Raoult's law, we can write $p_\text{A} = x_\text{A}p_\text{A}^*$, which implies that

$$\left(\frac{\partial\ln p_\text{A}}{\partial\ln x_\text{A}}\right)_{p,T} = \frac{\partial\ln x_\text{A}}{\partial\ln x_\text{A}} + \frac{\partial\ln p_\text{A}^*}{\partial\ln x_\text{A}} = 1 + 0$$

Therefore, $\left(\frac{\partial\ln p_\text{B}}{\partial\ln x_\text{B}}\right)_{p,T} = 1$

which is satisfied if $p_\text{B} = x_\text{B}p_\text{B}^*$ (by integration, or inspection). Hence, if A satisfies Raoult's law, so does B.

P7.20 $\ln x_A = \dfrac{-\Delta_{\mathrm{fus}}G}{RT}$ (Section 7.5 analogous to equation for $\ln x_B$ used in derivation of eqn 7.39)

$$\frac{\mathrm{d}\ln x_A}{\mathrm{d}T} = -\frac{1}{R} \times \frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\Delta_{\mathrm{fus}}G}{T}\right) = \boxed{\frac{\Delta_{\mathrm{fus}}H}{RT^2}} \quad \text{[Gibbs–Helmholtz equation]}$$

$$\int_1^{x_A} \mathrm{d}\ln x_A = \int_{T^*}^{T} \frac{\Delta_{\mathrm{fus}}H\,\mathrm{d}T}{RT^2} \approx \frac{\Delta_{\mathrm{fus}}H}{R}\int_{T^*}^{T}\frac{\mathrm{d}T}{T^2}$$

$$\boxed{\ln x_A = \frac{-\Delta_{\mathrm{fus}}H}{R} \times \left(\frac{1}{T} - \frac{1}{T^*}\right)}$$

The approximations $\ln x_A \approx -x_B$ and $T \approx T^*$ then lead to eqns 33 and 36, as in the text.

P7.22 Retrace the argument leading to eqn 7.40 of the text. Exactly the same process applies with a_A in place of x_A. At equilibrium

$$\mu_A^*(p) = \mu_A(x_A, p + \Pi)$$

which implies that, with $\mu = \mu^* + RT\ln a$ for a real solution,

$$\mu_A^*(p) = \mu_A^*(p + \Pi) + RT\ln a_A = \mu_A^*(p) + \int_p^{p+\Pi} V_m\,\mathrm{d}p + RT\ln a_A$$

and hence that $\displaystyle\int_p^{p+\Pi} V_m\,\mathrm{d}p = -RT\ln a_A$

For an incompressible solution, the integral evaluates to ΠV_m, so $\Pi V_m = -RT\ln a_A$

In terms of the osmotic coefficient ϕ (Problem 7.21)

$$\Pi V_m = r\phi RT \qquad r = \frac{x_B}{x_A} = \frac{n_B}{n_A} \qquad \phi = -\frac{x_A}{x_B}\ln a_A = -\frac{1}{r}\ln a_A$$

For a dilute solution, $n_A V_m \approx V$

Hence, $\Pi V = n_B \phi RT$

and therefore, with $[\mathrm{B}] = \dfrac{n_B}{V}$ $\quad \boxed{\Pi = \phi[\mathrm{B}]RT}$

Solutions to applications

P7.24 By the van't Hoff equation [7.40]

$$\Pi = [\mathrm{B}]RT = \frac{cRT}{M}$$

Division by the standard acceleration of free fall, g, gives

$$\frac{\Pi}{g} = \frac{c(R/g)T}{M}$$

(a) This expression may be written in the form

$$\Pi' = \frac{cR'T}{M}$$

which has the same form as the van't Hoff equation, but the unit of osmotic pressure (Π') is now

$$\frac{\text{force/area}}{\text{length/time}^2} = \frac{(\text{mass length})/(\text{area time}^2)}{\text{length/time}^2} = \frac{\text{mass}}{\text{area}}$$

This ratio can be specified in g cm^{-2}. Likewise, the constant of proportionality (R') would have the units of R/g

$$\frac{\text{energy K}^{-1}\,\text{mol}^{-1}}{\text{length/time}^2} = \frac{(\text{mass length}^2/\text{time}^2)\,\text{K}^{-1}\,\text{mol}^{-1}}{\text{length/time}^2} = \text{mass length K}^{-1}\text{mol}^{-1}$$

This result may be specified in $\boxed{\text{g cm K}^{-1}\,\text{mol}^{-1}}$

$$R' = \frac{R}{g} = \frac{8.314\,51\,\text{J K}^{-1}\,\text{mol}^{-1}}{9.806\,65\text{m s}^{-2}}$$
$$= 0.847\,844\,\text{kg m K}^{-1}\,\text{mol}^{-1}\left(\frac{10^3\,\text{g}}{\text{kg}}\right) \times \left(\frac{10^2\,\text{cm}}{\text{m}}\right)$$

$$\boxed{R' = 84\,784.4\,\text{g cm K}^{-1}\,\text{mol}^{-1}}$$

In the following we will drop the primes giving

$$\Pi = \frac{cRT}{M}$$

and use the Π units of g cm^{-2} and the R units g cm K^{-1} mol^{-1}.

(b) By extrapolating the low concentration plot of Π/c versus c (Fig. 7.4 (a)) to $c = 0$ we find the intercept 230 g cm^{-2}/g cm^{-3}. In this limit van't Hoff equation is valid so

$$\frac{RT}{\overline{M}_\text{n}} = \text{intercept} \quad \text{or} \quad \overline{M}_\text{n} = \frac{RT}{\text{intercept}}$$

$$\overline{M}_\text{n} = \frac{(84\,784.4\,\text{g cm K}^{-1}\,\text{mol}^{-1}) \times (298.15\,\text{K})}{(230\,\text{g cm}^{-2})/(\text{g cm}^{-3})}$$

$$\boxed{\overline{M}_\text{n} = 1.1 \times 10^{5\,\text{g mol}^{-1}}}$$

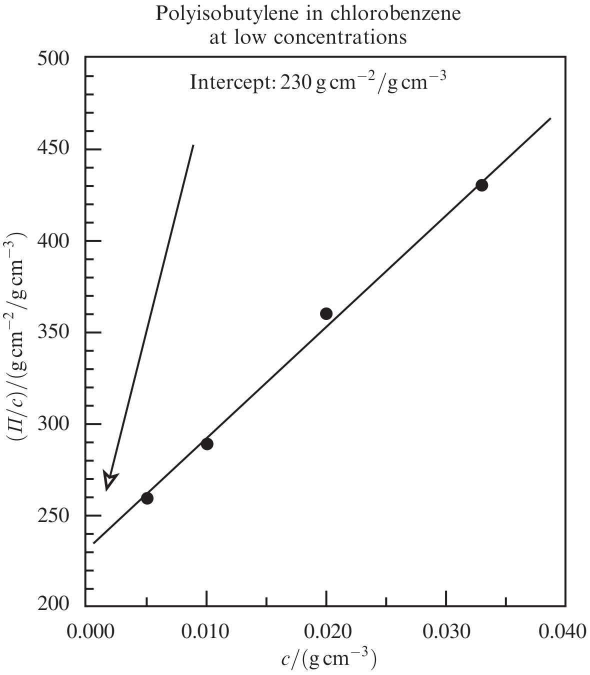
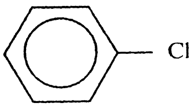
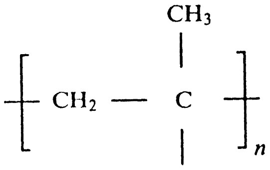


Figure 7.4(a)

(c) The plot of Π/c versus c for the full concentration range (Fig. 7.4(b)) is very nonlinear. We may conclude that the solvent is $\boxed{\text{good}}$. This may be due to the nonpolar nature of both solvent and solute.





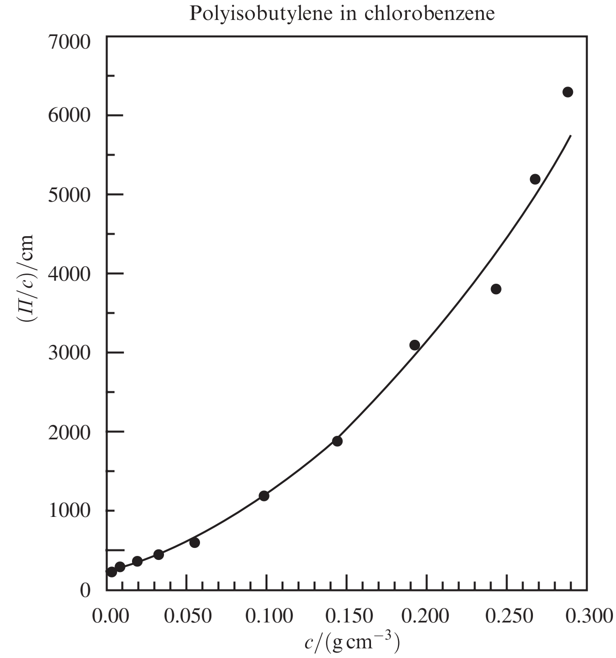


Figure 7.4(b)

(d) $\Pi/c = (RT/\overline{M}_\text{n})(1 + B'c + C'c^2)$

Since $RT/\overline{M}_\text{n}$ has been determined in part **(b)** by extrapolation to $c = 0$, it is best to determine the second and third virial coefficients with the linear regression fit

$$\frac{(\Pi/c)/(RT/\overline{M}_\text{n}) - 1}{c} = B' + C'c$$

$R = 0.9791$

$$\boxed{\begin{array}{l} B' = 21.4\,\text{cm}^3\,\text{g}^{-1}, \\ C' = 211\,\text{cm}^6\,\text{g}^{-2}, \end{array}} \quad \begin{array}{l} \text{standard deviation} = 2.4\,\text{cm}^3\,\text{g}^{-1} \\ \text{standard deviation} = 15\,\text{cm}^6\,\text{g}^{-2} \end{array}$$

(e) Using 1/4 for g and neglecting terms beyond the second power, we may write

$$\left(\frac{\Pi}{c}\right)^{1/2} = \left(\frac{RT}{\overline{M}_\text{n}}\right)^{1/2} \quad (1 + \tfrac{1}{2}B'c)$$

We can solve for B', then $g(B')^2 = C'$.

$$\left[\frac{\left(\frac{\Pi}{c}\right)^{1/2}}{\left(\frac{RT}{\overline{M}_\mathrm{n}}\right)^{1/2}}\right] - 1 = \tfrac{1}{2}B'c$$

$RT/\overline{M}_\mathrm{n}$ has been determined above as 230 g cm^{-2}/g cm^{-3}. We may analytically solve for B' from one of the data points, say, $\Pi/c = 430\,\mathrm{g\,cm^{-2}/g\,cm^{-3}}$ at $c = 0.033\,\mathrm{g\,cm^{-3}}$.

$$\left(\frac{430\,\mathrm{g\,cm^{-2}/g\,cm^{-3}}}{230\,\mathrm{g\,cm^{-2}/g\,cm^{-3}}}\right)^{1/2} - 1 = \tfrac{1}{2}B' \times (0.033\,\mathrm{g\,cm^{-3}})$$

$$B' = \frac{2 \times (1.367 - 1)}{0.033\,\mathrm{g\,cm^{-3}}} = 22.\bar{2}\,\mathrm{cm^3\,g^{-1}}$$

$$C' = g(B')^2 = 0.25 \times (22.\bar{2}\,\mathrm{cm^3\,g^{-1}})^2 = 12\bar{3}\,\mathrm{cm^6\,g^{-2}}$$

Better values of B' and C' can be obtained by plotting $\left(\frac{\Pi}{c}\right)^{1/2} \Big/ \left(\frac{RT}{\overline{M}_\mathrm{n}}\right)^{1/2}$ against c. This plot is shown in Fig. 7.4(c). The slope is $14.\overline{03}\,\mathrm{cm^3\,g^{-1}}$. $B' = 2 \times \text{slope} = \boxed{28.\bar{0}\,\mathrm{cm^3\,g^{-1}}}$ C' is then $\boxed{19\bar{6}\,\mathrm{cm^6\,g^{-2}}}$ The intercept of this plot should thereotically be 1.00, but it is in fact 0.916 with a standard deviation of 0.066. The overall consistency of the values of the parameters confirms that g is roughly 1/4 as assumed.

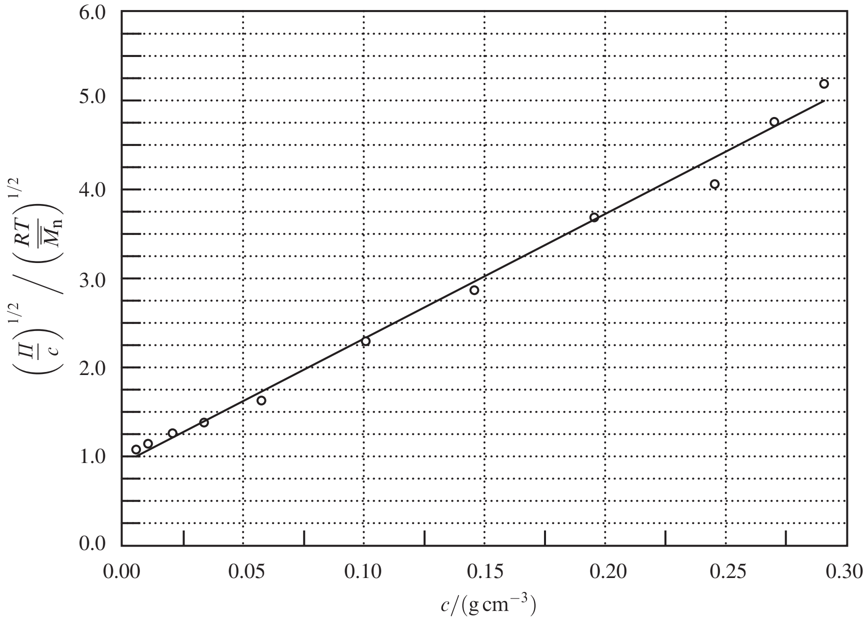


Figure 7.4(c)

8 Phase diagrams

Solutions to exercises

Discussion questions

E8.1(b) What factors determine the number of theoretical plates required to achieve a desired degree of separation in fractional distillation?

The principal factor is the shape of the two-phase liquid-vapor region in the phase diagram (usually a temperature-composition diagram). The closer the liquid and vapour lines are to each other, the more theoretical plates needed. See Fig. 8.15 of the text. But the presence of an azeotrope could prevent the desired degree of separation from being achieved. Incomplete miscibility of the components at specific concentrations could also affect the number of plates required.

E8.2(b) See Figs 8.1(a) and 8.1(b).

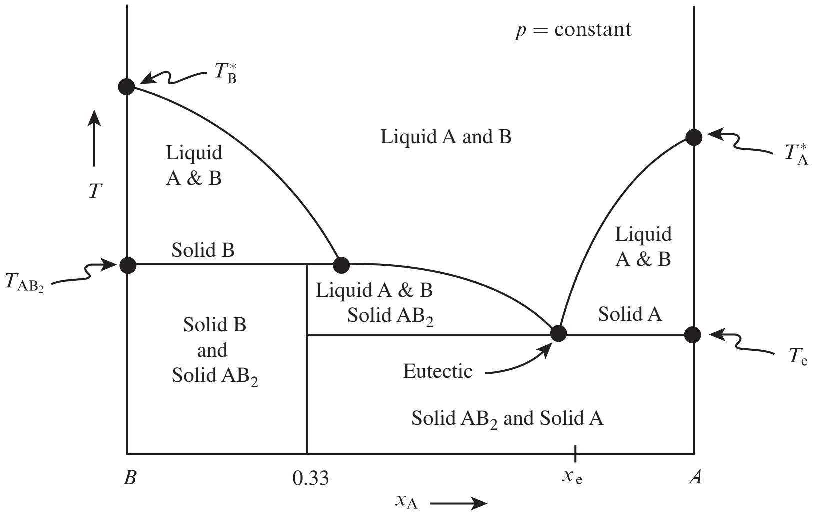


Figure 8.1(a)

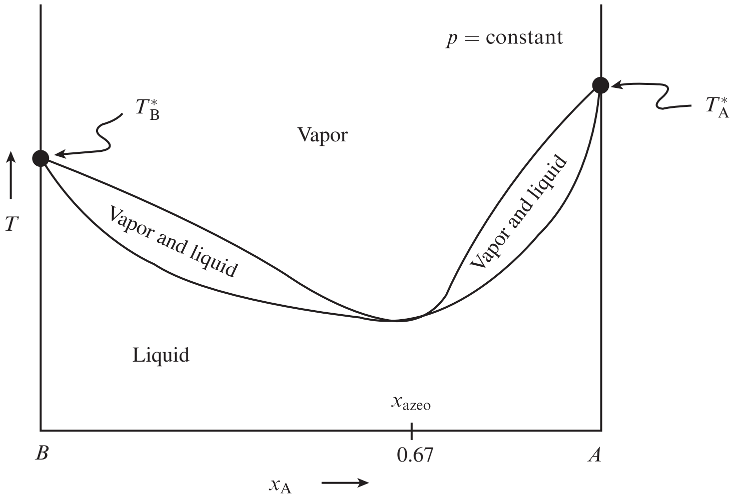


Figure 8.1(b)

E8.3(b) See Fig. 8.2.

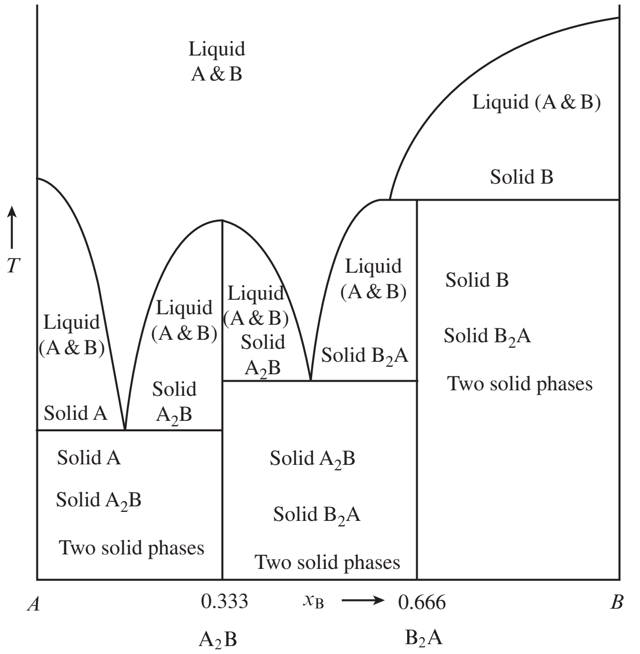


Figure 8.2

Numerical exercises

E8.4(b)

$$p = p_A + p_B = x_A p_A^* + (1 - x_A) p_B^*$$

$$x_A = \frac{p - p_B^*}{p_A^* - p_B^*}$$

$$x_A = \frac{19\,\text{kPa} - 18\,\text{kPa}}{20\,\text{kPa} - 18\,\text{kPa}} = \boxed{0.5} \qquad \text{A is 1,2-dimethylbenzene}$$

$$y_A = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*)x_A} = \frac{(0.5) \times (20\,\text{kPa})}{18\,\text{kPa} + (20\,\text{kPa} - 18\,\text{kPa})0.5} = 0.5\overline{26} \approx \boxed{0.5}$$

$$y_B = 1 - 0.5\overline{26} = 0.4\overline{74} \approx 0.5$$

E8.5(b)

$$p_A = y_A p = 0.612p = x_A p_A^* = x_A(68.8\,\text{kPa})$$

$$p_B = y_B p = (1 - y_A)p = 0.388p = x_B p_B^* = (1 - x_A) \times 82.1\,\text{kPa}$$

$$\frac{y_A p}{y_B p} = \frac{x_A p_A^*}{x_B p_B^*} \quad \text{and} \quad \frac{0.612}{0.388} = \frac{68.8 x_A}{82.1(1 - x_A)}$$

$$(0.388) \times (68.8)x_A = (0.612) \times (82.1) - (0.612) \times (82.1)x_A$$

$$26.6\overline{94}x_A = 50.2\overline{45} - 50.2\overline{45}x_A$$

$$x_A = \frac{50.2\overline{45}}{26.6\overline{94} + 50.2\overline{45}} = \boxed{0.653} \qquad x_B = 1 - 0.653 = \boxed{0.347}$$

$$p = x_A p_A^* + x_B p_B^* = (0.653) \times (68.8\,\text{kPa}) + (0.347) \times (82.1\,\text{kPa}) = \boxed{73.4\,\text{kPa}}$$

E8.6(b) **(a)** If Raoult's law holds, the solution is ideal.

$$p_A = x_A p_A^* = (0.4217) \times (110.1\,\text{kPa}) = 46.43\,\text{kPa}$$

$$p_B = x_B p_B^* = (1 - 0.4217) \times (94.93\,\text{kPa}) = 54.90\,\text{kPa}$$

$$p = p_A + p_B = (46.43 + 54.90)\,\text{kPa} = 101.33\,\text{kPa} = 1.000\,\text{atm}$$

Therefore, Raoult's law correctly predicts the pressure of the boiling liquid and $\boxed{\text{the solution is ideal}}$.

(b) $$y_A = \frac{p_A}{p} = \frac{46.43\,\text{kPa}}{101.33\,\text{kPa}} = \boxed{0.4582}$$

$$y_B = 1 - y_A = 1.000 - 0.4582 = \boxed{0.5418}$$

E8.7(b) Let B = benzene and T = toluene. Since the solution is equimolar $z_B = z_T = 0.500$

(a) Initially $x_B = z_B$ and $x_T = z_T$; thus

$$p = x_B p_B^* + x_T p_T^* \,[8.3] = (0.500) \times (74\,\text{Torr}) + (0.500) \times (22\,\text{Torr})$$
$$= 37\,\text{Torr} + 11\,\text{Torr} = \boxed{48\,\text{Torr}}$$

(b) $$y_B = \frac{p_B}{p}[4] = \frac{37\,\text{Torr}}{48\,\text{Torr}} = \boxed{0.77} \qquad y_T = 1 - 0.77 = \boxed{0.23}$$

(c) Near the end of the distillation

$$y_B = z_B = 0.500 \quad \text{and} \quad y_T = z_T = 0.500$$

Equation 5 may be solved for x_A [A = benzene = B here]

$$x_B = \frac{y_B p_T^*}{p_B^* + (p_T^* - p_B^*) y_B} = \frac{(0.500) \times (22\,\text{Torr})}{(75\,\text{Torr}) + (22 - 74)\,\text{Torr} \times (0.500)} = 0.23$$

$$x_T = 1 - 0.23 = 0.77$$

This result for the special case of $z_B = z_T = 0.500$ could have been obtained directly by realizing that

$$y_B(\text{initial}) = x_T(\text{final}) \qquad y_T(\text{initial}) = x_B(\text{final})$$

$$p(\text{final}) = x_B p_B^* + x_T p_T^* = (0.23) \times (74\,\text{Torr}) + (0.77) \times (22\,\text{Torr}) = \boxed{34\,\text{Torr}}$$

Thus in the course of the distillation the vapour pressure fell from 48 Torr to 34 Torr.

E8.8(b) See the phase diagram in Fig. 8.3.

(a) $y_A = \boxed{0.81}$

(b) $x_A = \boxed{0.67} \qquad y_A = \boxed{0.925}$

E8.9(b) Al^{3+}, H^+, $AlCl_3$, $Al(OH)_3$, OH^-, Cl^-, H_2O giving seven species. There are also three equilibria

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl$$

$$AlCl_3 \rightleftharpoons Al^{3+} + 3Cl^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

and one condition of electrical neutrality

$$[H^+] + 3[Al^{3+}] = [OH^-] + [Cl^-]$$

Hence, the number of independent components is

$$C = 7 - (3 + 1) = \boxed{3}$$

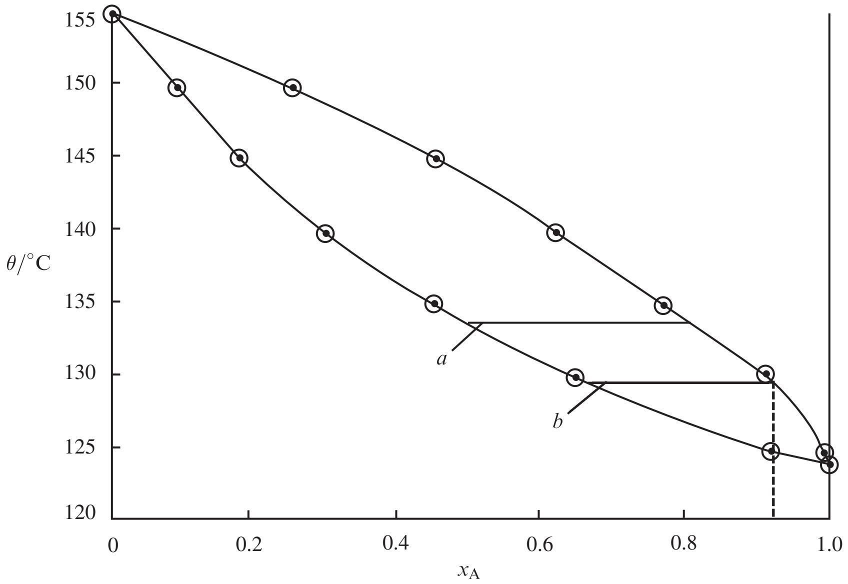


Figure 8.3

E8.10(b) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

(a) For this system $\boxed{C = 1}$ [Example 8.1] and $\boxed{P = 2}$ (s and g).

(b) If ammonia is added before heating, $\boxed{C = 2}$ (because NH_4Cl, NH_3 are now independent) and $\boxed{P = 2}$ (s and g).

E8.11(b) **(a)** Still $\boxed{C = 2}$ (Na_2SO_4, H_2O), but now there is no solid phase present, so $\boxed{P = 2}$ (liquid solution, vapour).

(b) The variance is $F = 2 - 2 + 2 = \boxed{2}$. We are free to change any two of the three variables, amount of dissolved salt, pressure, or temperature, but not the third. If we change the amount of dissolved salt and the pressure, the temperature is fixed by the equilibrium condition between the two phases.

E8.12(b) See Fig. 8.4.

E8.13(b) See Fig. 8.5. The phase diagram should be labelled as in Fig. 8.5. (a) Solid Ag with dissolved Sn begins to precipitate at a_1, and the sample solidifies completely at a_2. (b) Solid Ag with dissolved Sn begins to precipitate at b_1, and the liquid becomes richer in Sn. The peritectic reaction occurs at b_2, and as cooling continues Ag_3Sn is precipitated and the liquid becomes richer in Sn. At b_3 the system has its eutectic composition (e) and freezes without further change.

E8.14(b) See Fig. 8.6. The feature denoting incongruent melting is circled. Arrows on the tie line indicate the decomposition products. There are two eutectics: one at $x_B = \boxed{0.53}$, $T = \boxed{T_2}$; another at $x_B = \boxed{0.82}$, $T = \boxed{T_3}$.

E8.15(b) The cooling curves corresponding to the phase diagram in Fig. 8.7(a) are shown in Fig. 8.7(b). Note the breaks (abrupt change in slope) at temperatures corresponding to points a_1, b_1, and b_2. Also note the eutectic halts at a_2 and b_3.

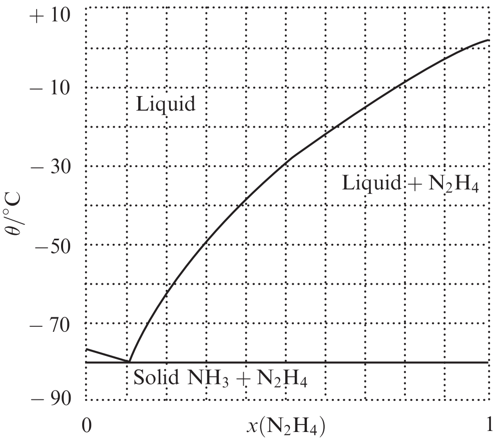


Figure 8.4

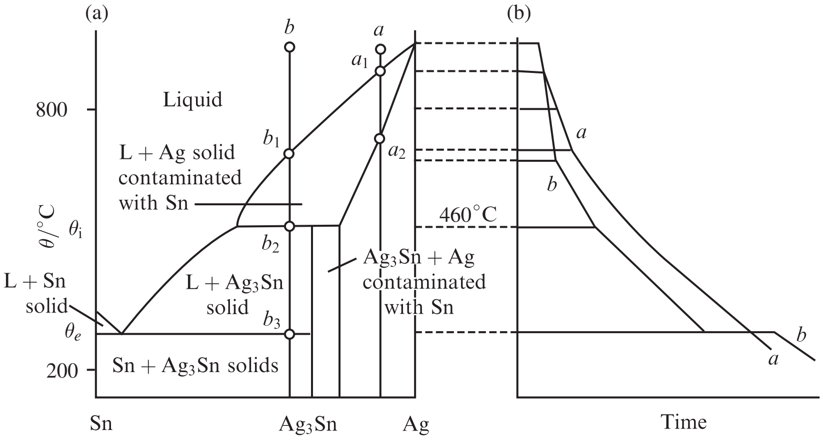


Figure 8.5

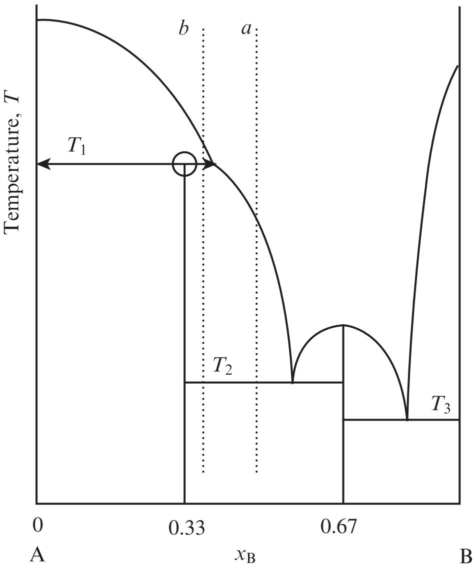


Figure 8.6

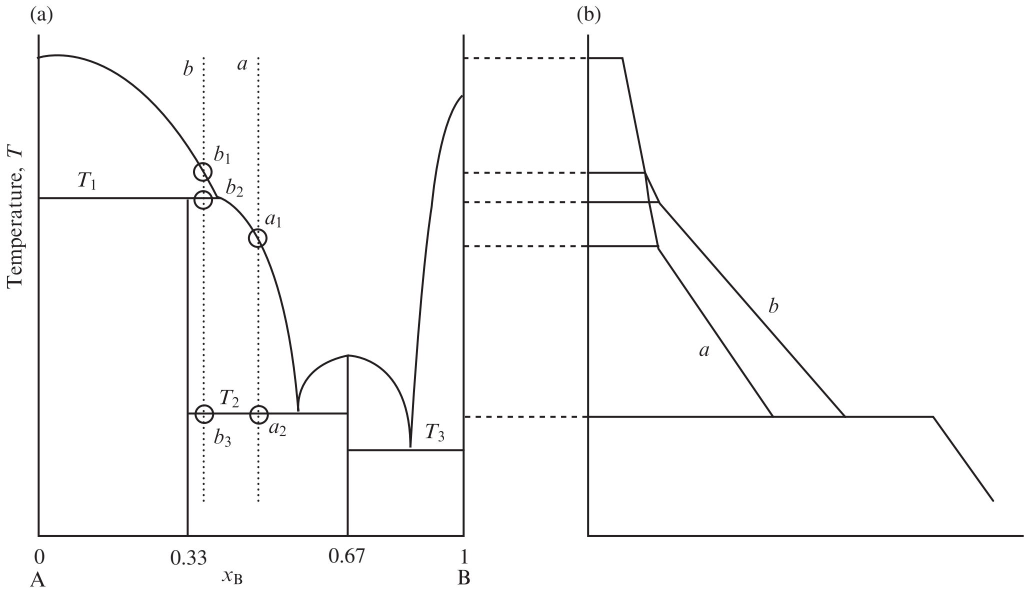


Figure 8.7

E8.16(b) Rough estimates based on Fig. 8.37 of the text are

(a) $x_B \approx \boxed{0.75}$ **(b)** $x_{AB_2} \approx \boxed{0.8}$ **(c)** $x_{AB_2} \approx \boxed{0.6}$

E8.17(b) The phase diagram is shown in Fig. 8.8. The given data points are circled. The lines are schematic at best.

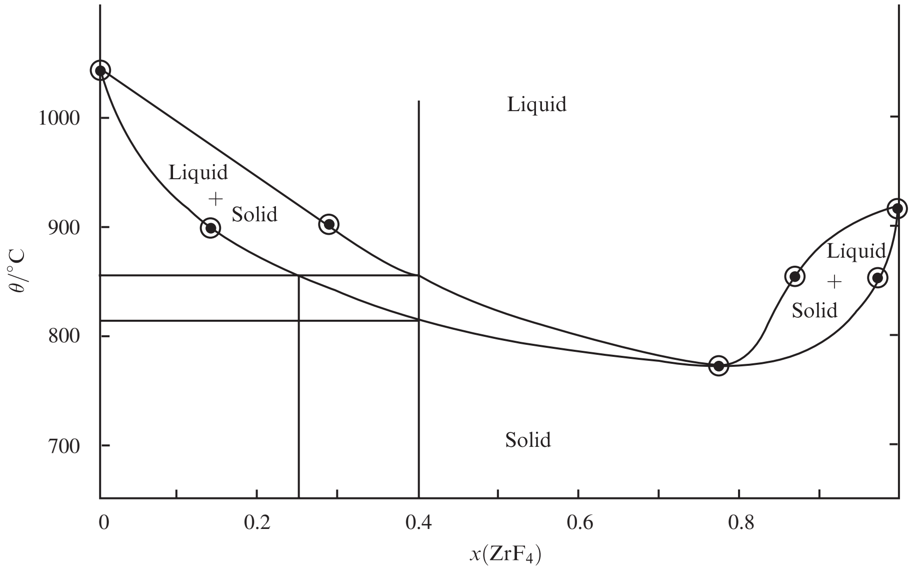


Figure 8.8

A solid solution with $x(\mathrm{ZrF_4}) = 0.24$ appears at 855°C. The solid solution continues to form, and its $\mathrm{ZrF_4}$ content increases until it reaches $x(\mathrm{ZrF_4}) = 0.40$ and 820° C. At that temperature, the entire sample is solid.

E8.18(b) The phase diagram for this system (Fig. 8.9) is very similar to that for the system methyl ethyl ether and diborane of Exercise 8.12(a). (See the *Student's Solutions Manual.*) The regions of the diagram contain analogous substances. The solid compound begins to crystallize at 120 K. The liquid becomes progressively richer in diborane until the liquid composition reaches 0.90 at 104 K. At that point the liquid disappears as heat is removed. Below 104 K the system is a mixture of solid compound and solid diborane.

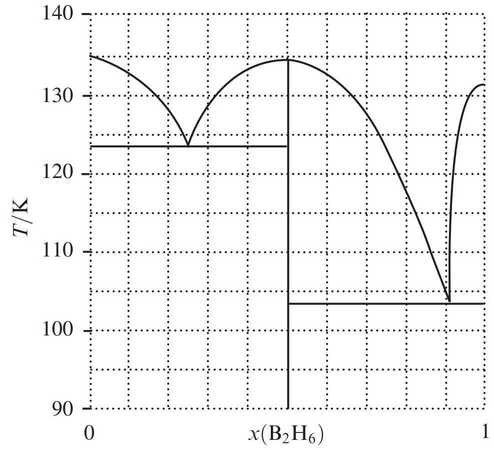


Figure 8.9

E8.19 Refer to the phase diagram in the solution to Exercise 8.17(a). (See the *Student's Solutions Manual.*) The cooling curves are sketched in Fig. 8.10.

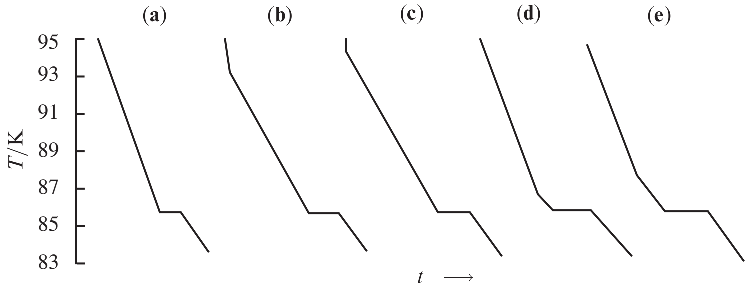


Figure 8.10

E8.20 **(a)** When x_A falls to 0.47, a second liquid phase appears. The amount of new phase increases as x_A falls and the amount of original phase decreases until, at $x_A = 0.314$, only one liquid remains.

(b) The mixture has a single liquid phase at all compositions.

The phase diagram is sketched in Fig. 8.11.

Solutions to problems

Solutions to numerical problems

P8.2 **(a)** The phase diagram is shown in Fig. 8.12.

(b) We need not interpolate data, for 296.0 K is a temperature for which we have experimental data. The mole fraction of *N*, *N*-dimethylacetamide in the heptane-rich phase (α, at the left of the phase diagram) is 0.168 and in the acetamide-rich phase (β, at right) 0.804. The proportions of the two

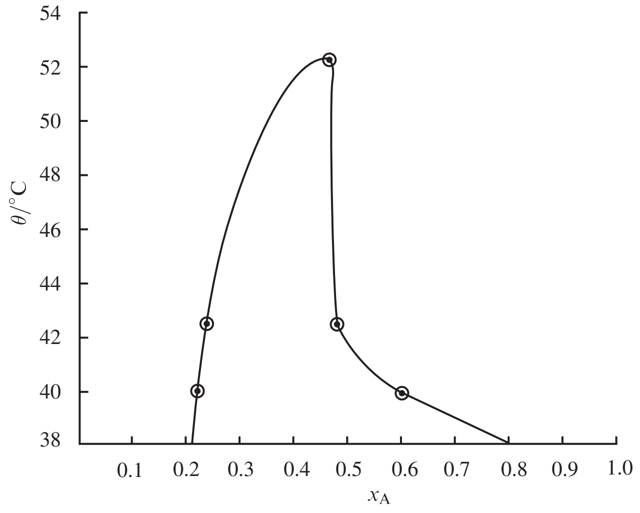


Figure 8.11

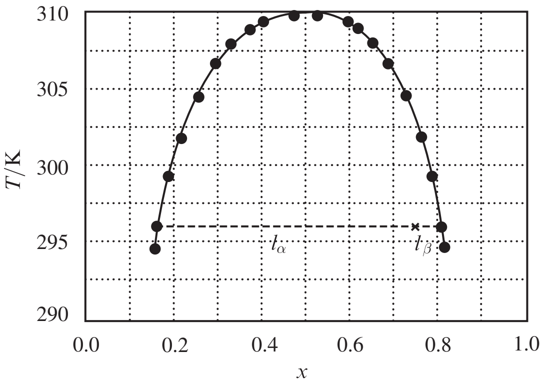


Figure 8.12

phases are in an inverse ratio of the distance their mole fractions are from the composition point in question, according to the lever rule. That is

$$n_\alpha/n_\beta = l_\beta/l_\alpha = (0.804 - 0.750)/(0.750 - 0.168) = \boxed{0.093}$$

The smooth curve through the data crosses $x = 0.750$ at $\boxed{302.5\,\text{K}}$, the temperature point at which the heptane-rich phase will vanish.

P8.6 See Fig. 8.13(a). The number of distinct chemical species (as opposed to components) and phases present at the indicated points are, respectively

$$b(3, 2),\ d(2, 2),\ e(4, 3),\ f(4, 3),\ g(4, 3),\ k(2, 2)$$

[Liquid A and solid A are here considered distinct species.]

The cooling curves are shown in Fig. 8.13(b).

P8.8 The information has been used to construct the phase diagram in Fig. 8.14(a). In $MgCu_2$ the mass percentage of Mg is $(100) \times \dfrac{24.3}{24.3 + 127} = \boxed{16}$, and in Mg_2Cu it is $(100) \times \dfrac{48.6}{48.6 + 63.5} = \boxed{43}$. The initial point is a_1, corresponding to a liquid single-phase system. At a_2 (at 720°C) $MgCu_2$ begins to come out of solution and the liquid becomes richer in Mg, moving toward e_2. At a_3 there is solid

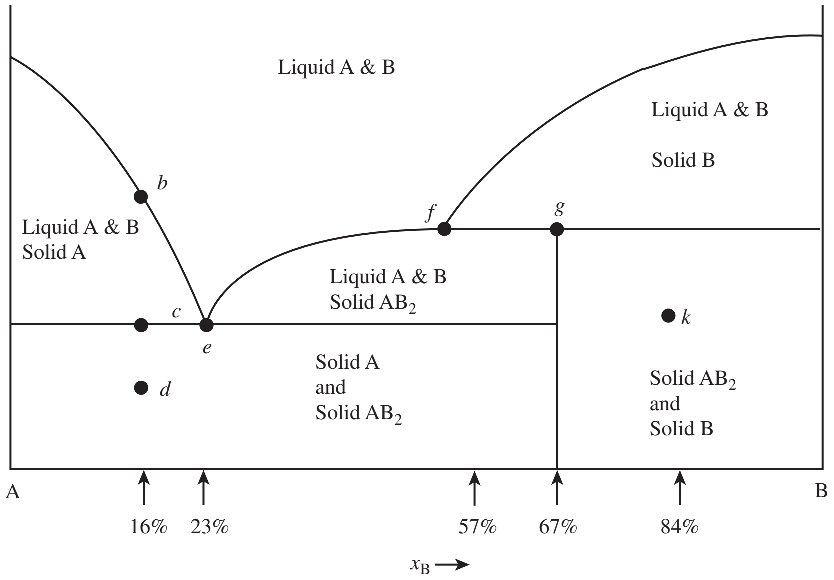


Figure 8.13(a)

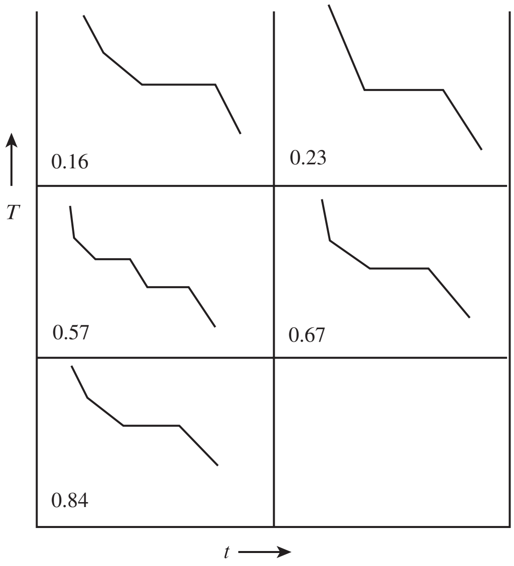


Figure 8.13(b)

$MgCu_2$ + liquid of composition e_2 (33 per cent by mass of Mg). This solution freezes without further change. The cooling curve will resemble that shown in Fig. 8.14(b).

P8.10 **(a)** $\boxed{\textbf{eutectic:}}$ **40.2 at % Si at 1268°C** $\boxed{\textbf{eutectic}\text{: 69.4 at \% Si at 1030°C}}$ [8.6]

$\boxed{\textbf{congruent melting compounds}\text{: } \begin{array}{ll} Ca_2Si & mp = 1314°C \\ CaSi & mp = 1324°C \end{array}}$ [8.7]

$\boxed{\textbf{incongruent melting compound}\text{: } CaSi_2 \quad mp = 1040°C}$ melts into CaSi(s) and liquid (68 at % Si)

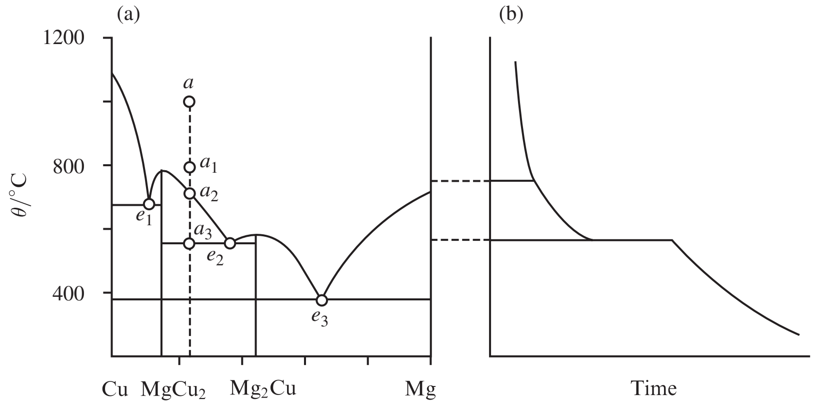


Figure 8.14

(b) At 1000°C the phases at equilibrium will be Ca(s) and liquid (13 at % Si). The **lever rule** gives the relative amounts:

$$\frac{n_{\text{Ca}}}{n_{\text{liq}}} = \frac{l_{\text{liq}}}{l_{\text{Ca}}} = \frac{0.2 - 0}{0.2 - 0.13} = \boxed{2.86}$$

(c) When an 80 at % Si melt it cooled in a manner that maintains equilibrium, Si(s) begins to appear at about 1250°C. Further cooling causes more Si(s) to freeze out of the melt so that the melt becomes more concentrated in Ca. There is a 69.4 at % Si eutectic at 1030°C. Just before the eutectic is reached, the lever rule says that the relative amounts of the Si(s) and liquid (69.4% Si) phases are:

$$\frac{n_{\text{Si}}}{n_{\text{liq}}} = \frac{l_{\text{liq}}}{l_{\text{Si}}} = \frac{0.80 - 0.694}{1.0 - 0.80} = \boxed{0.53 = \text{relative amounts at T slightly higher than } 1030^\circ\text{C}}$$

Just before 1030°C, the Si(s) is 34.6 mol% of the total heterogeneous mixture; the eutectic liquid is 65.4 mol%.

At the eutectic temperature a third phase appears - $CaSi_2$(s). As the melt cools at this temperature both Si(s) and $CaSi_2$(s) freeze out of the melt while the concentration of the melt remains constant. At a temperature slightly below 1030°C all the melt will have frozen to Si(s) and $CaSi_2$(s) with the relative amounts:

$$\frac{n_{\text{si}}}{n_{\text{CaSi}_2}} = \frac{l_{\text{CaSi}_2}}{l_{\text{Si}}} = \frac{0.80 - 0.667}{1.0 - 0.80}$$

$$= \boxed{0.665 = \text{relative amounts at } T \text{ slightly higher than } 1030^\circ\text{C}}$$

Just under 1030°C, the Si(s) is 39.9 mol% of the total heterogeneous mixture; the $CaSi_2$(s) is 60.1 mol%.

A graph of mol% Si(s) and mol% $CaSi_2$(s) vs. mol% eutectic liquid is a convenient way to show relative amounts of the three phases as the eutectic liquid freezes. Equations for the graph are derived with the law of conservation of mass. For the silicon mass,

$$n \cdot z_{\text{Si}} = n_{\text{liq}} \cdot w_{\text{Si}} + n_{\text{Si}} \cdot x_{\text{Si}} + n_{\text{CaSi}_2} \cdot y_{\text{Si}}$$

where n = total number of moles.

$$\boxed{\begin{aligned} w_{\mathrm{Si}} &= \text{Si fraction in eutectic liquid} = 0.694 \\ x_{\mathrm{Si}} &= \text{Si fraction in Si(s)} = 1.000 \\ y_{\mathrm{Si}} &= \text{Si fraction in CaSi}_2\text{(s)} = 0.667 \\ z_{\mathrm{Si}} &= \text{Si fraction in melt} = 0.800 \end{aligned}}$$

This equation may be rewritten in mole fractions of each phase by dividing by n:

$$z_{\mathrm{Si}} = (\text{mol fraction liq}) \cdot w_{\mathrm{Si}} + (\text{mol fraction Si}) \cdot x_{\mathrm{Si}} + (\text{mol fraction CaSi}_2) \cdot y_{\mathrm{Si}}$$

Since, $(\text{mol fraction liq}) + (\text{mol fraction Si}) + (\text{mol fraction CaSi}_2) = 1$
or $(\text{mol fraction CaSi}_2) = 1 - (\text{mol fraction liq} + \text{mol fraction Si})$, we may write :

$$\begin{aligned} z_{\mathrm{Si}} = {} & (\text{mol fraction liq}) \cdot w_{\mathrm{Si}} + (\text{mol fraction Si}) \cdot x_{\mathrm{Si}} \\ & +[1 - (\text{mol fraction liq} + \text{mol fraction Si})] \cdot y_{\mathrm{Si}} \end{aligned}$$

Solving for mol fraction Si:

$$\text{mol fraction Si} := \frac{(z_{\mathrm{Si}} - y_{\mathrm{Si}}) - (w_{\mathrm{Si}} - y_{\mathrm{Si}})(\text{mol fraction liq})}{x_{\mathrm{Si}} - y_{\mathrm{Si}}}$$

$$\text{mol fraction CaSi}_2 := 1 - (\text{mol fraction liq} + \text{mol fraction Si})$$

These two eqns are used to prepare plots of the mol fraction of Si and the mol fraction of $\mathrm{CaSi_2}$ against the mol fraction of the melt in the range 0–0.65.

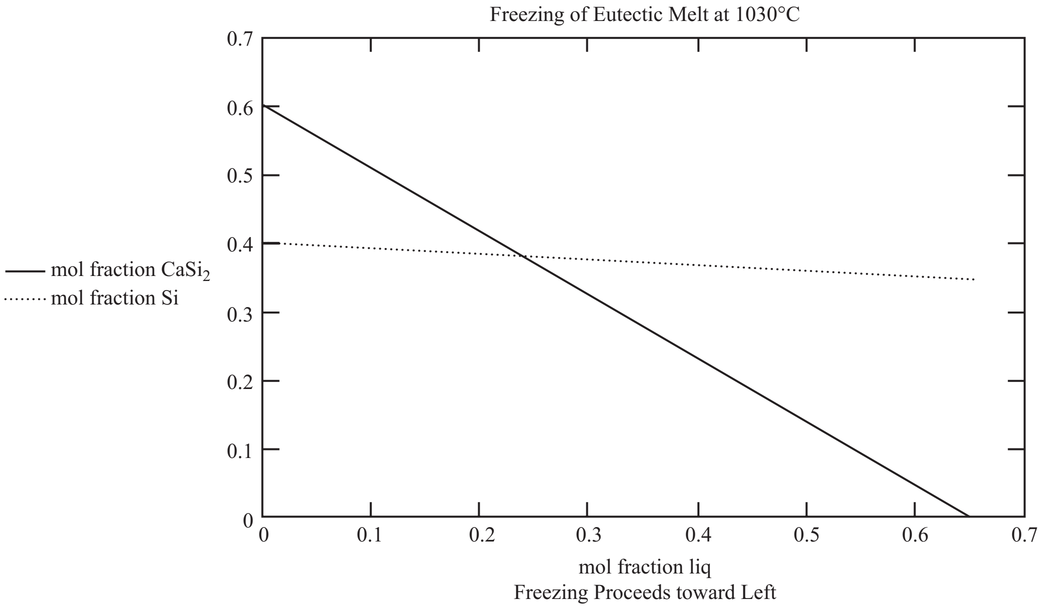


Figure 8.15

Solutions to theoretical problems

P8.12 The general condition of equilibrium in an isolated system is $\mathrm{d}S = 0$. Hence, if α and β constitute an isolated system, which are in thermal contact with each other

$$\mathrm{d}S = \mathrm{d}S_\alpha + \mathrm{d}S_\beta = 0 \qquad \text{(a)}$$

Entropy is an additive property and may be expressed in terms of U and V.

$$S = S(U, V)$$

The implication of this problem is that energy in the form of heat may be transferred from one phase to another, but that the phases are mechanically rigid, and hence their volumes are constant. Thus, $\mathrm{d}V = 0$, and

$$\mathrm{d}S = \left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)_V \mathrm{d}U_\alpha + \left(\frac{\partial S_\beta}{\partial U_\beta}\right)_V \mathrm{d}U_\beta = \frac{1}{T_\alpha}\,\mathrm{d}U_\alpha + \frac{1}{T_\beta}\,\mathrm{d}U_\beta \; [5.4]$$

But, $\mathrm{d}U_\alpha = -\mathrm{d}U_\beta$; therefore $\dfrac{1}{T_\alpha} = \dfrac{1}{T_\beta}$ or $\boxed{T_\alpha = T_\beta}$

Solutions to applications

P8.14 $C = 1$; hence, $F = C - P + 2 = 3 - P$

Since the tube is sealed there will always be some gaseous compound in equilibrium with the condensed phases. Thus when liquid begins to form upon melting, $P = 3$ (s, l, and g) and $F = 0$, corresponding to a definite melting temperature. At the transition to a normal liquid, $P = 3$ (l, l', and g) as well, so again $F = 0$.

P8.16 The temperature-composition lines can be calculated from the formula for the depression of freezing point [7.33].

$$\Delta T \approx \frac{RT^{*2}x_{\mathrm{B}}}{\Delta_{\mathrm{fus}}H}$$

For bismuth

$$\frac{RT^{*2}}{\Delta_{\mathrm{fus}}H} = \frac{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (544.5\,\mathrm{K})^2}{10.88 \times 10^3\,\mathrm{J\,mol^{-1}}} = 227\,\mathrm{K}$$

For cadmium

$$\frac{RT^{*2}}{\Delta_{\mathrm{fus}}H} = \frac{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (594\,\mathrm{K})^2}{6.07 \times 10^3\,\mathrm{J\,mol^{-1}}} = 483\,\mathrm{K}$$

We can use these constants to construct the following tables

$x(\mathrm{Cd})$	0.1	0.2	0.3	0.4	
$\Delta T/\mathrm{K}$	22.7	45.4	68.1	90.8	$(\Delta T = x(\mathrm{Cd}) \times 227\,\mathrm{K})$
$T_{\mathrm{f}}/\mathrm{K}$	522	499	476	454	$(T_{\mathrm{f}} = T_{\mathrm{f}}^* - \Delta T)$

$x(\mathrm{Bi})$	0.1	0.2	0.3	0.4	
$\Delta T/\mathrm{K}$	48.3	96.6	145	193	$(\Delta T = x(\mathrm{Bi}) \times 483\,\mathrm{K})$
$T_{\mathrm{f}}/\mathrm{K}$	546	497	449	401	$(T_{\mathrm{f}} = T_{\mathrm{f}}^* - \Delta T)$

These points are plotted in Fig. 8.16(a).

The eutectic temperature and concentration are located by extrapolation of the plotted freezing point lines until they intersect at e, which corresponds to $T_{\mathrm{E}} \approx 400\,\mathrm{K}$ and $x_{\mathrm{E}}(\mathrm{Cd}) \approx 0.60$.

Liquid at a cools without separation of a solid until a' is reached (at 476 K). Solid Bi then seperates, and the liquid becomes richer in Cd. At a'''(400 K) the composition is pure solid Bi + liquid of composition $x(\mathrm{Bi}) = 0.4$. The whole mass then solidfies to solid Bi + solid Cd.

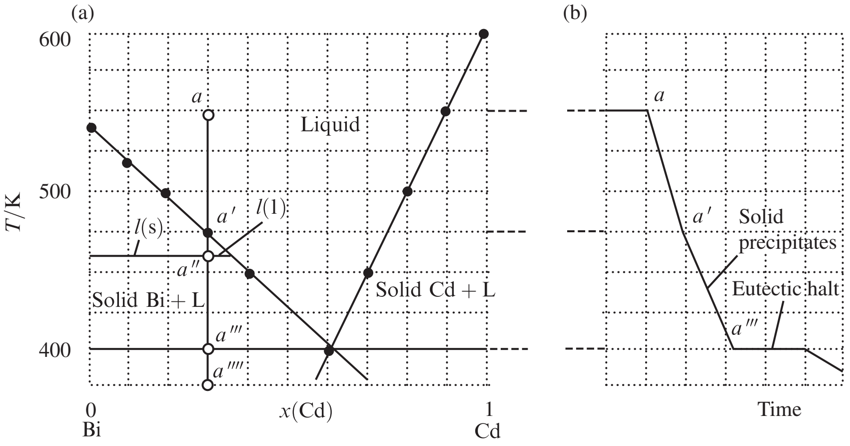


Figure 8.16

(a) At 460 K (point a''), $\dfrac{n(\mathrm{l})}{n(\mathrm{s})} = \dfrac{l(\mathrm{s})}{l(\mathrm{l})} \approx \boxed{5}$ by the lever rule.

(b) At 375 K (point a'''') there is $\boxed{\text{no liquid}}$. The cooling curve is shown in Fig. 8.16(b).

Comment. The experimental values of T_{E} and $x_{\mathrm{E}}(\mathrm{Cd})$ are 417 K and 0.55. The extrapolated values can be considered to be remarkably close to the experimental ones when one considers that the formulas employed apply only to dilute (ideal) solutions.

P8.17 **(a)** The data are plotted in Fig. 8.17.

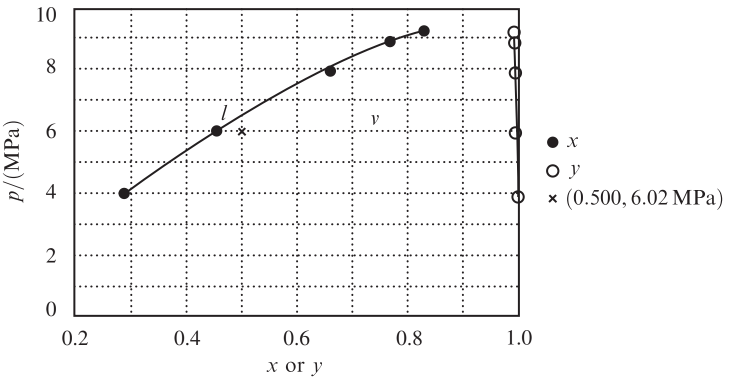


Figure 8.17

(b) We need not interpolate data, for 6.02 MPa is a pressure for which we have experimental data. The mole fraction of CO_2 in the liquid phase is 0.4541 and in the vapour phase 0.9980. The proportions of the two phases are in an inverse ratio of the distance their mole fractions are from the composition point in question, according to the lever rule. That is

$$\frac{n_{\mathrm{liq}}}{n_{\mathrm{vap}}} = \frac{v}{l} = \frac{0.9980 - 0.5000}{0.5000 - 0.4541} = \boxed{10.85}$$

P8.19 **(a)** As the solutions become either pure methanol ($x_{\mathrm{methanol}} = 1$) or pure TAME ($x_{\mathrm{methanol}} = 0$), the activity coefficients should become equal to 1 (Table 7.3). This means that the extremes in the range of $\ln \gamma(x)$ curves should approach zero as they do in the above plot (Fig. 8.18(a)).

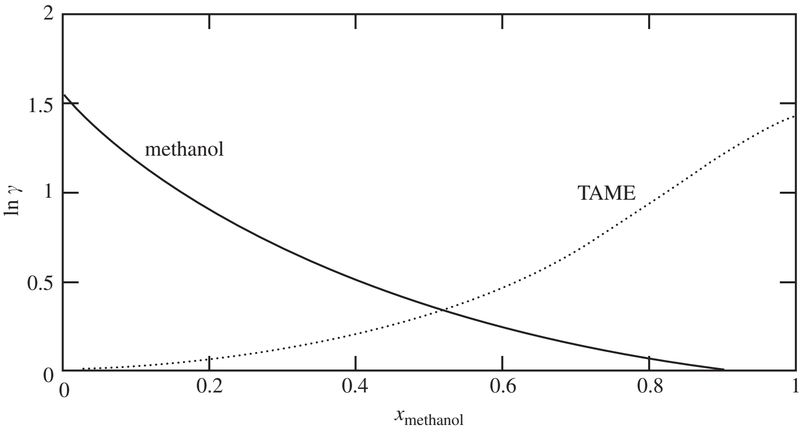


Figure 8.18(a)

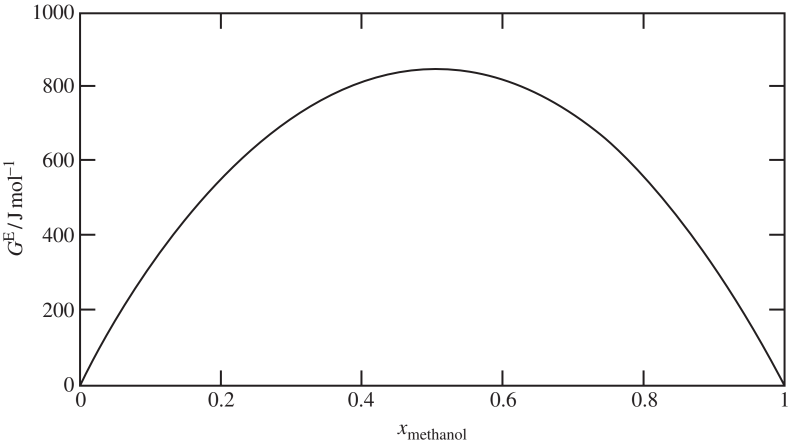


Figure 8.18(b)

(b) The large positive deviation of G^E from the ideal mixture ($G^E_{\text{ideal}} = 0$, Section 7.4) indicates that the mixing process is unfavorable. This may originate from the breakage of relatively strong methanol hydrogen bonding upon solution formation.

G^E for a regular solution is expected to be symmetrical about the point $x_{\text{methanol}} = 0.5$. Visual inspection of the $G^E(x_{\text{methanol}})$ plot reveals that methanol/TAME solutions are approximately "regular". The symmetry expectation can be demonstrated by remembering that $H^E_m = Wx_Ax_B$ and $S^E = 0$ for a regular solution (Section 7.4b). Then, for a regular solution $G^E_m = H^E_m - TS^E_m = H^E = Wx_Ax_B$, which is symmetrical about $x = 0.5$ in the sense that G^E_m at $x = 0.5 - \delta$ equals G^E_m at $x = 0.5 + \delta$.

(c) Azeotrope composition and vapor pressure:

$$x_{\text{methanol}} = y_{\text{methanol}} = 0.682$$
$$P = 11.59\,\text{kPa}$$

when $x_{\text{methanol}} = 0.2,\ \ P = 10.00\,\text{kPa}$.

(d) The vapor pressure plot shows positive deviations from ideality. The escaping tendency is stronger than that of an ideal solution.

To get the Henry's law constants, estimate values for the targets of P_{methanol} at $x_{\text{methanol}} = 0$ and P_{TAME} at $x_{\text{methanol}} = 1$.

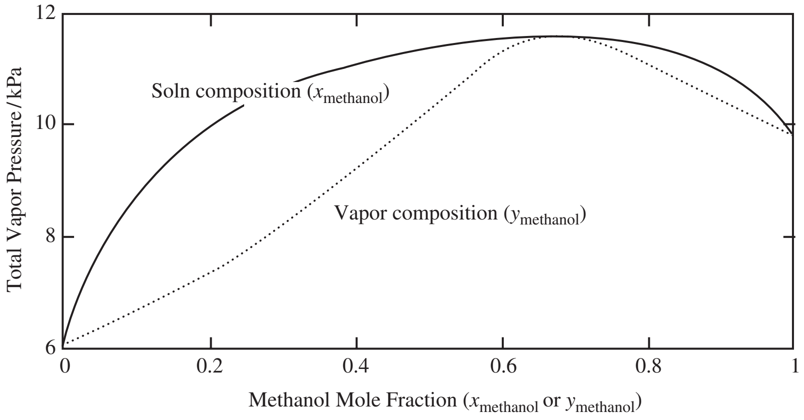


Figure 8.18(c)

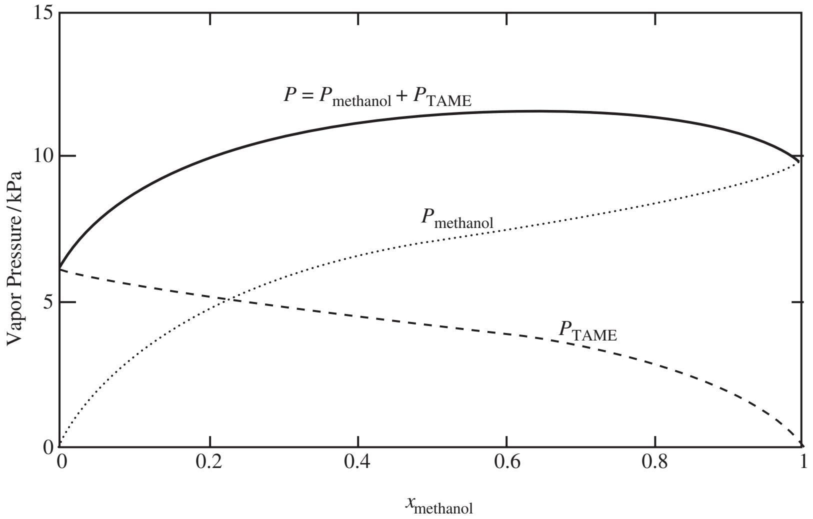


Figure 8.18(d)

For methanol in TAME (eqn 7.26):

$$K_{\text{methanol}} = \left(\frac{\mathrm{d}P_{\text{methanol}}}{\mathrm{d}x_{\text{methanol}}}\right)_{x_{\text{methanol}}=0} = 45.1\,\text{kPa}$$

For TAME in methanol:

$$K_{\text{TAME}} = \left(\frac{\mathrm{d}P_{\text{TAME}}}{\mathrm{d}x_{\text{TAME}}}\right)_{x_{\text{TAME}}=0} = -\left(\frac{\mathrm{d}P_{\text{TAME}}}{\mathrm{d}x_{\text{methanol}}}\right)_{x_{\text{methanol}}=1} = 25.3\,\text{kPa}$$

(e) According to eqn 6.3, the vapor pressure should increase when the applied pressure is increased. For TAME:

$$\begin{aligned} P &= P^{*}\,\mathrm{e}^{V_{\mathrm{m}}\Delta P/RT} \\ &= (6.09\,\text{kPa})\,\mathrm{e}^{(131.78\,\cancel{\text{cm}^3}\,\cancel{\text{mol}^{-1}})(2.0\,\cancel{\text{bar}})/[(83.1451\,\cancel{\text{cm}^3}\,\cancel{\text{bar}}\,\cancel{\text{K}^{-1}}\,\cancel{\text{mol}^{-1}})(288.15\,\cancel{\text{K}})]} \\ &= 6.16\,\text{kPa} \end{aligned}$$

The applied pressure increases the vapor pressure by about 1%, molecules have been "squeezed" out of the liquid phase and into the gas phase but only to a slight extent.

9 Chemical equilibrium

Solutions to exercises

Discussion questions

E9.1(b) The thermodynamic equilibrium constant involves activities rather than pressures. See eqn 9.18 and Example 9.1. For systems involving gases, the activities are the dimensionless fugacities. At low pressures, the fugacity may be replaced with pressures with little error, but at high pressures that is not a good approximation. The difference between the equilibrium constant expressed in activities and the constant expressed in pressures is dependent upon two factors: the stoichiometry of the reaction and the magnitude of the partial pressures. Thus there is no one answer to this question. For the example of the ammonia synthesis reaction, in a range of pressures where the fugacity coefficients are greater than one, an increase in pressure results in a greater shift to the product side than would be predicted by the constant expressed in partial pressures. For an exothermic reaction, such as the ammonia synthesis, an increase in temperature will shift the reaction to the reactant side, but the relative shift is independent of the fugacity coefficients. The ratio $\ln(K_2/K_1)$ depends only on $\Delta_r H$. See eqn 6.26.

E9.2(b) The physical basis of the dependence of the equilibrium constant on temperature as predicted by the van't Hoff equation can be seen when the expression $\Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$ is written in the form $R\ln K = -\Delta_r H^{\ominus}/T + \Delta_r S^{\ominus}$. When the reaction is exothermic and the temperature is raised, $\ln K$ and hence K decrease, since T occurs in the denominator, and the reaction shifts to favor the reactants. When the reaction is endothermic, increasing T makes $\ln K$ less negative, or K more positive, and products are favored. Another factor of importance when the reaction is endothermic is the increasing entropy of the reacting system resulting in a more positive $\ln K$, favoring products.

E9.3(b) A typical pH curve for the titration of a weak base with a strong acid is shown in Figure 9.1. The stoichiometric point S occurs on the acidic side of pH $= 7$ because the salt formed by the neutralization reaction has an acid cation.

E9.4(b) Buffers work best when $S \approx A'$, that is when the concentrations of the salt and acid are not widely different. An abundant supply of A^- ions can remove by reaction any H_3O^+ supplied by the addition of an acid; likewise an abundant supply of HA can remove by reaction any OH^- supplied by addition of base.

Indicators are weak acids which in their undissociated acid form have one colour, and in their dissociated anion form, another. In acidic solution, the indicator exists in the predominantly acid form (one colour), in basic solution in the predominantly anion form (the other colour). The ratio of the two forms is very pH sensitive because of the small value of $\mathrm{p}K_a$ of the indicator, so the colour change can occur very rapidly with change in pH.

Numerical exercises

E9.5(b) $\Delta_r G^{\ominus} = -RT\ln K = -(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (1600\,\mathrm{K}) \times \ln(0.255)$

$$= +18.17\overline{7}\,\mathrm{kJ\,mol^{-1}} = \boxed{+18.18\,\mathrm{kJ\,mol^{-1}}}$$

E9.6(b) $\Delta_r G^{\ominus} = -RT\ln K$

$$K = \mathrm{e}^{-(\Delta_r G^{\ominus}/RT)} = \exp\left\{-\frac{(0.178 \times 10^3\,\mathrm{J\,mol^{-1}})}{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (1173\,\mathrm{K})}\right\}$$

$$= 0.98\overline{2} = \boxed{0.98}$$

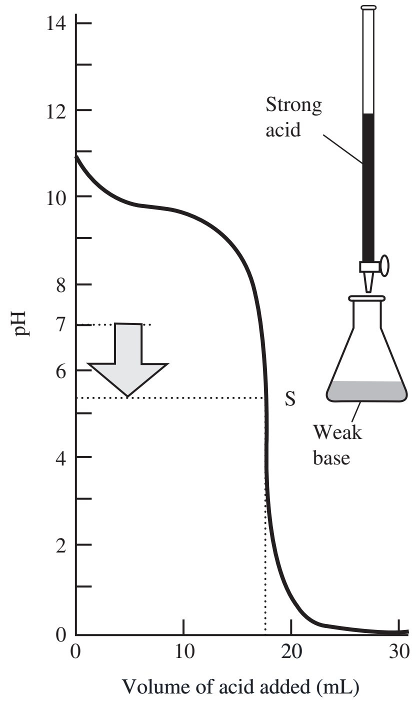


Figure 9.1

E9.7(b)

	$N_2O_4(g)$ $\rightleftharpoons$	$2NO_2(g)$
Amount at equilibrium	$(1-\alpha)n$	$2\alpha n$
Mole fraction	$\dfrac{1-\alpha}{1+\alpha}$	$\dfrac{2\alpha}{1+\alpha}$
Partial pressure	$\dfrac{(1-\alpha)p}{1+\alpha}$	$\dfrac{2\alpha p}{1+\alpha}$

Assuming that the gases are perfect, $a_J = \dfrac{p_J}{p^{\ominus}}$

$$K = \frac{(p_{NO_2}/p^{\ominus})^2}{(p_{N_2O_4}/p^{\ominus})} = \frac{4\alpha^2 p}{(1-\alpha^2)p^{\ominus}}$$

For $p = p^{\ominus}$, $K = \dfrac{4\alpha^2}{1-\alpha^2}$

(a) $\boxed{\Delta_r G = 0}$ at equilibrium

(b) $\alpha = 0.201 \qquad K = \dfrac{4(0.201)^2}{1-0.201^2} = \boxed{0.168\overline{41}}$

(c) $\Delta_r G^{\ominus} = -RT \ln K = -(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K}) \times \ln(0.168\overline{41})$
$= \boxed{4.41\,\mathrm{kJ\,mol^{-1}}}$

E9.8(b) **(a)**

	$Br_2(g)$ $\rightleftharpoons$	$2Br(g)$ $\quad \alpha = 0.24$
Amount at equilibrium	$(1-\alpha)n$	$2\alpha n$
Mole fraction	$\dfrac{1-\alpha}{1+\alpha}$	$\dfrac{2\alpha}{1+\alpha}$
Partial pressure	$\dfrac{(1-\alpha)p}{1+\alpha}$	$\dfrac{2\alpha p}{1+\alpha}$

Assuming both gases are perfect $a_J = \dfrac{p_J}{p^\ominus}$

$$\begin{aligned} K &= \frac{(p_{\mathrm{Br}}/p^\ominus)^2}{p_{\mathrm{Br}_2}/p^\ominus} = \frac{4\alpha^2 p}{(1-\alpha^2)p^\ominus} = \frac{4\alpha^2}{1-\alpha^2} \quad [p = p^\ominus] \\ &= \frac{4(0.24)^2}{1-(0.24)^2} = 0.24\overline{45} = \boxed{0.24} \end{aligned}$$

(b) $$\begin{aligned} \Delta_r G^\ominus &= -RT \ln K = -(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (1600\,\mathrm{K}) \times \ln(0.24\overline{45}) \\ &= \boxed{19\,\mathrm{kJ\,mol^{-1}}} \end{aligned}$$

(c) $$\begin{aligned} \ln K(2273\,\mathrm{K}) &= \ln K(1600\,\mathrm{K}) - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{2273\,\mathrm{K}} - \frac{1}{1600\,\mathrm{K}}\right) \\ &= \ln(0.24\overline{45}) - \left(\frac{112 \times 10^3\,\mathrm{J\,mol^{-1}}}{8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}}\right) \times (-1.851 \times 10^{-4}) \\ &= 1.08\overline{4} \end{aligned}$$

$$K(2273\,\mathrm{K}) = \mathrm{e}^{1.08\overline{4}} = \boxed{2.96}$$

E9.9(b) $\nu(\mathrm{CHCl_3}) = 1, \quad \nu(\mathrm{HCl}) = 3, \quad \nu(\mathrm{CH_4}) = -1, \quad \nu(\mathrm{Cl_2}) = -3$

(a) $$\begin{aligned} \Delta_r G^\ominus &= \Delta_f G^\ominus(\mathrm{CHCl_3, l}) + 3\Delta_f G^\ominus(\mathrm{HCl, g}) - \Delta_f G^\ominus(\mathrm{CH_4, g}) \\ &= (-73.66\,\mathrm{kJ\,mol^{-1}}) + (3) \times (-95.30\,\mathrm{kJ\,mol^{-1}}) - (-50.72\,\mathrm{kJ\,mol^{-1}}) \\ &= \boxed{-308.84\,\mathrm{kJ\,mol^{-1}}} \end{aligned}$$

$$\ln K = -\frac{\Delta_r G^\ominus}{RT}[8] = \frac{-(-308.84 \times 10^3\,\mathrm{J\,mol^{-1}})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298.15\,\mathrm{K})} = 124.58\overline{4}$$

$$K = \boxed{1.3 \times 10^{54}}$$

(b) $$\begin{aligned} \Delta_r H^\ominus &= \Delta_f H^\ominus(\mathrm{CHCl_3, l}) + 3\Delta_f H^\ominus(\mathrm{HCl, g}) - \Delta_f H^\ominus(\mathrm{CH_4, g}) \\ &= (-134.47\,\mathrm{kJ\,mol^{-1}}) + (3) \times (-92.31\,\mathrm{kJ\,mol^{-1}}) - (-74.81\,\mathrm{kJ\,mol^{-1}}) \\ &= -336.59\,\mathrm{kJ\,mol^{-1}} \end{aligned}$$

$$\begin{aligned} \ln K(50^\circ\mathrm{C}) &= \ln K(25^\circ\mathrm{C}) - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{323.2\,\mathrm{K}} - \frac{1}{298.2\,\mathrm{K}}\right) [9.28] \\ &= 124.58\overline{4} - \left(\frac{-336.59 \times 10^3\,\mathrm{J\,mol^{-1}}}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\right) \times (-2.594 \times 10^{-4}\,\mathrm{K^{-1}}) = 114.08\overline{3} \end{aligned}$$

$$K(50^\circ\mathrm{C}) = \boxed{3.5 \times 10^{49}}$$

$$\begin{aligned} \Delta_r G^\ominus(50^\circ\mathrm{C}) &= -RT \ln K(50^\circ\mathrm{C})[18] = -(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (323.15\,\mathrm{K}) \times (114.08\overline{3}) \\ &= \boxed{-306.52\,\mathrm{kJ\,mol^{-1}}} \end{aligned}$$

E9.10(b) Draw up the following table

	A	+	B	⇌	C	+	2D	Total
Initial amounts/mol	2.00		1.00		0		3.00	6.00
Stated change/mol					+0.79			
Implied change/mol	−0.79		−0.79		+0.79		+1.58	
Equilibrium amounts/mol	1.21		0.21		0.79		4.58	6.79
Mole fractions	$0.178\overline{2}$		$0.030\overline{9}$		$0.116\overline{3}$		$0.674\overline{5}$	0.9999

(a) Mole fractions are given in the table.

(b) $$K_x = \prod_{\mathrm{J}} x_{\mathrm{J}}^{\nu_{\mathrm{J}}}$$

$$K_x = \frac{(0.116\overline{3}) \times (0.674\overline{5})^2}{(0.178\overline{2}) \times (0.030\overline{9})} = \boxed{9.6}$$

(c) $p_{\mathrm{J}} = x_{\mathrm{J}} p$. Assuming the gases are perfect, $a_{\mathrm{J}} = \dfrac{p_{\mathrm{J}}}{p^{\ominus}}$, so

$$K = \frac{(p_{\mathrm{C}}/p^{\ominus}) \times (p_{\mathrm{D}}/p^{\ominus})^2}{(p_{\mathrm{A}}/p^{\ominus}) \times (p_{\mathrm{B}}/p^{\ominus})} = K_x\left(\frac{p}{p^{\ominus}}\right) = K_x \quad \text{when } p = 1.00\,\mathrm{bar}$$

$$K = K_x = \boxed{9.6}$$

(d) $$\Delta_{\mathrm{r}}G^{\ominus} = -RT\ln K = -(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K}) \times \ln(9.60\overline{9})$$
$$= \boxed{-5.6\,\mathrm{kJ\,mol^{-1}}}$$

E9.11(b) At 1120 K, $\Delta_{\mathrm{r}}G^{\ominus} = +22 \times 10^3\,\mathrm{J\,mol^{-1}}$

$$\ln K(1120\,\mathrm{K}) = \frac{-\Delta_{\mathrm{r}}G^{\ominus}}{RT} = -\frac{(22 \times 10^3\,\mathrm{J\,mol^{-1}})}{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (1120\,\mathrm{K})} = -2.3\overline{63}$$

$$K = \mathrm{e}^{-2.3\overline{63}} = 9.\overline{41} \times 10^{-2}$$

$$\ln K_2 = \ln K_1 - \frac{\Delta_{\mathrm{r}}H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Solve for T_2 at $\ln K_2 = 0$ $(K_2 = 1)$

$$\frac{1}{T_2} = \frac{R\ln K_1}{\Delta_{\mathrm{r}}H^{\ominus}} + \frac{1}{T_1} = \frac{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (-2.3\overline{63})}{(125 \times 10^3\,\mathrm{J\,mol^{-1}})} + \frac{1}{1120\,\mathrm{K}} = 7.3\overline{6} \times 10^{-4}$$

$$T_2 = \boxed{1.4 \times 10^3\,\mathrm{K}}$$

E9.12(b) Use $\dfrac{\mathrm{d}(\ln K)}{\mathrm{d}(1/T)} = \dfrac{-\Delta_{\mathrm{r}}H^{\ominus}}{R}$

We have $\ln K = -2.04 - 1176\,\mathrm{K}\left(\dfrac{1}{T}\right) + 2.1 \times 10^7\,\mathrm{K}^3\left(\dfrac{1}{T}\right)^3$

$$-\frac{\Delta_{\mathrm{r}}H^{\ominus}}{R} = -1176\,\mathrm{K} + 3 \times (2.1 \times 10^7\,\mathrm{K}^3) \times \left(\frac{1}{T}\right)^2$$

$T = 450\,\mathrm{K}$ so

$$-\frac{\Delta_{\mathrm{r}}H^{\ominus}}{R} = -1176\,\mathrm{K} + 3 \times (2.1 \times 10^7\,\mathrm{K}^3) \times \left(\frac{1}{450\,\mathrm{K}}\right)^2 = -86\overline{5}\,\mathrm{K}$$

$$\Delta_{\mathrm{r}}H^{\ominus} = +(86\overline{5}\,\mathrm{K}) \times (8.314\,\mathrm{J\,mol^{-1}K^{-1}}) = \boxed{7.1\overline{91}\,\mathrm{kJ\,mol^{-1}}}$$

Find $\Delta_r S^\ominus$ from $\Delta_r G^\ominus$

$$\begin{aligned}\Delta_r G^\ominus &= -RT\ln K\\ &= -(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (450\,\mathrm{K}) \times \left\{-2.04 - \frac{1176\,\mathrm{K}}{450\,\mathrm{K}} + \frac{2.1\times 10^{7}\,\mathrm{K^3}}{(450\,\mathrm{K})^3}\right\}\\ &= 16.\overline{55}\,\mathrm{kJ\,mol^{-1}}\\ \Delta_r G^\ominus &= \Delta_r H^\ominus - T\Delta_r S^\ominus\\ \Delta_r S^\ominus &= \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T} = \frac{7.1\overline{91}\,\mathrm{kJ\,mol^{-1}} - 16.5\overline{5}\,\mathrm{kJ\,mol^{-1}}}{450\,\mathrm{K}} = -20.\overline{79}\,\mathrm{J\,K^{-1}\,mol^{-1}}\\ &= \boxed{-21\,\mathrm{J\,K^{-1}\,mol^{-1}}}\end{aligned}$$

E9.13(b) $\mathrm{U(s)} + \frac{3}{2}\mathrm{H_2(g)} \rightleftharpoons \mathrm{UH_3(s)}, \quad \Delta_r G^\ominus = -RT\ln K$

At this low pressure, hydrogen is nearly a perfect gas, $a(\mathrm{H_2}) = \left(\dfrac{p}{p^\ominus}\right)$. The activities of the solids are 1.

Hence, $\ln K = \ln\left(\dfrac{p}{p^\ominus}\right)^{-3/2} = -\frac{3}{2}\ln\dfrac{p}{p^\ominus}$

$$\begin{aligned}\Delta G^\ominus &= \tfrac{3}{2}RT\ln\frac{p}{p^\ominus}\\ &= \left(\tfrac{3}{2}\right) \times (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (500\,\mathrm{K}) \times \ln\left(\frac{1.04\,\mathrm{Torr}}{750\,\mathrm{Torr}}\right)\\ &\qquad [p^\ominus = 1\,\mathrm{bar} \approx 750\,\mathrm{Torr}]\\ &= \boxed{-41.0\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

E9.14(b) $K_x = \prod_{\mathrm{J}} x_{\mathrm{J}}^{\nu_{\mathrm{J}}}$ [analogous to 17]

The relation of K_x to K is established in *Illustration* 9.4

$$\begin{aligned}K &= \prod_{\mathrm{J}}\left(\frac{p_{\mathrm{J}}}{p^\ominus}\right)^{\nu_{\mathrm{J}}} \quad \left[9.18 \text{ with } a_{\mathrm{J}} = \frac{p_{\mathrm{J}}}{p^\ominus}\right]\\ &= \prod_{\mathrm{J}} x_{\mathrm{J}}^{\nu_{\mathrm{J}}} \times \left(\frac{p}{p^\ominus}\right)^{\sum_{\mathrm{J}}\nu_{\mathrm{J}}} [p_{\mathrm{J}} = x_{\mathrm{J}}p] = K_x \times \left(\frac{p}{p^\ominus}\right)^{\nu} \quad \left[\nu \equiv \sum_{\mathrm{J}}\nu_{\mathrm{J}}\right]\end{aligned}$$

Therefore, $K_x = K\left(\dfrac{p}{p^\ominus}\right)^{-\nu}$, $K_x \propto p^{-\nu}$ [K and $p^\ominus$ are constants]

$$\nu = 1 + 1 - 1 - 1 = 0, \quad \text{thus} \quad \boxed{K_x(2\,\mathrm{bar}) = K_x(1\,\mathrm{bar})}$$

E9.15(b) $\mathrm{N_2(g)} + \mathrm{O_2(g)} \rightleftharpoons \mathrm{2NO(g)} \quad K = 1.69\times 10^{-3}$ at 2300 K

$$\text{Initial moles } \mathrm{N_2} = \frac{5.0\,\mathrm{g}}{28.01\,\mathrm{g\,mol^{-1}}} = 0.23\overline{80}\,\mathrm{mol\ N_2}$$

$$\text{Initial moles } \mathrm{O_2} = \frac{2.0\,\mathrm{g}}{32.00\,\mathrm{g\,mol^{-1}}} = 6.2\overline{50}\times 10^{-2}\,\mathrm{mol\ O_2}$$

	N_2	O_2	NO	Total
Initial amount/mol	$0.23\overline{80}$	$0.062\overline{5}$	0	0.300
Change/mol	$-z$	$-z$	$+2z$	0
Equilibrium amount/mol	$0.23\overline{80} - z$	$0.062\overline{5} - z$	$2z$	0.300
Mole fractions	$\frac{0.2380 - z}{0.300}$	$\frac{0.062\overline{5} - z}{0.300}$	$\frac{2z}{0.300}$	(1)

$$K = K_x\left(\frac{p}{p^{\ominus}}\right)^{\nu} \quad \left[\nu = \sum_{\mathrm{J}} \nu_{\mathrm{J}} = 0\right], \text{ then}$$

$$K = K_x = \frac{(2z/0.300)^2}{\left(\frac{0.2380-z}{0.300}\right) \times \left(\frac{0.0625-z}{0.300}\right)}$$

$$= \frac{4z^2}{(0.2380 - z) \times (0.0625 - z)} = 1.69 \times 10^{-3}$$

$$4z^2 = 1.69 \times 10^{-3}\left\{0.014\overline{88} - 0.30\overline{05}z + z^2\right\}$$

$$= 2.5\overline{14} \times 10^{-5} - (5.0\overline{78} \times 10^{-4})z + (1.69 \times 10^{-3})z^2$$

$$4.00 - 1.69 \times 10^{-3} = 4.00 \quad \text{so}$$

$$4z^2 + (5.0\overline{78} \times 10^{-4})z - 2.5\overline{14} \times 10^{-5} = 0$$

$$z = \frac{-5.0\overline{78} \times 10^{-4} \pm \left\{(5.078 \times 10^{-4})^2 - 4 \times (4) \times (-2.514 \times 10^{-5})\right\}^{1/2}}{8}$$

$$= \tfrac{1}{8}(-5.078 \times 10^{-4} \pm 2.0\overline{06} \times 10^{-2})$$

$$z > 0 \quad [z < 0 \text{ is physically impossible}] \quad \text{so}$$

$$z = 2.4\overline{44} \times 10^{-3}$$

$$x_{\mathrm{NO}} = \frac{2z}{0.300} = \frac{2(2.4\overline{44} \times 10^{-3})}{0.300} = \boxed{1.6 \times 10^{-2}}$$

E9.16(b) $\Delta_{\mathrm{r}}G^{\ominus} = -RT \ln K$ [9.8]

Hence, a value of $\Delta_{\mathrm{r}}G^{\ominus} < 0$ at 298 K corresponds to $K > 1$.

(a) $\Delta_{\mathrm{r}}G^{\ominus}/(\mathrm{kJ\,mol^{-1}}) = (2) \times (-33.56) - (-166.9) = +99.8, \quad K < 1$

(b) $\Delta_{\mathrm{r}}G^{\ominus}/(\mathrm{kJ\,mol^{-1}}) = (-690.00) - (-33.56) - (2) \times (-120.35) = -415.74, \quad \boxed{K > 1}$

E9.17(b) Le Chatelier's principle in the form of the rules in the first paragraph of Section 9.4 is employed. Thus we determine whether $\Delta_{\mathrm{r}}H^{\ominus}$ is positive or negative using the $\Delta_{\mathrm{f}}H^{\ominus}$ values of Table 2.6.

(a) $\Delta_{\mathrm{r}}H^{\ominus}/(\mathrm{kJ\,mol^{-1}}) = (2) \times (-20.63) - (-178.2) = +136.9$

(b) $\Delta_{\mathrm{r}}H^{\ominus}/(\mathrm{kJ\,mol^{-1}}) = (-813.99) - (-20.63) - (2) \times (-187.78) = -417.80$

Since **(a)** is endothermic, an increase in temperature favours the products, which implies that a reduction in temperature favours the reactants; since $\boxed{\textbf{(b)}}$ is exothermic, an increase in temperature favours the reactants, which implies that a reduction in temperature favours the products (in the sense of K increasing).

E9.18(b) $$\ln\frac{K'}{K}=\frac{\Delta_{\mathrm{r}}H^{\ominus}}{R}\left(\frac{1}{T}-\frac{1}{T'}\right)\quad\text{so}\quad\Delta_{\mathrm{r}}H^{\ominus}=\frac{R\ln\left(\frac{K'}{K}\right)}{\left(\frac{1}{T}-\frac{1}{T'}\right)}$$

$$T=310\,\mathrm{K},\qquad T'=325\,\mathrm{K};\qquad\text{let }\frac{K'}{K}=\kappa$$

$$\text{Now }\Delta_{\mathrm{r}}H^{\ominus}=\frac{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}})}{\left(\frac{1}{310\,\mathrm{K}}-\frac{1}{325\,\mathrm{K}}\right)}\times\ln\kappa=55.\overline{84}\,\mathrm{kJ\,mol^{-1}}\ \ln\kappa$$

(a) $\kappa=2,\qquad\Delta_{\mathrm{r}}H^{\ominus}=(55.\overline{84}\,\mathrm{kJ\,mol^{-1}})\times(\ln 2)=\boxed{39\,\mathrm{kJ\,mol^{-1}}}$

(b) $\kappa=\frac{1}{2},\qquad\Delta_{\mathrm{r}}H^{\ominus}=(55.\overline{84}\,\mathrm{kJ\,mol^{-1}})\times\left(\ln\frac{1}{2}\right)=\boxed{-39\,\mathrm{kJ\,mol^{-1}}}$

E9.19(b) $\mathrm{NH_4Cl(s)}\rightleftharpoons\mathrm{NH_3(g)}+\mathrm{HCl(g)}$

$p=p(\mathrm{NH_3})+p(\mathrm{HCl})=2p(\mathrm{NH_3})\quad[p(\mathrm{NH_3})=p(\mathrm{HCl})]$

(a) $$K=\prod_{\mathrm{J}}a_{\mathrm{J}}^{\nu_{\mathrm{J}}}[17];\qquad a(\text{gases})=\frac{p_{\mathrm{J}}}{p^{\ominus}};\qquad a(\mathrm{NH_4Cl,\,s})=1$$

$$K=\left(\frac{p(\mathrm{NH_3})}{p^{\ominus}}\right)\times\left(\frac{p(\mathrm{HCl})}{p^{\ominus}}\right)=\frac{p(\mathrm{NH_3})^2}{p^{\ominus 2}}=\frac{1}{4}\times\left(\frac{p}{p^{\ominus}}\right)^2$$

$$\text{At }427^{\circ}\mathrm{C}\ (700\,\mathrm{K}),\quad K=\frac{1}{4}\times\left(\frac{608\,\mathrm{kPa}}{100\,\mathrm{kPa}}\right)^2=\boxed{9.24}$$

$$\text{At }459^{\circ}\mathrm{C}\ (732\,\mathrm{K}),\quad K=\frac{1}{4}\times\left(\frac{1115\,\mathrm{kPa}}{100\,\mathrm{kPa}}\right)^2=31.08$$

(b) $$\Delta_{\mathrm{r}}G^{\ominus}=-RT\ln K[8]=(-8.314\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(700\,\mathrm{K})\times(\ln 9.24)$$
$$=\boxed{-12.9\,\mathrm{kJ\,mol^{-1}}}\quad(\text{at }427^{\circ}\mathrm{C})$$

(c) $$\Delta_{\mathrm{r}}H^{\ominus}\approx\frac{R\ln\frac{K'}{K}}{\left(\frac{1}{T}-\frac{1}{T'}\right)}[26]$$
$$\approx\frac{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}})\times\ln\left(\frac{31.08}{9.24}\right)}{\left(\frac{1}{700\,\mathrm{K}}-\frac{1}{732\,\mathrm{K}}\right)}=\boxed{+161\,\mathrm{kJ\,mol^{-1}}}$$

(d) $$\Delta_{\mathrm{r}}S^{\ominus}=\frac{\Delta_{\mathrm{r}}H^{\ominus}-\Delta_{\mathrm{r}}G^{\ominus}}{T}=\frac{(161\,\mathrm{kJ\,mol^{-1}})-(-12.9\,\mathrm{kJ\,mol^{-1}})}{700\,\mathrm{K}}=\boxed{+248\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

E9.20(b) The reaction is

$$\mathrm{CuSO_4\cdot 5H_2O(s)}\rightleftharpoons\mathrm{CuSO_4(s)}+\mathrm{5H_2O(g)}$$

For the purposes of this exercise we may assume that the required temperature is that temperature at which the $K=1$ which corresponds to a pressure of 1 bar for the gaseous products. For $K=1$, $\ln K=0$, and $\Delta_{\mathrm{r}}G^{\ominus}=0$.

$$\Delta_{\mathrm{r}}G^{\ominus}=\Delta_{\mathrm{r}}H^{\ominus}-T\Delta_{\mathrm{r}}S^{\ominus}=0\quad\text{when }\Delta_{\mathrm{r}}H^{\ominus}=T\Delta_{\mathrm{r}}S^{\ominus}$$

Therefore, the decomposition temperature (when $K=1$) is

$$T=\frac{\Delta_{\mathrm{r}}H^{\ominus}}{\Delta_{\mathrm{r}}S^{\ominus}}$$

$$CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(g)$$

$$\Delta_r H^\ominus = [(-771.36) + (5) \times (-241.82) - (-2279.7)]\,\text{kJ mol}^{-1} = +299.2\,\text{kJ mol}^{-1}$$

$$\Delta_r S^\ominus = [(109) + (5) \times (188.83) - (300.4)]\,\text{J K}^{-1}\,\text{mol}^{-1} = 752.\overline{8}\,\text{J K}^{-1}\,\text{mol}^{-1}$$

Therefore, $T = \dfrac{299.2 \times 10^3\,\text{J mol}^{-1}}{752.8\,\text{J K}^{-1}\,\text{mol}^{-1}} = \boxed{397\,\text{K}}$

Question. What would the decomposition temperature be for decomposition defined as the state at which $K = \frac{1}{2}$?

E9.21(b) **(a)** The half-way point corresponds to the condition

$$[\text{acid}] = [\text{salt}], \quad \text{for which} \quad \text{pH} = \text{p}K_a$$

Thus $\text{p}K_a = 4.82$ and $K_a = 10^{-4.82} = \boxed{1.5 \times 10^{-5}}$

(b) When $[\text{acid}] = 0.025\,\text{M}$

$$\text{pH} = \tfrac{1}{2}\text{p}K_a - \tfrac{1}{2}\log[\text{acid}] = \tfrac{1}{2}(4.82) - \tfrac{1}{2}(-1.60) = \boxed{3.21}$$

E9.22(b) **(a)** The HCO_2^- ion acts as a weak base.

$$HCO_2^-(aq) + H_2O(l) \rightleftharpoons HCOOH(aq) + OH^-(aq)$$

Then, since $[HCOOH] \approx [OH^-]$ and $[HCO_2^-] \approx S$, the nominal concentration of the salt,

$$K_b \approx \frac{[OH^-]^2}{S} \quad \text{and} \quad [OH^-] = (SK_b)^{1/2}$$

Therefore $\text{pOH} = \frac{1}{2}\text{p}K_b - \frac{1}{2}\log S$
However, $\text{pH} + \text{pOH} = \text{p}K_w$, so $\text{pH} = \text{p}K_w - \text{pOH}$
and $\text{p}K_a + \text{p}K_b = \text{p}K_w$, so $\text{p}K_b = \text{p}K_w - \text{p}K_a$
Thus $\text{pH} = \text{p}K_w - \frac{1}{2}(\text{p}K_w - \text{p}K_a) + \frac{1}{2}\log S = \frac{1}{2}\text{p}K_w + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log S$
$= \frac{1}{2}(14.00) + \frac{1}{2}(3.75) + \frac{1}{2}\log(0.10) = \boxed{8.37}$

(b) The same expression is obtained

$$\begin{aligned}\text{pH} &= \tfrac{1}{2}\text{p}K_w + \tfrac{1}{2}\text{p}K_a + \tfrac{1}{2}\log S \\ &= \tfrac{1}{2}(14.00) + \tfrac{1}{2}(4.19) + \tfrac{1}{2}\log(0.20) = \boxed{8.74}\end{aligned}$$

(c) 0.150 M HCN(aq)

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq) \quad K_a = \frac{[H_3O^+][CN^-]}{[HCN]}$$

Since we can ignore water autoprotolysis, $[H_3O^+] = [CN^-]$, so

$$K_a = \frac{[H_3O^+]^2}{A}$$

where $A = [HCN]$, the nominal acid concentration.

Thus $[H_3O^+] \approx (AK_a)^{1/2}$ and $\mathrm{pH} \approx \frac{1}{2}\mathrm{p}K_a - \frac{1}{2}\log A$

$$\mathrm{pH} = \tfrac{1}{2}(9.31) - \tfrac{1}{2}\log(0.150) = \boxed{5.07}$$

E9.23(b) The pH of a solution in which the nominal salt concentration is S is

$$\mathrm{pH} = \tfrac{1}{2}\mathrm{p}K_w + \tfrac{1}{2}\mathrm{p}K_a + \tfrac{1}{2}\log S$$

The volume of solution at the stoichiometric point is

$$V = (25.00\,\mathrm{mL}) + (25.00\,\mathrm{mL}) \times \left(\frac{0.100\,\mathrm{M}}{0.175\,\mathrm{M}}\right) = 39.2\overline{86}\,\mathrm{mL}$$

$$S = (0.100\,\mathrm{M}) \times \left(\frac{25.00\,\mathrm{mL}}{39.2\overline{86}\,\mathrm{mL}}\right) = 6.36\overline{4} \times 10^{-2}\,\mathrm{M}$$

$\mathrm{p}K_a = 1.96$ for chlorous acid.

$$\begin{aligned}\mathrm{pH} &= \tfrac{1}{2}(14.00) + \tfrac{1}{2}(1.96) + \tfrac{1}{2}\log(6.36\overline{4} \times 10^{-2}) \\ &= \boxed{7.38}\end{aligned}$$

E9.24(b) When only the salt is present, use $\mathrm{pH} = \frac{1}{2}\mathrm{p}K_a + \frac{1}{2}\mathrm{p}K_w + \frac{1}{2}\log S$

$$\mathrm{pH} = \tfrac{1}{2}(4.19) + \tfrac{1}{2}(14.00) + \tfrac{1}{2}\log(0.15) = 8.68 \qquad \text{(a)}$$

When $A \approx S$, use the Henderson–Hasselbalch equation

$$\mathrm{pH} = \mathrm{p}K_a - \log\frac{A}{S} = 4.19 - \log\frac{A}{0.15} = 3.36\overline{6} - \log A \qquad \text{(b)}$$

When so much acid has been added that $A \gg S$, use

$$\mathrm{pH} = \tfrac{1}{2}\mathrm{p}K_a - \tfrac{1}{2}\log A \qquad \text{(c)}$$

We can make up a table of values

$A/(\mathrm{mol\,L^{-1}})$	0	0.06	0.08	0.10	0.12	0.14	0.6	0.8	1.0
pH	8.68	4.59	4.46	4.36	4.29	4.21	2.21	2.14	2.09
Formula	(a)	(b)					(c)		

These values are plotted in Fig. 9.2.

E9.25(b) According to the Henderson–Hasselbalch equation the pH of a buffer varies about a central value given by $\mathrm{p}K_a$. For the $\dfrac{[\text{acid}]}{[\text{salt}]}$ ratio to be neither very large nor very small we require $\mathrm{p}K_a \approx \mathrm{pH}$ (buffer)

(a) For pH = 4.6, use $\boxed{\text{aniline and anilinium ion}}$, $\mathrm{p}K_a = 4.63$.

(b) For pH = 10.8, use $\boxed{\text{ethylammonium ion and ethylamine}}$, $\mathrm{p}K_a = 10.81$

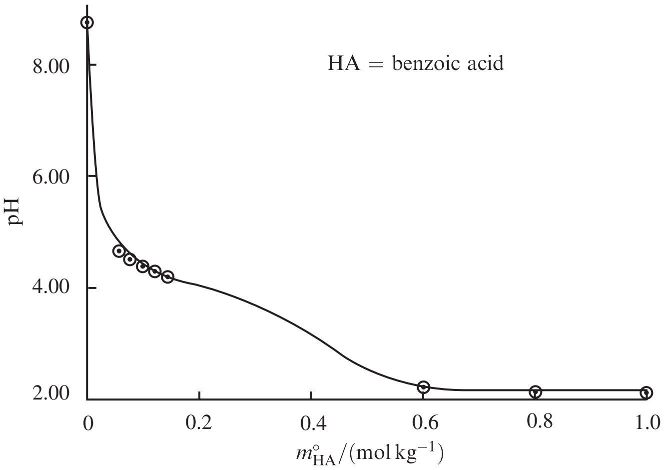


Figure 9.2

Solutions to problems

Solutions to numerical problems

P9.2 $\mathrm{CH_4(g) \rightleftharpoons C(s) + 2H_2(g)}$

This reaction is the reverse of the formation reaction.

(a)
$$\Delta_r G^\ominus = -\Delta_f G^\ominus$$
$$\begin{aligned}\Delta_f G^\ominus &= \Delta_f H^\ominus - T\Delta_f S^\ominus \\ &= -74\,850\,\mathrm{J\,mol^{-1}} - 298\,\mathrm{K} \times (-80.67\,\mathrm{J\,K^{-1}\,mol^{-1}}) \\ &= -5.08 \times 10^4\,\mathrm{J\,mol^{-1}}\end{aligned}$$
$$\ln K = \frac{\Delta_r G^\ominus}{-RT}[9.8] = \frac{5.08 \times 10^4\,\mathrm{J\,mol^{-1}}}{-8.314\,\mathrm{J\,K^{-1}\,mol^{-1}} \times 298\,\mathrm{K}} = -20.508$$
$$K = \boxed{1.24 \times 10^{-9}}$$

(b)
$$\Delta_r H^\ominus = -\Delta_f H^\ominus = 74.85\,\mathrm{kJ\,mol^{-1}}$$
$$\ln K(50^\circ\mathrm{C}) = \ln K(298\,\mathrm{K}) - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{323\,\mathrm{K}} - \frac{1}{298\,\mathrm{K}}\right)\ [9.28]$$
$$= -20.508 - \left(\frac{7.4850 \times 10^4\,\mathrm{J\,mol^{-1}}}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\right) \times (-2.59\overline{7} \times 10^{-4}) = -18.17\overline{0}$$
$$K(50^\circ\mathrm{C}) = \boxed{1.29 \times 10^{-8}}$$

(c) Draw up the equilibrium table

	$\mathrm{CH_4(g)}$	$\mathrm{H_2(g)}$
Amounts	$(1-\alpha)n$	$2\alpha n$
Mole fractions	$\dfrac{1-\alpha}{1+\alpha}$	$\dfrac{2\alpha}{1+\alpha}$
Partial pressures	$\left(\dfrac{1-\alpha}{1+\alpha}\right)p$	$\dfrac{2\alpha p}{1+\alpha}$

$$K = \prod_J a_J^{\nu_J}\,[9.18] = \frac{\left(\frac{p_{H_2}}{p^{\ominus}}\right)^2}{\left(\frac{p_{CH_4}}{p^{\ominus}}\right)}$$

$$1.24 \times 10^{-9} = \frac{(2\alpha)^2}{1-\alpha^2}\left(\frac{p}{p^{\ominus}}\right) \approx 4\alpha^2 p \quad [\alpha \ll 1]$$

$$\alpha = \frac{1.24 \times 10^{-9}}{4 \times 0.010} = \boxed{1.8 \times 10^{-4}}$$

(d) Le Chatelier's principle provides the answers:

As pressure increases, α decreases, since the more compact state (less moles of gas) is favoured at high pressures. As temperature increases the side of the reaction which can absorb heat is favoured. Since $\Delta_r H^{\ominus}$ is positive, that is the right-hand side, hence α increases. This can also be seen from the results of parts **(a)** and **(b)**, K increased from 25°C to 50°C, implying that α increased.

P9.3 $U(s) + \frac{3}{2}H_2(g) \rightleftharpoons UH_3(s) \quad K = (p/p^{\ominus})^{-3/2}$ [Exercise 9.13(b)]

$$\Delta_f H^{\ominus} = RT^2 \frac{d\ln K}{dT}[9.26] = RT^2 \frac{d}{dT}\left(-\tfrac{3}{2}\ln p/p^{\ominus}\right)$$

$$= -\tfrac{3}{2}RT^2 \frac{d\ln p}{dT}$$

$$= -\tfrac{3}{2}RT^2\left(\frac{14.64 \times 10^3\,K}{T^2} - \frac{5.65}{T}\right)$$

$$= -\tfrac{3}{2}R(14.64 \times 10^3\,K - 5.65T)$$

$$= \boxed{-(2.196 \times 10^4\,K - 8.48T)R}$$

$$d(\Delta_f H^{\ominus}) = \Delta_r C_p^{\ominus} dT \text{ [from 2.44]}$$

$$\text{or } \Delta_r C_p^{\ominus} = \left(\frac{\partial \Delta_f H^{\ominus}}{\partial T}\right)_p = \boxed{8.48R}$$

P9.5 $CaCl_2 \cdot NH_3(s) \rightleftharpoons CaCl_2(s) + NH_3(g) \qquad K = \frac{p}{p^{\ominus}}$

$$\Delta_r G^{\ominus} = -RT\ln K = -RT\ln\frac{p}{p^{\ominus}}$$

$$= -(8.314\,J\,K^{-1}\,mol^{-1}) \times (400\,K) \times \ln\left(\frac{12.8\,Torr}{750\,Torr}\right) \quad [p^{\ominus} = 1\,bar = 750.3\,Torr]$$

$$= +13.5\,kJ\,mol^{-1} \quad \text{at } 400\,K$$

Since $\Delta_r G^{\ominus}$ and $\ln K$ are related as above, the dependence of $\Delta_r G^{\ominus}$ on temperature can be determined from the dependence of $\ln K$ on temperature.

$$\frac{\Delta_r G^{\ominus}(T)}{T} - \frac{\Delta_r G^{\ominus}(T')}{T'} = \Delta_r H^{\ominus}\left(\frac{1}{T} - \frac{1}{T'}\right) [26]$$

Therefore, taking $T' = 400\,\mathrm{K}$,

$$\begin{aligned}\Delta_\mathrm{r}G^\ominus(T) &= \left(\frac{T}{400\,\mathrm{K}}\right) \times (13.5\,\mathrm{kJ\,mol^{-1}}) + (78\,\mathrm{kJ\,mol^{-1}}) \times \left(1 - \frac{T}{400\,\mathrm{K}}\right)\\ &= (78\,\mathrm{kJ\,mol^{-1}}) + \left(\frac{(13.5-78)\,\mathrm{kJ\,mol^{-1}}}{400}\right) \times \left(\frac{T}{\mathrm{K}}\right)\end{aligned}$$

That is, $\Delta_\mathrm{r}G^\ominus(T)/(\mathrm{kJ\,mol^{-1}}) = \boxed{78 - 0.161(T/\mathrm{K})}$

P9.7 The equilibrium we need to consider is $A_2(g) \rightleftharpoons 2A(g)$. A = acetic acid

It is convenient to express the equilibrium constant in terms of α, the degree of dissociation of the dimer, which is the predominant species at low temperatures.

	A	A_2	Total
At equilibrium	$2\alpha n$	$(1-\alpha)n$	$(1+\alpha)n$
Mole fraction	$\dfrac{2\alpha}{1+\alpha}$	$\dfrac{1-\alpha}{1+\alpha}$	1
Partial pressure	$\dfrac{2\alpha p}{1+\alpha}$	$\left(\dfrac{1-\alpha}{1+\alpha}\right)p$	p

The equilibrium constant for the dissociation is

$$K_p = \frac{\left(\frac{p_\mathrm{A}}{p^\ominus}\right)^2}{\frac{p_{\mathrm{A}_2}}{p^\ominus}} = \frac{p_\mathrm{A}^2}{p_{\mathrm{A}_2}p^\ominus} = \frac{4\alpha^2\left(\frac{p}{p^\ominus}\right)}{1-\alpha^2}$$

We also know that

$$pV = n_\mathrm{total}RT = (1+\alpha)nRT, \quad \text{implying that} \quad \alpha = \frac{pV}{nRT} - 1 \quad \text{and} \quad n = \frac{m}{M}$$

In the first experiment,

$$\alpha = \frac{pVM}{mRT} - 1 = \frac{(764.3\,\mathrm{Torr}) \times (21.45 \times 10^{-3}\,\mathrm{L}) \times (120.1\,\mathrm{g\,mol^{-1}})}{(0.0519\,\mathrm{g}) \times (62.364\,\mathrm{L\,Torr\,K^{-1}\,mol^{-1}}) \times (437\,\mathrm{K})} - 1 = 0.392$$

Hence, $K = \dfrac{(4) \times (0.392)^2 \times \left(\frac{764.3}{750.1}\right)}{1-(0.392)^2} = \boxed{0.740}$

In the second experiment,

$$\alpha = \frac{pVM}{mRT} - 1 = \frac{(764.3\,\mathrm{Torr}) \times (21.45 \times 10^{-3}\,\mathrm{L}) \times (120.1\,\mathrm{g\,mol^{-1}})}{(0.038\,\mathrm{g}) \times (62.364\,\mathrm{L\,Torr\,K^{-1}\,mol^{-1}}) \times (471\,\mathrm{K})} - 1 = 0.764$$

Hence, $K = \dfrac{(4) \times (0.764)^2 \times \left(\frac{764.3}{750.1}\right)}{1-(0.764)^2} = \boxed{5.71}$

The enthalpy of dissociation is

$$\Delta_\mathrm{r}H^\ominus = \frac{R\ln\frac{K'}{K}}{\left(\frac{1}{T}-\frac{1}{T'}\right)}[9.28, \text{Exercise 9.18(a)}] = \frac{R\ln\left(\frac{5.71}{0.740}\right)}{\left(\frac{1}{437\,\mathrm{K}}-\frac{1}{471\,\mathrm{K}}\right)} = +103\,\mathrm{kJ\,mol^{-1}}$$

The enthalpy of dimerization is the negative of this value, or $\boxed{-103\,\mathrm{kJ\,mol^{-1}}}$ (i.e. per mole of dimer).

P9.9 Draw up the following equilibrium table

	A	B	C	D	Total
Initial amounts/mol	1.00	2.00	0	1.00	4.00
Stated change/mol			+0.90		
Implied change/mol	−0.60	−0.30	+0.90	+0.60	
Equilibrium amounts/mol	0.40	1.70	0.90	1.60	4.60
Mole fractions	0.087	0.370	0.196	0.348	1.001

The mole fractions are given in the table.

$$K_x = \prod_{\mathrm{J}} x_{\mathrm{J}}^{\nu_{\mathrm{J}}} \quad \text{[analogous to eqn 9.18 and \textit{Illustration} 9.4]}$$

$$K_x = \frac{(0.196)^3 \times (0.348)^2}{(0.087)^2 \times (0.370)} = 0.32\overline{6} = \boxed{0.33}$$

$$p_{\mathrm{J}} = x_{\mathrm{J}} p, \quad p = 1\,\mathrm{bar}, \quad p^{\ominus} = 1\,\mathrm{bar}$$

Assuming that the gases are perfect, $a_{\mathrm{J}} = \dfrac{p_{\mathrm{J}}}{p^{\ominus}}$, hence

$$K = \frac{(p_{\mathrm{C}}/p^{\ominus})^3 \times (p_{\mathrm{D}}/p^{\ominus})^2}{(p_{\mathrm{A}}/p^{\ominus})^2 \times (p_{\mathrm{B}}/p^{\ominus})}$$

$$= \frac{x_{\mathrm{C}}^3 x_{\mathrm{D}}^2}{x_{\mathrm{A}}^2 x_{\mathrm{B}}} \times \left(\frac{p}{p^{\ominus}}\right)^2 = K_x \quad \text{when } p = 1.00\,\mathrm{bar} = \boxed{0.33}$$

P9.10 The equilibrium $I_2(g) \rightleftharpoons 2I(g)$ is described by the equilibrium constant

$$K = \frac{x(\mathrm{I})^2}{x(\mathrm{I_2})} \times \frac{p}{p^{\ominus}} = \frac{4\alpha^2\left(\frac{p}{p^{\ominus}}\right)}{1-\alpha^2} \quad \text{[Problem 9.7]}$$

If $p^0 = \dfrac{nRT}{V}$, then $p = (1+\alpha)p^0$, implying that

$$\alpha = \frac{p - p^0}{p^0}$$

We therefore draw up the following table

	973 K	1073 K	1173 K	
p/atm	0.06244	0.07500	0.09181	
$10^4 n_{\mathrm{I}}$	2.4709	2.4555	2.4366	
p^0/atm	0.05757	0.06309	0.06844	$\left[p^0 = \dfrac{nRT}{V}\right]$
α	0.08459	0.1888	0.3415	
K	$\boxed{1.800 \times 10^{-3}}$	$\boxed{1.109 \times 10^{-2}}$	$\boxed{4.848 \times 10^{-2}}$	

$$\Delta H^{\ominus} = RT^2 \times \left(\frac{\mathrm{d}\ln K}{\mathrm{d}T}\right) = (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (1073\,\mathrm{K})^2 \times \left(\frac{-3.027 - (-6.320)}{200\,\mathrm{K}}\right)$$

$$= \boxed{+158\,\mathrm{kJ\,mol^{-1}}}$$

P9.13 The reaction is

$$\mathrm{Si(s)} + \mathrm{H_2(g)} \rightleftharpoons \mathrm{SiH_2(g)}$$

The equilibrium constant is

$$K = \exp\left(\frac{-\Delta_r G^\ominus}{RT}\right) = \exp\left(\frac{-\Delta_r H^\ominus}{RT}\right)\exp\left(\frac{-\Delta_r S^\ominus}{R}\right)$$

Let h be the uncertainty in $\Delta_f H^\ominus$, so that the high value is $h+$ the low value. The K based on the low value is

$$K_{\mathrm{low}\,H} = \exp\left(\frac{-\Delta_r H^\ominus_{\mathrm{low}}}{RT}\right)\exp\left(\frac{\Delta_r S^\ominus}{R}\right) = \exp\left(\frac{-\Delta_r H^\ominus_{\mathrm{high}}}{RT}\right)\exp\left(\frac{h}{RT}\right)\exp\left(\frac{\Delta_r S^\ominus}{R}\right)$$

$$= \exp\left(\frac{h}{RT}\right) K_{\mathrm{high}\,H}$$

So $\dfrac{K_{\mathrm{low}\,H}}{K_{\mathrm{high}\,H}} = \exp\left(\dfrac{h}{RT}\right)$

(a) At 298 K, $\dfrac{K_{\mathrm{low}H}}{K_{\mathrm{high}H}} = \exp\left(\dfrac{(289-243)\,\mathrm{kJ\,mol^{-1}}}{(8.3145\times10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})}\right) = \boxed{1.2\times10^{8}}$

(b) At 700 K, $\dfrac{K_{\mathrm{low}H}}{K_{\mathrm{high}H}} = \exp\left(\dfrac{(289-243)\,\mathrm{kJ\,mol^{-1}}}{(8.3145\times10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}})\times(700\,\mathrm{K})}\right) = \boxed{2.7\times10^{3}}$

Solutions to theoretical problems

P9.16 $K = \dfrac{p(\mathrm{NO_2})^2}{p(\mathrm{N_2O_4})p^\ominus}$ with $p(\mathrm{NO_2}) + p(\mathrm{N_2O_4}) = p$

Since $p(\mathrm{NO_2})^2 + p(\mathrm{NO_2})K - pK = 0$ $[p \equiv p/p^\ominus]$

$$p(\mathrm{NO_2}) = \frac{\left(1+\frac{4p}{K}\right)^{1/2} - 1}{\left(\frac{2}{K}\right)}$$

We choose the root with the positive sign because p must be positive.

For equal absorptions

$$l_1 p_1(\mathrm{NO_2}) = l_2 p_2(\mathrm{NO_2}), \quad \text{or} \quad \rho p_1 = p_2 \ \ [\rho = l_1/l_2]$$

Therefore

$$\rho\left(1+\frac{4p_1}{K}\right)^{1/2} - \rho = (1+4p_2/K)^{1/2} - 1$$

$$\rho\left(1+\frac{4p_1}{K}\right)^{1/2} = \rho - 1 + \left(1+\frac{4p_2}{K}\right)^{1/2}$$

$$\rho^2\left(1+\frac{4p_1}{K}\right) = (\rho-1)^2 + \left(1+\frac{4p_2}{K}\right) + 2(\rho-1)\times\left(1+\frac{4p_2}{K}\right)^{1/2}$$

$$\rho - 1 + \frac{2(p_1\rho^2 - p_2)}{K} = (\rho - 1) \times \left(1 + \frac{4p_2}{K}\right)^{1/2}$$

$$\left(\rho - 1 + \frac{2(p_1\rho^2 - p_2)}{K}\right)^2 = (\rho - 1)^2 \times \left(1 + \frac{4p_2}{K}\right)$$

$$\frac{(p_1\rho^2 - p_2)^2}{K^2} + \frac{(\rho - 1) \times (p_1\rho^2 - p_2) - (\rho - 1)^2 p_2}{K} = 0$$

Hence, $K = \dfrac{(p_1\rho^2 - p_2)^2}{\rho(\rho - 1) \times (p_2 - p_1\rho)p^{\ominus}}$ [reinstating $p^{\ominus}$]

Since $\rho = \dfrac{395\,\text{mm}}{75\,\text{mm}} = 5.2\overline{7}$

$$p^{\ominus}K = \frac{(27.8p_1 - p_2)^2}{22.5(p_2 - 5.27p_1)}$$

We can therefore draw up the following table

Absorbance	p_1/Torr	p_2/Torr	$p^{\ominus}K$/Torr
0.05	1.00	5.47	110.8
0.10	2.10	12.00	102.5
0.15	3.15	18.65	103.0
			Mean: 105

Hence, since $p^{\ominus} = 750\,\text{Torr (1 bar)}$, $K = \boxed{0.140}$

P9.18 The five conditions are:

(a) Electrical neutrality: $[\text{BH}^+] + [\text{H}_3\text{O}^+] = [\text{A}^-] + [\text{OH}^-]$

(b) Conservation of B groups: $[\text{B}] + [\text{BH}^+] = \dfrac{\text{B}_\text{o}V_\text{B}}{V_\text{A} + V_\text{B}}$

where V_B is the (fixed) initial volume of base and V_A is the volume of titrant (acid) added.

(c) Concentration of A^-groups : $[\text{A}^-] = \dfrac{\text{A}_\text{o}V_\text{A}}{V_\text{A} + V_\text{B}}$

(d) Protonation equilibrium of B: $[\text{B}]K_\text{b} = [\text{BH}^+][\text{OH}^-]$

(e) Autoprotolysis equilibrium: $K_\text{w} = [\text{H}_3\text{O}^+][\text{OH}^-]$

First we express condition **(b)** in terms of $[\text{BH}^+]$ and $[\text{OH}^-]$ by using condition **(d)** to eliminate [B]

$$[\text{BH}^+] = \frac{\text{B}_\text{o}K_\text{b}V_\text{B}}{(V_\text{A} + V_\text{B})([\text{OH}^-] + K_\text{b})}$$

Next we use this relation and condition **(c)**, and at the same time we use condition **(e)** to eliminate $[\text{H}_3\text{O}^+]$

$$\frac{\text{B}_\text{o}K_\text{b}V_\text{B}}{(V_\text{A} + V_\text{B})([\text{OH}^-] + K_\text{b})} + \frac{K_\text{w}}{[\text{OH}^-]} = \frac{\text{A}_\text{o}V_\text{A}}{V_\text{A} + V_\text{B}} + [\text{OH}^-]$$

Now we multiply through by $\left(\dfrac{V_\text{A} + V_\text{B}}{V_\text{B}}\right)[\text{OH}^-]$, expand the fraction $\left(\dfrac{V_\text{A} + V_\text{B}}{V_\text{B}}\right)$, and collect terms in $\nu = \dfrac{V_\text{A}}{V_\text{B}}$ and obtain $\boxed{\nu = \dfrac{\text{B}_\text{o}K_\text{b}[\text{OH}^-] + (K_\text{w} - [\text{OH}^-]^2)([\text{OH}^-] + K_\text{b})}{([\text{OH}^-] + K_\text{b})([\text{OH}^-]^2 + \text{A}_\text{o}[\text{OH}^-] - K_\text{w})}}$

If desired, this formula for ν can be rewritten in terms of $[\mathrm{H_3O^+}]$ and pH by using relation **(e)** and the definition $\mathrm{pH} = -\log[\mathrm{H_3O^+}]$, or $[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}}$

Solutions to applications

P9.20 Refer to Box 9.2 for information necessary to the solution of this problem. The biological standard value of the Gibbs energy for ATP hydrolysis is $\approx -30\,\mathrm{kJ\,mol^{-1}}$. The standard Gibbs energy of combustion of glucose is $-2880\,\mathrm{kJ\,mol^{-1}}$.

(a) If we assume that each mole of ATP formed during the aerobic breakdown of glucose produces $-30\,\mathrm{kJ\,mol^{-1}}$, then

$$\text{efficiency} = \frac{38 \times (-30\,\mathrm{kJ\,mol^{-1}})}{-2880\,\mathrm{kJ\,mol^{-1}}} \times 100\% \approx \boxed{40\%}$$

(b) For the oxidation of glucose under the biological conditions of $p_{\mathrm{CO_2}} = 5.3 \times 10^{-2}\,\mathrm{atm}$, $p_{\mathrm{O_2}} = 0.132\,\mathrm{atm}$, and $[\text{glucose}] = 5.6 \times 10^{-2}\,\mathrm{mol\,L^{-1}}$ we have

$$\Delta_r G' = \Delta_r G^{\ominus} + RT \ln Q$$

$$\text{where } Q = \frac{(p_{\mathrm{CO_2}}/p^{\ominus})^6}{[\text{glucose}] \times (p_{\mathrm{O_2}}/p^{\ominus})^9} = \frac{(5.3 \times 10^{-2})^6}{5.6 \times 10^{-2} \times (0.132)^9} = 32.\overline{5}$$

Then

$$\begin{aligned}\Delta_r G' &= -2880\,\mathrm{kJ\,mol^{-1}} + 8.314\,\mathrm{J\,K^{-1}\,mol^{-1}} \times 310\,\mathrm{K} \times \ln(32.\overline{5}) \\ &= \boxed{-2871\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

which is not much different from the standard value.

For the ATP → ADP conversion under the given conditions

$$\Delta_r G' = \Delta_r G^{\oplus} + RT \ln\left(\frac{Q'}{Q^{\oplus}}\right)$$

$$\text{where } Q^{\oplus} = \frac{[\mathrm{ADP}][\mathrm{Pi}][\mathrm{H_3O^+}]}{[\mathrm{ATP}]} = \frac{1 \times 1 \times 10^{-7}}{1} = 10^{-7}$$

$$\text{and } Q' = \frac{1.0 \times 10^{-4} \times 1.0 \times 10^{-4} \times 10^{-7.4}}{1.0 \times 10^{-4}} = 10^{-11.4}$$

then

$$\begin{aligned}\Delta_r G' &= -30\,\mathrm{kJ\,mol^{-1}} + RT \ln(10^{-4.4}) \\ &= -30\,\mathrm{kJ\,mol^{-1}} + 8.314\,\mathrm{J\,K^{-1}\,mol^{-1}} \times 310\,\mathrm{K} \times (-10.1) \\ &= \boxed{-56\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

With this value for $\Delta_r G'$, the efficiency becomes

$$\text{efficiency} = \frac{38 \times (-56\,\mathrm{kJ\,mol^{-1}})}{-2871\,\mathrm{kJ\,mol^{-1}}} = \boxed{74\%}$$

(c) The theoretical limit of the diesel engine is

$$\epsilon = 1 - \frac{T_c}{T_h} = 1 - \frac{873\,\text{K}}{1923\,\text{K}} = 55\%$$

75% of the theoretical limit is 41%.

We see that the biological efficiency under the conditions given is greater than that of the diesel engine. What limits the efficiency of the diesel engine, or any heat engine, is that heat engines must convert heat ($q \approx \Delta_c H$) into useful work ($W_{\text{add,max}} = \Delta_r G$). Because of the second law, a substantial fraction of that heat is wasted. The biological process involves $\Delta_r G$ directly and does not go through a heat step.

P9.22 **(a)** The equilibrium constant is given by

$$K = \exp\left(\frac{-\Delta_r G^\ominus}{RT}\right) = \exp\left(\frac{-\Delta_r H^\ominus}{RT}\right)\exp\left(\frac{\Delta_r S^\ominus}{R}\right)$$

so $\ln K = -\dfrac{\Delta_r H^\ominus}{RT} + \dfrac{\Delta_r S^\ominus}{R}$

A plot of $\ln K$ against $1/T$ should be a straight line with a slope of $-\Delta_r H^\ominus/R$ and a y-intercept of $\Delta_r S^\ominus/R$ (Fig. 9.3).

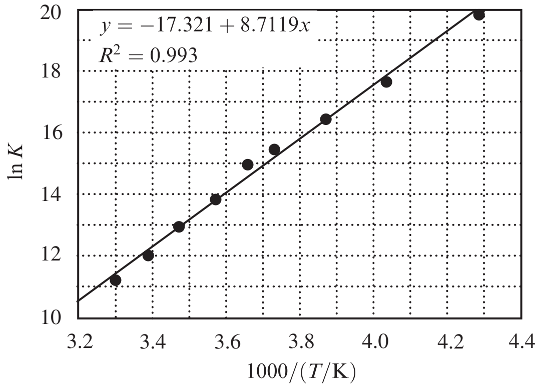


Figure 9.3

So $\Delta_r H^\ominus = -R \times \text{slope} = -(8.3145 \times 10^{-3}\,\text{kJ mol}^{-1}\,\text{K}^{-1}) \times (8.71 \times 10^3\,\text{K})$

$$= \boxed{-72.4\,\text{kJ mol}^{-1}}$$

and $\Delta_r S^\ominus = R \times \text{intercept} = (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (-17.3) = \boxed{-144\,\text{J K}^{-1}\,\text{mol}^{-1}}$

(b) $\Delta_r H^\ominus = \Delta_f H^\ominus((\text{ClO})_2) - 2\Delta_f H^\ominus(\text{ClO})$ so $\Delta_f H^\ominus((\text{ClO})_2) = \Delta_r H^\ominus + 2\Delta_f H^\ominus(\text{ClO})$,

$\Delta_f H^\ominus((\text{ClO})_2) = [-72.4 + 2(101.8)]\,\text{kJ mol}^{-1} = \boxed{131.2\,\text{kJ mol}^{-1}}$

$S^\ominus((\text{ClO})_2) = [-144 + 2(226.6)]\,\text{J K}^{-1}\,\text{mol}^{-1} = \boxed{309.2\,\text{J K}^{-1}\,\text{mol}^{-1}}$

P9.24 A reaction proceeds spontaneously if its reaction Gibbs function is negative.

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q$$

Note that under the given conditions, $RT = 1.58\,\text{kJ mol}^{-1}$.

(1) $\Delta_r G/(\text{kJ mol}^{-1}) = \Delta_r G^\ominus(1) - RT \ln p_{\text{H}_2\text{O}} = -23.6 - 1.58 \ln 1.3 \times 10^{-7} = +1.5$

(2) $\Delta_r G/(\text{kJ mol}^{-1}) = \Delta_r G^\ominus(2) - RT \ln p_{\text{H}_2\text{O}} p_{\text{HNO}_3}$

$$= -57.2 - 1.58 \ln[(1.3 \times 10^{-7}) \times (4.1 \times 10^{-10})] = +2.0$$

$$
\begin{aligned}
(3)\quad \Delta_r G/(\text{kJ mol}^{-1}) &= \Delta_r G^{\ominus}(3) - RT \ln p^2_{H_2O}p_{HNO_3} \\
&= -85.6 - 1.58 \ln[(1.3 \times 10^{-7})^2 \times (4.1 \times 10^{-10})] = -1.3 \\
(4)\quad \Delta_r G/(\text{kJ mol}^{-1}) &= \Delta_r G^{\ominus}(4) - RT \ln p^3_{H_2O}p_{HNO_3} \\
&= -85.6 - 1.58 \ln[(1.3 \times 10^{-7})^3 \times (4.1 \times 10^{-10})] = -3.5
\end{aligned}
$$

So both the dihydrate and trihydrate form spontaneously from the vapour. Does one convert spontaneously into the other? Consider the reaction

$$HNO_3 \cdot 2H_2O(s) + H_2O(g) \rightleftharpoons HNO_3 \cdot 3H_2O(s)$$

which may be considered as reaction (4) − reaction (3). Therefore $\Delta_r G$ for this reaction is

$$\Delta_r G = \Delta_r G(4) - \Delta_r G(3) = -2.2\,\text{kJ mol}^{-1}$$

We conclude that the dihydrate converts spontaneously to the $\boxed{\text{trihydrate}}$, the most stable solid (at least of the four we considered).

P9.26 **(a)** The following four equilibria are needed for the construction of the Ellingham diagram for the smelting reduction of silica with graphite (Box 9.1).

(1) $\frac{1}{2}Si(\text{s or l}) + \frac{1}{2}O_2(g) \rightarrow \frac{1}{2}SiO_2(\text{s or l})$

$$
\begin{aligned}
\Delta_1 G(T) &= 0.5\left[GH_{SiO_2(l)}(T) - GH_{Si(l)}(T) - GH_{O_2}(T)\right] \text{ if } T > \text{mpSiO}_2 \\
&= 0.5\left[GH_{SiO_2(s)}(T) - GH_{Si(l)}(T) - GH_{O_2}(T)\right] \text{ if mpSi} \le T \le \text{mpSiO}_2 \\
&= 0.5\left[GH_{SiO_2(s)}(T) - GH_{Si(s)}(T) - GH_{O_2}(T)\right] \text{ if } T < \text{mpSi}
\end{aligned}
$$

(2) $\frac{1}{2}C(s) + \frac{1}{2}O_2(g) \rightarrow \frac{1}{2}CO_2(g)$

$$\Delta_2 G(T) = 0.5\left[GH_{CO_2(g)}(T) - GH_{C(s)}(T) - GH_{O_2}(T)\right]$$

(3) $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$

$$\Delta_3 G(T) = GH_{CO(g)}(T) - GH_{C(s)}(T) - \tfrac{1}{2}GH_{O_2}(T)$$

(4) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

$$\Delta_4 G(T) = GH_{CO_2(g)}(T) - GH_{CO(g)}(T) - \tfrac{1}{2}GH_{O_2}(T)$$

$\Delta_3 G(T)$ alone lies above $\Delta_1 G(T)$ and then only above 1900 K. Thus, the smelting reaction.

(5) $\frac{1}{2}SiO_2 + \frac{1}{2}C(s) \rightarrow \frac{1}{2}Si + CO(g)$

$(\Delta_5 G(T) = \Delta_3 G(T) - \Delta_1 G(T))$

will have an equilibrium that lies to the right at temperatures higher than the temperature for which $\Delta_5 G(T) = 0$. Algebra or the root function can be used to show that this temperature equals 1892 K. The minimum smelting temperature of silica is about 1892 K. Furthermore, $\Delta_2 G$ never lies above $\Delta_1 G$ so we do not expect appreciable amounts of CO_2 is formed during smelting of silica.

(b) This problem is related to P8.18. Begin by making the definition $GH(T) = G(T) - H_{SER} = a + bT$. Write the important equilibria and calculate equilibrium contents at 2000 K. Silica and

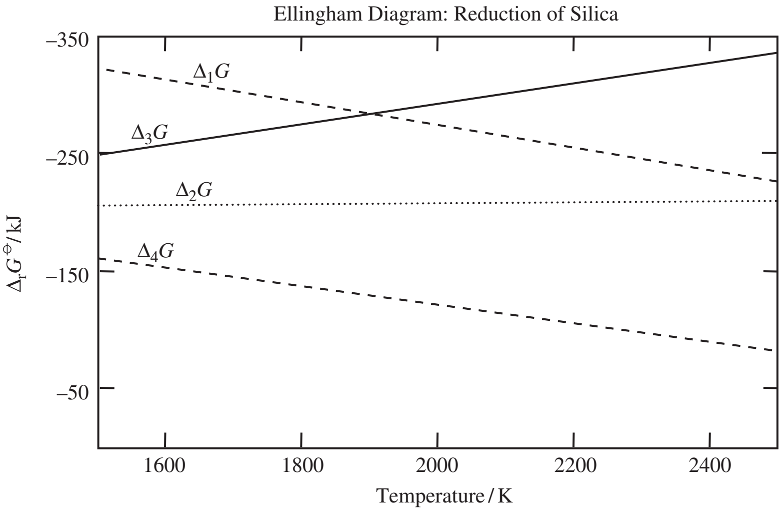


Figure 9.4

silicon are molten at this temperature. We assume that carbon forms an ideal solution with molten silicon and make the initial estimate:

$$\{\text{initial estimate of carbon mole function in molten Si}\} = x_{\text{est}} = 0.02$$

according to eqn 7.27,

$$\Delta_{\text{mix}} G(\text{C}) = RT x_{\text{est}} \ln x_{\text{est}} \quad \text{and} \quad \Delta_{\text{mix}} G(\text{Si}) = RT(1 - x_{\text{est}}) \ln(1 - x_{\text{est}})$$

There are three unknowns (x_C, P_{CO}, P_{SiO}) so we select three independent equilibria that involve the silicon melt and solve them self-consistently with the ideal solution estimate. The estimate is used to calculate the small mixing Gibbs energy only.

$$\begin{aligned} GH_{\text{C in melt}} &= GH_{\text{graphite}} + \Delta_{\text{mix}} G(\text{C}) \equiv GH_{\text{C}} \\ GH_{\text{Si in melt}} &= GH_{\text{Si(l)}} + \Delta_{\text{mix}} G(\text{Si}) \equiv GH_{\text{Si}} \end{aligned}$$

The independent equilibria are used to calculate a new estimate for the mole fraction of carbon in silicon, x_C. The new value is used in a repeat calculation in order to have a better estimate for x_{est}. This iteration procedure is repeated until the estimate and the calculated value of x_C agree to within 1%.

With the initial estimate:

(1) $SiO_2(l) + 2C(\text{Si melt}) \rightarrow Si(\text{melt}) + 2CO(g)$

$$\Delta_1 G = GH_{\text{Si}} + 2GH_{\text{CO(g)}} - GH_{\text{SiO}_2\text{(l)}} - 2GH_{\text{C}} = -37.69\,\text{kJ mol}^{-1}$$

$$K_1 = e^{-\Delta_1 G/RT} = 9.646 \quad \text{and} \quad x_{\text{Si}} P_{\text{CO}}^2 = K_1 x_{\text{C}}^2$$

(2) $SiO_2(l) + 3C(\text{Si melt}) \rightarrow SiC(s) + 2CO(g)$

$$\Delta_2 G = GH_{\text{SiC(s)}} + 2GH_{\text{CO(g)}} - GH_{\text{SiO}_2\text{(e)}} - 3GH_{\text{C}} = -85.72\,\text{kJ mol}^{-1}$$

$$K_2 = e^{-\Delta_2 G/RT} = 173.26 \quad \text{and} \quad P_{\text{CO}}^2 = K_2 x_{\text{C}}^3$$

Dividing the equilibrium constant expression of Reaction (1) by the one for Reaction (2), and using $x_{\mathrm{C}} = 1 - x_{\mathrm{Si}}$, gives

$$(1 - x_{\mathrm{Si}})(x_{\mathrm{Si}}) = K_1/K_2$$

Solving for x_{Si} gives:

$$\begin{aligned} x_{\mathrm{Si}} &= \tfrac{1}{2}\left\{1 + \sqrt{1 - 4K_1/K_2}\right\} = 0.9408 \\ x_{\mathrm{C}} &= 1 - x_{\mathrm{Si}} = 0.0592 \end{aligned}$$

The initial estimate of x_{C} (0.02) and the calculated value do not agree to within 1%, so the calculation is repeated (iterated) with the new estimate: $x_{\mathrm{est}} = 0.0592$. After several additional iterations, it is found that with $x_{\mathrm{est}} = 0.0695$ the calculated value is $\boxed{x_{\mathrm{C}} = 0.0698}$. Since these do agree to within 1%, the calculation is self-consistent and further iteration is unnecessary.

The equilibrium expression for reaction (2) gives:

$$P_{\mathrm{CO}} = \sqrt{K_2 x_{\mathrm{C}}^3}\,\mathrm{bar} = \sqrt{(125.66)(0.0698)^3}\,\mathrm{bar}$$

$$\boxed{P_{\mathrm{CO}} = 0.207\,\mathrm{bar}}$$

The third equilibrium is used to acquire P_{Si}, it is:

(3) $\mathrm{SiO_2(l) + C(Si\ melt) \rightarrow SiO(g) + CO(g)}$

$$\Delta_3 G = GH_{\mathrm{SiO(g)}} + GH_{\mathrm{CO(g)}} - GH_{\mathrm{SiO_2(l)}} - GH_{\mathrm{C}} = -8.415\,\mathrm{KJ\ mol^{-1}}$$

$$K_3 = \mathrm{e}^{-\Delta G_3/RT} = 1.659$$

$$P_{\mathrm{SiO}} = \left(\frac{K_3 x_{\mathrm{C}}}{P_{\mathrm{CO}}}\right)\mathrm{bar}^2 = \frac{1.659(0.0698)}{0.207}\,\mathrm{bar}$$

$$\boxed{P_{\mathrm{SiO}} = 0.559\,\mathrm{bar}}$$

10 Equilibrium electrochemistry

Solutions to exercises

Discussion questions

E10.1(b) The Debye–Hückel theory is a theory of the activity coefficients of ions in solution. It is the coulombic (electrostatic) interaction of the ions in solution with each other and also the interaction of the ions with the solvent that is responsible for the deviation of their activity coefficients from the ideal value of 1. The electrostatic ion–ion interaction is the stronger of the two and is fundamentally responsible for the deviation. Because of this interaction there is a build up of charge of opposite sign around any given ion 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 non-zero value of $RT \ln \gamma_\pm$. This non-zero value implies that $\gamma_\pm$ will have a value different from unity which is its ideal value. The role of the solvent is more indirect. The solvent determines the dielectric constant, ϵ, of the solution. Looking at the details of the theory as outlined in *Justification* 10.2 we see that ϵ enters into a number of the basic equations, in particular, Coulomb's law, Poisson's equation, and the equation for the Debye length. The larger the dielectric constant, the smaller (in magnitude) is $\ln \gamma_\pm$.

E10.2(b) The potential difference between the electrodes in a working electrochemical cell is called the **cell potential**. The cell potential is not a constant and changes with time as the cell reaction proceeds. Thus the cell potential is a potential difference measured under non-equilibrium conditions as electric current is drawn from the cell. **Electromotive force** is the zero-current cell potential and corresponds to the potential difference of the cell when the cell (not the cell reaction) is at equilibrium.

E10.3(b) The pH of an aqueous solution can in principle be measured with any electrode having an emf that is sensitive to $H^+(aq)$ concentration (activity). In principle, the hydrogen gas electrode is the simplest and most fundamental. A cell is constructed with the hydrogen electrode being the right-hand electrode and any reference electrode with known potential as the left-hand electrode. A common choice is the saturated calomel electrode. The pH can then be obtained from eqn 10.43 by measuring the emf (zero-current potential difference), E, of the cell. The hydrogen gas electrode is not convenient to use, so in practice glass electrodes are used because of ease of handling.

Numerical exercises

E10.4(b) $$\mathrm{NaCl(aq)} + \mathrm{AgNO_3(aq)} \rightarrow \mathrm{AgCl(s)} + \mathrm{NaNO_3(aq)}$$

NaCl, $AgNO_3$ and $NaNO_3$ are strong electrolytes; therefore the net ionic equation is

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

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

E10.5(b) $$\mathrm{PbS(s)} \rightleftharpoons \mathrm{Pb^{2+}(aq)} + \mathrm{S^{2-}(aq)}$$

$$K_S = \prod_J a_J^{\nu_J}$$

Since the solubility is expected to be low, we may (initially) ignore activity coefficients. Hence

$$K_S = \frac{b(\mathrm{Pb^{2+}})}{b^\ominus} \times \frac{b(\mathrm{S^{2-}})}{b^\ominus} \qquad b(\mathrm{Pb^{2+}}) = b(\mathrm{S^{2-}}) = S$$

$$K_S = \frac{S^2}{(b^\ominus)^2}$$

$$S = (K_S)^{1/2} b^\ominus$$

Use $\ln K_S = \dfrac{-\Delta_r G^\ominus}{RT}$ to obtain K_S

$$\begin{aligned}\Delta_r G^\ominus &= \Delta_f G^\ominus(\mathrm{S^{2-}, aq}) + \Delta_f G^\ominus(\mathrm{Pb^{2+}, aq}) - \Delta_r G^\ominus(\mathrm{PbS, s})\\ &= (+85.8\,\mathrm{kJ\,mol^{-1}}) + (-24.43\,\mathrm{kJ\,mol^{-1}}) - (-98.7\,\mathrm{kJ\,mol^{-1}})\\ &= 160.07\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

$$\ln K_S = \frac{-160.07 \times 10^3\,\mathrm{J\,mol^{-1}}}{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})} = -64.61$$

$$K_S = \mathrm{e}^{-64.61} = 8.7 \times 10^{-29}$$

$$K_S = \frac{S^2}{b^{\ominus 2}} \qquad S = (K_S)^{1/2} b^\ominus = (8.7\overline{35} \times 10^{-29})^{1/2} = \boxed{9.3 \times 10^{-15}\,\mathrm{mol\,kg^{-1}}}$$

E10.6(b) The ratio of hydration Gibbs energies is

$$\frac{\Delta_{\mathrm{hyd}} G^\ominus(\mathrm{NO_3^-})}{\Delta_{\mathrm{hyd}} G^\ominus(\mathrm{Cl^-})} = \frac{r(\mathrm{Cl^-})}{r(\mathrm{NO_3^-})} = \frac{181\,\mathrm{pm}}{189\,\mathrm{pm}} = 0.958$$

We have $\Delta_{\mathrm{hyd}} G^\ominus(\mathrm{Cl^-}) = -379\,\mathrm{kJ\,mol^{-1}}$ [Exercise 10.6a]

So $\Delta_{\mathrm{hyd}} G^\ominus(\mathrm{NO_3^-}) = (0.958) \times (-379\,\mathrm{kJ\,mol^{-1}}) = \boxed{-363\,\mathrm{kJ\,mol^{-1}}}$

E10.7(b) $I = \frac{1}{2}\sum_i (b_i/b^\ominus) z_i^2$ [10.18]

and for an $\mathrm{M}_p\mathrm{X}_q$ salt, $b_+/b^\ominus = pb/b^\ominus$, $b_-/b^\ominus = qb/b^\ominus$, so

$$I = \tfrac{1}{2}(pz_+^2 + qz_-^2) b/b^\ominus$$

(a) $I(\mathrm{MgCl_2}) = \frac{1}{2}(1 \times 2^2 + 2 \times 1) b/b^\ominus = 3b/b^\ominus$

(b) $I(\mathrm{Al_2(SO_4)_3}) = \frac{1}{2}(2 \times 3^2 + 3 \times 2^2) b/b^\ominus = 15b/b^\ominus$

(c) $I(\mathrm{Fe_2(SO_4)_3}) = \frac{1}{2}(2 \times 3^2 + 3 \times 2^2) b/b^\ominus = 15b/b^\ominus$

E10.8(b) $I = I(\mathrm{K_3[Fe(CN)_6]}) + I(\mathrm{KCl}) + I(\mathrm{NaBr}) = \frac{1}{2}(3 + 3^2)\dfrac{b(\mathrm{K_3[Fe(CN)_6]})}{b^\ominus} + \dfrac{b(\mathrm{KCl})}{b^\ominus} + \dfrac{b(\mathrm{NaBr})}{b^\ominus}$

$= (6) \times (0.040) + (0.030) + (0.050) = \boxed{0.320}$

Question. Can you establish that the statement in the comment following the solution to Exercise 10.8a (in the *Student's Solutions Manual*) holds for the solution of this exercise?

E10.9(b) $I = I(\mathrm{KNO_3}) = \dfrac{b}{b^\ominus}(\mathrm{KNO_3}) = 0.110$

Therefore, the ionic strengths of the added salts must be 0.890.

(a) $I(\mathrm{KNO_3}) = \dfrac{b}{b^\ominus}$, so $b(\mathrm{KNO_3}) = 0.890\,\mathrm{mol\,kg^{-1}}$

and $(0.890\,\mathrm{mol\,kg^{-1}}) \times (0.500\,\mathrm{kg}) = 0.445\,\mathrm{mol\ KNO_3}$

So $(0.445\,\mathrm{mol}) \times (101.11\,\mathrm{g\,mol^{-1}}) = \boxed{45.0\,\mathrm{g\ KNO_3}}$ must be added.

(b) $I(\text{Ba(NO}_3)_2) = \frac{1}{2}(2^2 + 2\times 1^2)\frac{b}{b^\ominus} = 3\frac{b}{b^\ominus} = 0.890$

$$b = \frac{0.890}{3}b^\ominus = 0.296\overline{7}\,\text{mol kg}^{-1}$$

and $(0.296\overline{7}\,\text{mol kg}^{-1})\times(0.500\,\text{kg}) = 0.148\overline{4}\,\text{mol Ba(NO}_3)_2$

So $(0.148\overline{4}\,\text{mol})\times(261.32\,\text{g mol}^{-1}) = \boxed{38.8\,\text{g Ba(NO}_3)_2}$

E10.10(b) $I(\text{Al}_2(\text{SO}_4)_3) = \frac{1}{2}((2\times 3^3)+(3\times 2^2))b/b^\ominus = 15b/b^\ominus$

$I(\text{Ca(NO}_3)_2) = \frac{1}{2}(2^2+2)b/b^\ominus = 3b/b^\ominus$

$3(0.500\,\text{mol kg}^{-1}) = 15(b(\text{Al}_2(\text{SO}_4)_3))$

$b(\text{Al}_2(\text{SO}_4)_3) = \frac{3}{15}(0.500\,\text{mol kg}^{-1}) = \boxed{0.100\,\text{mol kg}^{-1}}$

E10.11(b) $\gamma_\pm = (\gamma_+^p\gamma_-^q)^{1/s} \quad s = p+q$

For $\text{Al}_2(\text{SO}_4)_3$ $p=2, q=3, s=5$

$$\boxed{\gamma_\pm = (\gamma_+^2\gamma_-^3)^{1/5}}$$

E10.12(b) Since the solutions are dilute, use the Debye–Hückel limiting law

$$\log\gamma_\pm = -|z_+z_-|AI^{1/2}$$

$$I = \frac{1}{2}\sum_i z_i^2(b_i/b^\ominus) = \frac{1}{2}\{1\times(0.020)+1\times(0.020)+4\times(0.035)+2\times(0.035)\}$$

$$= 0.125$$

$$\log\gamma_\pm = -1\times 1\times 0.509\times(0.125)^{1/2} = -0.179\overline{96}$$

(For NaCl) $\gamma_\pm = 10^{-0.179\overline{96}}$

$= \boxed{0.661}$

E10.13(b) $I(\text{CaCl}_2) = \frac{1}{2}(4+2)b/b^\ominus = 3b/b^\ominus$

$\log\gamma_\pm = -2\times 1\times 0.509\times(0.300)^{1/2} = -0.557\overline{6}$

$\gamma_\pm = 10^{-0.557\overline{6}} = 0.277\overline{0} = 0.277$

$\text{Error} = \dfrac{0.524-0.277}{0.524}\times 100\text{ per cent} = \boxed{47.1\text{ per cent}}$

E10.14(b) The extended Debye–Hückel law is $\log\gamma_\pm = -\dfrac{A|z_+z_-|I^{1/2}}{1+BI^{1/2}}$

Solving for B

$$B = -\left(\frac{1}{I^{1/2}} + \frac{A|z_+z_-|}{\log\gamma_\pm}\right) = -\left(\frac{1}{(b/b^\ominus)^{1/2}} + \frac{0.509}{\log\gamma_\pm}\right)$$

Draw up the following table

$b/(\mathrm{mol\,kg^{-1}})$	5.0×10^{-3}	10.0×10^{-3}	50.0×10^{-3}
$\gamma_{\pm}$	0.927	0.902	0.816
B	$1.3\overline{2}$	$1.3\overline{6}$	$1.2\overline{9}$

$$B = \boxed{1.3}$$

E10.15(b) $\mathrm{PbI_2(s)} \rightleftharpoons \mathrm{PbI_2(aq)} \qquad K_\mathrm{S} = 1.4 \times 10^{-8}$

$$\begin{aligned}
\Delta_\mathrm{r}G^\ominus &= -RT\ln K_\mathrm{S} = -(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298.15\,\mathrm{K}) \times \ln(1.4 \times 10^{-8}) \\
&= 44.83\,\mathrm{kJ\,mol^{-1}} \\
\Delta_\mathrm{r}G^\ominus &= \Delta_\mathrm{f}G^\ominus(\mathrm{PbI_2, aq}) - \Delta_\mathrm{f}G^\ominus(\mathrm{PbI_2, s}) \\
\Delta_\mathrm{f}G^\ominus(\mathrm{PbI_2, aq}) &= \Delta_\mathrm{r}G^\ominus + \Delta_\mathrm{f}G^\ominus(\mathrm{PbI_2, s}) \\
&= 44.8\overline{3}\,\mathrm{kJ\,mol^{-1}} - 173.64\,\mathrm{kJ\,mol^{-1}} \\
&= \boxed{-128.8\,\mathrm{kJ\,mol^{-1}}}
\end{aligned}$$

E10.16(b) The Nernst equation may be applied to half-cell potentials as well as to overall cell potentials.

$$E(\mathrm{H^+/H_2}) = \frac{RT}{F}\ln\frac{a(\mathrm{H^+})}{(f_{\mathrm{H_2}}/p^\ominus)^{1/2}}$$

$$\Delta E = E_2 - E_1 = \frac{RT}{F}\ln\frac{a_2(\mathrm{H^+})}{a_1(\mathrm{H^+})}[f_{\mathrm{H_2}}\text{is constant}] = \frac{RT}{F}\ln\frac{\gamma_\pm b_2}{\gamma_\pm b_1}$$

$$= (25.7\,\mathrm{mV}) \times \ln\left[\frac{(0.830) \times (5.0 \times 10^{-2})}{(0.929) \times (5.0 \times 10^{-3})}\right] = \boxed{+56.3\,\mathrm{mV}}$$

E10.17(b) Identify electrodes using species with the desired oxidation states.

L: $\mathrm{Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-}$

R: $\mathrm{Ni(OH)_3(s) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)}$

$\mathrm{Cd(s)|Cd(OH)_2(s)|OH^-(aq)|Ni(OH)_2(s)|Ni(OH)_3(s)|Pt}$

E10.18(b) The cell notation specifies the right and left electrodes. Note that for proper cancellation we must equalize the number of electrons in half-reactions being combined.

(a)
R: $\mathrm{Ag_2CrO_4(s) + 2e^- \rightarrow 2Ag(s) + CrO_4^{2-}(aq)}$ $\quad +0.45\,\mathrm{V}$
L: $\mathrm{Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)}$ $\quad +1.36\,\mathrm{V}$
Overall (R − L): $\mathrm{Ag_2CrO_4(s) + 2Cl^-(aq) \rightarrow 2Ag(s) + CrO_4^{2-}(aq) + Cl_2(g)}$ $\quad -0.91\,\mathrm{V}$

(b)
R: $\mathrm{Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)}$ $\quad +0.15\,\mathrm{V}$
L: $\mathrm{2Fe^{3+}(aq) + 2e^- \rightarrow 2Fe^{2+}(aq)}$ $\quad +0.77\,\mathrm{V}$
Overall (R − L): $\mathrm{Sn^{4+}(aq) + 2Fe^{2+}(aq) \rightarrow Sn^{2+}(aq) + 2Fe^{3+}(aq)}$ $\quad -0.62\,\mathrm{V}$

(c)
R: $\mathrm{MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)}$ $\quad +1.23\,\mathrm{V}$
L: $\mathrm{Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)}$ $\quad +0.34\,\mathrm{V}$
Overall (R − L): $\mathrm{Cu(s) + MnO_2(s) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + Mn^{2+}(aq)}$
$\mathrm{+ 2H_2O(l)}$ $\quad +0.89\,\mathrm{V}$

Comment. Those cells for which $E^{\ominus} > 0$ may operate as spontaneous galvanic cells under standard conditions. Those for which $E^{\ominus} < 0$ may operate as nonspontaneous electrolytic cells. Recall that $E^{\ominus}$ informs us of the spontaneity of a cell under standard conditions only. For other conditions we require E.

E10.19(b) The conditions (concentrations, etc.) under which these reactions occur are not given. For the purposes of this exercise we assume standard conditions. The specification of the right and left electrodes is determined by the direction of the reaction as written. As always, in combining half-reactions to form an overall cell reaction we must write half-reactions with equal number of electrons to ensure proper cancellation. We first identify the half-reactions, and then set up the corresponding cell.

(a) R: $2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$ $\quad -0.83\,V$
L: $2Na^+(aq) + 2e^- \rightarrow 2Na(s)$ $\quad -2.71\,V$

and the cell is

$Na(s)|Na^+(aq), OH^-(aq)|H_2(g)|Pt$ $\quad \boxed{+1.88\,V}$

or more simply

$$\boxed{Na(s)|NaOH(aq)|H_2(g)|Pt}$$

(b) R: $I_2(s) + 2e^- \rightarrow 2I^-(aq)$ $\quad +0.54\,V$
L: $2H^+(aq) + 2e^- \rightarrow H_2(g)$ $\quad 0$

and the cell is

$Pt|H_2(g)|H^+(aq), I^-(aq)|I_2(s)|Pt$ $\quad \boxed{+0.54\,V}$

or more simply

$$\boxed{Pt|H_2(g)|HI(aq)|I_2(s)|Pt}$$

(c) R: $2H^+(aq) + 2e^- \rightarrow H_2(g)$ $\quad 0.00\,V$
L: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $\quad -0.083\,V$

and the cell is

$Pt|H_2(g)|H^+(aq), OH^-(aq)|H_2(g)|Pt$ $\quad \boxed{0.083\,V}$

or more simply

$$\boxed{Pt|H_2(g)|H_2O(l)|H_2(g)|Pt}$$

Comment. All of these cells have $E^{\ominus} > 0$, corresponding to a spontaneous cell reaction under standard conditions. If $E^{\ominus}$ had turned out to be negative, the spontaneous reaction would have been the reverse of the one given, with the right and left electrodes of the cell also reversed.

E10.20(b) See the solutions for Exercise 10.18(b), where we have used $E^{\ominus} = E_R^{\ominus} - E_L^{\ominus}$, with standard electrode potentials from Table 10.7.

E10.21(b) See the solutions for Exercise 10.19(b), where we have used $E^{\ominus} = E_R^{\ominus} - E_L^{\ominus}$, with standard electrode potentials from Table 10.7.

E10.22(b) In each case find $E^{\ominus} = E_R^{\ominus} - E_L^{\ominus}$ from the data in Table 10.7, then use

$$\Delta_r G^{\ominus} = -\nu F E^{\ominus} \text{ [10.32]}$$

(a) $$\left.\begin{array}{lll} \text{R:} & S_2O_8^{2-}(aq) + 2e^- \rightarrow 2SO_4^{2-}(aq) & +2.05\,V \\ \text{L:} & I_2(s) + 2e^- \rightarrow 2I^-(aq) & +0.54\,V \end{array}\right\} +1.51\,V$$

$$\Delta_r G^{\ominus} = (-2) \times (96.485\,kC\,mol^{-1}) \times (1.51\,V) = \boxed{-291\,kJ\,mol^{-1}}$$

(b)
$$\left.\begin{array}{lr}\mathrm{Zn^{2+}(aq)} + 2\mathrm{e^-} \rightarrow \mathrm{Zn(s)} & -0.76\,\mathrm{V} \\ \mathrm{Pb^{2+}(aq)} + 2\mathrm{e^-} \rightarrow \mathrm{Pb(s)} & -0.13\,\mathrm{V}\end{array}\right\} E^{\ominus} = -0.63\,\mathrm{V}$$

$$\Delta_r G^{\ominus} = (-2) \times (96.485\,\mathrm{kC\,mol^{-1}}) \times (-0.63\,\mathrm{V}) = \boxed{+122\,\mathrm{kJ\,mol^{-1}}}$$

E10.23(b) **(a)** A new half-cell may be obtained by the process (3) = (1) − (2), that is

$$(3)\ 2\mathrm{H_2O(l)} + \mathrm{Ag(s)} + \mathrm{e^-} \rightarrow \mathrm{H_2(g)} + 2\mathrm{OH^-(aq)} + \mathrm{Ag^+(aq)}$$

But, $E_3^{\ominus} \neq E_1^{\ominus} - E_2^{\ominus}$, for the reason that the reduction potentials are intensive, as opposed to extensive, quantities. Only extensive quantities are additive. However, the $\Delta_r G^{\ominus}$ values of the half-reactions are extensive properties, and thus

$$\Delta_r G_3^{\ominus} = \Delta_r G_1^{\ominus} - \Delta_r G_2^{\ominus}$$
$$-\nu_3 F E_3^{\ominus} = -\nu_1 F E_1^{\ominus} - (-\nu_2 F E_2^{\ominus})$$

Solving for $E_3^{\ominus}$ we obtain

$$E_3^{\ominus} = \frac{\nu_1 E_1^{\ominus} - \nu_2 E_2^{\ominus}}{\nu_3} = \frac{(2) \times (-0.828\,\mathrm{V}) - (1) \times (0.799\,\mathrm{V})}{1} = \boxed{-2.455\,\mathrm{V}}$$

(b) The complete cell reactions is obtained in the usual manner. We take (2) × (2) − (1) to obtain

$$2\mathrm{Ag^+(aq)} + \mathrm{H_2(g)} + 2\mathrm{OH^-(aq)} \rightarrow 2\mathrm{Ag(s)} + 2\mathrm{H_2O(l)}$$
$$E^{\ominus}(\text{cell}) = E_R^{\ominus} - E_L^{\ominus} = E_2^{\ominus} - E_1^{\ominus} = (0.799\,\mathrm{V}) - (-0.828\,\mathrm{V}) = \boxed{+1.627\,\mathrm{V}}$$

Comment. The general relation for $E^{\ominus}$ of a new half-cell obtained from two others is

$$E_3^{\ominus} = \frac{\nu_1 E_1^{\ominus} \pm \nu_2 E_2^{\ominus}}{\nu_3}$$

E10.24(b) **(a)**
$$E = E^{\ominus} - \frac{RT}{\nu F}\ln Q \quad \nu = 2$$
$$Q = \prod_J a_J^{\nu_J} = a_{\mathrm{H^+}}^2 a_{\mathrm{Cl^-}}^2 \quad [\text{all other activities} = 1]$$
$$= a_+^2 a_-^2 = (\gamma_+ b_+)^2 \times (\gamma_- b_-)^2 \quad \left[b \equiv \frac{b}{b^{\ominus}} \text{ here and below}\right]$$
$$= (\gamma_+\gamma_-)^2 \times (b_+ b_-)^2 = \gamma_\pm^4 b^4 \quad [16,\ b_+ = b, b_- = b]$$

Hence, $E = E^{\ominus} - \dfrac{RT}{2F}\ln(\gamma_\pm^4 b^4) = \boxed{E^{\ominus} - \dfrac{2RT}{F}\ln(\gamma_\pm b)}$

(b) $\Delta_r G = -\nu F E[10.32] = -(2) \times (9.6485 \times 10^4\,\mathrm{C\,mol^{-1}}) \times (0.4658\,\mathrm{V}) = \boxed{-89.89\,\mathrm{kJ\,mol^{-1}}}$

(c) $\log \gamma_\pm = -|z_+ z_-| A I^{1/2}$ [19] $= -(0.509) \times (0.010)^{1/2}$ [$I = b$ for HCl(aq)] $= -0.0509$
$\gamma_\pm = 0.889$

$$E^{\ominus} = E + \frac{2RT}{F}\ln(\gamma_\pm b) = (0.4658\,\mathrm{V}) + (2) \times (25.693 \times 10^{-3}\,\mathrm{V}) \times \ln(0.889 \times 0.010)$$
$$= \boxed{+0.223\,\mathrm{V}}$$

The value compares favourably to that given in Table 10.7.

E10.25(b) R: $\mathrm{Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)}$

L: $\mathrm{2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)}$

R − L: $\mathrm{2Ag(s) + Fe^{2+}(aq) \rightarrow 2Ag^+(aq) + Fe(s)}$

$$E^\ominus = E^\ominus_\mathrm{R} - E^\ominus_\mathrm{L} = (-0.44\,\mathrm{V}) - (0.80\,\mathrm{V}) = \boxed{-1.24\,\mathrm{V}}$$

$$\Delta_\mathrm{r}G^\ominus = -\nu F E^\ominus = -2 \times (9.65 \times 10^4\,\mathrm{C\,mol^{-1}}) \times (-1.24\,\mathrm{V})$$

$$= \boxed{+239\,\mathrm{kJ\,mol^{-1}}}$$

$$\Delta_\mathrm{r}H^\ominus = 2\Delta_\mathrm{f}H^\ominus(\mathrm{Ag^+, aq}) - \Delta_\mathrm{f}H^\ominus(\mathrm{Fe^{2+}, aq}) = [(2) \times (105.58) - (-89.1)]\,\mathrm{kJ\,mol^{-1}}$$

$$= \boxed{+300.3\,\mathrm{kJ\,mol^{-1}}}$$

$$\left(\frac{\partial \Delta_\mathrm{r}G^\ominus}{\partial T}\right)_p = -\Delta_\mathrm{r}S^\ominus = \frac{\Delta_\mathrm{r}G^\ominus - \Delta_\mathrm{r}H^\ominus}{T} \quad [\Delta_\mathrm{r}G^\ominus = \Delta_\mathrm{r}H - T\Delta_\mathrm{r}S]$$

$$= \frac{(239 - 300.3)\,\mathrm{kJ\,mol^{-1}}}{298.15\,\mathrm{K}} = -0.206\,\mathrm{kJ\,mol^{-1}\,K^{-1}}$$

Therefore, $\Delta_\mathrm{r}G^\ominus(308\,\mathrm{K}) \approx (239) + (10\,\mathrm{K}) \times (-0.206\,\mathrm{K^{-1}})\,\mathrm{kJ\,mol^{-1}} \approx \boxed{+237\,\mathrm{kJ\,mol^{-1}}}$

E10.26(b) In each case $\ln K = \dfrac{\nu F E^\ominus}{RT}$ [10.36]

(a) $\mathrm{Sn(s) + CuSO_4(aq) \rightleftharpoons Cu(s) + SnSO_4(aq)}$

$$\left.\begin{array}{lll} \mathrm{R:} & \mathrm{Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)} & +0.34\,\mathrm{V} \\ \mathrm{L:} & \mathrm{Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)} & -0.14\,\mathrm{V} \end{array}\right\} +0.48\,\mathrm{V}$$

$$\ln K = \frac{(2) \times (0.48\,\mathrm{V})}{25.693\,\mathrm{mV}} = +37.\bar{4}, \qquad K = \boxed{1.7 \times 10^{16}}$$

(b) $\mathrm{Cu^{2+}(aq) + Cu(s) \rightleftharpoons 2Cu^+(aq)}$

$$\left.\begin{array}{lll} \mathrm{R:} & \mathrm{Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)} & +0.16\,\mathrm{V} \\ \mathrm{L:} & \mathrm{Cu^+(aq) + e^- \rightarrow Cu(s)} & +0.52\,\mathrm{V} \end{array}\right\} -0.36\,\mathrm{V}$$

$$\ln K = \frac{-0.36\,\mathrm{V}}{25.693\,\mathrm{mV}} = -14.\bar{0}, \qquad K = \boxed{8.2 \times 10^{-7}}$$

E10.27(b) We need to obtain $E^\ominus$ for the couple

(3) $\mathrm{Co^{3+}(aq) + 3e^- \rightarrow Co(s)}$

from the values of $E^\ominus$ for the couples

(1) $\mathrm{Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)}$ $\quad E^\ominus_1 = 1.81\,\mathrm{V}$

(2) $\mathrm{Co^{2+}(aq) + 2e^- \rightarrow Co(s)}$ $\quad E^\ominus_2 = -0.28\,\mathrm{V}$

We see that (3) = (1) + (2); therefore (see the solution to Exercise 10.23(b))

$$E_3 = \frac{\nu_1 E^\ominus_1 + \nu_2 E^\ominus_2}{\nu_3} = \frac{(1) \times (1.81\,\mathrm{V}) + (2) \times (-0.28\,\mathrm{V})}{3} = 0.42\,\mathrm{V}$$

Then,

R: $\mathrm{Co^{3+}(aq) + 3e^- \rightarrow Co(s)}$ $\qquad E_R^{\ominus} = 0.42\,\mathrm{V}$
L: $\mathrm{3AgCl(s) + 3e^- \rightarrow 3Ag(s) + 3Cl^-(aq)}$ $\qquad E_L^{\ominus} = 0.22\,\mathrm{V}$
R − L: $\mathrm{Co^{3+}(aq) + 3Cl^-(aq) + 3Ag(s) \rightarrow 3AgCl(s) + Co(s)}$
$E^{\ominus} = E_R^{\ominus} - E_L^{\ominus} = (0.42\,\mathrm{V}) - (0.22\,\mathrm{V}) = \boxed{+0.20\,\mathrm{V}}$

E10.28(b) First assume all activity coefficients are 1 and calculate K_S°, the ideal solubility product constant.

(1) $\mathrm{AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)}$
$S(\mathrm{AgI}) = b(\mathrm{Ag^+}) = b(\mathrm{I^-})$ because all stoichiometric coefficients are 1.

$$\text{Thus } K_S^{\circ} = \frac{b(\mathrm{Ag^+})b(\mathrm{I^-})}{b^{\ominus 2}} = \frac{S^2}{b^{\ominus 2}} = (1.2 \times 10^{-8})^2 = \boxed{1.4\overline{4} \times 10^{-16}}$$

(2) $\mathrm{Bi_2S_3(s) \rightleftharpoons 2Bi^{3+}(aq) + 3S^{2-}(aq)}$

$b(\mathrm{Bi^{3+}}) = 2S(\mathrm{Bi_2S_3})$

$b(\mathrm{S^{2-}}) = 3S(\mathrm{Bi_2S_3})$

$$K_S^{\circ} = \frac{(b(\mathrm{Bi^{3+}}))^2 \times (b(\mathrm{S^{2-}}))^3}{b^{\ominus 5}} = \frac{(2S)^2 \times (3S)^3}{b^{\ominus 5}} = 108\left(\frac{S}{b^{\ominus}}\right)^5$$

$$= \boxed{1.1\overline{3} \times 10^{-97}}$$

For AgI, $K_S = \gamma_{\pm}^2 K_S^{\circ}$

$\log \gamma_{\pm} = -|z_+z_-|AI^{1/2} \qquad A = 0.509$

$I = Sb^{\ominus}, \qquad |z_+z_-| = 1$ so

$\log \gamma_{\pm} = -(0.509) \times (1.2 \times 10^{-8})^{1/2} = -5.58 \times 10^{-5}$

$\gamma_{\pm} = 0.999\overline{9}$

$K_S = (0.999\overline{9})^2 K_S^{\circ} = 0.999\overline{7} K_S^{\circ}$

For $\mathrm{Bi_2S_3}$, $I = 15b/b^{\ominus} = 15Sb^{\ominus}$, $|z_+z_-| = 6$
so $\log \gamma_{\pm} = -(0.509) \times (6) \times [15(1.6 \times 10^{-20})]^{1/2} = -1.49\overline{6} \times 10^{-9}$

$\gamma_{\pm} = 1.0$

$K_S = \gamma_{\pm}^5 K_S^{\circ} = K_S^{\circ}$

Neglect of activity coefficients is not significant for AgI and $\mathrm{Bi_2S_3}$.

E10.29(b) The Nernst equation applies to half-reactions as well as whole reactions; thus for

$\mathrm{8H^+ + MnO_4^-(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O}$

$$E = E^{\ominus} - \frac{RT}{5F}\ln\frac{a(\mathrm{Mn^{2+}})}{a(\mathrm{MnO_4^-})a(\mathrm{H^+})^8}$$

E10.30(b) R: $\mathrm{2AgI(s) + 2e^- \rightarrow 2Ag(s) + 2I^-(aq)}$ $\quad -0.15\,\mathrm{V}$
L: $\mathrm{2H^+(aq) + 2e^- \rightarrow H_2(g)}$ $\quad 0\,\mathrm{V}$

Overall(R − L): $\mathrm{2AgI(s) + H_2(g) \rightarrow 2Ag(s) + 2H^+(aq) + 2I^-(aq)}$

$Q = a(\mathrm{H^+})^2 a(\mathrm{I^-})^2 \qquad \nu = 2$

Assume $a(\mathrm{H^+}) = a(\mathrm{I^-})$, $Q = a(\mathrm{H^+})^4$

$$E = E^{\ominus} - \frac{RT}{2F}\ln a(\mathrm{H}^+)^4 = E^{\ominus} - \frac{2RT}{F}\ln a(\mathrm{H}^+) = E^{\ominus} + 2 \times (2.303) \times \left(\frac{RT}{F}\right) \times \mathrm{pH}$$

$$\mathrm{pH} = \left(\frac{F}{2 \times (2.303RT)}\right) \times (E - E^{\ominus}) = \frac{E + 0.15\,\mathrm{V}}{0.1183\,\mathrm{V}} = \frac{1.15\,\mathrm{V}}{0.1183\,\mathrm{V}} = \boxed{9.72}$$

E10.31(b) The electrode reactions are

L: $\mathrm{Ag^+(aq) + e^- \rightarrow Ag(s)}$

R: $\mathrm{AgI(s) + e^- \rightarrow Ag(s) + I^-(aq)}$

Overall(R − L): $\mathrm{AgI(s) \rightarrow Ag^+(aq) + I^-(aq)}$

Since the cell reaction is a solubility equilibrium, for a saturated solution there is no further tendency to dissolve and so $E = \boxed{0}$

E10.32(b) R: $\mathrm{2Bi^{3+}(aq) + 6e^- \rightarrow 2Bi(s)}$

L: $\mathrm{Bi_2S_3(s) + 6e^- \rightarrow 2Bi(s) + 3S^{2-}(aq)}$

Overall(R − L): $\mathrm{2Bi^{3+}(aq) + 3S^{2-}(aq) \rightarrow Bi_2S_3(s)}$ $\quad \nu = 6$

$$\begin{aligned}\ln K &= \frac{\nu F E^{\ominus}}{RT}\\ &= \frac{6(0.96\,\mathrm{V})}{(25.693 \times 10^{-3}\,\mathrm{V})}\\ &= 22\bar{4}\\ K &= \mathrm{e}^{22\bar{4}}\end{aligned}$$

It is convenient to give the solution for **(b)** first.

(b) $K_\mathrm{S} = K^{-1} = \mathrm{e}^{-22\bar{4}} \approx \boxed{10^{-98}}$, since the cell reaction is the reverse of the solubility equilibrium.

(a) $$K_\mathrm{S} \approx 10^{-98} = \left[\frac{b}{b^{\ominus}}(\mathrm{Bi^{3+}})\right]^2 \times \left[\frac{b}{b^{\ominus}}(\mathrm{S^{2-}})\right]^3 = (2S)^2 \times (3S)^3 = 108S^5$$

$$S = \left(\frac{10^{-98}}{108}\right)^{1/5} \approx \boxed{10^{-20}\,\mathrm{mol\,L^{-1}}}$$

Solutions to problems

Solutions to numerical problems

P10.1 We require two half-cell reactions, which upon subtracting one (left) from the other (right), yields the given overall reaction (Section 10.4). The half-reaction at the right electrode corresponds to reduction, that at the left electrode to oxidation, though all half-reactions are listed in Table 10.7 as reduction reactions.

	$E^{\ominus}$
R: $\mathrm{Hg_2SO_4(s) + 2e^- \rightarrow 2Hg(l) + SO_4^{2-}(aq)}$	+0.62 V
L: $\mathrm{PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)}$	−0.36 V
R − L: $\mathrm{Pb(s) + Hg_2SO_4(s) \rightarrow PbSO_4(s) + 2Hg(l)}$	+0.98 V

Hence, a suitable cell would be

$$\mathrm{Pb(s)|PbSO_4(s)|H_2SO_4(aq)|Hg_2SO_4(s)|Hg(l)}$$

or, alternatively,

$$\mathrm{Pb(s)|PbSO_4(s)|H_2SO_4(aq)\|H_2SO_4(aq)\|Hg_2SO_4(s)|Hg(l)}$$

For the cell in which the only sources of electrolyte are the slightly soluble salts, $PbSO_4$ and Hg_2SO_4, the cell would be

$$\mathrm{Pb(s)|PbSO_4(s)|PbSO_4(aq)\|Hg_2SO_4(aq)|Hg_2SO_4(s)|Hg(l)}$$

The potential of this cell is given by the Nernst equation [10.34].

$$E = E^{\ominus} - \frac{RT}{\nu F}\ln Q\ [10.34]; \quad \nu = 2$$

$$Q = \frac{a_{\mathrm{Pb^{2+}}}a_{\mathrm{SO_4^{2-}}}}{a_{\mathrm{Hg_2^{2+}}}a_{\mathrm{SO_4^{2-}}}} = \frac{K_{\mathrm{S}}(\mathrm{PbSO_4})}{K_{\mathrm{S}}(\mathrm{Hg_2SO_4})}$$

$$E = (0.98\,\mathrm{V}) - \frac{RT}{2F}\ln\frac{K_{\mathrm{S}}(\mathrm{PbSO_4})}{K_{\mathrm{S}}(\mathrm{Hg_2SO_4})}$$

$$= (0.98\,\mathrm{V}) - \left(\frac{25.693\times10^{-3}\,\mathrm{V}}{2}\right)\times\ln\left(\frac{1.6\times10^{-8}}{6.6\times10^{-7}}\right)$$

[Table 10.6, 4th Edition, or *CRC Handbook*]

$$= (0.98\,\mathrm{V}) + (0.05\,\mathrm{V}) = \boxed{+1.03\,\mathrm{V}}$$

P10.6 $\mathrm{Pt|H_2(g)|NaOH(aq), NaCl(aq)|AgCl(s)|Ag(s)}$

$\mathrm{H_2(s) + 2AgCl(s) \rightarrow 2Ag(s) + 2Cl^-(aq) + 2H^+(aq)} \quad \nu = 2$

$$E = E^{\ominus} - \frac{RT}{2F}\ln Q, \quad Q = a(\mathrm{H^+})^2a(\mathrm{Cl^-})^2 \qquad [f/p^{\ominus} = 1]$$

$$= E^{\ominus} - \frac{RT}{F}\ln a(\mathrm{H^+})a(\mathrm{Cl^-}) = E^{\ominus} - \frac{RT}{F}\ln\frac{K_{\mathrm{w}}a(\mathrm{Cl^-})}{a(\mathrm{OH^-})} = E^{\ominus} - \frac{RT}{F}\ln\frac{K_{\mathrm{w}}\gamma_{\pm}b(\mathrm{Cl^-})}{\gamma_{\pm}b(\mathrm{OH^-})}$$

$$= E^{\ominus} - \frac{RT}{F}\ln\frac{K_{\mathrm{w}}b(\mathrm{Cl^-})}{b(\mathrm{OH^-})} = E^{\ominus} - \frac{RT}{F}\ln K_{\mathrm{w}} - \frac{RT}{F}\ln\frac{b(\mathrm{Cl^-})}{b(\mathrm{OH^-})}$$

$$= E^{\ominus} + (2.303)\frac{RT}{F}\times \mathrm{p}K_{\mathrm{w}} - \frac{RT}{F}\ln\frac{b(\mathrm{Cl^-})}{b(\mathrm{OH^-})} \qquad \left(\mathrm{p}K_{\mathrm{w}} = -\log K_{\mathrm{w}} = \frac{-\ln K_{\mathrm{w}}}{2.303}\right)$$

Hence, $\mathrm{p}K_{\mathrm{w}} = \dfrac{E - E^{\ominus}}{2.303RT/F} + \dfrac{\ln\left(\frac{b(\mathrm{Cl^-})}{b(\mathrm{OH^-})}\right)}{2.303} = \dfrac{E - E^{\ominus}}{2.303RT/F} + 0.05114$

$$E^{\ominus} = E^{\ominus}_{\mathrm{R}} - E^{\ominus}_{\mathrm{L}} = E^{\ominus}(\mathrm{AgCl, Ag}) - E^{\ominus}(\mathrm{H^+/H_2}) = +0.22\,\mathrm{V} - 0\ [\text{Table 10.7}]$$

We then draw up the following table with the more precise value for $E^{\ominus} = +0.2223\,\mathrm{V}$ [Problem 10.8]

$\theta/^{\circ}\mathrm{C}$	20.0	25.0	30.0
E/V	1.04774	1.04864	1.04942
$\dfrac{\frac{2.303RT}{F}}{\mathrm{V}}$	0.05819	0.05918	0.06018
$\mathrm{p}K_{\mathrm{w}}$	$\boxed{14.23}$	14.01	13.79

$$\frac{\mathrm{d}\ln K_{\mathrm{w}}}{\mathrm{d}T} = \frac{\Delta_{\mathrm{r}}H^{\ominus}}{RT^2}\ [9.26]$$

Hence, $\Delta_{\mathrm{r}}H^{\ominus} = -(2.303)RT^2\dfrac{\mathrm{d}}{\mathrm{d}T}(\mathrm{p}K_{\mathrm{w}})$

then with $\dfrac{\mathrm{d\,p}K_{\mathrm{w}}}{\mathrm{d}T} \approx \dfrac{\Delta \mathrm{p}K_{\mathrm{w}}}{\Delta T}$

$$\Delta_{\mathrm{r}}H^{\ominus} \approx -(2.303)\times(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298.15\,\mathrm{K})^2\times\frac{13.79-14.23}{10\,\mathrm{K}}$$

$$= \boxed{+74.9\,\mathrm{kJ\,mol^{-1}}}$$

$$\Delta_{\mathrm{r}}G^{\ominus} = -RT\ln K_{\mathrm{w}} = 2.303RT\times \mathrm{p}K_{\mathrm{w}} = \boxed{+80.0\,\mathrm{kJ\,mol^{-1}}}$$

$$\Delta_{\mathrm{r}}S^{\ominus} = \frac{\Delta_{\mathrm{r}}H^{\ominus}-\Delta_{\mathrm{r}}G^{\ominus}}{T} = \boxed{-17.1\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

See the original reference for a careful analysis of the precise data.

P10.7 The cells described in the problem are back-to-back pairs of cells each of the type

$$\mathrm{Ag(s)|AgX(s)|MX}(b_1)|\mathrm{M}_x\mathrm{Hg(s)}$$

R: $\mathrm{M}^+(b_1) + \mathrm{e}^- \xrightarrow{\mathrm{Hg}} \mathrm{M}_x\mathrm{Hg(s)}$ (Reduction of M^+ and formation of amalgam)

L: $\mathrm{AgX(s)} + \mathrm{e}^- \rightarrow \mathrm{Ag(s)} + \mathrm{X}^-(b_1)$

R − L: $\mathrm{Ag(s)} + \mathrm{M}^+(b_1) + \mathrm{X}^-(b_1) \xrightarrow{\mathrm{Hg}} \mathrm{M}_x\mathrm{Hg(s)} + \mathrm{AgX(s)} \quad \nu = 1$

$$Q = \frac{a(\mathrm{M}_x\mathrm{Hg})}{a(\mathrm{M}^+)a(\mathrm{X}^-)}$$

$$E = E^{\ominus} - \frac{RT}{F}\ln Q$$

For a pair of such cells back to back,

$$\mathrm{Ag(s)|AgX(s)|MX}(b_1)|\mathrm{M}_x\mathrm{Hg(s)|MX}(b_2)|\mathrm{AgX(s)|Ag(s)}$$

$$E_{\mathrm{R}} = E^{\ominus} - \frac{RT}{F}\ln Q_{\mathrm{R}} \qquad E_{\mathrm{L}} = E^{\ominus} - \frac{RT}{F}\ln Q_{\mathrm{L}}$$

$$E = \frac{-RT}{F}\ln\frac{Q_{\mathrm{L}}}{Q_{\mathrm{R}}} = \frac{RT}{F}\ln\frac{(a(\mathrm{M}^+)a(\mathrm{X}^-))_{\mathrm{L}}}{(a(\mathrm{M}^+)a(\mathrm{X}^-))_{\mathrm{R}}}$$

(Note that the unknown quantity $a(\mathrm{M}_x\mathrm{Hg})$ drops out of the expression for E.)

$$a(\mathrm{M}^+)a(\mathrm{X}^-) = \left(\frac{\gamma_+b_+}{b^{\ominus}}\right)\left(\frac{\gamma_-b_-}{b^{\ominus}}\right) = \gamma_{\pm}^2\left(\frac{b}{b^{\ominus}}\right)^2 \quad (b_+ = b_-)$$

With L = (1) and R = (2) we have

$$E = \frac{2RT}{F}\ln\frac{b_1}{b_2} + \frac{2RT}{F}\ln\frac{\gamma_{\pm}(1)}{\gamma_{\pm}(2)}$$

Take $b_2 = 0.09141\,\mathrm{mol\,kg^{-1}}$ (the reference value), and write $b = \dfrac{b_1}{b^{\ominus}}$

$$E = \frac{2RT}{F}\left(\ln\frac{b}{0.09141} + \ln\frac{\gamma_{\pm}}{\gamma_{\pm}(\mathrm{ref})}\right)$$

For $b = 0.09141$, the extended Debye–Hückel law gives

$$\log \gamma_{\pm}(\text{ref}) = \frac{(-1.461) \times (0.09141)^{1/2}}{(1) + (1.70) \times (0.09141)^{1/2}} + (0.20) \times (0.09141) = -0.273\overline{5}$$

$$\gamma_{\pm}(\text{ref}) = 0.532\overline{8}$$

$$\text{then } E = (0.05139\,\text{V}) \times \left(\ln \frac{b}{0.09141} + \ln \frac{\gamma_{\pm}}{0.5328}\right)$$

$$\ln \gamma_{\pm} = \frac{E}{0.05139\,\text{V}} - \ln \frac{b}{(0.09141) \times (0.05328)}$$

We then draw up the following table

$b/(\text{mol/kg}^{-1})$	0.0555	0.09141	0.1652	0.2171	1.040	1.350
E/V	−0.0220	0.0000	0.0263	0.0379	0.1156	0.1336
γ	0.572	$\boxed{0.533}$	0.492	0.469	0.444	0.486

A more precise procedure is described in the original references for the temperature dependence of $E^{\ominus}(\text{Ag, AgCl, Cl}^-)$, see Problem 10.10.

P10.10 The method of the solution is first to determine $\Delta_r G^{\ominus}$, $\Delta_r H^{\ominus}$, and $\Delta_r S^{\ominus}$ for the cell reaction

$$\tfrac{1}{2}\text{H}_2(\text{g}) + \text{AgCl(s)} \rightarrow \text{Ag(s)} + \text{HCl(aq)}$$

and then, from the values of these quantities and the known values of $\Delta_f G^{\ominus}$, $\Delta_f H^{\ominus}$, and $S^{\ominus}$ for all the species other than $\text{Cl}^-(\text{aq})$, to calculate $\Delta_f G^{\ominus}$, $\Delta_f H^{\ominus}$, and $S^{\ominus}$ for $\text{Cl}^-(\text{aq})$.

$$\Delta_r G^{\ominus} = -\nu F E^{\ominus}$$

At 298.15 K(25.00°C)

$$E^{\ominus}/\text{V} = (0.23659) - (4.8564 \times 10^{-4}) \times (25.00) - (3.4205 \times 10^{-6}) \times (25.00)^2$$
$$+ (5.869 \times 10^{-9}) \times (25.00)^3 = +0.22240\,\text{V}$$

Therefore, $\Delta G^{\ominus} = -(96.485\,\text{kC mol}^{-1}) \times (0.22240\,\text{V}) = -21.46\,\text{kJ mol}^{-1}$

$$\Delta_r S^{\ominus} = -\left(\frac{\partial \Delta_r G^{\ominus}}{\partial T}\right)_p = \left(\frac{\partial E^{\ominus}}{\partial T}\right)_p \times \nu F = \nu F \left(\frac{\partial E^{\ominus}}{\partial \theta}\right)_p \frac{{}^\circ\text{C}}{\text{K}} \quad [\text{d}\theta/{}^\circ\text{C} = \text{d}T/\text{K}] \qquad \text{(a)}$$

$$\frac{\left(\frac{\partial E^{\ominus}}{\partial \theta}\right)_p}{\text{V}} = (-4.8564 \times 10^{-4}/{}^\circ\text{C}) - (2) \times (3.4205 \times 10^{-6}\theta/({}^\circ\text{C})^2)$$
$$+ (3) \times (5.869 \times 10^{-9}\theta^2/({}^\circ\text{C})^3)$$

$$\frac{\left(\frac{\partial E^{\ominus}}{\partial \theta}\right)_p}{\text{V}/{}^\circ\text{C}} = (-4.8564 \times 10^{-4}) - (6.8410 \times 10^{-6}(\theta/{}^\circ\text{C})) + (1.7607 \times 10^{-8}(\theta/{}^\circ\text{C})^2)$$

Therefore, at 25.00°C,

$$\left(\frac{\partial E^{\ominus}}{\partial \theta}\right)_p = -6.4566 \times 10^{-4}\,\text{V}/{}^\circ\text{C}$$

and

$$\left(\frac{\partial E^{\ominus}}{\partial T}\right)_p = (-6.4566 \times 10^{-4}\,\text{V}/{}^\circ\text{C}) \times ({}^\circ\text{C/K}) = -6.4566 \times 10^{-4}\,\text{V K}^{-1}$$

Hence, from equation (a)

$$\Delta_r S^\ominus = (-96.485\,\mathrm{kC\,mol^{-1}}) \times (6.4566 \times 10^{-4}\,\mathrm{V\,K^{-1}}) = -62.30\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

and $\Delta_r H^\ominus = \Delta_r G^\ominus + T\Delta_r S^\ominus$

$$= -(21.46\,\mathrm{kJ\,mol^{-1}}) + (298.15\,\mathrm{K}) \times (-62.30\,\mathrm{J\,K^{-1}\,mol^{-1}}) = -40.03\,\mathrm{kJ\,mol^{-1}}$$

For the cell reaction

$$\tfrac{1}{2}\mathrm{H_2(g)} + \mathrm{AgCl(s)} \rightarrow \mathrm{Ag(s)} + \mathrm{HCl(aq)}$$

$$\begin{aligned}\Delta_r G^\ominus &= \Delta_f G^\ominus(\mathrm{H^+}) + \Delta_f G^\ominus(\mathrm{Cl^-}) - \Delta_f G^\ominus(\mathrm{AgCl})\\ &= \Delta_f G^\ominus(\mathrm{Cl^-}) - \Delta_f G^\ominus(\mathrm{AgCl}) \quad [\Delta_f G^\ominus(\mathrm{H^+}) = 0]\end{aligned}$$

Hence, $\Delta_f G^\ominus(\mathrm{Cl^-}) = \Delta_r G^\ominus + \Delta_f G^\ominus(\mathrm{AgCl}) = [(-21.46) - (109.79)]\,\mathrm{kJ\,mol^{-1}}$

$$= \boxed{-131.25\,\mathrm{kJ\,mol^{-1}}}$$

Similarly, $\Delta_f H^\ominus(\mathrm{Cl^-}) = \Delta_r H^\ominus + \Delta_f H^\ominus(\mathrm{AgCl}) = (-40.03) - (127.07\,\mathrm{kJ\,mol^{-1}})$

$$= \boxed{-167.10\,\mathrm{kJ\,mol^{-1}}}$$

For the entropy of $\mathrm{Cl^-}$ in solution we use

$$\Delta_r S^\ominus = S^\ominus(\mathrm{Ag}) + S^\ominus(\mathrm{H^+}) + S^\ominus(\mathrm{Cl^-}) - \tfrac{1}{2}S^\ominus(\mathrm{H_2}) - S^\ominus(\mathrm{AgCl})$$

with $S^\ominus(\mathrm{H^+}) = 0$. Then,

$$\begin{aligned}S^\ominus(\mathrm{Cl^-}) &= \Delta_r S^\ominus - S^\ominus(\mathrm{Ag}) + \tfrac{1}{2}S^\ominus(\mathrm{H_2}) + S^\ominus(\mathrm{AgCl})\\ &= (-62.30) - (42.55) + \left(\tfrac{1}{2}\right) \times (130.68) + (96.2) = \boxed{+56.7\,\mathrm{J\,K^{-1}\,mol^{-1}}}\end{aligned}$$

P10.12 **(a)** From $\left(\dfrac{\partial G}{\partial p}\right)_T = V$ [5.10]

we obtain $\left(\dfrac{\partial \Delta_r G}{\partial p}\right)_T = \Delta_r V$

Substituting $\Delta_r G = -\nu FE$ [10.32] yields

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

(b) The plot (Fig. 10.1) of E against p appears to fit a straight line very closely. A linear regression analysis yields

Slope = $\boxed{2.840 \times 10^{-3}\,\mathrm{mV\,atm^{-1}}}$, standard deviation = $3 \times 10^{-6}\,\mathrm{mV\,atm^{-1}}$
Intercept = 8.5583 mV, standard deviation = 2.8×10^{-3} mV
$R = 0.999\,997\,01$ (an extremely good fit)

From $\Delta_r V$

$$\left(\frac{\partial E}{\partial p}\right)_{T,n} = -\frac{(-2.66\overline{6} \times 10^{-6}\,\mathrm{m^3\,mol^{-1}})}{1 \times 9.6485 \times 10^{4}\,\mathrm{C\,mol^{-1}}}$$

Since $\mathrm{J} = \mathrm{V\,C} = \mathrm{Pa\,m^3}$, $\mathrm{C} = \dfrac{\mathrm{Pa\,m^3}}{\mathrm{V}}$ or $\dfrac{\mathrm{m^3}}{\mathrm{C}} = \dfrac{\mathrm{V}}{\mathrm{Pa}}$

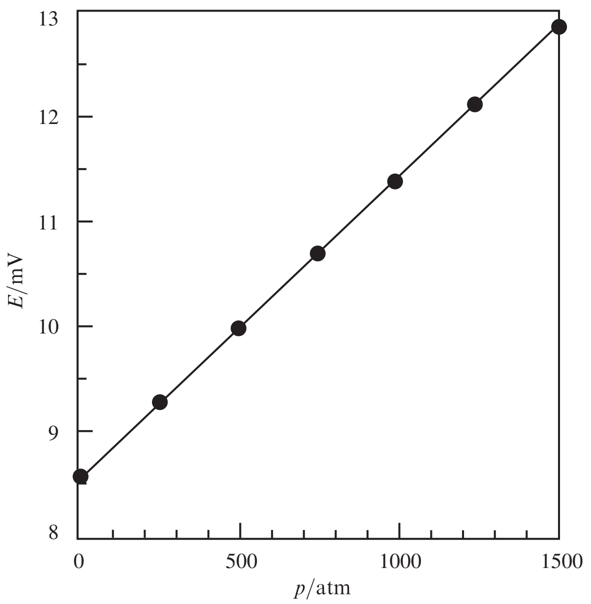


Figure 10.1

Therefore

$$\left(\frac{\partial E}{\partial p}\right)_{T,n} = \left(\frac{2.66\overline{6} \times 10^{-6}}{9.648\overline{5} \times 10^{4}}\right)\frac{\mathrm{V}}{\mathrm{Pa}} \times \frac{1.01325 \times 10^{5}\,\mathrm{Pa}}{\mathrm{atm}} = 2.80 \times 10^{-6}\,\mathrm{V\,atm^{-1}}$$

$$= \boxed{2.80 \times 10^{-3}\,\mathrm{mV\,atm^{-1}}}$$

This compares closely to the result from the potential measurements.

(c) A fit to a second-order polynomial of the form

$$E = a + bp + cp^2$$

yields

$a = 8.5592\,\mathrm{mV}$,	standard deviation $= 0.0039\,\mathrm{mV}$
$b = 2.835 \times 10^{-3}\,\mathrm{mV\,atm^{-1}}$,	standard deviation $= 0.012 \times 10^{-3}\,\mathrm{mV\,atm^{-1}}$
$c = 3.02 \times 10^{-9}\,\mathrm{mV\,atm^{-2}}$,	standard deviation $= 7.89 \times 10^{-9}\,\mathrm{mV\,atm^{-1}}$
$R = 0.999\,997\,11$	

This regression coefficient is only marginally better than that for the linear fit, but the uncertainty in the quadratic term is > 200 per cent.

$$\left(\frac{\partial E}{\partial p}\right)_{T} = b + 2cp$$

The slope changes from $\left(\frac{\partial E}{\partial p}\right)_{\min} = b = 2.835 \times 10^{-3}\,\mathrm{mV\,atm^{-1}}$

to $\left(\frac{\partial E}{\partial p}\right)_{\max} = b + 2c(1500\,\mathrm{atm}) = 2.836 \times 10^{-3}\,\mathrm{mV\,atm^{-1}}$

We conclude that the linear fit and constancy of $\left(\frac{\partial E}{\partial p}\right)$ are very good.

(d) We can obtain an order of magnitude value for the isothermal compressibility from the value of c.

$$\frac{\partial^2 E}{\partial p^2} = -\frac{1}{\nu F}\left(\frac{\partial \Delta_r V}{\partial p}\right)_T = 2c$$

$$(\kappa_T)_{\text{cell}} = -\frac{1}{V}\left(\frac{\partial \Delta_r V}{\partial p}\right)_T = \frac{2\nu c F}{\mathrm{V}}$$

$$(\kappa_T)_{\text{cell}} = \frac{2(1)\times(3.02\times10^{-12}\,\mathrm{V\,atm^{-2}})\times(9.6485\times10^4\,\mathrm{C\,mol^{-1}})\times\left(\frac{82.058\,\mathrm{cm^3\,atm}}{8.3145\,\mathrm{J}}\right)}{\left(\frac{1\,\mathrm{cm^3}}{0.996\,\mathrm{g}}\right)\times\left(\frac{18.016\,\mathrm{g}}{1\,\mathrm{mol}}\right)}$$

$$= \boxed{3.2\times10^{-7}\,\mathrm{atm^{-1}}} \qquad \text{standard deviation} \approx 200 \text{ per cent}$$

where we have assumed the density of the cell to be approximately that of water at 30°C.

Comment. It is evident from these calculations that the effect of pressure on the potentials of cells involving only liquids and solids is not important; for this reaction the change is only $\sim 3\times10^{-6}\,\mathrm{V\,atm^{-1}}$. The effective isothermal compressibility of the cell is of the order of magnitude typical of solids rather than liquids; other than that, little significance can be attached to the calculated numerical value.

P10.15 The equilibrium is

$$K = \frac{a(\mathrm{H_2O})^4 a(\mathrm{V_4O_{12}}^{-4})}{a(\mathrm{H_2VO_4}^-)^4} \approx \frac{\gamma(\mathrm{V_4O_{12}}^{-4})b(\mathrm{V_4O_{12}}^{-4})}{\gamma(\mathrm{H_2VO_4}^-)^4 b(\mathrm{H_2VO_4}^-)^4}$$

Let x be $b(\mathrm{H_2VO_4}^-)$; then $b(\mathrm{V_4O_{12}}^{-4}) = (0.010 - x)/4$. Then the equilibrium equation can be expressed as

$$x^4\left(\frac{K\gamma(\mathrm{H_2VO_4}^-)^4}{\gamma(\mathrm{V_4O_{12}}^{-4})}\right) = (0.010 - x)/4$$

which can be solved numerically once the constants are determined. The activity coefficients are

$$\log\gamma(\mathrm{H_2VO_4}^-) = -\frac{0.5373}{2} = -0.269 \quad \text{so} \quad \gamma(\mathrm{H_2VO_4}^-) = 0.538$$

and $\log\gamma(\mathrm{V_4O_{12}}^{-4}) = -\dfrac{0.5373(4^2)}{2} = -1.075 \quad \text{so} \quad \gamma(\mathrm{V_4O_{12}}^{-4}) = 0.0842$

The equation is

$$x^4(2.5\times10^6) = (0.010 - x)/4$$

Its solution is

$$x = \boxed{0.0048\,\mathrm{mol\,kg^{-1}}} = b(\mathrm{H_2VO_4}^-)$$

and $b(\mathrm{V_4O_{12}}^{-4}) = 0.010 - (0.010 - 0.0048)/4 = \boxed{0.0013\,\mathrm{mol\,kg^{-1}}}$

P10.18 The reduction reaction is

$$\mathrm{Sb_2O_3(s) + 3H_2O(l) + 6e^- \rightarrow 2Sb(s) + 6OH^-(aq)} \qquad Q = a(\mathrm{OH^-})^6 \quad \nu = 6$$

Therefore

(a) $$E = E^\ominus - \frac{RT}{6F}\ln a(\mathrm{OH^-})^6 = E^\ominus - \frac{RT}{F}\ln a(\mathrm{OH^-}) = \boxed{E^\ominus + \frac{2.303RT}{F}\mathrm{pOH}}$$

$[\ln a(\mathrm{OH^-}) = 2.303\log a(\mathrm{OH^-}) = -2.303\mathrm{pOH}]$

(b) Since $\mathrm{pOH} + \mathrm{pH} = \mathrm{p}K_\mathrm{w}$

$$\boxed{E = E^{\ominus} + \frac{2.303RT}{F}(\mathrm{p}K_\mathrm{w} - \mathrm{pH})}$$

(c) The change in potential is

$$\Delta E = \frac{2.303RT}{F}(\mathrm{pOH_f} - \mathrm{pOH_i}) = (59.17\,\mathrm{mV}) \times (\mathrm{pOH_f} - \mathrm{pOH_i})$$

$$\mathrm{pOH_f} = -\log(0.050\gamma_\pm) = -\log 0.050 - \log\gamma_\pm = -\log 0.050 + A\sqrt{(0.050)} = 1.41\bar{5}$$

$$\mathrm{pOH_i} = -\log(0.010\gamma_\pm) = -\log 0.010 - \log\gamma_\pm = -\log 0.010 + A\sqrt{(0.010)} = 2.05\bar{1}$$

Hence, $\Delta E = (59.17\,\mathrm{mV}) \times (1.41\bar{5} - 2.05\bar{1}) = \boxed{-37.6\,\mathrm{mV}}$

P10.19 We need to obtain $\Delta_\mathrm{r}H^{\ominus}$ for the reaction

$$\tfrac{1}{2}\mathrm{H_2(g)} + \mathrm{Uup^+(aq)} \rightarrow \mathrm{Uup(s)} + \mathrm{H^+(aq)}$$

We draw up the thermodynamic cycle shown in Fig. 10.2.

Data are obtained from Table 13.4, 14.3, 2.6, and 2.6b. The conversion factor between eV and $\mathrm{kJ\,mol^{-1}}$ is

$$1\,\mathrm{eV} = 96.485\,\mathrm{kJ\,mol^{-1}}$$

The distance from A to B in the cycle is given by

$$\Delta_\mathrm{r}H^{\ominus} = x = (3.22\,\mathrm{eV}) + \left(\tfrac{1}{2}\right) \times (4.5\,\mathrm{eV}) + (13.6\,\mathrm{eV}) - (11.3\,\mathrm{eV}) - (5.52\,\mathrm{eV}) - (1.5\,\mathrm{eV})$$
$$= 0.75\,\mathrm{eV}$$

$$\Delta_\mathrm{r}S^{\ominus} = S^{\ominus}(\mathrm{Uup, s}) + S^{\ominus}(\mathrm{H^+, aq}) - \tfrac{1}{2}S^{\ominus}(\mathrm{H_2, g}) - S^{\ominus}(\mathrm{Uup^+, aq})$$
$$= (0.69) + (0) - \left(\tfrac{1}{2}\right) \times (1.354) - (1.34)\,\mathrm{meV\,K^{-1}} = -1.33\,\mathrm{meV\,K^{-1}}$$

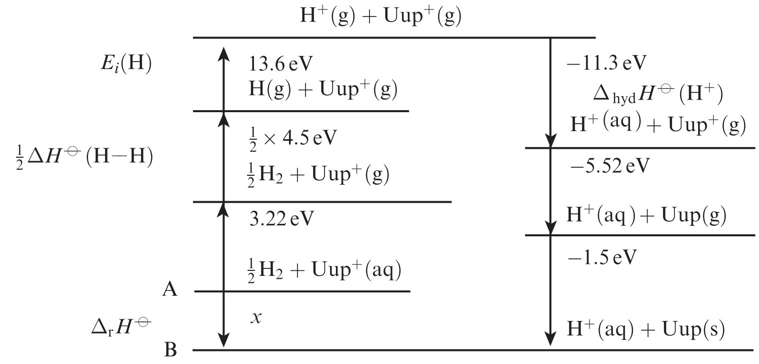


Figure 10.2

$$\Delta_\mathrm{r}G^{\ominus} = \Delta_\mathrm{r}H^{\ominus} - T\Delta_\mathrm{r}S^{\ominus} = (0.75\,\mathrm{eV}) + (298.15\,\mathrm{K}) \times (1.33\,\mathrm{meV\,K^{-1}}) = +1.1\bar{5}\,\mathrm{eV}$$

which corresponds to $\boxed{+111\,\mathrm{kJ\,mol^{-1}}}$

The electrode potential is therefore $\dfrac{-\Delta_\mathrm{r}G^{\ominus}}{\nu F}$, with $\nu = 1$, or $\boxed{-1.1\bar{5}\,\mathrm{V}}$

Solutions to theoretical problems

P10.21 $\mathrm{MX(s)} \rightleftharpoons \mathrm{M^+(aq)} + \mathrm{X^-(aq)}, \qquad K_s \approx b(\mathrm{M^+})b(\mathrm{X^-}) \quad \left[b \equiv \dfrac{b}{b^\ominus}\right]$

$$b(\mathrm{M^+}) = S, \qquad b(\mathrm{X^-}) = S + C$$

$$K_s = S(S+C), \quad \text{or} \quad S^2 + CS - K_s = 0$$

which solves to $\boxed{S = \tfrac{1}{2}(C^2 + 4K_s)^{1/2} - \tfrac{1}{2}C}$ or $S = \tfrac{1}{2}C\left(1 + \dfrac{4K_s}{C^2}\right)^{1/2} - \tfrac{1}{2}C$

If $4K_s \ll C^2$,

$$S \approx \tfrac{1}{2}C\left(1 + \frac{2K_s}{C^2}\right) - \tfrac{1}{2}C\left[(1+x)^{1/2} \approx 1 + \tfrac{1}{2}x + \cdots\right] \approx \boxed{\frac{K_s}{C}}$$

P10.22 $K_s = a(\mathrm{M^+})a(\mathrm{X^-}) = b(\mathrm{M^+})b(\mathrm{X^-})\gamma_\pm^2; \qquad b(\mathrm{M^+}) = S', \quad b(\mathrm{X^-}) = S' + C$

$$\log \gamma_\pm = -AI^{1/2} = -AC^{1/2} \qquad \ln \gamma_\pm = -2.303AC^{1/2}$$

$$\gamma_\pm = \mathrm{e}^{-2.303AC^{1/2}} \qquad \gamma_\pm^2 = \mathrm{e}^{-4.606AC^{1/2}}$$

$$K_s = S'(S'+C) \times \mathrm{e}^{-4.606AC^{1/2}}$$

We solve $S'^2 + S'C - \dfrac{K_s}{\gamma_\pm^2} = 0$

to get $S' = \dfrac{1}{2}\left(C^2 + \dfrac{4K_s}{\gamma_\pm^2}\right)^{1/2} - \dfrac{1}{2}C \approx \dfrac{K_s}{C\gamma_\pm^2}$ [as in Problem 10.21]

Therefore, since $\gamma_\pm^2 = \mathrm{e}^{-4.606AC^{1/2}}$ $\boxed{S' \approx \dfrac{K_s\mathrm{e}^{-4.606AC^{1/2}}}{C}}$

P10.25 The half-reactions involved are:

R: $\mathrm{cyt_{ox}} + \mathrm{e^-} \rightarrow \mathrm{cyt_{red}} \quad E^\ominus_{\mathrm{cyt}}$
L: $\mathrm{D_{ox}} + \mathrm{e^-} \rightarrow \mathrm{D_{red}} \quad E^\ominus_{\mathrm{D}}$

The overall cell reaction is:

$$\mathrm{R - L = cyt_{ox} + D_{red} \rightleftharpoons cyt_{red} + D_{ox}} \quad E^{\ominus -} = E^\ominus_{\mathrm{cyt}} - E^\ominus_{\mathrm{D}}$$

(a) The Nernst equation for the cell reaction is

$$E = E - \frac{RT}{F}\ln\frac{[\mathrm{cyt_{red}}][\mathrm{D_{ox}}]}{[\mathrm{cyt_{ox}}][\mathrm{D_{red}}]}$$

at equilibrium, $E = 0$; therefore

$$\ln\frac{[\mathrm{cyt_{red}}]_{\mathrm{eq}}[\mathrm{D_{ox}}]_{\mathrm{eq}}}{[\mathrm{cyt_{ox}}]_{\mathrm{eq}}[\mathrm{D_{red}}]_{\mathrm{eq}}} = \frac{F}{RT}\left(E^\ominus_{\mathrm{cyt}} - E^\ominus_{\mathrm{D}}\right)$$

$$\ln\left(\frac{[\mathrm{D_{ox}}]_{\mathrm{eq}}}{[\mathrm{D_{red}}]_{\mathrm{eq}}}\right) = \ln\left(\frac{[\mathrm{cyt}]_{\mathrm{ox}}}{[\mathrm{cyt}]_{\mathrm{red}}}\right) + \frac{F}{RT}\left(E^\ominus_{\mathrm{cyt}} - E^\ominus_{\mathrm{D}}\right)$$

Therefore a plot of $\ln\left(\dfrac{[\mathrm{D_{ox}}]_{\mathrm{eq}}}{[\mathrm{D_{red}}]_{\mathrm{eq}}}\right)$ against $\ln\left(\dfrac{[\mathrm{cyt}]_{\mathrm{ox}}}{[\mathrm{cyt}]_{\mathrm{red}}}\right)$ is linear with a slope of one and an intercept of $\dfrac{F}{RT}\left(E^\ominus_{\mathrm{cyt}} - E^\ominus_{\mathrm{D}}\right)$

(b) Draw up the following table:

$\ln\left(\frac{[D_{ox}]_{eq}}{[D_{red}]_{eq}}\right)$	−5.882	−4.776	−3.661	−3.002	−2.593	−1.436	−0.6274
$\ln\left(\frac{[cyt_{ox}]_{eq}}{[cyt_{red}]_{eq}}\right)$	−4.547	−3.772	−2.415	−1.625	−1.094	−0.2120	−0.3293

The plot of $\ln\left(\frac{[D_{ox}]_{eq}}{[D_{red}]_{eq}}\right)$ against $\ln\left(\frac{[cyt_{ox}]_{eq}}{[cyt_{red}]_{eq}}\right)$ is shown in Fig. 10.3. The intercept is −1.2124. Hence

$$
\begin{aligned}
E^{\ominus}_{cyt} &= \frac{RT}{F} \times (-1.2124) + 0.237\,\mathrm{V} \\
&= 0.0257\,\mathrm{V} \times (-1.2124) + 0.237\,\mathrm{V} \\
&= \boxed{+0.206\,\mathrm{V}}
\end{aligned}
$$

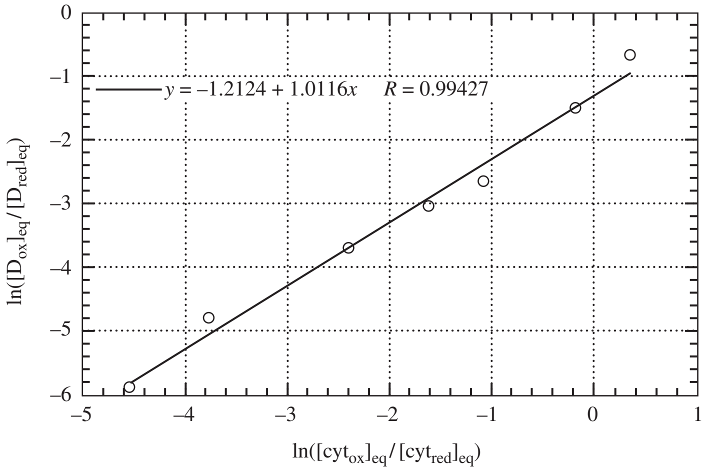


Figure 10.3

Solutions to application

P10.27 **(a)** $\text{molality}_{H_2SO_4} = b(d) = a(d - d_{25}) + c(d - d_{25})^2$

where d is density in $\mathrm{g\,cm^{-3}}$ at 25 °C, $a = 14.523\,\mathrm{mol\,kg^{-1}(g\,cm^{-3})^{-1}}$, $c = 25.031\,\mathrm{mol\,kg^{-1}(g\,cm^{-3})^{-2}}$, and $d_{25} = 0.99707\,\mathrm{g\,cm^{-3}}$.

For 1 kg solvent ($m_{H_2O} = 1$ kg):

$$
\text{mass }\%_{H_2SO_4} = \left(\frac{m_{H_2SO_4}}{m_{H_2SO_4} + m_{H_2O}}\right)100 = \frac{b \times 100}{b + \frac{\cancel{m_{H_2O}}}{m_{H_2SO_4}\cancel{m_{H_2O}}}}
$$

$$
\text{mass }\%_{H_2SO_4}(d) = \frac{100 \times b(d)}{b(d) + \frac{1}{m_{H_2SO_4}}} \quad \text{where } m_{H_2SO_4} = 0.09807\,\mathrm{kg\,mol^{-1}}
$$

an equation for the solution molarity is deduced with a unit analysis.

$$
\text{molarity}_{H_2SO_4}(d) = b(d) \times \left(1 - \frac{\text{mass }\%_{H_2SO_4}(d)}{100}\right) d \times \left(\frac{\cancel{10^3}\,\mathrm{cm^3}}{\mathrm{L}}\right)\left(\frac{\mathrm{kg}}{\cancel{10^3}\,\mathrm{g}}\right)
$$

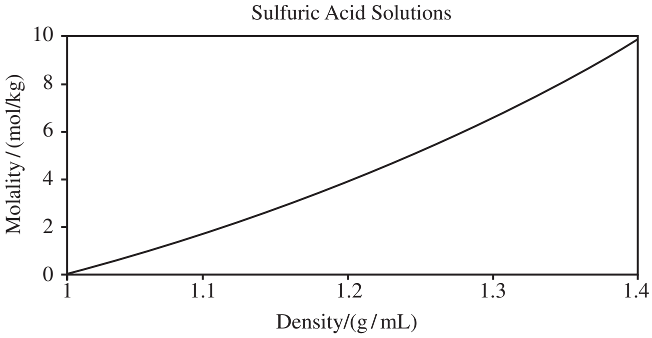


Figure 10.4(a)

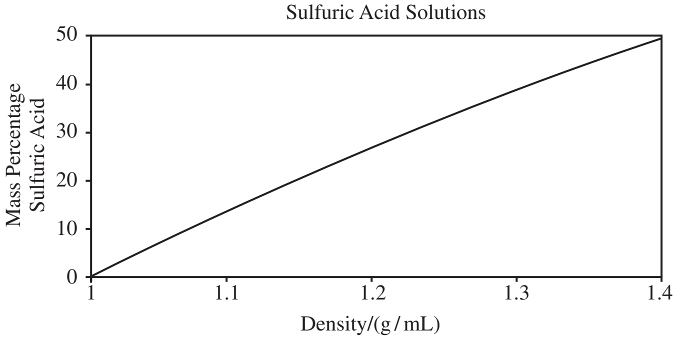


Figure 10.4(b)

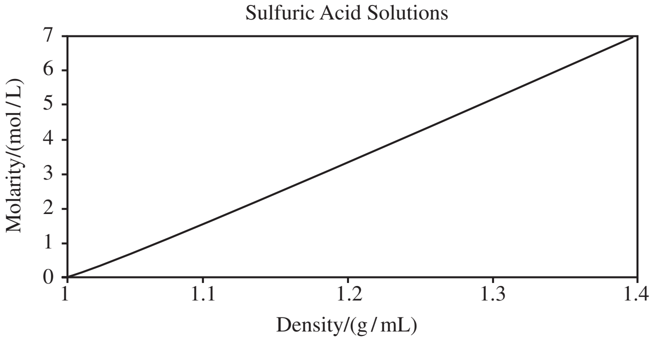


Figure 10.4(c)

(b) cell: $Pb(s) \mid PbSO_4(s) \mid H_2SO_4(aq) \mid PbO_2(s) \mid PbSO_4(s) \mid Pb(s)$

cathode: $PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

$E^{\ominus}_{\text{cathode}} = 1.6913\,\text{V}$

anode: $PbSO_4(s) + H^+(aq) + 2e^- \rightarrow Pb(s) + HSO_4^-$

$E^{\ominus}_{\text{anode}} = -0.3588\,\text{V}$

net: $PbO_2(s) + Pb(s) + 2H^+(aq) + 2HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

$$E^{\ominus} = E^{\ominus}_{\text{cathode}} - E^{\circ}_{\text{anode}} = \boxed{2.0501\,V} \qquad \text{(eqn 10.38)}$$

$$\begin{aligned}\Delta_r G^{\ominus} &= -\nu F E^{\ominus} = -(2)(9.64853 \times 10^4\,\text{C mol}^{-1})(2.0501\,\text{V}) \\ &= -3.956 \times 10^5\,\text{C V mol}^{-1} = -3.956 \times 10^5\,\text{J mol}^{-1} = \boxed{-395.6\,\text{kJ mol}^{-1}}\end{aligned}$$

$\Delta_f H^\ominus$ values of Table 2.6 and the *CRC Handbook of Chemistry and Physics* are used in the $\Delta_r H^\ominus$ calculation.

$$\begin{aligned}
\Delta_r H^\ominus &= 2\Delta_f H^\ominus(\mathrm{PbSO_4}) + 2\Delta_f H^\ominus(\mathrm{H_2O(l)}) - \Delta_f H^\ominus(\mathrm{PbO_2}) - \Delta_f H^\ominus(\mathrm{Pb}) \\
&\quad -2\Delta_f H^\ominus(\mathrm{H^+}) - 2\Delta_f H^\ominus(\mathrm{HSO_4^-}) \\
&= 2(-919.94\,\mathrm{kJ\,mol^{-1}}) + 2(-285.83\,\mathrm{kJ\,mol^{-1}}) - (-277.4\,\mathrm{kJ\,mol^{-1}}) \\
&\quad -2(-887.34\,\mathrm{kJ\,mol^{-1}}) \\
\Delta_r H^\ominus &= \boxed{-359.5\,\mathrm{kJ\,mol^{-1}}} \\
\Delta_r S^\ominus &= \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T} = \frac{-359.5\,\mathrm{kJ\,mol^{-1}} - (-395.6\,\mathrm{kJ\,mol^{-1}})}{298.15\,\mathrm{K}} \\
&= \boxed{121\,\mathrm{J\,K^{-1}\,mol^{-1}}} \quad \text{(eqn 4.39)}
\end{aligned}$$

$$\begin{aligned}
E^\ominus(15^\circ\mathrm{C}) &= E^\ominus(25^\circ\mathrm{C}) + \Delta E^\ominus = E^\ominus(25^\circ\mathrm{C}) + \frac{\Delta_r S^\ominus}{\nu F}\Delta T \qquad \text{(eqn 10.45)} \\
&= 2.0501\,\mathrm{V} + \frac{(121\,\mathrm{J}\,\cancel{\mathrm{K^{-1}}}\,\cancel{\mathrm{mol^{-1}}})}{2(96485\,\mathrm{C}\,\cancel{\mathrm{mol^{-1}}})}(10\,\cancel{\mathrm{K}}) \\
&= 2.0501\mathrm{V} + 0.006\mathrm{V} = \boxed{2.0507\mathrm{V}}
\end{aligned}$$

The temperature difference makes a negligibly small difference in the cell potential.
When $Q = 6.0 \times 10^{-5}$,

$$\begin{aligned}
E &= E^\ominus - \frac{RT}{\nu F}\ln Q \quad \text{(eqn 10.34)} \\
&= 2.0501\,\mathrm{V} - \frac{(8.31451\,\mathrm{J}\,\cancel{\mathrm{K^{-1}}}\,\cancel{\mathrm{mol^{-1}}})(298.15\,\cancel{\mathrm{K}})}{2(96485\,\mathrm{C}\,\cancel{\mathrm{mol^{-1}}})}\ln(6.0 \times 10^{-5}) \\
&= \boxed{2.1750\,\mathrm{V}}
\end{aligned}$$

(c) The general form of the reduction half-reaction is: ox + $\nu\mathrm{e^-} + \nu_\mathrm{H}\mathrm{H^+} + \mathrm{aA} \rightarrow \mathrm{red} + \mathrm{xX}$ using eqn 10.34,

$$\begin{aligned}
E &= E^\ominus - \frac{RT}{\nu F}\ln \mathrm{Q} = E^\ominus - \frac{RT}{\nu F}\ln\left(\frac{a_\mathrm{red}a_\mathrm{X}^x}{a_\mathrm{ox}a_\mathrm{H^+}^{\nu_\mathrm{H}}a_\mathrm{A}^a}\right) \\
&= E^\ominus - \frac{RT}{\nu F}\ln\left(\frac{1}{a_\mathrm{H^+}^{\nu_\mathrm{H}}}\right)
\end{aligned}$$

(all species other than acids are at unit activity in a Pourboix diagram)

$$\begin{aligned}
&= E^\ominus + \frac{\nu_\mathrm{H}RT}{\nu F}\ln a_\mathrm{H^+} = E^\ominus + \frac{\nu_\mathrm{H}RT\ln^{(10)}}{\nu F}\log a_\mathrm{H^+} \\
&= E^\ominus - \frac{\nu_\mathrm{H}}{\nu}\left(\frac{RT\ln^{(10)}}{F}\right)\mathrm{pH} \quad \text{(eqn 9.29)}
\end{aligned}$$

$$\boxed{E = E^\ominus - (0.05916\mathrm{V})\left(\frac{\nu_\mathrm{H}}{\nu}\right)\mathrm{pH}}$$

For the $PbO_2 \mid PbSO_4$ couple,

$$PbO_2(s) + 4H^+ + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$$

$$E^{\ominus} = 1.6913\,V,\ \nu_H = 4,\ \nu = 2$$

$$E = 1.6913\,V - (0.11832\,V)pH$$

For pH = 5, $\boxed{E = 1.0997\ V}$

For pH = 8, $\boxed{E = 0.7447\ V}$

For the $PbSO_4/Pb$ couple,

$$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$$

Since $\nu_H = O$, $\boxed{E = E^{\ominus} = -0.3588\,V}$ at all pH values in the Pourboix diagram.

Part 2: Structure

11 Quantum theory: introduction and principles

Solutions to exercises

Discussion questions

E11.1(b) A successful theory of black-body radiation must be able to explain the energy density distribution of the radiation as a function of wavelength, in particular, the observed drop to zero as $\lambda \to 0$. Classical theory predicts the opposite. However, if we assume, as did Planck, that the energy of the oscillators that constitute electromagnetic radiation are quantized according to the relation $E = nh\nu = nhc/\lambda$, we see that at short wavelengths the energy of the oscillators is very large. This energy is too large for the walls to supply it, so the short-wavelength oscillators remain unexcited. The effect of quantization is to reduce the contribution to the total energy emitted by the black-body from the high-energy short-wavelength oscillators, for they cannot be sufficiently excited with the energy available.

E11.2(b) In quantum mechanics all dynamical properties of a physical system have associated with them a corresponding operator. The system itself is described by a wavefunction. The observable properties of the system can be obtained in one of two ways from the wavefunction depending upon whether or not the wavefunction is an eigenfunction of the operator.

When the function representing the state of the system is an eigenfunction of the operator Ω, we solve the eigenvalue equation (eqn 11.30)

$$\Omega\Psi = \omega\Psi$$

in order to obtain the observable values, ω, of the dynamical properties.

When the function is not an eigenfunction of Ω, we can only find the average or expectation value of dynamical properties by performing the integration shown in eqn 11.39

$$\langle\Omega\rangle = \int \Psi^*\Omega\Psi\,\mathrm{d}\tau.$$

E11.3(b) No answer.

Numerical exercises

E11.4(b) The power is equal to the excitance M times the emitting area

$$\begin{aligned} P &= MA = \sigma T^4(2\pi rl) \\ &= (5.67\times10^{-8}\,\mathrm{W\,m^{-2}\,K^{-4}})\times(3300\,\mathrm{K})^4\times(2\pi)\times(0.12\times10^{-3}\,\mathrm{m})\times(5.0\times10^{-2}\,\mathrm{m}) \\ &= \boxed{2.5\times10^2\,\mathrm{W}} \end{aligned}$$

Comment. This could be a 250 W incandescent light bulb.

E11.5(b) Wien's displacement law is

$$T\lambda_{\max} = c_2/5 \quad \text{so} \quad \lambda_{\max} = \frac{c_2}{5T} = \frac{1.44\times10^{-2}\,\mathrm{m\,K}}{5(2500\,\mathrm{K})} = 1.15\times10^{-6}\,\mathrm{m} = \boxed{1.15\,\mu\mathrm{m}}$$

E11.6(b) The de Broglie relation is

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad \text{so} \quad v = \frac{h}{m\lambda} = \frac{6.626\times10^{-34}\,\mathrm{J\,s}}{(1.675\times10^{-27}\,\mathrm{kg})\times(3.0\times10^{-2}\,\mathrm{m})}$$

$$v = \boxed{1.3\times10^{-5}\,\mathrm{m\,s^{-1}}}$$

E11.7(b) The de Broglie relation is

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad \text{so} \quad v = \frac{h}{m\lambda} = \frac{6.626\times 10^{-34}\,\text{J s}}{(9.11\times 10^{-31}\,\text{kg})\times(0.45\times 10^{-9}\,\text{m})}$$

$$v = \boxed{1.6\times 10^{6}\,\text{m s}^{-1}}$$

E11.8(b) The momentum of a photon is

$$p = \frac{h}{\lambda} = \frac{6.626\times 10^{-34}\,\text{J s}}{350\times 10^{-9}\,\text{m}} = \boxed{1.89\times 10^{-27}\,\text{kg m s}^{-1}}$$

The momentum of a particle is

$$p = mv \quad \text{so} \quad v = \frac{p}{m} = \frac{1.89\times 10^{-27}\,\text{kg m s}^{-1}}{2(1.0078\times 10^{-3}\,\text{kg mol}^{-1}/6.022\times 10^{23}\,\text{mol}^{-1})}$$

$$v = \boxed{0.565\,\text{m s}^{-1}}$$

E11.9(b) The energy of the photon is equal to the ionization energy plus the kinetic energy of the ejected electron

$$E_{\text{photon}} = E_{\text{ionize}} + E_{\text{electron}} \quad \text{so} \quad \frac{hc}{\lambda} = E_{\text{ionize}} + \tfrac{1}{2}mv^2$$

$$\text{and } \lambda = \frac{hc}{E_{\text{ionize}} + \frac{1}{2}mv^2} = \frac{(6.626\times 10^{-34}\,\text{J s})\times(2.998\times 10^{8}\,\text{m s}^{-1})}{5.12\times 10^{-18}\,\text{J} + \frac{1}{2}(9.11\times 10^{-31}\,\text{kg})\times(345\times 10^{3}\,\text{m s}^{-1})^2}$$

$$= 3.48\times 10^{-8}\,\text{m} = \boxed{38.4\,\text{nm}}$$

E11.10(b) The uncertainty principle is

$$\Delta p \Delta x \geq \tfrac{1}{2}\hbar$$

so the minimum uncertainty in position is

$$\Delta x = \frac{\hbar}{2\Delta p} = \frac{\hbar}{2m\Delta v} = \frac{1.0546\times 10^{-34}\,\text{J s}}{2(9.11\times 10^{-31}\,\text{kg})\times(0.000\,010)\times(995\times 10^{3}\,\text{m s}^{-1})}$$

$$= \boxed{5.8\times 10^{-6}\,\text{m}}$$

E11.11(b) $E = h\nu = \dfrac{hc}{\lambda}; \qquad E(\text{per mole}) = N_{\text{A}}E = \dfrac{N_{\text{A}}hc}{\lambda}$

$$hc = (6.62608\times 10^{-34}\,\text{J s})\times(2.99792\times 10^{8}\,\text{m s}^{-1}) = 1.986\times 10^{-25}\,\text{J m}$$

$$N_{\text{A}}hc = (6.02214\times 10^{23}\,\text{mol}^{-1})\times(1.986\times 10^{-25}\,\text{J m}) = 0.1196\,\text{J m mol}^{-1}$$

Thus, $E = \dfrac{1.986\times 10^{-25}\,\text{J m}}{\lambda}; \ E(\text{per mole}) = \dfrac{0.1196\,\text{J m mol}^{-1}}{\lambda}$

We can therefore draw up the following table

λ	E/J	$E/(\mathrm{kJ\,mol^{-1}})$
(a) 200 nm	9.93×10^{-19}	598
(b) 150 pm	1.32×10^{-15}	7.98×10^{5}
(c) 1.00 cm	1.99×10^{-23}	0.012

E11.12(b) Assuming that the ^{4}He atom is free and stationary, if a photon is absorbed, the atom acquires its momentum p, achieving a speed v such that $p = mv$.

$$v = \frac{p}{m} \qquad m = 4.00 \times 1.6605 \times 10^{-27}\,\mathrm{kg} = 6.64\bar{2} \times 10^{-27}\,\mathrm{kg}$$

$$p = \frac{h}{\lambda}$$

(a)
$$p = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{200 \times 10^{-9}\,\mathrm{m}} = 3.31\bar{3} \times 10^{-27}\,\mathrm{kg\,m\,s^{-1}}$$
$$v = \frac{p}{m} = \frac{3.31\bar{3} \times 10^{-27}\,\mathrm{kg\,m\,s^{-1}}}{6.642 \times 10^{-27}\,\mathrm{kg}} = \boxed{0.499\,\mathrm{m\,s^{-1}}}$$

(b)
$$p = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{150 \times 10^{-12}\,\mathrm{m}} = 4.41\bar{7} \times 10^{-24}\,\mathrm{kg\,m\,s^{-1}}$$
$$v = \frac{p}{m} = \frac{4.41\bar{7} \times 10^{-24}\,\mathrm{kg\,m\,s^{-1}}}{6.642 \times 10^{-27}\,\mathrm{kg}} = \boxed{665\,\mathrm{m\,s^{-1}}}$$

(c)
$$p = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{1.00 \times 10^{-2}\,\mathrm{m}} = 6.626 \times 10^{-32}\,\mathrm{kg\,m\,s^{-1}}$$
$$v = \frac{p}{m} = \frac{6.626 \times 10^{-32}\,\mathrm{kg\,m\,s^{-1}}}{6.642 \times 10^{-27}\,\mathrm{kg}} = \boxed{9.98 \times 10^{-6}\,\mathrm{m\,s^{-1}}}$$

E11.13(b) Each emitted photon increases the momentum of the rocket by h/λ. The final momentum of the rocket will be Nh/λ, where N is the number of photons emitted, so the final speed will be $\dfrac{Nh}{\lambda m_{\text{rocket}}}$. The rate of photon emission is the power (rate of energy emission) divided by the energy per photon (hc/λ), so

$$N = \frac{tP\lambda}{hc} \quad \text{and} \quad v = \left(\frac{tP\lambda}{hc}\right) \times \left(\frac{h}{\lambda m_{\text{rocket}}}\right) = \frac{tP}{cm_{\text{rocket}}}$$

$$v = \frac{(10.0\,\mathrm{yr}) \times (365\,\mathrm{day\,yr^{-1}}) \times (24\,\mathrm{h\,day^{-1}}) \times (3600\,\mathrm{s\,h^{-1}}) \times (1.50 \times 10^{3}\,\mathrm{W})}{(2.998 \times 10^{8}\,\mathrm{m\,s^{-1}}) \times (10.0\,\mathrm{kg})}$$
$$= \boxed{158\,\mathrm{m\,s^{-1}}}$$

E11.14(b) Rate of photon emission is rate of energy emission (power) divided by energy per photon (hc/λ)

(a)
$$\text{rate} = \frac{P\lambda}{hc} = \frac{(0.10\,\mathrm{W}) \times (700 \times 10^{-9}\,\mathrm{m})}{(6.626 \times 10^{-34}\,\mathrm{J\,s}) \times (2.998 \times 10^{8}\,\mathrm{m\,s^{-1}})} = \boxed{3.52 \times 10^{17}\,\mathrm{s^{-1}}}$$

(b)
$$\text{rate} = \frac{(1.0\,\mathrm{W}) \times (700 \times 10^{-9}\,\mathrm{m})}{(6.626 \times 10^{-34}\,\mathrm{J\,s}) \times (2.998 \times 10^{8}\,\mathrm{m\,s^{-1}})} = \boxed{3.52 \times 10^{18}\,\mathrm{s^{-1}}}$$

E11.15(b) Wien's displacement law is

$$T\lambda_{\max} = c_2/5 \quad \text{so} \quad T = \frac{c_2}{5\lambda_{\max}} = \frac{1.44 \times 10^{-2}\,\mathrm{m\,K}}{5(1600 \times 10^{-9}\,\mathrm{m})} = \boxed{1800\,\mathrm{K}}$$

E11.16(b) Conservation of energy requires

$$E_{\text{photon}} = \Phi + E_{\text{K}} = h\nu = hc/\lambda \quad \text{so} \quad E_{\text{K}} = hc/\lambda - \Phi$$

and $E_{\text{K}} = \frac{1}{2}m_{\text{e}}v^2$ so $v = \left(\dfrac{2E_{\text{K}}}{m_{\text{e}}}\right)^{1/2}$

(a) $$E_{\text{K}} = \frac{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^8\,\text{m s}^{-1})}{650 \times 10^{-9}\,\text{m}} - (2.09\,\text{eV}) \times (1.60 \times 10^{-19}\,\text{J eV}^{-1})$$

But this expression is negative, which is unphysical. There is no kinetic energy or velocity because the photon does not have enough energy to dislodge the electron.

(b) $$E_{\text{K}} = \frac{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^8\,\text{m s}^{-1})}{195 \times 10^{-9}\,\text{m}} - (2.09\,\text{eV}) \times (1.60 \times 10^{-19}\,\text{J eV}^{-1})$$

$$= \boxed{6.84 \times 10^{-19}\,\text{J}}$$

and $v = \left(\dfrac{2(3.20 \times 10^{-19}\,\text{J})}{9.11 \times 10^{-31}\,\text{kg}}\right)^{1/2} = \boxed{1.23 \times 10^6\,\text{m s}^{-1}}$

E11.17(b) $E = h\nu = h/\tau$, so

(a) $E = 6.626 \times 10^{-34}\,\text{J s}/2.50 \times 10^{-15}\,\text{s} = \boxed{2.65 \times 10^{-19}\,\text{J} = 160\,\text{kJ mol}^{-1}}$

(b) $E = 6.626 \times 10^{-34}\,\text{J s}/2.21 \times 10^{-15}\,\text{s} = \boxed{3.00 \times 10^{-19}\,\text{J} = 181\,\text{kJ mol}^{-1}}$

(c) $E = 6.626 \times 10^{-34}\,\text{J s}/1.0 \times 10^{-3}\,\text{s} = \boxed{6.62 \times 10^{-31}\,\text{J} = 4.0 \times 10^{-10}\,\text{kJ mol}^{-1}}$

E11.18(b) The de Broglie wavelength is

$$\lambda = \frac{h}{p}$$

The momentum is related to the kinetic energy by

$$E_{\text{K}} = \frac{p^2}{2m} \quad \text{so} \quad p = (2mE_{\text{K}})^{1/2}$$

The kinetic energy of an electron accelerated through 1 V is $1\,\text{eV} = 1.60 \times 10^{-19}\,\text{J}$, so

$$\lambda = \frac{h}{(2mE_{\text{K}})^{1/2}}$$

(a) $$\lambda = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{(2(9.11 \times 10^{-31}\,\mathrm{kg}) \times (100\,\mathrm{eV}) \times (1.60 \times 10^{-19}\,\mathrm{J\,eV^{-1}}))^{1/2}} = \boxed{1.23 \times 10^{-10}\,\mathrm{m}}$$

(b) $$\lambda = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{(2(9.11 \times 10^{-31}\,\mathrm{kg}) \times (1.0 \times 10^{3}\,\mathrm{eV}) \times (1.60 \times 10^{-19}\,\mathrm{J\,eV^{-1}}))^{1/2}} = \boxed{3.9 \times 10^{-11}\,\mathrm{m}}$$

(c) $$\lambda = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{(2(9.11 \times 10^{-31}\,\mathrm{kg}) \times (100 \times 10^{3}\,\mathrm{eV}) \times (1.60 \times 10^{-19}\,\mathrm{J\,eV^{-1}}))^{1/2}} = \boxed{3.88 \times 10^{-12}\,\mathrm{m}}$$

E11.19(b) The minimum uncertainty in position is $\boxed{100\,\mathrm{pm}}$. Therefore, since $\Delta x \Delta p \geq \frac{1}{2}\hbar$

$$\Delta p \geq \frac{\hbar}{2\Delta x} = \frac{1.0546 \times 10^{-34}\,\mathrm{J\,s}}{2(100 \times 10^{-12}\,\mathrm{m})} = 5.3 \times 10^{-25}\,\mathrm{kg\,m\,s^{-1}}$$

$$\Delta v = \frac{\Delta p}{m} = \frac{5.3 \times 10^{-25}\,\mathrm{kg\,m\,s^{-1}}}{9.11 \times 10^{-31}\,\mathrm{kg}} = \boxed{5.8 \times 10^{-5}\,\mathrm{m\,s^{-1}}}$$

E11.20(b) Conservation of energy requires

$$E_{\mathrm{photon}} = E_{\mathrm{binding}} + \tfrac{1}{2}m_{\mathrm{e}}v^2 = h\nu = hc/\lambda \quad \text{so} \quad E_{\mathrm{binding}} = hc/\lambda - \tfrac{1}{2}m_{\mathrm{e}}v^2$$

and $$E_{\mathrm{binding}} = \frac{(6.626 \times 10^{-34}\,\mathrm{J\,s}) \times (2.998 \times 10^{8}\,\mathrm{m\,s^{-1}})}{121 \times 10^{-12}\,\mathrm{m}} - \tfrac{1}{2}(9.11 \times 10^{-31}\,\mathrm{kg}) \times (5.69 \times 10^{7}\,\mathrm{m\,s^{-1}})^2 = \boxed{1.67 \times 10^{-16}\,\mathrm{J}}$$

Comment. This calculation uses the non-relativistic kinetic energy, which is only about 3 per cent less than the accurate (relativistic) value of 1.52×10^{-15} J. In this exercise, however, E_{binding} is a small difference of two larger numbers, so a small error in the kinetic energy results in a larger error in E_{binding}: the accurate value is $E_{\mathrm{binding}} = 1.26 \times 10^{-16}$ J.

Solutions to problems

Solutions to numerical problems

P11.3 $$\theta_{\mathrm{E}} = \frac{h\nu}{k}, \qquad [\theta_{\mathrm{E}}] = \frac{\mathrm{J\,s} \times \mathrm{s^{-1}}}{\mathrm{J\,K^{-1}}} = \mathrm{K}$$

In terms of θ_{E} the Einstein equation [11.9] for the heat capacity of solids is

$$C_V = 3R\left(\frac{\theta_{\mathrm{E}}}{T}\right)^2 \times \left(\frac{\mathrm{e}^{\theta_{\mathrm{E}}/2T}}{\mathrm{e}^{\theta_{\mathrm{E}}/T} - 1}\right)^2, \quad \text{classical value} = 3R$$

It reverts to the classical value when $T \gg \theta_{\mathrm{E}}$ or when $\dfrac{h\nu}{kT} \ll 1$ as demonstrated in the text (Section 11.1). The criterion for classical behaviour is therefore that $\boxed{T \gg \theta_{\mathrm{E}}}$.

$$\theta_{\mathrm{E}} = \frac{h\nu}{k} = \frac{(6.626 \times 10^{-34}\,\mathrm{J\,Hz^{-1}}) \times \nu}{1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}} = 4.798 \times 10^{-11}\,(\nu/\mathrm{Hz})\mathrm{K}$$

(a) For $\nu = 4.65 \times 10^{13}\,\text{Hz}$, $\theta_\text{E} = (4.798 \times 10^{-11}) \times (4.65 \times 10^{13}\,\text{K}) = \boxed{2231\,\text{K}}$

(b) For $\nu = 7.15 \times 10^{12}\,\text{Hz}$, $\theta_\text{E} = (4.798 \times 10^{-11}) \times (7.15 \times 10^{12}\,\text{K}) = \boxed{343\,\text{K}}$

Hence

(a) $$\frac{C_V}{3R} = \left(\frac{2231\,\text{K}}{298\,\text{K}}\right)^2 \times \left(\frac{\text{e}^{223\bar{1}/(2\times298)}}{\text{e}^{2231/298} - 1}\right)^2 = \boxed{0.031}$$

(b) $$\frac{C_V}{3R} = \left(\frac{343\,\text{K}}{298\,\text{K}}\right)^2 \times \left(\frac{\text{e}^{343/(2\times298)}}{\text{e}^{343/298} - 1}\right)^2 = \boxed{0.897}$$

Comment. For many metals the classical value is approached at room temperature; consequently, the failure of classical theory became apparent only after methods for achieving temperatures well below 25°C were developed in the latter part of the nineteenth century.

P11.5 The hydrogen atom wavefunctions are obtained from the solution of the Schrödinger equation in Chapter 13. Here we need only the wavefunction which is provided. It is the square of the wavefunction that is related to the probability (Section 11.4).

$$\psi^2 = \frac{1}{\pi a_0^3}\text{e}^{-2r/a_0}, \qquad \delta\tau = \frac{4}{3}\pi r_0^3, \quad r_0 = 1.0\,\text{pm}$$

If we assume that the volume $\delta\tau$ is so small that ψ does not vary within it, the probability is given by

$$\psi^2\delta\tau = \frac{4r_0^3}{3a_0^3}\text{e}^{-2r/a_0} = \frac{4}{3} \times \left(\frac{1.0}{53}\right)^3 \text{e}^{-2r/a_0}$$

(a) $r = 0:$ $$\psi^2\delta\tau = \frac{4}{3}\left(\frac{1.0}{53}\right)^3 = \boxed{9.0 \times 10^{-6}}$$

(b) $r = a_0:$ $$\psi^2\delta\tau = \frac{4}{3}\left(\frac{1.0}{53}\right)^3 \text{e}^{-2} = \boxed{1.2 \times 10^{-6}}$$

Question. If there is a nonzero probability that the electron can be found at $r = 0$ how does it avoid destruction at the nucleus? (*Hint.* See Chapter 13 for part of the solution to this difficult question.)

P11.7 According to the uncertainty principle,

$$\Delta p \Delta q \geq \tfrac{1}{2}\hbar,$$

where Δq and Δp are root-mean-square deviations:

$$\Delta q = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2} \quad \text{and} \quad \Delta p = (\langle p^2 \rangle - \langle p \rangle^2)^{1/2}.$$

To verify whether the relationship holds for the particle in a state whose wavefunction is

$$\Psi = (2a/\pi)^{1/4}\text{e}^{-ax^2},$$

We need the quantum-mechanical averages $\langle x \rangle$, $\langle x^2 \rangle$, $\langle p \rangle$, and $\langle p^2 \rangle$.

$$\langle x \rangle = \int \Psi^* x^2 \Psi \, \text{d}\tau = \int_{\infty-}^{\infty} \left(\frac{2a}{\pi}\right)^{1/4} \text{e}^{-ax^2} x \left(\frac{2a}{\pi}\right)^{1/4} \text{e}^{-ax^2} \text{d}x,$$

$$\langle x\rangle = \left(\frac{2a}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} x\mathrm{e}^{-2ax^2}\mathrm{d}x = 0;$$

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

$$\langle x^2\rangle = \left(\frac{2a}{\pi}\right)^{1/2}\frac{\pi^{1/2}}{2(2a)^{3/2}} = \frac{1}{4a};$$

so $\quad \Delta q = \dfrac{1}{2a^{1/2}}.$

$$\langle p\rangle = \int_{-\infty}^{\infty}\Psi^*\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\Psi}{\mathrm{d}x}\right)\mathrm{d}x \quad \text{and} \quad \langle p^2\rangle = \int_{-\infty}^{\infty}\Psi^*\left(-\hbar^2\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2}\right)\mathrm{d}x.$$

We need to evaluate the derivatives:

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

and $\quad \dfrac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} = \left(\dfrac{2a}{\pi}\right)^{1/4}[(-2ax)^2\mathrm{e}^{-ax^2} + (-2a)\mathrm{e}^{-ax^2}] = \left(\dfrac{2a}{\pi}\right)^{1/4}(4a^2x^2 - 2a)\mathrm{e}^{-ax^2}.$

So $\quad \langle p\rangle = \displaystyle\int_{-\infty}^{\infty}\left(\frac{2a}{\pi}\right)^{1/4}\mathrm{e}^{-ax^2}\left(\frac{\hbar}{\mathrm{i}}\right)\left(\frac{2a}{\pi}\right)^{1/4}(-2ax)\mathrm{e}^{-ax^2}\,\mathrm{d}x$

$$= -\frac{2\hbar}{\mathrm{i}}\left(\frac{2a}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} x\mathrm{e}^{-2ax^2}\mathrm{d}x = 0;$$

$$\langle p^2\rangle = \int_{-\infty}^{\infty}\left(\frac{2a}{\pi}\right)^{1/4}\mathrm{e}^{-ax^2}(-\hbar^2)\left(\frac{2a}{\pi}\right)^{1/4}(4a^2x^2 - 2a)\mathrm{e}^{-ax^2}\mathrm{d}x,$$

$$\langle p^2\rangle = (-2a\hbar^2)\left(\frac{2a}{\pi}\right)^{1/2}\int_{-\infty}^{\infty}(2ax^2 - 1)\mathrm{e}^{-2ax^2}\mathrm{d}x,$$

$$\langle p^2\rangle = (-2a\hbar^2)\left(\frac{2a}{\pi}\right)^{1/2}\left(2a\frac{\pi^{1/2}}{2(2a)^{3/2}} - \frac{\pi^{1/2}}{(2a)^{1/2}}\right) = a\hbar^2;$$

and $\quad \Delta p = a^{1/2}\hbar.$

Finally, $\quad \Delta q\,\Delta p = \dfrac{1}{2a^{1/2}} \times a^{1/2}\hbar = 1/2\hbar,$

which is the minimum product consistent with the uncertainty principle.

Solutions to theoretical problems

P11.9 We look for the value of λ at which ρ is a maximum, using (as appropriate) the short-wavelength (high-frequency) approximation

$$\rho = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT}-1}\right) \quad [11.5]$$

$$\frac{d\rho}{d\lambda} = -\frac{5}{\lambda}\rho + \frac{hc}{\lambda^2 kT}\left(\frac{e^{hc/\lambda kT}}{e^{hc/\lambda kT}-1}\right)\rho = 0 \quad \text{at } \lambda = \lambda_{\max}$$

Then, $-5 + \dfrac{hc}{\lambda kT} \times \dfrac{e^{hc/\lambda kT}}{e^{hc/\lambda kT}-1} = 0$

Hence, $5 - 5e^{hc/\lambda kT} + \dfrac{hc}{\lambda kT}e^{hc/\lambda kT} = 0$

If $\dfrac{hc}{\lambda kT} \gg 1$ [short wavelengths, high frequencies], this expression simplifies. We neglect the initial 5, cancel the two exponents, and obtain

$$hc = 5\lambda kT \quad \text{for} \quad \lambda = \lambda_{\max} \quad \text{and} \quad \frac{hc}{\lambda kT} \gg 1$$

or $\boxed{\lambda_{\max}T = \dfrac{hc}{5k} = 2.88\,\text{mm K}}$, in accord with observation.

Comment. Most experimental studies of black-body radiation have been done over a wavelength range of a factor of 10 to 100 of the wavelength of visible light and over a temperature range of 300 K to 10 000 K.

Question. Does the short-wavelength approximation apply over all of these ranges? Would it apply to the cosmic background radiation of the universe at 2.7 K where $\lambda_{\max} \approx 0.2$ cm?

P11.10

$$\rho = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT}-1}\right) \quad [11.5]$$

As λ increases, $\dfrac{hc}{\lambda kT}$ decreases, and at very long wavelength $hc/\lambda kT \ll 1$. Hence we can expand the exponential in a power series. Let $x = hc/\lambda kT$, then

$$e^x = 1 + x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \cdots$$

$$\rho = \frac{8\pi hc}{\lambda^5}\left[\frac{1}{1 + x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \cdots - 1}\right]$$

$$\lim_{\lambda\to\infty}\rho = \frac{8\pi hc}{\lambda^5}\left[\frac{1}{1+x-1}\right] = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{hc/\lambda kT}\right)$$

$$= \frac{8\pi kT}{\lambda^4}$$

This is the Rayleigh–Jeans law [11.3].

P11.12 $\rho = \dfrac{8\pi hc}{\lambda^5} \times \dfrac{1}{e^{hc/\lambda kT} - 1}$ [11.5]

$$\begin{aligned}\frac{\partial\rho}{\partial\lambda} &= -\frac{40\pi hc}{\lambda^6} \times \left(\frac{1}{e^{hc/\lambda kT} - 1}\right) - \left(\frac{8\pi hc}{\lambda^5}\right) \times \frac{e^{hc/\lambda kT} \times \left(-\frac{hc}{\lambda^2 kT}\right)}{\left(e^{hc/\lambda kT} - 1\right)^2} \\ &= \frac{8\pi hc}{\lambda^5} \times \left(\frac{1}{e^{hc/\lambda kT} - 1}\right) \times \left[-\frac{5}{\lambda} + \frac{hc}{\lambda^2 kT}\frac{e^{hc/\lambda kT}}{e^{hc/\lambda kT} - 1}\right] \\ &= \left(-\frac{5}{\lambda}\right) \times \rho\left[1 - \frac{hc}{5\lambda kT}\frac{1}{1 - e^{-hc/\lambda kT}}\right]\end{aligned}$$

$$\frac{\partial\rho}{\partial\lambda} = 0 \quad \text{when } \lambda = \lambda_{\max} \quad \text{and}$$

$$\frac{hc}{5\lambda_{\max}kT}\left[\frac{1}{1 - e^{-hc/\lambda_{\max}kT}}\right] = 1$$

$$\frac{5\lambda_{\max}kT}{hc}\left(1 - e^{-hc/\lambda_{\max}kT}\right) = 1$$

Let $x = \dfrac{hc}{\lambda_{\max}kT}$; then $\dfrac{5}{x}\left(1 - e^{-x}\right) = 1$ or $\dfrac{5}{x} = \dfrac{1}{1 - e^{-x}}$

The solution of this equation is $x = 4.965$.

Then $h = \dfrac{4.965\lambda_{\max}kT}{c}$ (1)

However

$M = \sigma T^4 = \left(\dfrac{2\pi^5 k^4}{15c^2h^3}\right)T^4$ (2)

Substituting (1) into (2) yields

$$\begin{aligned}M &\approx \left(\frac{2\pi^5 k^4}{15c^2}\right) \times \left(\frac{c}{4.965\lambda_{\max}kT}\right)^3 T^4 \\ &\approx \frac{2\pi^5 ckT}{1835.9\lambda_{\max}^3}\end{aligned}$$

$$\begin{aligned}k &\approx \frac{1835.9\lambda_{\max}^3 M}{2\pi^5 cT} \\ &\approx \frac{1835.9(1.451 \times 10^{-6}\,\text{m})^3 \times (904.48 \times 10^3\,\text{W})}{2\pi^5(2.998 \times 10^8\,\text{m s}^{-1}) \times (2000\,\text{K}) \times (1.000\,\text{m}^2)}\end{aligned}$$

$\boxed{k \approx 1.382 \times 10^{-23}\,\text{J K}^{-1}}$ (3)

Substituting (3) into (1)

$$h \approx \frac{5(1.451 \times 10^{-6}\,\mathrm{m}) \times (1.382 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (2000\,\mathrm{K})}{2.998 \times 10^{8}\,\mathrm{m\,s^{-1}}}$$

$$\boxed{h \approx 6.69 \times 10^{-34}\,\mathrm{J\,s}}$$

Comment. These calculated values are very close to the currently accepted values for these constants.

P11.14 In each case form $N\psi$; integrate

$$\int (N\psi)^*(N\psi)\,\mathrm{d}\tau$$

set the integral equal to 1 and solve for N.

(a)
$$\psi = N\left(2 - \frac{r}{a_0}\right)\mathrm{e}^{-r/2a_0}$$

$$\psi^2 = N^2\left(2 - \frac{r}{a_0}\right)^2\mathrm{e}^{-r/a_0}$$

$$\int \psi^2\,\mathrm{d}\tau = N^2\int_0^\infty\left(4r^2 - \frac{4r^3}{a_0} + \frac{r^4}{a_0^2}\right)\mathrm{e}^{-r/a_0}\,\mathrm{d}r\int_0^\pi \sin\theta\,\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\phi$$

$$= N^2\left(4 \times 2a_0^3 - 4 \times \frac{6a_0^4}{a_0} + \frac{24a_0^5}{a_0^2}\right) \times (2) \times (2\pi) = 32\pi a_0^3N^2;$$

hence $\boxed{N = \left(\frac{1}{32\pi a_0^3}\right)^{1/2}}$

where we have used

$$\int_0^\infty x^n\mathrm{e}^{-ax}\,\mathrm{d}x = \frac{n!}{a^{n+1}} \text{ [Problem 11.13]}$$

(b)
$$\psi = Nr\sin\theta\cos\phi\,\mathrm{e}^{-r/(2a_0)}$$

$$\int \psi^2\,\mathrm{d}\tau = N^2\int_0^\infty r^4\mathrm{e}^{-r/a_0}\,\mathrm{d}r\int_0^\pi \sin^2\theta\sin\theta\,\mathrm{d}\theta\int_0^{2\pi}\cos^2\phi\,\mathrm{d}\phi$$

$$= N^2 4!a_0^5\int_{-1}^{1}(1 - \cos^2\theta)\,\mathrm{d}\cos\theta \times \pi$$

$$= N^2 4!a_0^5\left(2 - \frac{2}{3}\right)\pi = 32\pi a_0^5N_0^2; \quad \text{hence} \quad \boxed{N = \left(\frac{1}{32\pi a_0^5}\right)^{1/2}}$$

where we have used $\int_0^\pi \cos^n\theta\sin\theta\,\mathrm{d}\theta = -\int_1^{-1}\cos^n\theta\,\mathrm{d}\cos\theta = \int_{-1}^{1}x^n\,\mathrm{d}x$

and the relations at the end of the solution to Problem 11.8. [See *Student's solutions manual*.]

P11.16 Operate on each function with i; if the function is regenerated multiplied by a constant, it is an eigenfunction of i and the constant is the eigenvalue.

(a) $f = x^3 - kx$

$i(x^3 - kx) = -x^3 + kx = -f$

Therefore, f is an eigenfunction with eigenvalue, $\boxed{-1}$

(b) $f = \cos kx$

$i\cos kx = \cos(-kx) = \cos kx = f$

Therefore, f is an eigenfunction with eigenvalue, $\boxed{+1}$

(c) $f = x^2 + 3x - 1$

$i(x^2 + 3x - 1) = x^2 - 3x - 1 \neq \text{constant} \times f$

Therefore, f is not an eigenfunction of i.

P11.19 The kinetic energy operator, $\hat{T}$, is obtained from the operator analogue of the classical equation

$$E_K = \frac{p^2}{2m}$$

that is,

$$\hat{T} = \frac{(\hat{p})^2}{2m}$$

$$\hat{p}_x = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x} \text{ [11.32]}; \quad \text{hence} \quad \hat{p}_x^2 = -\hbar^2\frac{\mathrm{d}^2}{\mathrm{d}x^2} \quad \text{and} \quad \hat{T} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$$

Then

$$\langle T\rangle = N^2\int\psi^*\left(\frac{\hat{p}_x^2}{2m}\right)\psi\,\mathrm{d}\tau = \frac{\int\psi^*\left(\frac{\hat{p}^2}{2m}\right)\psi\,\mathrm{d}\tau}{\int\psi^*\psi\,\mathrm{d}\tau} \quad \left[N^2 = \frac{1}{\int\psi^*\psi\,\mathrm{d}\tau}\right]$$

$$= \frac{\frac{-\hbar^2}{2m}\int\psi^*\frac{\mathrm{d}^2}{\mathrm{d}x^2}(\mathrm{e}^{\mathrm{i}kx}\cos\chi + \mathrm{e}^{-\mathrm{i}kx}\sin\chi)\,\mathrm{d}\tau}{\int\psi^*\psi\,\mathrm{d}\tau}$$

$$= \frac{\frac{-\hbar^2}{2m}\int\psi^*(-k^2)\times(\mathrm{e}^{\mathrm{i}kx}\cos\chi + \mathrm{e}^{-\mathrm{i}kx}\sin\chi)\,\mathrm{d}\tau}{\int\psi^*\psi\,\mathrm{d}\tau} = \frac{\hbar^2k^2\int\psi^*\psi\,\mathrm{d}\tau}{2m\int\psi^*\psi\,\mathrm{d}\tau} = \boxed{\frac{\hbar^2k^2}{2m}}$$

P11.20 $p_x = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}$ [11.32]

$$\langle p_x\rangle = N^2\int\psi^*\hat{p}_x\psi\,\mathrm{d}x; \quad N^2 = \frac{1}{\int\psi^*\psi\,\mathrm{d}\tau}$$

$$= \frac{\int\psi^*\hat{p}_x\psi\,\mathrm{d}x}{\int\psi^*\psi\,\mathrm{d}x} = \frac{\frac{\hbar}{\mathrm{i}}\int\psi^*\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)\mathrm{d}x}{\int\psi^*\psi\,\mathrm{d}x}$$

(a) $\psi = \mathrm{e}^{\mathrm{i}kx}, \quad \frac{\mathrm{d}\psi}{\mathrm{d}x} = \mathrm{i}k\psi$

Hence,

$$\langle p_x\rangle = \frac{\frac{\hbar}{\mathrm{i}}\times\mathrm{i}k\int\psi^*\psi\,\mathrm{d}x}{\int\psi^*\psi\,\mathrm{d}x} = \boxed{k\hbar}$$

(b) $\psi = \cos kx, \qquad \dfrac{\mathrm{d}\psi}{\mathrm{d}x} = -k \sin kx$

$$\int_{-\infty}^{\infty} \psi^* \frac{\mathrm{d}\psi}{\mathrm{d}x}\,\mathrm{d}x = -k \int_{-\infty}^{\infty} \cos kx \sin kx\,\mathrm{d}x = 0$$

Therefore, $\langle p_x \rangle = \boxed{0}$

(c) $\psi = \mathrm{e}^{-\alpha x^2}, \quad \dfrac{\mathrm{d}\psi}{\mathrm{d}x} = -2\alpha x \mathrm{e}^{-\alpha x^2}$

$$\int_{-\infty}^{\infty} \psi^* \frac{\mathrm{d}\psi}{\mathrm{d}x}\,\mathrm{d}x = -2\alpha \int_{-\infty}^{\infty} x\mathrm{e}^{-2\alpha x^2}\,\mathrm{d}x = 0 \quad \text{[by symmetry, since } x \text{ is an odd function]}$$

Therefore, $\langle p_x \rangle = \boxed{0}$

P11.23 No solution.

Solution to applications

P11.27 **(a)** Consider any infinitesimal volume element $\mathrm{d}x\ \mathrm{d}y\ \mathrm{d}z$ within the hemisphere (Figure 11.1) that has a radius equal to the distance traveled by light in the time $\mathrm{d}t$ ($c\,\mathrm{d}t$). The objective is to find the total radiation flux perpendicular to the hemisphere face at its center. Imagine an infinitesimal area A at that point. Let r be the distance from $\mathrm{d}x\ \mathrm{d}y\ \mathrm{d}z$ to A and imagine the infinitesimal area A' perpendicular to $\vec{r}$. E is the total isotropic energy density in $\mathrm{d}x\ \mathrm{d}y\ \mathrm{d}z$. $E\ \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$ is the energy emitted in $\mathrm{d}t$. $A'/4\pi r^2$ is the fraction of this radiation that passes through A'. The radiation flux that originates from $\mathrm{d}x\ \mathrm{d}y\ \mathrm{d}z$ and passes through A' in $\mathrm{d}t$ is given by:

$$J_{A'} = \frac{\left(\frac{\cancel{A'}}{4\pi r^2}\right) E\ \mathrm{d}x\ \mathrm{d}y\ \mathrm{d}z}{\cancel{A'}\,\mathrm{d}t} = \frac{E\ \mathrm{d}x\ \mathrm{d}y\ \mathrm{d}z}{4\pi r^2\,\mathrm{d}t}$$

The contribution of $J_{A'}$ to the radiation flux through A, J_A, is given by the expression $J_{A'} \times (\cancel{A}\cos\theta)/\cancel{A} = J_{A'}\cos\theta$. The integration of this expression over the whole hemisphere gives an

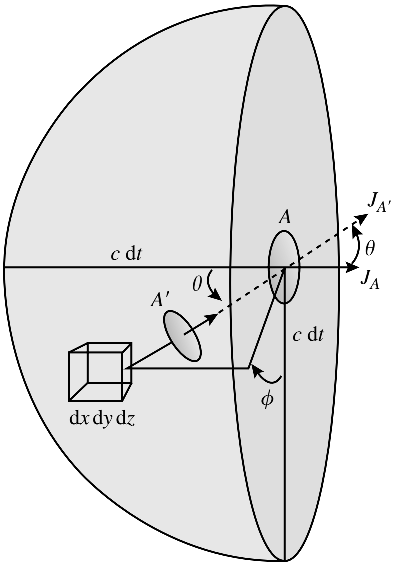


Figure 11.1

expression for J_A. Spherical coordinates facilitate to integration: $\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z = r^2 \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\,\mathrm{d}r = -r^2\mathrm{d}(\cos\theta)\,\mathrm{d}\phi\,\mathrm{d}r$ where $0 \le \theta \le 2\pi$ and $0 \le \theta \le \pi/2$.

$$\begin{aligned}
J_A &= \int\limits_{\text{hemisphere}} \cos(\theta)\left\{\frac{E\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z}{4\pi r^2\,\mathrm{d}t}\right\} \\
&= \int\limits_{\text{hemisphere}} \cos(\theta)\left\{\frac{E}{4\pi \cancel{r^2}\mathrm{d}t}\right\}\{-\cancel{r^2}\mathrm{d}(\cos\theta)\,\mathrm{d}\phi\,\mathrm{d}r\} \\
&= -\left(\frac{E}{4\pi\,\mathrm{d}t}\right)\int\limits_{\cos(0)}^{\cos(\pi/2)} \cos(\theta)\,\mathrm{d}(\cos\theta)\int\limits_0^{2\pi}\mathrm{d}\phi\int\limits_0^{c\,dt}\mathrm{d}r \\
&= -\left(\frac{E}{\cancel{4\pi\mathrm{d}t}}\right)\left[\int\limits_1^0 w\,\mathrm{d}w\right](2\cancel{\pi})\,(c\cancel{\mathrm{d}t}) \\
J_A &= -\frac{cE}{4}\left(\frac{-1}{\cancel{2}}\right)(\cancel{2})\ \{\text{Subscript “A” has been a bookkeeping device. It may be dropped.}\}
\end{aligned}$$

$$\boxed{J = \frac{cE}{4}} \quad \text{or} \quad \boxed{\mathrm{d}J = \frac{c}{4}\,\mathrm{d}E}$$

$$\mathrm{d}E = \frac{8\pi hc\,\mathrm{d}\lambda}{\lambda^5(\mathrm{e}^{hc/\lambda RT}-1)} \quad [\text{eqn 11.5}]$$

By eqn 16.1 $\tilde{\nu} = 1/\lambda$. Taking differentials to be positive, $\mathrm{d}\tilde{\nu} = \mathrm{d}\lambda/\lambda^2$ or $\mathrm{d}\lambda = \lambda^2\,\mathrm{d}\tilde{\nu} = \mathrm{d}\tilde{\nu}/\tilde{\nu}^2$. The substitution of $\tilde{\nu}$ for λ gives:

$$\mathrm{d}E = \frac{8\pi hc\tilde{\nu}^3}{\mathrm{e}^{hc\tilde{\nu}/kT}-1}\,\mathrm{d}\tilde{\nu}$$

Thus, $\mathrm{d}J = \mathrm{f}(\tilde{\nu})\,\mathrm{d}\tilde{\nu}$ where $\boxed{\mathrm{f}(\tilde{\nu}) = \dfrac{2\pi hc^2\tilde{\nu}^3}{\mathrm{e}^{hc\tilde{\nu}/kT}-1}}$

The value of the Stefan–Boltzmann constant σ is defined by the low $n = \int_0^\infty \mathrm{d}J(\tilde{\nu}) = \sigma T^4$. n is called the total exitance. Let $x = hc\tilde{\nu}/kT$ (or $\tilde{\nu} = kTx/hc$), substitute the above equation for $\mathrm{d}J(\tilde{\nu})$ into the Stefan–Boltzmann low, and integrate.

$$\begin{aligned}
n &= \int\limits_o^\infty \frac{2\pi hc^2\tilde{\nu}^3\mathrm{d}\tilde{\nu}}{\mathrm{e}^{hc\tilde{\nu}/kT}-1} = \frac{2\pi k^4T^4}{h^3c^2}\int\limits_0^\infty \frac{x^3\mathrm{d}x}{e^x-1} \\
&= \left(\frac{2\pi k^4T^4}{h^3c^2}\right)\left(\frac{\pi^4}{15}\right) = \left(\frac{2\pi^5k^4}{15\,h^3c^2}\right)T^4
\end{aligned}$$

Thus, $\boxed{\sigma = \dfrac{2\pi^5k^4}{15h^3c^2} = 5.6704\times10^{-8}\ \mathrm{W\,m^{-2}\,K^{-4}}}$

The function $f(\tilde{\nu})$ gives radiation density in units that are compatible with those often used in discussions of infrared radiation which lies between about 33 $\mathrm{cm^{-1}}$ and 12 800 $\mathrm{cm^{-1}}$ (Fig. 11.2).

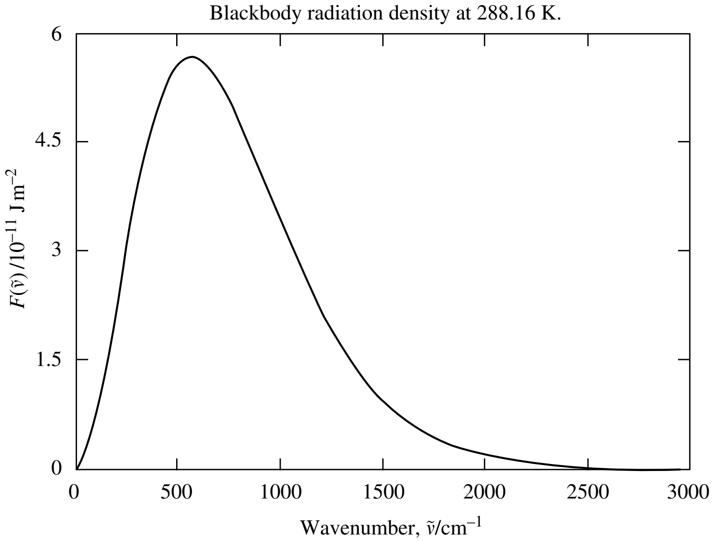


Figure 11.2

By graphing $f(\tilde{\nu})$ at the observed average temperature of the Earth's surface (288.16 K) we easily see that the Earth's black-body emissions are in the infrared with a maximum at about 600 cm^{-1}.

(b) Let R represent the radius of the Earth. Assuming an average balance between the Earth's absorption of solar radiation and Earth's emission of black-body radiation into space gives:

Solar energy absorbed = black-body energy lost

$\pi R^2(1 - \text{albedo})(\text{solar energy flux}) = (4\pi R^2)(\sigma T^4)$

Solving for T gives:

$$\begin{aligned} T &= \left[\frac{(1-\text{albedo})(\text{solar energy flux})}{4\sigma}\right]^{1/4} \\ &= \left[\frac{(1-0.29)(0.1353\ \text{W cm}^{-2})}{4(5.67\times10^{-12}\ \text{W cm}^{-2}\ \text{K}^{-4})}\right]^{1/4} = \boxed{255\ \text{K}} \end{aligned}$$

This is an estimate of what the Earth's temperature would be in the absence of the greenhouse effect.

12 Quantum theory: techniques and applications

Solutions to exercises

Discussion questions

E12.1(b) The correspondence principle states that in the limit of very large quantum numbers quantum mechanics merges with classical mechanics. An example is a molecule of a gas in a box. At room temperature, the particle-in-a-box quantum numbers corresponding to the average energy of the gas molecules ($\frac{1}{2}$ kT per degree of freedom) are extremely large; consequently the separation between the levels is relatively so small (n is always small compared to n^2, compare eqn 12.10 to eqn 12.4) that the energy of the particle is effectively continuous, just as in classical mechanics. We may also look at these equations from the point of view of the mass of the particle. As the mass of the particle increases to macroscopic values, the separation between the energy levels approaches zero. The quantization disappears as we know it must. Tennis balls do not show quantum mechanical effects. (Except those served by Pete Sampras.) We can also see the correspondence principle operating when we examine the wavefunctions for large values of the quantum numbers. The probability density becomes uniform over the path of motion, which is again the classical result. This aspect is discussed in more detail in Section 12.1(c).

The harmonic oscillator provides another example of the correspondence principle. The same effects mentioned above are observed. We see from Fig. 12.22 of the text that probability distribution for large values on n approaches the classical picture of the motion. (Look at the graph for $n = 20$.)

E12.2(b) The physical origin of tunnelling is related to the probability density of the particle which according to the Born interpretation is the square of the wavefunction that represents the particle. This interpretation requires that the wavefunction of the system be everywhere continuous, event at barriers. Therefore, if the wavefunction is non-zero on one side of a barrier it must be non-zero on the other side of the barrier and this implies that the particle has tunnelled through the barrier. The transmission probability depends upon the mass of the particle (specifically $m^{1/2}$, through eqns 12.24 and 12.28): the greater the mass the smaller the probability of tunnelling. Electrons and protons have small masses, molecular groups large masses; therefore, tunnelling effects are more observable in process involving electrons and protons.

E12.3(b) The essential features of the derivation are:

(1) The separation of the hamiltonian into large (unperturbed) and small (perturbed) parts which are independent of each other.

(2) The expansion of the wavefunctions and energies as a power series in an unspecified parameters, λ, which in the end effectively cancels or is set equal to 1.

(3) The calculation of the first-order correction to the energies by an integration of the perturbation over the zero-order wavefunctions.

(4) The expansion of the first-order correction to the wavefunction in terms of the complete set of functions which are a solution of the unperturbed Schrodinger equation.

(5) The calculation of the second-order correction to the energies with use of the corrected first order wavefunctions.

See *Justification* 12.7 and *Further reading* for a more complete discussion of the method.

Numerical exercises

E12.4(b)

$$E = \frac{n^2h^2}{8m_eL^2}$$

$$\frac{h^2}{8m_eL^2} = \frac{(6.626 \times 10^{-34}\,\mathrm{J\,s})^2}{8(9.109 \times 10^{-31}\,\mathrm{kg}) \times (1.50 \times 10^{-9}\,\mathrm{m})^2} = 2.67\overline{8} \times 10^{-20}\,\mathrm{J}$$

Conversion factors

$$\frac{E}{\mathrm{kJ\,mol^{-1}}} = \frac{N_A}{10^3}E/\mathrm{J}$$

$$1\,\mathrm{eV} = 1.602 \times 10^{-19}\,\mathrm{J}$$

$$1\,\mathrm{cm^{-1}} = 1.986 \times 10^{-23}\,\mathrm{J}$$

(a) $$E_3 - E_1 = (9-1)\frac{h^2}{8m_eL^2} = 8(2.678 \times 10^{-20}\,\mathrm{J})$$

$$= \boxed{2.14 \times 10^{-19}\,\mathrm{J}} = \boxed{129\,\mathrm{kJ\,mol^{-1}}} = \boxed{1.34\,\mathrm{eV}} = \boxed{1.08 \times 10^4\,\mathrm{cm^{-1}}}$$

(b) $$E_7 - E_6 = (49-36)\frac{h^2}{8m_eL^2}$$

$$= 13(2.678 \times 10^{-20}\,\mathrm{J})$$

$$= \boxed{3.48 \times 10^{-19}\,\mathrm{J}} = \boxed{210\,\mathrm{kJ\,mol^{-1}}} = \boxed{2.17\,\mathrm{eV}} = \boxed{1.75 \times 10^4\,\mathrm{cm^{-1}}}$$

E12.5(b) The probability is

$$P = \int \psi^*\psi\,\mathrm{d}x = \frac{2}{L}\int \sin^2\left(\frac{n\pi x}{L}\right)\mathrm{d}x = \frac{2\Delta x}{L}\sin^2\left(\frac{n\pi x}{L}\right)$$

where $\Delta x = 0.02L$ and the function is evaluated at $x = 0.66L$.

(a) For $n = 1$

$$P = \frac{2(0.02L)}{L}\sin^2(0.66\pi) = \boxed{0.03\overline{1}}$$

(b) For $n = 2$

$$P = \frac{2(0.02L)}{L}\sin^2[2(0.66\pi)] = \boxed{0.02\overline{9}}$$

E12.6(b) The expectation value is

$$\langle \hat{p} \rangle = \int \psi^*\hat{p}\psi\,\mathrm{d}x$$

but first we need $\hat{p}\psi$

$$\hat{p}\psi = -\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right) = -\mathrm{i}\hbar\left(\frac{2}{L}\right)^{1/2}\frac{n\pi}{L}\cos\left(\frac{n\pi x}{L}\right)$$

$$\text{so } \langle \hat{p} \rangle = \frac{-2\mathrm{i}\hbar n\pi}{L^2}\int_0^L \sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)\mathrm{d}x = \boxed{0} \text{ for all } n$$

$$\langle \hat{p}^2 \rangle = 2m\langle \hat{H} \rangle = 2mE_n = \frac{h^2n^2}{4L^2}$$

for all n. So for $n = 2$

$$\langle \hat{p}^2 \rangle = \boxed{\frac{h^2}{L^2}}$$

E12.7(b) $n = 5$

$$\psi_5 = \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{5\pi x}{L}\right)$$

$$P(x) \propto \psi_5^2 \propto \sin^2\left(\frac{5\pi x}{L}\right)$$

Maxima and minima in $P(x)$ correspond to $\dfrac{\mathrm{d}P(x)}{\mathrm{d}x} = 0$

$$\frac{\mathrm{d}}{\mathrm{d}x}P(x) \propto \frac{\mathrm{d}\psi^2}{\mathrm{d}x} \propto \sin\left(\frac{5\pi x}{L}\right)\cos\left(\frac{5\pi x}{L}\right) \propto \sin\left(\frac{10\pi x}{L}\right) \quad (2\sin\alpha\cos\alpha = \sin 2\alpha)$$

$$\sin\theta = 0 \quad \text{when } \theta = 0, \pi, 2\pi, \ldots = n'\pi \quad (n' = 0, 1, 2, \ldots)$$

$$\frac{10\pi x}{L} = n'\pi \quad n' \leq 10$$

$$x = \frac{n'L}{10}$$

Minima at $x = 0,\ x = L$

Maxima and minima alternate: maxima correspond to

$$n' = 1, 3, 5, 7, 9 \qquad x = \boxed{\frac{L}{10}}, \boxed{\frac{3L}{10}}, \boxed{\frac{L}{2}}, \boxed{\frac{7L}{10}}, \boxed{\frac{9L}{10}}$$

E12.8(b) The energy levels are

$$E_{n_1,n_2,n_3} = \frac{(n_1^2 + n_2^2 + n_3^2)h^2}{8mL^2} = E_1(n_1^2 + n_2^2 + n_3^2)$$

where E_1 combines all constants besides quantum numbers. The minimum value for all the quantum numbers is 1, so the lowest energy is

$$E_{1,1,1} = 3E_1$$

The question asks about an energy 14/3 times this amount, namely $14E_1$. This energy level can be obtained by any combination of allowed quantum numbers such that

$$n_1^2 + n_2^2 + n_3^2 = 14 = 3^2 + 2^2 + 1^2$$

The degeneracy, then, is $\boxed{6}$, corresponding to $(n_1, n_2, n_3) = (1, 2, 3), (2, 1, 3), (1, 3, 2), (2, 3, 1), (3, 1, 2)$, or $(3, 2, 1)$.

E12.9(b) $E = \frac{3}{2}kT$ is the average translational energy of a gaseous molecule (see Chapter 20).

$$E = \tfrac{3}{2}kT = \frac{(n_1^2 + n_2^2 + n_3^2)h^2}{8mL^2} = \frac{n^2h^2}{8mL^2}$$

$$E = \left(\tfrac{3}{2}\right) \times (1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (300\,\mathrm{K}) = 6.21\bar{4} \times 10^{-21}\,\mathrm{J}$$

$$n^2 = \frac{8mL^2}{h^2}E$$

If $L^3 = 1.00\,\mathrm{m}^3,\ L^2 = 1.00\,\mathrm{m}^2$

$$\frac{h^2}{8mL^2} = \frac{(6.626 \times 10^{-34}\,\mathrm{J\,s})^2}{(8) \times \left(\frac{0.02802\,\mathrm{kg\,mol^{-1}}}{6.022\times10^{23}\,\mathrm{mol^{-1}}}\right) \times (1.00\,\mathrm{m}^2)} = 1.18\bar{0} \times 10^{-42}\,\mathrm{J}$$

$$n^2 = \frac{6.21\bar{4} \times 10^{-21}\,\mathrm{J}}{1.180 \times 10^{-42}\,\mathrm{J}} = 5.26\bar{5} \times 10^{21}; \qquad n = \boxed{7.26 \times 10^{10}}$$

$$\Delta E = E_{n+1} - E_n = E_{7.26\times10^{10}+1} - E_{7.26\times10^{10}}$$

$$\Delta E = (2n+1) \times \left(\frac{h^2}{8mL^2}\right) = [(2) \times (7.26 \times 10^{10} + 1)] \times \left(\frac{h^2}{8mL^2}\right) = \frac{14.5\bar{2} \times 10^{10}h^2}{8mL^2}$$

$$= (14.5\bar{2} \times 10^{10}) \times (1.18\bar{0} \times 10^{-42}\,\mathrm{J}) = \boxed{1.71 \times 10^{-31}\,\mathrm{J}}$$

The de Broglie wavelength is obtained from

$$\lambda = \frac{h}{p} = \frac{h}{mv}\ \text{[Section 11.2]}$$

The velocity is obtained from

$$E_\mathrm{K} = \tfrac{1}{2}mv^2 = \tfrac{3}{2}kT = 6.21\bar{4} \times 10^{-21}\,\mathrm{J}$$

$$v^2 = \frac{6.21\bar{4} \times 10^{-21}\,\mathrm{J}}{\left(\frac{1}{2}\right) \times \left(\frac{0.02802\,\mathrm{kg\,mol^{-1}}}{6.022\times10^{23}\,\mathrm{mol^{-1}}}\right)} = 2.67\bar{1} \times 10^5; \qquad v = 517\,\mathrm{m\,s^{-1}}$$

$$\lambda = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{(4.65 \times 10^{-26}\,\mathrm{kg}) \times (517\,\mathrm{m\,s^{-1}})} = 2.75 \times 10^{-11}\,\mathrm{m} = \boxed{27.5\,\mathrm{pm}}$$

The conclusion to be drawn from all of these calculations is that the translational motion of the nitrogen molecule can be described classically. The energy of the molecule is essentially continuous, $\frac{\Delta E}{E} \lll 1$.

E12.10(b) The zero-point energy is

$$E_0 = \tfrac{1}{2}\hbar\omega = \tfrac{1}{2}\hbar\left(\frac{k}{m}\right)^{1/2} = \tfrac{1}{2}(1.0546 \times 10^{-34}\,\mathrm{J\,s}) \times \left(\frac{285\,\mathrm{N\,m^{-1}}}{5.16 \times 10^{-26}\,\mathrm{kg}}\right)^{1/2}$$

$$= \boxed{3.92 \times 10^{-21}\,\mathrm{J}}$$

E12.11(b) The difference in adjacent energy levels is

$$\Delta E = \hbar\omega = \hbar\left(\frac{k}{m}\right)^{1/2} \quad \text{so} \quad k = \frac{m(\Delta E)^2}{\hbar^2} = \frac{(2.88\times 10^{-25}\,\text{kg})\times(3.17\times 10^{-21}\,\text{J})^2}{(1.0546\times 10^{-34}\,\text{J s})^2}$$

$$k = \boxed{260\,\text{N m}^{-1}}$$

E12.12(b) The difference in adjacent energy levels, which is equal to the energy of the photon, is

$$\Delta E = \hbar\omega = h\nu \quad \text{so} \quad \hbar\left(\frac{k}{m}\right)^{1/2} = \frac{hc}{\lambda}$$

$$\text{and } \lambda = \frac{hc}{\hbar}\left(\frac{k}{m}\right)^{1/2} = 2\pi c\left(\frac{m}{k}\right)^{1/2}$$

$$= 2\pi(2.998\times 10^{8}\,\text{m s}^{-1})\times\left(\frac{(15.9949\,\text{u})\times(1.66\times 10^{-27}\,\text{kg u}^{-1})}{544\,\text{N m}^{-1}}\right)^{1/2}$$

$$\lambda = 1.32\times 10^{-5}\,\text{m} = \boxed{13.2\,\mu\text{m}}$$

E12.13(b) The difference in adjacent energy levels, which is equal to the energy of the photon, is

$$\Delta E = \hbar\omega = h\nu \quad \text{so} \quad \hbar\left(\frac{k}{m}\right)^{1/2} = \frac{hc}{\lambda}$$

$$\text{and } \lambda = \frac{hc}{\hbar}\left(\frac{k}{m}\right)^{1/2} = 2\pi c\left(\frac{m}{k}\right)^{1/2}$$

Doubling the mass, then, increases the wavelength by $2^{1/2}$. So taking the result from Ex. 12.12(b), the new wavelength is

$$\lambda = 2^{1/2}(13.2\,\mu\text{m}) = \boxed{18.7\,\mu\text{m}}$$

E12.14(b) $\omega = \left(\frac{g}{l}\right)^{1/2}$ [elementary physics]

$$\Delta E = \hbar\omega = h\nu$$

(a) $\Delta E = h\nu = (6.626\times 10^{-34}\,\text{J Hz}^{-1})\times(33\times 10^{3}\,\text{Hz}) = \boxed{2.2\times 10^{-29}\,\text{J}}$

(b) $\Delta E = \hbar\omega = \hbar\left(\frac{k}{m_{\text{eff}}}\right)^{1/2} \quad \left[\frac{1}{m_{\text{eff}}} = \frac{1}{m_1} + \frac{1}{m_2} \text{ with } m_1 = m_2\right]$

For a two-particle oscillator m_{eff}, replaces m in the expression for ω. (See Chapter 16 for a more complete discussion of the vibration of a diatomic molecule.)

$$\Delta E = \hbar\left(\frac{2k}{m}\right)^{1/2} = (1.055\times 10^{-34}\,\text{J s})\times\left(\frac{(2)\times(1177\,\text{N m}^{-1})}{(16.00)\times(1.6605\times 10^{-27}\,\text{kg})}\right)^{1/2}$$

$$= \boxed{3.14\times 10^{-20}\,\text{J}}$$

E12.15(b) The first excited-state wavefunction has the form

$$\psi = 2N_1 y \exp\left(-\tfrac{1}{2}y^2\right)$$

where N_1 is a collection of constants and $y \equiv x\left(\dfrac{m\omega}{\hbar}\right)^{1/2}$. To see if it satisfies Schrödinger's equation, we see what happens when we apply the energy operator to this function

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \tfrac{1}{2}m\omega^2 x^2\psi$$

We need derivatives of ψ

$$\frac{\mathrm{d}\psi}{\mathrm{d}x} = \frac{\mathrm{d}\psi}{\mathrm{d}y}\frac{\mathrm{d}y}{\mathrm{d}x} = \left(\frac{m\omega}{\hbar}\right)^{1/2}(2N_1)\times(1-y^2)\times\exp\left(-\tfrac{1}{2}y^2\right)$$

and $\dfrac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \dfrac{\mathrm{d}^2\psi}{\mathrm{d}y^2}\left(\dfrac{\mathrm{d}y}{\mathrm{d}x}\right)^2 = \left(\dfrac{m\omega}{\hbar}\right)\times(2N_1)\times(-3y+y^3)\times\exp\left(-\tfrac{1}{2}y^2\right) = \left(\dfrac{m\omega}{\hbar}\right)\times(y^2-3)\psi$

$$\begin{aligned}\text{So } \hat{H}\psi &= -\frac{\hbar^2}{2m}\times\left(\frac{m\omega}{\hbar}\right)\times(y^2-3)\psi + \tfrac{1}{2}m\omega^2x^2\psi \\ &= -\tfrac{1}{2}\hbar\omega\times(y^2-3)\times\psi + \tfrac{1}{2}\hbar\omega y^2\psi = \tfrac{3}{2}\hbar\omega\psi\end{aligned}$$

Thus, ψ is an eigenfunction of $\hat{H}$ (i.e. it obeys the Schrödinger equation) with eigenvalue

$$E = \boxed{\tfrac{3}{2}\hbar\omega}$$

E12.16(b) The zero-point energy is

$$E_0 = \tfrac{1}{2}\hbar\omega = \tfrac{1}{2}\hbar\left(\frac{k}{m_{\text{eff}}}\right)^{1/2}$$

For a homonuclear diatomic molecule, the effective mass is half the mass of an atom, so

$$E_0 = \tfrac{1}{2}(1.0546\times10^{-34}\,\mathrm{J\,s})\times\left(\frac{2293.8\,\mathrm{N\,m^{-1}}}{\tfrac{1}{2}(14.0031\,\mathrm{u})\times(1.66054\times10^{-27}\,\mathrm{kg\,u^{-1}})}\right)^{1/2}$$

$$E_0 = \boxed{2.3421\times10^{-20}\,\mathrm{J}}$$

E12.17(b) Orthogonality requires that

$$\int \psi_m^*\psi_n\,\mathrm{d}\tau = 0$$

if $m \neq n$.

Performing the integration

$$\int \psi_m^*\psi_n\,\mathrm{d}\tau = \int_0^{2\pi} N\mathrm{e}^{-\mathrm{i}m\phi}N\mathrm{e}^{\mathrm{i}n\phi}\,\mathrm{d}\phi = N^2\int_0^{2\pi}\mathrm{e}^{\mathrm{i}(n-m)\phi}\,\mathrm{d}\phi$$

If $m \neq n$, then

$$\int \psi_m^* \psi_n \, \mathrm{d}\tau = \frac{N^2}{\mathrm{i}(n-m)} \mathrm{e}^{\mathrm{i}(n-m)\phi}\Big|_0^{2\pi} = \frac{N^2}{\mathrm{i}(n-m)}(1-1) = 0$$

Therefore, they are orthogonal.

E12.18(b) The magnitude of angular momentum is

$$\langle \hat{L}^2 \rangle^{1/2} = (l(l+1))^{1/2}\hbar = (2(3))^{1/2}(1.0546 \times 10^{-34}\,\mathrm{J\,s}) = \boxed{2.58 \times 10^{-34}\,\mathrm{J\,s}}$$

Possible projections on to an arbitrary axis are

$$\langle \hat{L}_z \rangle = m_l \hbar$$

where $m_l = 0$ or ± 1 or ± 2. So possible projections include

$$\boxed{0,\ \pm 1.0546 \times 10^{-34}\,\mathrm{J\,s} \text{ and } 2.1109 \times 10^{-34}\,\mathrm{J\,s}}$$

E12.19(b) The cones are constructed as described in Section 12.7(c) and Fig. 12.36 of the text; their edges are of length $\{6(6+1)\}^{1/2} = 6.48$ and their projections are $m_j = +6, +5, \ldots, -6$. See Fig. 12.1(a).

The vectors follow, in units of $\hbar$. From the highest-pointing to the lowest-pointing vectors (Fig. 12.1(b)), the values of m_l are 6, 5, 4, 3, 2, 1, 0, −1, −2, −3, −4, −5, and −6.

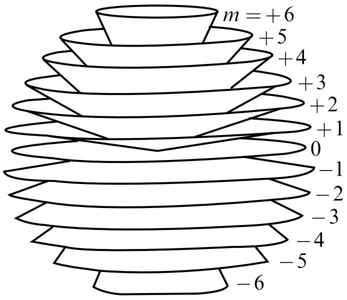


Figure 12.1(a)

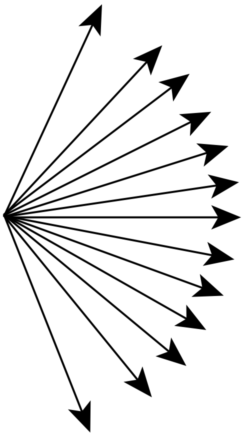


Figure 12.1(b)

Solutions to problems

Solutions to numerical problems

P12.4 $$E = \frac{l(l+1)\hbar^2}{2I}[12.65] = \frac{l(l+1)\hbar^2}{2m_{\text{eff}}R^2} \quad [I = m_{\text{eff}}R^2,\ m_{\text{eff}} \text{ in place of } m]$$

$$= \left(\frac{l(l+1)\times(1.055\times10^{-34}\,\text{J s})^2}{(2)\times(1.6605\times10^{-27}\,\text{kg})\times(160\times10^{-12}\,\text{m})^2}\right)\times\left(\frac{1}{1.008}+\frac{1}{126.90}\right)$$

$$\left[\frac{1}{m_{\text{eff}}} = \frac{1}{m_1}+\frac{1}{m_2}\right]$$

The energies may be expressed in terms of equivalent frequencies with $\nu = \frac{E}{h} = 1.509\times10^{33}\,E$.

Therefore,

$$E = l(l+1)\times(1.31\times10^{-22}\,\text{J}) = l(l+1)\times(198\,\text{GHz})$$

Hence, the energies and equivalent frequencies are

l	0	1	2	3
$10^{22}\,E/\text{J}$	$\boxed{0}$	$\boxed{2.62}$	$\boxed{7.86}$	$\boxed{15.72}$
ν/GHz	0	396	1188	2376

P12.6 Treat the gravitational potential energy as a perturbation in the energy operator:

$$H^{(1)} = mgx.$$

The first-order correction to the ground-state energy, E_1, is:

$$E_1{}^{(1)} = \int_0^L \Psi_1^{(0)*}H^{(1)}\Psi_1^{(0)}\text{d}x = \int_0^L \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{\pi x}{L}\right)mgx\left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{\pi x}{L}\right)dx,$$

$$E_1{}^{(1)} = \frac{2mg}{L}\int_0^L x\sin^2\left(\frac{\pi x}{L}\right)dx,$$

$$E_1{}^{(1)} = \frac{2mg}{L}\left(\frac{x^2}{4}-\frac{xL}{2\pi}\cos\left(\frac{\pi x}{L}\right)\sin\left(\frac{\pi x}{L}\right)-\frac{L^2}{4\pi^2}\cos^2\left(\frac{\pi x}{L}\right)\right)\Bigg|_0^L,$$

$$E_1{}^{(1)} = \boxed{\tfrac{1}{2}mgL}$$

Not surprisingly, this amounts to the energy perturbation evaluated at the midpoint of the box. For $m = m_e$, $E_1{}^{(1)}/\text{L} = 4.47\times10^{-30}\,\text{J m}^{-1}$.

Solutions to theoretical problems

P12.8 $$-\left(\frac{\hbar^2}{2m}\right)\times\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi=E\psi\quad [V=0]$$

We try the solution $\psi=X(x)Y(y)Z(z)$

$$-\frac{\hbar^2}{2m}(X''YZ+XY''Z+XYZ'')=EXYZ$$

$$-\frac{\hbar^2}{2m}\left(\frac{X''}{X}+\frac{Y''}{Y}+\frac{Z''}{Z}\right)=E$$

$\frac{X''}{X}$ depends only on x; therefore, when x changes only this term changes, but the sum of the three terms is constant. Therefore, $\frac{X''}{X}$ must also be constant. We write

$$-\frac{\hbar^2}{2m}\frac{X''}{X}=E^X,\quad \text{with analogous terms for } y,\ z$$

Hence we solve

$$\left.\begin{aligned}-\frac{\hbar^2}{2m}X''&=E^XX\\-\frac{\hbar^2}{2m}Y''&=E^YY\\-\frac{\hbar^2}{2m}Z''&=E^ZZ\end{aligned}\right\}E=E^X+E^Y+E^Z,\quad \psi=XYZ$$

The three-dimensional equation has therefore separated into three one-dimensional equations, and we can write

$$\boxed{E=\frac{h^2}{8m}\left(\frac{n_1^2}{L_1^2}+\frac{n_2^2}{L_2^2}+\frac{n_3^2}{L_3^2}\right)}\quad n_1,n_2,n_3=1,2,3,\ldots$$

$$\psi=\left(\frac{8}{L_1L_2L_3}\right)^{1/2}\sin\left(\frac{n_1\pi x}{L_1}\right)\sin\left(\frac{n_2\pi y}{L_2}\right)\sin\left(\frac{n_3\pi z}{L_3}\right)$$

For a cubic box

$$\boxed{E=(n_1^2+n_2^2+n_3^2)\frac{h^2}{8mL^2}}$$

P12.10 The wavefunctions in each region (see Fig. 12.2(a)) are (eqns 12.22–12.25):

$$\psi_1(x)=e^{ik_1x}+B_1e^{-ik_2x}$$
$$\psi_2(x)=A_2e^{k_2x}+B_2e^{-k_2x}$$
$$\psi_3(x)=A_3e^{ik_3x}$$

with the above choice of $A_1=1$ the transmission probability is simply $T=|A_3|^2$. The wavefunction coefficients are determined by the criteria that both the wavefunctions and their first derivatives w/r/t

x be continuous at potential boundaries

$$\psi_1(0) = \psi_2(0); \quad \psi_2(L) = \psi_3(L)$$

$$\frac{d\psi_1(0)}{dx} = \frac{d\psi_2(0)}{dx}; \quad \frac{d\psi_2(L)}{dx} = \frac{d\psi_3(L)}{dx}$$

These criteria establish the algebraic relationships:

$$1 + B_1 - A_2 - B_2 = 0$$

$$(-ik_1 - k_2)A_2 + (-ik_1 + k_2)B_2 + 2ik_1 = 0$$

$$A_2 e^{k_2 L} + B_2 e^{-k_2 L} - A_3 e^{ik_3 L} = 0$$

$$A_2 k_2 e^{k_2 L} - B_2 k_2 e^{-k_2 L} - iA_3 k_3 e^{ik_3 L} = 0$$

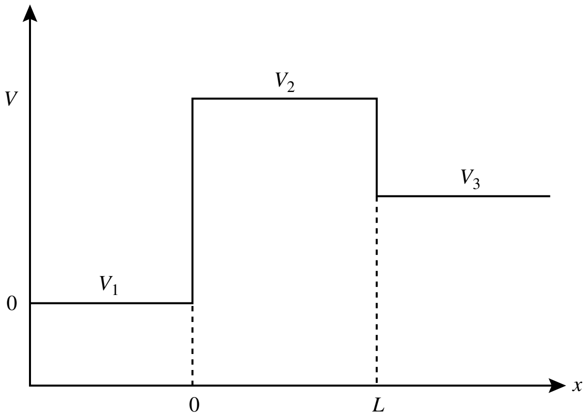


Figure 12.2(a)

Solving the simultaneous equations for A_3 gives

$$A_3 = \frac{4k_1k_2\, e^{ik_3L}}{(ia + b)\, e^{k_2L} - (ia - b)\, e^{-k_2L}}$$

where $a = k_2^2 - k_1k_3$ and $b = k_1k_2 + k_2k_3$.

since $\sinh(z) = (e^z - e^{-z})/2$ or $e^z = 2\sinh(z) + e^{-z}$, substitute $e^{k_2L} = 2\sinh(k_2L) + e^{-k_2L}$ giving:

$$A_3 = \frac{2k_1k_2 e^{ik_3L}}{(ia + b)\sinh(k_2L) + b\, e^{-k_2L}}$$

$$\boxed{\begin{array}{l} T = |A_3|^2 = A_3\bar{A}_3 = \dfrac{4k_1^2k_2^2}{(a^2 + b^2)\sinh^2(k_2L) + b^2} \\ \text{where } a^2 + b^2 = (k_1^2 + k_2^2)(k_2^2 + k_3^2) \text{ and } b^2 = k_2^2(k_1 + k_3)^2 \end{array}}$$

(b) In the special case for which $V_1 = V_3 = 0$, eqns 12.22 and 12.25 require that $k_1 = k_3$. Additionally,

$$\left(\frac{k_1}{k_2}\right)^2 = \frac{E}{V_2 - E} = \frac{\varepsilon}{1 - \varepsilon} \text{ where } \varepsilon = E/V_2.$$

$$a^2 + b^2 = (k_1^2 + k_2^2)^2 = k_2^4\left\{1 + \left(\frac{k_1}{k_2}\right)^2\right\}^2$$

$$b^2 = 4k_1^2 k_2^2$$

$$\frac{a^2+b^2}{b^2} = \frac{k_2^2\left\{1+\left(\frac{k_1}{k_2}\right)^2\right\}^2}{4k_1^2} = \frac{1}{4\varepsilon(1-\varepsilon)}$$

$$T = \frac{b^2}{b^2+(a^2+b^2)\sinh^2(k_2L)} = \frac{1}{1+\left(\frac{a^2+b^2}{b^2}\right)\sinh^2(k_2L)}$$

$$T = \left\{1+\frac{\sinh^2(k_2L)}{4\varepsilon(1-\varepsilon)}\right\}^{-1} = \left\{1+\frac{(e^{k_2L}-e^{-k_2L})^2}{16\varepsilon(1-\varepsilon)}\right\}^{-1}$$

This proves eqn 12.28a where $V_1 = V_3 = 0$

In the high wide barrier limit $k_2L \gg 1$. This implies both that e^{-k_2L} is negligibly small compared to e^{k_2L} and that 1 is negligibly small compared to $e^{2\,k_2L}/\{16\varepsilon(1-\varepsilon)\}$. The previous equation simplifies to

$$T = 16\,\varepsilon(1-\varepsilon)e^{-2\,k_2L} \quad \text{[eqn12.28b]}$$

(c)

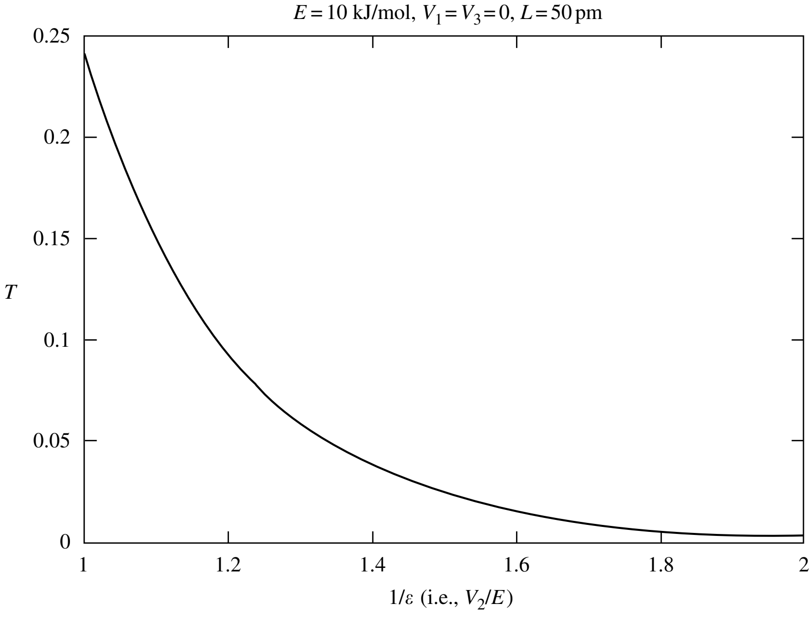


Figure 12.2(b)

P12.12 The Schrödinger equation is $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi$

and we write $\psi = e^{-gx^2}$, so $\frac{d\psi}{dx} = -2gxe^{-gx^2}$

$$\frac{d^2\psi}{dx^2} = -2ge^{-gx^2} + 4g^2x^2e^{-gx^2} = -2g\psi + 4g^2x^2\psi$$

$$\left(\frac{\hbar^2 g}{m}\right)\psi - \left(\frac{2\hbar^2 g^2}{m}\right)x^2\psi + \tfrac{1}{2}kx^2\psi = E\psi$$

$$\left[\left(\frac{\hbar^2 g}{m}\right) - E\right]\psi + \left(\tfrac{1}{2}k - \frac{2\hbar^2 g^2}{m}\right)x^2\psi = 0$$

This equation is satisfied if

$$E = \frac{\hbar^2 g}{m} \quad \text{and} \quad 2\hbar^2 g^2 = \tfrac{1}{2}mk, \quad \text{or} \quad \boxed{g = \tfrac{1}{2}\left(\frac{mk}{\hbar^2}\right)^{1/2}}$$

Therefore,

$$E = \tfrac{1}{2}\hbar\left(\frac{k}{m}\right)^{1/2} = \tfrac{1}{2}\hbar\omega \quad \text{if } \omega = \left(\frac{k}{m}\right)^{1/2}$$

P12.14

$$\langle x^n\rangle = \alpha^n\langle y^n\rangle = \alpha^n\int_{-\infty}^{+\infty}\psi y^n\psi\,\mathrm{d}x = \alpha^{n+1}\int_{-\infty}^{+\infty}\psi^2 y^n\,\mathrm{d}y \quad [x = \alpha y]$$

$$\langle x^3\rangle \propto \int_{-\infty}^{+\infty}\psi^2 y^3\,\mathrm{d}y = \boxed{0} \text{ by symmetry} \quad [y^3 \text{ is an odd function of } y]$$

$$\langle x^4\rangle = \alpha^5\int_{-\infty}^{+\infty}\psi y^4\psi\,\mathrm{d}y$$

$$y^4\psi = y^4 N H_v \mathrm{e}^{-y^2/2}$$

$$\begin{aligned}
y^4 H_v &= y^3\left(\tfrac{1}{2}H_{v+1} + vH_{v-1}\right) = y^2\left[\tfrac{1}{2}\left(\tfrac{1}{2}H_{v+2} + (v+1)H_v\right) + v\left(\tfrac{1}{2}H_v + (v-1)H_{v-2}\right)\right] \\
&= y^2\left[\tfrac{1}{4}H_{v+2} + \left(v + \tfrac{1}{2}\right)H_v + v(v-1)H_{v-2}\right] \\
&= y\left[\tfrac{1}{4}\left(\tfrac{1}{2}H_{v+3} + (v+2)H_{v+1}\right) + \left(v + \tfrac{1}{2}\right) \times \left(\tfrac{1}{2}H_{v+1} + vH_{v-1}\right)\right. \\
&\qquad \left. + v(v-1) \times \left(\tfrac{1}{2}H_{v-1} + (v-2)H_{v-3}\right)\right] \\
&= y\left(\tfrac{1}{8}H_{v+3} + \tfrac{3}{4}(v+1)H_{v+1} + \tfrac{3}{2}v^2 H_{v-1} + v(v-1) \times (v-2)H_{v-3}\right)
\end{aligned}$$

Only yH_{v+1} and yH_{v-1} lead to H_v and contribute to the expectation value (since H_v is orthogonal to all except H_v) [Table 12.1]; hence

$$\begin{aligned}
y^4 H_v &= \tfrac{3}{4}y\{(v+1)H_{v+1} + 2v^2 H_{v-1}\} + \cdots \\
&= \tfrac{3}{4}\left[(v+1)\left(\tfrac{1}{2}H_{v+2} + (v+1)H_v\right) + 2v^2\left(\tfrac{1}{2}H_v + (v-1)H_{v-2}\right)\right] + \cdots \\
&= \tfrac{3}{4}\{(v+1)^2 H_v + v^2 H_v\} + \cdots \\
&= \tfrac{3}{4}(2v^2 + 2v + 1)H_v + \cdots
\end{aligned}$$

Therefore

$$\int_{-\infty}^{+\infty}\psi y^4\psi\,\mathrm{d}y = \tfrac{3}{4}(2v^2 + 2v + 1)N^2\int_{-\infty}^{+\infty}H_v^2\mathrm{e}^{-y^2}\,\mathrm{d}y = \frac{3}{4\alpha}(2v^2 + 2v + 1)$$

and so

$$\langle x^4\rangle = (\alpha^5) \times \left(\frac{3}{4\alpha}\right) \times (2v^2 + 2v + 1) = \boxed{\tfrac{3}{4}(2v^2 + 2v + 1)\alpha^4}$$

P12.17 $V = -\dfrac{e^2}{4\pi\varepsilon_0}\cdot\dfrac{1}{r}$ [13.5 with $Z = 1$] $= \alpha x^b$ with $b = -1$ $[x \to r]$

Since $2\langle T\rangle = b\langle V\rangle$ [12.45, $\langle T\rangle \equiv E_\mathrm{K}$]

$$2\langle T\rangle = -\langle V\rangle$$

Therefore, $\boxed{\langle T\rangle = -\tfrac{1}{2}\langle V\rangle}$

P12.18 In each case, if the function is an eigenfunction of the operator, the eigenvalue is also the expectation value; if it is not an eigenfunction we form

$$\langle\Omega\rangle = \int \psi^*\hat{\Omega}\psi\,\mathrm{d}\tau \text{ [11.39]}$$

(a) $\hat{l}_z\mathrm{e}^{\mathrm{i}\phi} = \dfrac{\hbar}{\mathrm{i}}\dfrac{\mathrm{d}}{\mathrm{d}\phi}\mathrm{e}^{\mathrm{i}\phi} = \hbar\mathrm{e}^{\mathrm{i}\phi}$; hence $J_z = \boxed{+\hbar}$

(b) $\hat{l}_z\mathrm{e}^{-2\mathrm{i}\phi} = \dfrac{\hbar}{\mathrm{i}}\dfrac{\mathrm{d}}{\mathrm{d}\phi}\mathrm{e}^{-2\mathrm{i}\phi} = -2\hbar\mathrm{e}^{-2\mathrm{i}\phi}$; hence $J_z = \boxed{-2\hbar}$

(c) $\langle l_z\rangle \propto \displaystyle\int_0^{2\pi}\cos\phi\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}\phi}\cos\phi\right)\mathrm{d}\phi \propto -\frac{\hbar}{\mathrm{i}}\int_0^{2\pi}\cos\phi\sin\phi\,\mathrm{d}\phi = \boxed{0}$

(d)
$$\begin{aligned}\langle l_z\rangle &= N^2\int_0^{2\pi}(\cos\chi\,\mathrm{e}^{\mathrm{i}\phi} + \sin\chi\,\mathrm{e}^{-\mathrm{i}\phi})^*\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}\phi}\right)\times(\cos\chi\,\mathrm{e}^{\mathrm{i}\phi} + \sin\chi\,\mathrm{e}^{-\mathrm{i}\phi})\,\mathrm{d}\phi\\
&= \frac{\hbar}{\mathrm{i}}N^2\int_0^{2\pi}(\cos\chi\,\mathrm{e}^{-\mathrm{i}\phi} + \sin\chi\,\mathrm{e}^{\mathrm{i}\phi})\times(\mathrm{i}\cos\chi\,\mathrm{e}^{\mathrm{i}\phi} - \mathrm{i}\sin\chi\,\mathrm{e}^{-\mathrm{i}\phi})\,\mathrm{d}\phi\\
&= \hbar N^2\int_0^{2\pi}(\cos^2\chi - \sin^2\chi + \cos\chi\ \sin\chi[\mathrm{e}^{2\mathrm{i}\phi} - \mathrm{e}^{-2\mathrm{i}\phi}])\,\mathrm{d}\phi\\
&= \hbar N^2(\cos^2\chi - \sin^2\chi)\times(2\pi) = 2\pi\hbar N^2\cos 2\chi\end{aligned}$$

$$\begin{aligned}N^2&\int_0^{2\pi}(\cos\chi\,\mathrm{e}^{\mathrm{i}\phi} + \sin\chi\,\mathrm{e}^{-\mathrm{i}\phi})^*(\cos\chi\,\mathrm{e}^{\mathrm{i}\phi} + \sin\chi\,\mathrm{e}^{-\mathrm{i}\phi})\,\mathrm{d}\phi\\
&= N^2\int_0^{2\pi}(\cos^2\chi + \sin^2\chi + \cos\chi\sin\chi[\mathrm{e}^{2\mathrm{i}\phi} + \mathrm{e}^{-2\mathrm{i}\phi}])\,\mathrm{d}\phi\\
&= 2\pi N^2(\cos^2\chi + \sin^2\chi) = 2\pi N^2 = 1 \quad \text{if } N^2 = \frac{1}{2\pi}\end{aligned}$$

Therefore

$$\langle l_z\rangle = \boxed{\hbar\cos 2\chi}\ [\chi \text{ is a parameter}]$$

For the kinetic energy we use $\hat{T} \equiv \hat{E}_\mathrm{K} = \dfrac{\hat{J}_z^2}{2I}$[12.47] $= -\dfrac{\hbar^2}{2I}\dfrac{\mathrm{d}^2}{\mathrm{d}\phi^2}$ [12.52]

(a) $\hat{T}\mathrm{e}^{\mathrm{i}\phi} = -\dfrac{\hbar^2}{2I}(\mathrm{i}^2\mathrm{e}^{\mathrm{i}\phi}) = \dfrac{\hbar^2}{2I}\mathrm{e}^{\mathrm{i}\phi}$; hence $\langle T\rangle = \boxed{\dfrac{\hbar^2}{2I}}$

(b) $\hat{T}\mathrm{e}^{-2\mathrm{i}\phi} = -\dfrac{\hbar^2}{2I}(2\mathrm{i})^2\mathrm{e}^{-2\mathrm{i}\phi} = \dfrac{4\hbar^2}{2I}\mathrm{e}^{-2\mathrm{i}\phi}$; hence $\langle T\rangle = \boxed{\dfrac{2\hbar^2}{I}}$

(c) $\hat{T}\cos\phi = -\dfrac{\hbar^2}{2I}(-\cos\phi) = \dfrac{\hbar^2}{2I}\cos\phi$; hence $\langle T\rangle = \boxed{\dfrac{\hbar^2}{2I}}$

(d) $$\hat{T}(\cos\chi e^{i\phi}+\sin\chi e^{-i\phi})=-\frac{\hbar^2}{2I}(-\cos\chi e^{i\phi}-\sin\chi e^{-i\phi})=\frac{\hbar^2}{2I}(\cos\chi e^{i\phi}+\sin\chi e^{-i\phi})$$

and hence $\langle T\rangle=\boxed{\dfrac{\hbar^2}{2I}}$

Comment. All of these functions are eigenfunctions of the kinetic energy operator, which is also the total energy or Hamiltonian operator, since the potential energy is zero for this system.

P12.20
$$\int_0^{\pi}\int_0^{2\pi}Y_{3,3}^{*}Y_{3,3}\sin\theta\,d\theta\,d\phi=\int_0^{\pi}\left(\tfrac{1}{64}\right)\times\left(\frac{35}{\pi}\right)\sin^6\theta\sin\theta\,d\theta\int_0^{2\pi}d\phi\text{ [Table 12.3]}$$
$$=\left(\tfrac{1}{64}\right)\times\left(\frac{35}{\pi}\right)\times(2\pi)\int_{-1}^{1}(1-\cos^2\theta)^3\,d\cos\theta$$
$$[\sin\theta\,d\theta=d\cos\theta,\ \sin^2\theta=1-\cos^2\theta]$$
$$=\tfrac{35}{32}\int_{-1}^{1}(1-3x^2+3x^4-x^6)\,dx\quad[x=\cos\theta]$$
$$=\tfrac{35}{32}\left(x-x^3+\tfrac{3}{5}x^5-\tfrac{1}{7}x^7\right)\Big|_{-1}^{1}=\frac{35}{32}\times\frac{32}{35}=\boxed{1}$$

P12.22
$$\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$
$$\frac{\partial^2}{\partial x^2}f=-a^2f\qquad\frac{\partial^2}{\partial y^2}f=-b^2f\qquad\frac{\partial^2}{\partial y^2}f=-c^2f$$

and f is an eigenfunction with eigenvalue $\boxed{-(a^2+b^2+c^2)}$

P12.25 **(a)** Suppose that a particle moves classically at the constant speed v. It starts at $x=0$ at $t=0$ and at $t=\tau$ is at position $x=L$. $v=\dfrac{L}{\tau}$ and $x=vt$.

$$\langle x\rangle=\frac{1}{\tau}\int_{t=0}^{\tau}x\,dt=\frac{1}{\tau}\int_{t=0}^{\tau}vt\,dt$$
$$=\frac{v}{\tau}\int_{t=0}^{\tau}t\,dt=\frac{v}{2\tau}t^2\Big|_{t=0}^{\tau}$$
$$=\frac{v\tau^2}{2\tau}=\frac{v\tau}{2}=\boxed{\frac{L}{2}=\langle x\rangle}$$
$$\langle x^2\rangle=\frac{1}{\tau}\int_{t=0}^{\tau}x^2\,dt=\frac{v^2}{\tau}\int_{t=0}^{\tau}t^2\,dt$$
$$=\frac{v^2}{3\tau}t^3\Big|_{t=0}^{\tau}=\frac{(v\tau)^2}{3}=\frac{L^2}{3}$$
$$\boxed{\langle x^2\rangle^{1/2}=\frac{L}{3^{1/2}}}$$

(b) $$\psi_n = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \quad \text{for } 0 \le x \le L \text{ [12.7]}$$

$$\begin{aligned}
\langle x\rangle_n &= \int_{x=0}^{L} \psi_n^* x \psi_n \, \mathrm{d}x = \frac{2}{L}\int_0^L x \sin^2\left(\frac{n\pi x}{L}\right) \mathrm{d}x \\
&= \frac{2}{L}\left[\frac{x^2}{4} - \frac{x\sin\left(\frac{2n\pi x}{L}\right)}{4(n\pi/L)} - \frac{\cos\left(\frac{2n\pi x}{L}\right)}{8(n\pi/L)^2}\right]_{x=0}^{x=L} \\
&= \frac{2}{L}\left[\frac{L^2}{4}\right] = \boxed{\frac{L}{2} = \langle x\rangle_n}
\end{aligned}$$

This agrees with the classical result.

$$\begin{aligned}
\langle x^2\rangle_n &= \int_{x=0}^{L} \psi_n^* x^2 \psi_n \, \mathrm{d}x = \frac{2}{L}\int_{x=0}^{L} x^2 \sin^2\left(\frac{n\pi x}{L}\right) \mathrm{d}x \\
&= \frac{2}{L}\left[\frac{x^3}{6} - \left(\frac{x^2}{4(n\pi/L)} - \frac{1}{8(n\pi/L)^3}\right)\sin\left(\frac{2n\pi x}{L}\right) - \frac{x\cos\left(\frac{2n\pi x}{L}\right)}{8(n\pi/L)^2}\right]_{x=0}^{x=L} \\
&= \frac{2}{L}\left[\frac{L^3}{6} - \frac{L}{8(n\pi/L)^2}\right] \\
&= \frac{L^2}{3} - \frac{1}{4(n\pi/L)^2}
\end{aligned}$$

$$\boxed{\langle x^2\rangle_n^{1/2} = \left(\frac{L^2}{3} - \frac{1}{4(n\pi/L)^2}\right)^{1/2}}$$

$$\lim_{n\to\infty} \langle x^2\rangle_n^{1/2} = \frac{L}{3^{1/2}}$$

This agrees with the classical result.

P12.27 **(a)** The energy levels are given by:

$$E_n = \frac{h^2 n^2}{8mL^2},$$

and we are looking for the energy difference between $n = 6$ and $n = 7$:

$$\Delta E = \frac{h^2(7^2 - 6^2)}{8mL^2}.$$

Since there are 12 atoms on the conjugated backbone, the length of the box is 11 times the bond length:

$$L = 11(140 \times 10^{-12}\,\mathrm{m}) = 1.54 \times 10^{-9}\,\mathrm{m},$$

$$\text{so} \quad \Delta E = \frac{(6.626 \times 10^{-34}\,\mathrm{J\,s})^2(49 - 36)}{8(9.11 \times 10^{-31}\,\mathrm{kg})(1.54 \times 10^{-9}\,\mathrm{m})^2} = \boxed{3.30 \times 10^{-19}\,\mathrm{J}}.$$

(b) The relationship between energy and frequency is:

$$\Delta E = h\nu \qquad \text{so} \qquad \nu = \frac{\Delta E}{h} = \frac{3.30 \times 10^{-19}\,\mathrm{J}}{6.626 \times 10^{-34}\,\mathrm{J\,s}} = \boxed{4.95 \times 10^{-14}\,\mathrm{s}^{-1}}.$$

(c) The frequency computed in this problem is about twice that computed in problem 12.26b, suggesting that *the absorption spectrum of a linear polyene shifts to* $\boxed{\textit{lower}}$ *frequency as the number of conjugated atoms* $\boxed{\textit{increases}}$. The reason for this is apparent if we look at the terms in the energy expression (which is proportional to the frequency) that change with the number of conjugated atoms, N. The energy and frequency are inversely proportional to L^2 and directly proportional to $(n+1)^2 - n^2 = 2n+1$, where n is the quantum number of the highest occupied state. Since n is proportional to N (equal to $N/2$) and L is approximately proportional to N (strictly to $N-1$), the energy and frequency are approximately proportional to N^{-1}.

P12.29 In effect, we are looking for the vibrational frequency of an O atom bound, with a force constant equal to that of free CO, to an infinitely massive and immobile protein complex. The angular frequency is

$$\omega = \left(\frac{k}{m}\right)^{1/2},$$

where m is the mass of the O atom.

$$m = (16.0\,\mathrm{u})(1.66\times10^{-27}\,\mathrm{kg\,u^{-1}}) = 2.66\times10^{-26}\,\mathrm{kg},$$

and k is the same force constant as in problem 12.2, namely $1902\,\mathrm{N\,m^{-1}}$:

$$\omega = \left(\frac{1902\,\mathrm{N\,m^{-1}}}{2.66\times10^{-26}\,\mathrm{kg}}\right)^{1/2} = \boxed{2.68\times10^{14}\,\mathrm{s^{-1}}}.$$

13 Atomic structure and atomic spectra

Solutions to exercises

Discussion questions

E13.1(b) (1) The principal quantum number, n, determines the energy of a hydrogenic atomic orbital through eqn 13.13.

(2) The azimuthal quantum number, l, determines the magnitude of the angular momentum of a hydrogenic atomic orbital through the relation $\{l(l+1)\}^{1/2}\hbar$.

(3) The magnetic quantum number, m_l, determines the z-component of the angular momentum of a hydrogenic orbital through the relation $m_l\hbar$.

(4) The spin quantum number, s, determines the magnitude of the spin angular momentum through the relation $\{s(s+1)\}^{1/2}\hbar$. For a hydrogenic atomic orbitals, s can only be $1/2$.

(5) The spin quantum number, m_s, determines the z-component of the spin angular momentum through the relation $m_s\hbar$. For hydrogenic atomic orbitals, m_s can only be $\pm 1/2$.

E13.2(b) **(a)** A boundary surface for a hydrogenic orbital is drawn so as to contain most (say 90%) of the probability density of an electron in that orbital. Its shape varies from orbital to orbital because the electron density distribution is different for different orbitals.

(b) The radial distribution function gives the probability that the electron will be found anywhere within a shell of radius r around the nucleus. It gives a better picture of where the electron is likely to be found with respect to the nucleus than the probability density which is the square of the wavefunction.

E13.3(b) The first ionization energies increase markedly from Li to Be, decrease slightly from Be to B, again increase markedly from B to N, again decrease slightly from N to O, and finally increase markedly from N to Ne. The general trend is an overall increase of I_1 with atomic number across the period. That is to be expected since the principal quantum number (electron shell) of the outer electron remains the same, while its attraction to the nucleus increases. The slight decrease from Be to B is a reflection of the outer electron being in a higher energy subshell (larger l value) in B than in Be. The slight decrease from N to O is due to the half-filled subshell effect; half-filled sub-shells have increased stability. O has one electron outside of the half-filled p subshell and that electron must pair with another resulting in strong electron–electron repulsions between them.

E13.4(b) An electron has a magnetic moment and magnetic field due to its orbital angular momentum. It also has a magnetic moment and magnetic field due to its spin angular momentum. There is an interaction energy between magnetic moments and magnetic fields. That between the spin magnetic moment and the magnetic field generated by the orbital motion is called spin–orbit coupling. The energy of interaction is proportional to the scalar product of the two vectors representing the spin and orbital angular momenta and hence depends upon the orientation of the two vectors. See Fig. 13.29. The total angular momentum of an electron in an atom is the vector sum of the orbital and spin angular momenta as illustrated in Fig. 13.30 and expressed in eqn 13.46. The spin–orbit coupling results in a splitting of the energy levels associated with atomic terms as shown in Figs 13.31 and 13.32. This splitting shows up in atomic spectra as a fine structure as illustrated in Fig. 13.32.

Numerical exercises

E13.5(b) The energy of the photon that struck the Xe atom goes into liberating the bound electron and giving it any kinetic energy it now possesses

$$E_{\text{photon}} = I + E_{\text{kinetic}} \quad I = \text{ionization energy}$$

The energy of a photon is related to its frequency and wavelength

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

and the kinetic energy of an electron is related to its mass and speed

$$E_{\text{kinetic}} = \tfrac{1}{2}m_{\text{e}}s^2$$

So $\dfrac{hc}{\lambda} = I + \tfrac{1}{2}m_{\text{e}}s^2 \Rightarrow I = \dfrac{hc}{\lambda} - \tfrac{1}{2}m_{\text{e}}s^2$

$$\begin{aligned} I &= \frac{(6.626\times10^{-34}\,\text{J s})\times(2.998\times10^{8}\,\text{m s}^{-1})}{58.4\times10^{-9}\,\text{m}} \\ &\quad -\tfrac{1}{2}(9.11\times10^{-31}\,\text{kg})\times(1.79\times10^{6}\,\text{m s}^{-1})^2 \\ &= \boxed{1.94\times10^{-18}\,\text{J}} = 12.1\,\text{eV} \end{aligned}$$

E13.6(b) The radial wavefunction is [Table 13.1]

$R_{3,0} = A\left(6-2\rho+\tfrac{1}{9}\rho^2\right)\text{e}^{-\rho/6}$ where $\rho \equiv \dfrac{2Zr}{a_0}$, and A is a collection of constants. Differentiating with respect to ρ yields

$$\begin{aligned} \frac{\text{d}R_{3,0}}{\text{d}\rho} = 0 &= A(6-2\rho+\tfrac{1}{9}\rho^2)\times\left(-\tfrac{1}{6}\right)\text{e}^{-\rho/6} + \left(-2+\tfrac{2}{9}\rho\right)A\text{e}^{-\rho/6} \\ &= A\text{e}^{-\rho/6}\left(-\tfrac{\rho^2}{54}+\tfrac{5}{9}\rho-3\right) \end{aligned}$$

This is a quadratic equation

$$0 = a\rho^2 + b\rho + c \quad \text{where} \quad a = -\frac{1}{54}, \quad b = \frac{5}{9}, \quad \text{and} \quad c = -3.$$

The solution is

$$\rho = \frac{-b \pm (b^2-4ac)^{1/2}}{2a} = 15 \pm 3\sqrt{7}$$

so $r = \boxed{\left(\dfrac{15}{2} \pm \dfrac{3(7^{1/2})}{2}\right)\dfrac{a_0}{Z}}$.

Numerically, this works out to $\rho = 7.65$ and 2.35, so $r = \boxed{11.5a_0/Z}$ and $\boxed{3.53a_0/Z}$. Substituting $Z = 1$ and $a_0 = 5.292\times10^{-11}$ m, $r = 607$ pm and 187 pm.

The other maximum in the wavefunction is at $\boxed{r = 0}$. It is a physical maximum, but not a calculus maximum: the first derivative of the wavefunction does not vanish there, so it cannot be found by differentiation.

E13.7(b) The radial wavefunction is [Table 13.1]

$$R_{3,1} = A\left(4 - \tfrac{1}{3}\rho\right)\rho e^{-\rho/6} \quad \text{where} \quad \rho = \frac{2Zr}{a_0}$$

The radial nodes occur where the radial wavefunction vanishes. This occurs at

$$\rho = 0, \qquad \boxed{r = 0}$$

and when

$$\left(4 - \tfrac{1}{3}\rho\right) = 0, \quad \text{or} \quad \frac{\rho}{3} = 4, \quad \text{or} \quad \rho = 12$$

then $r = \dfrac{\rho a_0}{2Z} = \dfrac{\rho a_0}{2} = \dfrac{12a_0}{2} = \boxed{6a_0} = 3.18 \times 10^{-10}\,\text{m}$

E13.8(b) Normalization requires

$$\int |\psi|^2\,d\tau = 1 = \int_0^\infty \int_0^\pi \int_0^{2\pi} [N(2 - r/a_0)e^{-r/2a_0}]^2\,d\phi\,\sin\theta\,d\theta\,r^2\,dr$$

$$1 = N^2 \int_0^\infty e^{-r/a_0}(2 - r/a_0)^2 r^2\,dr \int_0^\pi \sin\theta\,d\theta \int_0^{2\pi} d\phi$$

Integrating over angles yields

$$\begin{aligned} 1 &= 4\pi N^2 \int_0^\infty e^{-r/a_0}(2 - r/a_0)^2 r^2\,dr \\ &= 4\pi N^2 \int_0^\infty e^{-r/a_0}(4 - 4r/a_0 + r^2/a_0^2) r^2\,dr = 4\pi N^2(8a_0^3) \end{aligned}$$

In the last step, we used $\int_0^\infty e^{-r/k} r^2\,dr = 2k^3$, $\int_0^\infty e^{-r/k} r^3\,dr = 6k^4$, and $\int_0^\infty e^{-r/k} r^4\,dr = 24k^5$

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

E13.9(b) The average kinetic energy is

$$\langle \hat{E}_K \rangle = \int \psi^* \hat{E}_K \psi\,d\tau$$

where $\psi = N(2 - \rho)e^{-\rho/2}$ with $N = \dfrac{1}{4}\left(\dfrac{Z^3}{2\pi a_0^3}\right)^{1/2}$ and $\rho \equiv \dfrac{Zr}{a_0}$ here

$$\hat{E}_K = -\frac{\hbar^2}{2m}\nabla^2 \qquad d\tau = r^2 \sin\theta\,dr\,d\theta\,d\phi = \frac{a_0^3 \rho^2 \sin\theta\,d\rho\,d\theta\,d\phi}{Z^3}$$

In spherical polar coordinates, three of the derivatives in ∇^2 are derivatives with respect to angles, so those parts of $\nabla^2\psi$ vanish. Thus

$$\nabla^2\psi = \frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r} = \frac{\partial^2\psi}{\partial\rho^2}\left(\frac{\partial\rho}{\partial r}\right)^2 + \frac{2Z}{\rho a_0}\left(\frac{\partial\psi}{\partial\rho}\right)\frac{\partial\rho}{\partial r} = \left(\frac{Z}{a_0}\right)^2 \times \left(\frac{\partial^2\psi}{\partial\rho^2} + \frac{2}{\rho}\frac{\partial\psi}{\partial\rho}\right)$$

$$\frac{\partial \rho}{\partial r} = N(2-\rho)\times\left(-\tfrac{1}{2}\right)\mathrm{e}^{-\rho/2} - N\,\mathrm{e}^{-\rho/2} = N\left(\tfrac{1}{2}\rho - 2\right)\mathrm{e}^{-\rho/2}$$

$$\frac{\partial^2 \psi}{\partial \rho^2} = N\left(\tfrac{1}{2}\rho - 2\right)\times\left(-\tfrac{1}{2}\right)\mathrm{e}^{-\rho/2} + \tfrac{1}{2}N\,\mathrm{e}^{-\rho/2} = N\left(\tfrac{3}{2} - \tfrac{1}{4}\rho\right)\mathrm{e}^{-\rho/2}$$

$$\nabla^2\psi = \left(\frac{Z}{a_0}\right)^2 N\mathrm{e}^{-\rho/2}(-4/\rho + 5/2 - \rho/4)$$

and

$$\langle \hat{E}_\mathrm{K}\rangle = \int_0^\infty\int_0^\pi\int_0^{2\pi} N(2-\rho)\mathrm{e}^{-\rho/2}\left(\frac{Z}{a_0}\right)^2\times\left(\frac{-\hbar^2}{2m}\right)$$

$$\times\, N\mathrm{e}^{-\rho/2}(-4/\rho + 5/2 - \rho/4)\frac{a_0^3\,\mathrm{d}\phi\,\sin\theta\,\mathrm{d}\theta\,\rho^2\,\mathrm{d}\rho}{Z^3}$$

The integrals over angles give a factor of 4π, so

$$\langle \hat{E}_\mathrm{K}\rangle = 4\pi N^2\left(\frac{a_0}{Z}\right)\times\left(-\frac{\hbar^2}{2m}\right)\int_0^\infty (2-\rho)\times\left(-4 + \tfrac{5}{2}\rho - \tfrac{1}{4}\rho^2\right)\rho\mathrm{e}^{-\rho}\,\mathrm{d}\rho$$

The integral in this last expression works out to -2, using $\int_0^\infty \mathrm{e}^{-\rho}\rho^n\,\mathrm{d}\rho = n!$ for $n = 1, 2,$ and 3. So

$$\langle \hat{E}_\mathrm{K}\rangle = 4\pi\left(\frac{Z^3}{32\pi a_0^3}\right)\times\left(\frac{a_0}{Z}\right)\times\left(\frac{\hbar^2}{m}\right) = \boxed{\frac{\hbar^2 Z^2}{8ma_0^2}}$$

The average potential energy is

$$\langle V\rangle = \int \psi^* V\psi\,\mathrm{d}\tau \quad \text{where} \quad V = -\frac{Ze^2}{4\pi\varepsilon_0 r} = -\frac{Z^2e^2}{4\pi\varepsilon_0 a_0\rho}$$

and $\langle V\rangle = \int_0^\infty\int_0^\pi\int_0^{2\pi} N(2-\rho)\mathrm{e}^{-\rho/2}\left(-\frac{Z^2e^2}{4\pi\varepsilon_0 a_0\rho}\right)N(2-\rho)\mathrm{e}^{-\rho/2}\frac{a_0^3\rho^2\sin\theta\,\mathrm{d}\rho\,\mathrm{d}\theta\,\mathrm{d}\phi}{Z^3}$

The integrals over angles give a factor of 4π, so

$$\langle V\rangle = 4\pi N^2\left(-\frac{Z^2e^2}{4\pi\varepsilon_0 a_0}\right)\times\left(\frac{a_0^3}{Z^3}\right)\int_0^\infty (2-\rho)^2\rho\mathrm{e}^{-\rho}\,\mathrm{d}\rho$$

The integral in this last expression works out to 2, using $\int_0^\infty \mathrm{e}^{-\rho}\rho^n\,\mathrm{d}\rho = n!$ for $n = 1, 2, 3,$ and 4. So

$$\langle V\rangle = 4\pi\left(\frac{Z^3}{32\pi a_0^3}\right)\times\left(-\frac{Z^2e^2}{4\pi\varepsilon_0 a_0}\right)\times\left(\frac{a_0^3}{Z^3}\right)\times(2) = \boxed{-\frac{Z^2e^2}{16\pi\varepsilon_0 a_0}}$$

E13.10(b) The radial distribution function is defined as

$$P = 4\pi r^2\psi^2 \quad \text{so} \quad P_{3s} = 4\pi r^2(Y_{0,0}R_{3,0})^2,$$

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

where $\rho \equiv \dfrac{2Zr}{na_0} = \dfrac{2Zr}{3a_0}$ here.

But we want to find the most likely radius, so it would help to simplify the function by expressing it in terms either of r or ρ, but not both. To find the most likely radius, we could set the derivative of P_{3s} equal to zero; therefore, we can collect all multiplicative constants together (including the factors of a_0/Z needed to turn the initial r^2 into ρ^2) since they will eventually be divided into zero

$$P_{3s} = C^2\rho^2(6 - 6\rho + \rho^2)^2\mathrm{e}^{-\rho}$$

Note that not all the extrema of P are maxima; some are minima. But all the extrema of $(P_{3s})^{1/2}$ correspond to maxima of P_{3s}. So let us find the extrema of $(P_{3s})^{1/2}$

$$\frac{\mathrm{d}(P_{3s})^{1/2}}{\mathrm{d}\rho} = 0 = \frac{\mathrm{d}}{\mathrm{d}\rho}C\rho(6 - 6\rho + \rho^2)\mathrm{e}^{-\rho/2}$$

$$= C[\rho(6 - 6\rho + \rho^2) \times (-\tfrac{1}{2}) + (6 - 12\rho + 3\rho^2)]\mathrm{e}^{-\rho/2}$$

$$0 = C(6 - 15\rho + 6\rho^2 - \tfrac{1}{2}\rho^3)\mathrm{e}^{-\rho/2} \quad \text{so} \quad 12 - 30\rho + 12\rho^2 - \rho^3 = 0$$

Numerical solution of this cubic equation yields

$$\rho = 0.49,\ 2.79,\ \text{and } 8.72$$

corresponding to

$$r = \boxed{0.74a_0/Z,\ 4.19a_0/Z,\ \text{and } 13.08a_0/Z}$$

Comment. If numerical methods are to be used to locate the roots of the equation which locates the extrema, then graphical/numerical methods might as well be used to locate the maxima directly. That is, the student may simply have a spreadsheet compute P_{3s} and examine or manipulate the spreadsheet to locate the maxima.

E13.11(b) Orbital angular momentum is

$$\langle\hat{L}^2\rangle^{1/2} = \hbar(l(l+1))^{1/2}$$

There are l angular nodes and $n - l - 1$ radial nodes

(a) $n = 4,\ l = 2,$ so $\langle\hat{L}^2\rangle^{1/2} = 6^{1/2}\hbar = \boxed{2.45 \times 10^{-34}\,\mathrm{J\,s}}$ $\boxed{2}$ angular nodes $\boxed{1}$ radial node

(b) $n = 2,\ l = 1,$ so $\langle\hat{L}^2\rangle^{1/2} = 2^{1/2}\hbar = \boxed{1.49 \times 10^{-34}\,\mathrm{J\,s}}$ $\boxed{1}$ angular node $\boxed{0}$ radial nodes

(c) $n = 3,\ l = 1,$ so $\langle\hat{L}^2\rangle^{1/2} = 2^{1/2}\hbar = \boxed{1.49 \times 10^{-34}\,\mathrm{J\,s}}$ $\boxed{1}$ angular node $\boxed{1}$ radial node

E13.12(b) For $l > 0$, $j = l \pm 1/2$, so

(a) $l = 1$, so $j = \boxed{1/2 \text{ or } 3/2}$

(b) $l = 5$, so $j = \boxed{9/2 \text{ or } 11/2}$

E13.13(b) Use the Clebsch–Gordan series in the form

$$J = j_1 + j_2,\ j_1 + j_2 - 1, \ldots, |j_1 - j_2|$$

Then, with $j_1 = 5$ and $j_2 = 3$

$$J = \boxed{8, 7, 6, 5, 4, 3, 2}$$

E13.14(b) The degeneracy g of a hydrogenic atom with principal quantum number n is $g = n^2$. The energy E of hydrogenic atoms is

$$E = -\frac{hcZ^2\mathcal{R}_H}{n^2} = -\frac{hcZ^2\mathcal{R}_H}{g}$$

so the degeneracy is

$$g = -\frac{hcZ^2\mathcal{R}_H}{E}$$

(a) $$g = -\frac{hc(2)^2\mathcal{R}_H}{-4hc\mathcal{R}_H} = \boxed{1}$$

(b) $$g = -\frac{hc(4)^2\mathcal{R}_H}{-\frac{1}{4}hc\mathcal{R}_H} = \boxed{64}$$

(c) $$g = -\frac{hc(5)^2\mathcal{R}_H}{-hc\mathcal{R}_H} = \boxed{25}$$

E13.15(b) The letter F indicates that the total orbital angular momentum quantum number L is 3; the superscript 3 is the multiplicity of the term, $2S+1$, related to the spin quantum number $S = 1$; and the subscript 4 indicates the total angular momentum quantum number J.

E13.16(b) The radial distribution function varies as

$$P = 4\pi r^2\psi^2 = \frac{4}{a_0^3}r^2\mathrm{e}^{-2r/a_0}$$

The maximum value of P occurs at $r = a_0$ since

$$\frac{\mathrm{d}P}{\mathrm{d}r} \propto \left(2r - \frac{2r^2}{a_0}\right)\mathrm{e}^{-2r/a_0} = 0 \quad \text{at } r = a_0 \text{ and } P_{\max} = \frac{4}{a_0}\mathrm{e}^{-2}$$

P falls to a fraction f of its maximum given by

$$f = \frac{\frac{4r^2}{a_0^3}\mathrm{e}^{-2r/a_0}}{\frac{4}{a_0}\mathrm{e}^{-2}} = \frac{r^2}{a_0^2}\mathrm{e}^2\mathrm{e}^{-2r/a_0}$$

and hence we must solve for r in

$$\frac{f^{1/2}}{\mathrm{e}} = \frac{r}{a_0}\mathrm{e}^{-r/a_0}$$

(a) $f = 0.50$

$$0.260 = \frac{r}{a_0}\mathrm{e}^{-r/a_0} \text{ solves to } r = 2.08a_0 = \boxed{110\,\text{pm}} \text{ and to } r = 0.380a_0 = \boxed{20.1\,\text{pm}}$$

(b) $f = 0.75$

$$0.319 = \frac{r}{a_0}\mathrm{e}^{-r/a_0} \text{ solves to } r = 1.63a_0 = \boxed{86\,\text{pm}} \text{ and to } r = 0.555a_0 = \boxed{29.4\,\text{pm}}$$

In each case the equation is solved numerically (or graphically) with readily available personal computer software. The solutions above are easily checked by substitution into the equation for f. The radial distribution function is readily plotted and is shown in Fig. 13.1.

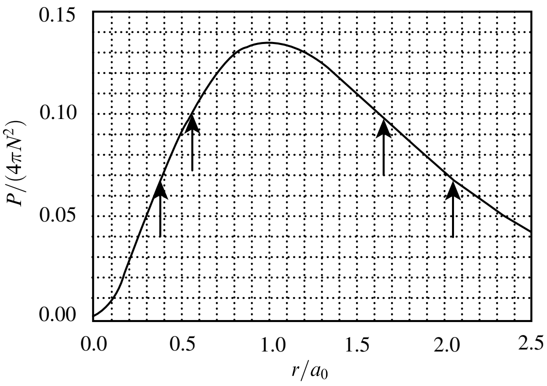


Figure 13.1

E13.17(b) **(a)** $5d \rightarrow 2s$ is $\boxed{\text{not}}$ an allowed transition, for $\Delta l = -2$ (Δl must equal ±1).

(b) $5p \rightarrow 3s$ is $\boxed{\text{allowed}}$, since $\Delta l = -1$.

(c) $5p \rightarrow 3f$ is $\boxed{\text{not}}$ allowed, for $\Delta l = +2$ (Δl must equal ±1).

E13.18(b) For each l, there are $2l + 1$ values of m_l and hence $2l + 1$ orbitals—each of which can be occupied by two electrons, so maximum occupancy is $2(2l + 1)$

(a) $2s\!: l = 0$; maximum occupancy $= \boxed{2}$

(b) $4d\!: l = 2$; maximum occupancy $= \boxed{10}$

(c) $6f\!: l = 3$; maximum occupancy $= \boxed{14}$

(d) $6h\!: l = 5$; maximum occupancy $= \boxed{22}$

E13.19(b) $V^{2+}: 1s^22s^22p^63s^23p^63d^3 = [\mathrm{Ar}]3d^3$

The only unpaired electrons are those in the $3d$ subshell. There are three. $S = \boxed{\frac{3}{2}}$ and $\frac{3}{2} - 1 = \boxed{\frac{1}{2}}$.

For $S = \frac{3}{2}$, $M_S = \boxed{\pm\frac{1}{2} \text{ and } \pm\frac{3}{2}}$

for $S = \frac{1}{2}$, $M_S = \boxed{\pm\frac{1}{2}}$

E13.20(b) **(a)** Possible values of S for four electrons in different orbitals are $\boxed{2, 1, \text{and } 0}$; the multiplicity is $2S + 1$, so multiplicities are $\boxed{5, 3, \text{and } 1}$ respectively.

(b) Possible values of S for five electrons in different orbitals are $\boxed{5/2, 3/2, \text{and } 1/2}$; the multiplicity is $2S + 1$, so multiplicities are $\boxed{6, 4, \text{and } 2}$ respectively.

E13.21(b) The coupling of a p electron ($l = 1$) and a d electron ($l = 2$) gives rise to $L = 3$ (F), 2 (D), and 1 (P) terms. Possible values of S include 0 and 1. Possible values of J (using Russell–Saunders coupling) are 3, 2, and 1 ($S = 0$) and 4, 3, 2, 1, and 0 ($S = 1$). The term symbols are

$$\boxed{{}^1\mathrm{F}_3;\ {}^3\mathrm{F}_4,\ {}^3\mathrm{F}_3,\ {}^3\mathrm{F}_2;\ {}^1\mathrm{D}_2;\ {}^3\mathrm{D}_3,\ {}^3\mathrm{D}_2,\ {}^3\mathrm{D}_1;\ {}^1\mathrm{P}_1;\ {}^3\mathrm{P}_2,\ {}^3\mathrm{P}_1,\ {}^3\mathrm{P}_0}.$$

Hund's rules state that the lowest energy level has maximum multiplicity. Consideration of spin–orbit coupling says the lowest energy level has the lowest value of $J(J + 1) - L(L + 1) - S(S + 1)$. So the lowest energy level is $\boxed{{}^3\mathrm{F}_2}$

E13.22(b) **(a)** ^{3}D has $S = 1$ and $L = 2$, so $J = \boxed{3, 2, \text{and } 1}$ are present. $J = 3$ has $\boxed{7}$ states, with $M_J = 0$, ±1, ±2, or ±3; $J = 2$ has $\boxed{5}$ states, with $M_J = 0$, ±1, or ±2; $J = 1$ has $\boxed{3}$ states, with $M_J = 0$, or ±1.

(b) ^{4}D has $S = 3/2$ and $L = 2$, so $J = \boxed{7/2, 5/2, 3/2, \text{and } 1/2}$ are present. $J = 7/2$ has $\boxed{8}$ possible states, with $M_J = \pm7/2, \pm5/2, \pm3/2$ or $\pm1/2$; $J = 5/2$ has $\boxed{6}$ possible states, with $M_J = \pm5/2$ $\pm3/2$ or $\pm1/2$; $J = 3/2$ has $\boxed{4}$ possible states, with $M_J = \pm3/2$ or $\pm1/2$; $J = 1/2$ has $\boxed{2}$ possible states, with $M_J = \pm1/2$.

(c) ^{2}G has $S = 1/2$ and $L = 4$, so $J = \boxed{9/2 \text{ and } 7/2}$ are present. $J = 9/2$ had $\boxed{10}$ possible states, with $M_J = \pm9/2, \pm7/2, \pm5/2, \pm3/2$ or $\pm1/2$; $J = 7/2$ has $\boxed{8}$ possible states, with $M_J = \pm7/2, \pm5/2, \pm3/2$ or $\pm1/2$.

E13.23(b) Closed shells and subshells do not contribute to either L or S and thus are ignored in what follows.

(a) Sc[Ar]$3d^1 4s^2$: $S = \frac{1}{2}$, $L = 2$; $J = \frac{5}{2}, \frac{3}{2}$, so the terms are $\boxed{^2\text{D}_{5/2} \text{ and } ^2\text{D}_{3/2}}$

(b) Br[Ar]$3d^{10}4s^2 4p^5$. We treat the missing electron in the $4p$ subshell as equivalent to a single "electron" with $l = 1$, $s = \frac{1}{2}$. Hence $L = 1$, $S = \frac{1}{2}$, and $J = \frac{3}{2}, \frac{1}{2}$, so the terms are $\boxed{^2\text{P}_{3/2} \text{ and } ^2\text{P}_{1/2}}$

Solutions to problems

Solutions to numerical problems

P13.2 All lines in the hydrogen spectrum fit the Rydberg formula

$$\frac{1}{\lambda} = \mathcal{R}_\text{H}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \left[13.1,\ \text{with } \tilde{\nu} = \frac{1}{\lambda}\right] \qquad \mathcal{R}_\text{H} = 109\,677\ \text{cm}^{-1}$$

Find n_1 from the value of λ_max, which arises from the transition $n_1 + 1 \to n_1$

$$\frac{1}{\lambda_\text{max}\mathcal{R}_\text{H}} = \frac{1}{n_1^2} - \frac{1}{(n_1+1)^2} = \frac{2n_1 + 1}{n_1^2(n_1+1)^2}$$

$$\lambda_\text{max}\mathcal{R}_\text{H} = \frac{n_1^2(n_1+1)^2}{2n_1+1} = (656.46 \times 10^{-9}\ \text{m}) \times (109\,677 \times 10^2\ \text{m}^{-1}) = 7.20$$

and hence $n_1 = 2$, as determined by trial and error substitution. Therefore, the transitions are given by

$$\tilde{\nu} = \frac{1}{\lambda} = (109\,677\ \text{cm}^{-1}) \times \left(\frac{1}{4} - \frac{1}{n_2^2}\right), \quad n_2 = 3, 4, 5, 6$$

The next line has $n_2 = 7$, and occurs at

$$\tilde{\nu} = \frac{1}{\lambda} = (109\,677\ \text{cm}^{-1}) \times \left(\frac{1}{4} - \frac{1}{49}\right) = \boxed{397.13\ \text{nm}}$$

The energy required to ionize the atom is obtained by letting $n_2 \to \infty$. Then

$$\tilde{\nu}_\infty = \frac{1}{\lambda_\infty} = (109\,677\ \text{cm}^{-1}) \times \left(\frac{1}{4} - 0\right) = 27\,419\ \text{cm}^{-1}, \quad \text{or} \quad \boxed{3.40\ \text{eV}}$$

(The answer, 3.40 eV, is the ionization energy of an H atom that is already in an excited state, with $n = 2$.)

Comment. The series with $n_1 = 2$ is the Balmer series.

P13.4 The lowest possible value of n in $1s^2nd^1$ is 3; thus the series of ^{2}D terms correspond to $1s^23d$, $1s^24d$, etc. Figure 13.2 is a description consistent with the data in the problem statement.

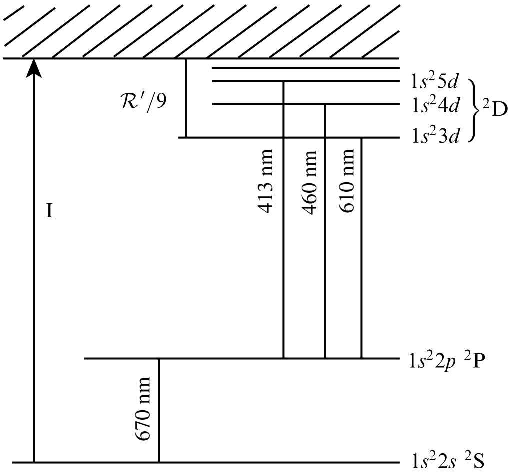


Figure 13.2

If we assume that the energies of the d orbitals are hydrogenic we may write

$$E(1s^2nd^1, {}^2\text{D}) = -\frac{hc\mathcal{R}'}{n^2} \qquad [n = 3, 4, 5, \ldots]$$

Then for the $^2\text{D} \to {}^2\text{P}$ transitions

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{|E(1s^22p^1, {}^2\text{P})|}{hc} - \frac{\mathcal{R}'}{n^2} \qquad \left[\Delta E = h\nu = \frac{hc}{\lambda} = hc\tilde{\nu}, \tilde{\nu} = \frac{\Delta E}{hc}\right]$$

from which we can write

$$\frac{|E(1s^22p^1, {}^2\text{P})|}{hc} = \frac{1}{\lambda} + \frac{\mathcal{R}'}{n^2} = \begin{cases} \dfrac{1}{610.36 \times 10^{-7}\,\text{cm}} + \dfrac{\mathcal{R}'}{9} & \text{(a)} \\ \dfrac{1}{460.29 \times 10^{-7}\,\text{cm}} + \dfrac{\mathcal{R}'}{16} & \text{(b)} \\ \dfrac{1}{413.23 \times 10^{-7}\,\text{cm}} + \dfrac{\mathcal{R}'}{25} & \text{(c)} \end{cases}$$

$$\text{Then} \quad \left.\begin{array}{l} \text{(b)} - \text{(a) solves to } \mathcal{R}' = 109\,886\,\text{cm}^{-1} \\ \text{(a)} - \text{(c) solves to } \mathcal{R}' = 109\,910\,\text{cm}^{-1} \\ \text{(b)} - \text{(c) solves to } \mathcal{R}' = 109\,963\,\text{cm}^{-1} \end{array}\right\} \text{Mean} = 109\,920\,\text{cm}^{-1}$$

The binding energies are therefore

$$E(1s^23d^1, {}^2\text{D}) = \frac{\mathcal{R}'}{9} = -12\,213\,\text{cm}^{-1}$$

$$E(1s^22p, {}^2\text{P}) = -\frac{1}{610.36 \times 10^{-7}\,\text{cm}} - 12\,213\,\text{cm}^{-1} = -28\,597\,\text{cm}^{-1}$$

$$E(1s^22s^1, {}^2\text{S}) = -\frac{1}{670.78 \times 10^{-7}\,\text{cm}} - 28\,597\,\text{cm}^{-1} = -43\,505\,\text{cm}^{-1}$$

Therefore, the ionization energy is

$$I(1s^2 2s^1, {}^2\mathrm{S}) = 43\,505\ \mathrm{cm^{-1}}, \quad \text{or} \quad \boxed{5.39\ \mathrm{eV}}$$

P13.5 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 $J = 1/2$ or $3/2$. The term symbols are $\boxed{{}^2\mathrm{P}_{1/2} \text{ and } {}^2\mathrm{P}_{3/2}}$, 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 $J = 3/2$ or $5/2$. The term symbols are $\boxed{{}^2\mathrm{D}_{3/2} \text{ and } {}^2\mathrm{D}_{5/2}}$, of which the former has the lower energy. According to the simple treatment of spin–orbit coupling, the energy is given by

$$E_{l,s,j} = \tfrac{1}{2}hcA[j(j+1) - l(l+1) - s(s+1)]$$

where A is the spin–orbit coupling constant. So

$$E({}^2\mathrm{P}_{1/2}) = \tfrac{1}{2}hcA[\tfrac{1}{2}(1/2+1) - 1(1+1) - \tfrac{1}{2}(1/2+1)] = -hcA$$

and $E({}^2\mathrm{D}_{3/2}) = \tfrac{1}{2}hcA[\tfrac{3}{2}(3/2+1) - 2(2+1) - \tfrac{1}{2}(1/2+1)] = -\tfrac{3}{2}hcA$

This approach would predict the ground state to be $\boxed{{}^2\mathrm{D}_{3/2}}$

Comment. The computational study cited above finds the ${}^2\mathrm{P}_{1/2}$ level to be lowest, but the authors caution that the error of similar calculations on Y and Lu is comparable to the computed difference between levels.

P13.7 $\mathcal{R}_\mathrm{H} = k\mu_\mathrm{H}, \quad \mathcal{R}_\mathrm{D} = k\mu_\mathrm{D}, \quad \mathcal{R} = k\mu$ [18]

where $\mathcal{R}$ corresponds to an infinitely heavy nucleus, with $\mu = m_\mathrm{e}$.

Since $\mu = \dfrac{m_\mathrm{e} m_\mathrm{N}}{m_\mathrm{e} + m_\mathrm{N}}$ [N = p or d]

$$\mathcal{R}_\mathrm{H} = k\mu_\mathrm{H} = \frac{km_\mathrm{e}}{1 + \frac{m_\mathrm{e}}{m_\mathrm{p}}} = \frac{\mathcal{R}}{1 + \frac{m_\mathrm{e}}{m_\mathrm{p}}}$$

Likewise, $\mathcal{R}_\mathrm{D} = \dfrac{\mathcal{R}}{1 + \frac{m_\mathrm{e}}{m_\mathrm{d}}}$ where m_p is the mass of the proton and m_d the mass of the deuteron. The two lines in question lie at

$$\frac{1}{\lambda_\mathrm{H}} = \mathcal{R}_\mathrm{H}\left(1 - \tfrac{1}{4}\right) = \tfrac{3}{4}\mathcal{R}_\mathrm{H} \qquad \frac{1}{\lambda_\mathrm{D}} = \mathcal{R}_\mathrm{D}\left(1 - \tfrac{1}{4}\right) = \tfrac{3}{4}\mathcal{R}_\mathrm{D}$$

and hence

$$\frac{\mathcal{R}_\mathrm{H}}{\mathcal{R}_\mathrm{D}} = \frac{\lambda_\mathrm{D}}{\lambda_\mathrm{H}} = \frac{\tilde{\nu}_\mathrm{H}}{\tilde{\nu}_\mathrm{D}}$$

Then, since

$$\frac{\mathcal{R}_\mathrm{H}}{\mathcal{R}_\mathrm{D}} = \frac{1 + \frac{m_\mathrm{e}}{m_\mathrm{d}}}{1 + \frac{m_\mathrm{e}}{m_\mathrm{p}}}, \qquad m_\mathrm{d} = \frac{m_\mathrm{e}}{\left(1 + \frac{m_\mathrm{e}}{m_\mathrm{p}}\right)\frac{\mathcal{R}_\mathrm{H}}{\mathcal{R}_\mathrm{D}} - 1}$$

and we can calculate m_d from

$$m_\mathrm{d} = \frac{m_\mathrm{e}}{\left(1+\frac{m_\mathrm{e}}{m_\mathrm{p}}\right)\frac{\lambda_\mathrm{D}}{\lambda_\mathrm{H}}-1} = \frac{m_\mathrm{e}}{\left(1+\frac{m_\mathrm{e}}{m_\mathrm{p}}\right)\frac{\tilde{\nu}_\mathrm{H}}{\tilde{\nu}_\mathrm{D}}-1}$$

$$= \frac{9.10939\times10^{-31}\,\mathrm{kg}}{\left(1+\frac{9.10939\times10^{-31}\,\mathrm{kg}}{1.67262\times10^{-27}\,\mathrm{kg}}\right)\times\left(\frac{82\,259.098\,\mathrm{cm}^{-1}}{82\,281.476\,\mathrm{cm}^{-1}}\right)-1} = \boxed{3.3429\times10^{-27}\,\mathrm{kg}}$$

Since $I = Rhc$,

$$\frac{I_\mathrm{D}}{I_\mathrm{H}} = \frac{\mathcal{R}_\mathrm{D}}{\mathcal{R}_\mathrm{H}} = \frac{\tilde{\nu}_\mathrm{D}}{\tilde{\nu}_\mathrm{H}} = \frac{82\,281.476\,\mathrm{cm}^{-1}}{82\,259.098\,\mathrm{cm}^{-1}} = \boxed{1.000\,272}$$

P13.10 If we assume that the innermost electron is a hydrogen-like $1s$ orbital we may write

$$r^* = \frac{a_0}{Z}[\text{Example 13.3}] = \frac{52.92\,\mathrm{pm}}{126} = \boxed{0.420\,\mathrm{pm}}$$

Solutions to theoretical problems

P13.12 Consider $\psi_{2p_z} = \psi_{2,1,0}$ which extends along the z-axis. The most probable point along the z-axis is where the radial function has its maximum value (for ψ^2 is also a maximum at that point). From Table 13.1 we know that

$$R_{21} \propto \rho\mathrm{e}^{-\rho/4}$$

and so $\dfrac{\mathrm{d}R}{\mathrm{d}\rho} = \left(1-\frac{1}{4}\rho\right)\mathrm{e}^{-\rho/4} = 0$ when $\rho = 4$.

Therefore, $r^* = \dfrac{2a_0}{Z}$, and the point of maximum probability lies at $z = \pm\dfrac{2a_0}{Z} = \boxed{\pm106\,\mathrm{pm}}$

Comment. Since the radial portion of a $2p$ function is the same, the same result would have been obtained for all of them. The direction of the most probable point would, however, be different.

P13.13 In each case we need to show that

$$\int_{\text{all space}} \psi_1^*\psi_2\,\mathrm{d}\tau = 0$$

(a) $$\int_0^\infty\int_0^\pi\int_0^{2\pi}\psi_{1s}\psi_{2s}r^2\,\mathrm{d}r\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi \overset{?}{=} 0$$

$$\left.\begin{aligned}\psi_{1s} &= R_{1,0}Y_{0,0}\\ \psi_{2s} &= R_{2,0}Y_{0,0}\end{aligned}\right\} Y_{0,0} = \left(\frac{1}{4\pi}\right)^{1/2} \quad [\text{Table 12.3}]$$

Since $Y_{0,0}$ is a constant, the integral over the radial functions determines the orthogonality of the functions.

$$\int_0^\infty R_{1,0}R_{2,0}r^2\,\mathrm{d}r$$

$$R_{1,0} \propto \mathrm{e}^{-\rho/2} = \mathrm{e}^{-Zr/a_0} \qquad \left[\rho = \frac{2Zr}{a_0}\right]$$

$$R_{2,0} \propto (2-\rho/2)\mathrm{e}^{-\rho/4} = \left(2-\frac{Zr}{a_0}\right)\mathrm{e}^{-Zr/2a_0} \qquad \left[\rho = \frac{2Zr}{a_0}\right]$$

$$\begin{aligned}\int_0^\infty R_{1,0}R_{2,0}r^2\,\mathrm{d}r &\propto \int_0^\infty \mathrm{e}^{-Zr/a_0}\left(2-\frac{Zr}{a_0}\right)\mathrm{e}^{-Zr/2a_0}r^2\,\mathrm{d}r\\ &= \int_0^\infty 2\mathrm{e}^{-(3/2)Zr/a_0}r^2\,\mathrm{d}r - \int_0^\infty \frac{Z}{a_0}\mathrm{e}^{-(3/2)Zr/a_0}r^3\,\mathrm{d}r\\ &= \frac{2\times 2!}{\left(\frac{3}{2}\frac{Z}{a_0}\right)^3} - \left(\frac{Z}{a_0}\right)\times\frac{3!}{\left(\frac{3}{2}\frac{Z}{a_0}\right)^4} = \boxed{0}\end{aligned}$$

Hence, the functions are orthogonal.

(b) We use the p_x and p_y orbitals in the form given in Section 13.2(f), eqn 25

$$p_x \propto x, \qquad p_y \propto y$$

Thus

$$\int_{\text{all space}} p_x p_y\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \propto \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} xy\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$$

This is an integral of an odd function of x and y over the entire range of variable from $-\infty$ to $+\infty$, therefore, the $\boxed{\text{integral is zero}}$. More explicitly we may perform the integration using the orbitals in the form (Section 13.2(f), eqn 13.25)

$$p_x = f(r)\sin\theta\cos\phi \qquad p_y = f(r)\sin\theta\sin\phi$$

$$\int_{\text{all space}} p_x p_y r^2\,\mathrm{d}r\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi = \int_0^\infty f(r)^2r^2\,\mathrm{d}r\int_0^\pi \sin^2\theta\,\mathrm{d}\theta\int_0^{2\pi}\cos\phi\sin\phi\,\mathrm{d}\phi$$

The first factor is nonzero since the radial functions are normalized. The second factor is $\frac{\pi}{2}$. The third factor is zero. Therefore, the product of the integrals is $\boxed{\text{zero}}$ and the functions are orthogonal.

P13.14

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r}\right)+V_{\text{eff}}\right]R = ER\ [13.11] \qquad (1)$$

where $V_{\text{eff}} = -\dfrac{Ze^2}{4\pi\varepsilon_0 r}+\dfrac{l(l+1)\hbar^2}{2\mu r^2} = -\dfrac{Z\hbar^2}{\mu a_0 r}+\dfrac{l(l+1)\hbar^2}{2\mu r^2}$

Using $\rho = Zr/a_0$, the derivative term of the Hamiltonian can be written in the form

$$\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r} = \left(\frac{Z}{a_0}\right)^2\times\left[\frac{\mathrm{d}^2}{\mathrm{d}\rho^2}+\frac{2}{\rho}\frac{\mathrm{d}}{\mathrm{d}\rho}\right] \equiv D_{\text{op}} \qquad (2)$$

To determine E_{2s} and E_{2p}, we will evaluate the left side of (1) and compare the result to the right side.

$2s$ orbital. $\quad R_{2s} = N_{2s}(2-\rho)\mathrm{e}^{-\rho/2} \quad$ where $\rho \equiv Zr/a_0$ here

$$\frac{\mathrm{d}R_{2s}}{\mathrm{d}\rho} = N_{2s}\left\{-1-\tfrac{1}{2}(2-\rho)\right\}\mathrm{e}^{-\rho/2} = N_{2s}\left\{\frac{\rho-4}{2}\right\}\mathrm{e}^{-\rho/2} = \frac{\rho-4}{2(2-\rho)}R_{2s}$$

$$\frac{\mathrm{d}^2R_{2s}}{\mathrm{d}\rho^2} = N_{2s}\left\{\tfrac{1}{2}-\tfrac{1}{4}(\rho-4)\right\}\mathrm{e}^{-\rho/2} = N_{2s}\left\{\tfrac{3}{2}-\frac{\rho}{4}\right\}\mathrm{e}^{-\rho/2} = \frac{6-\rho}{4(2-\rho)}R_{2s}$$

$$-\frac{\hbar^2}{2\mu}D_{\text{op}}R_{2s} = -\frac{\hbar^2}{2\mu}\left\{\frac{6-\rho}{4(2-\rho)} + \frac{\rho-4}{\rho(2-\rho)}\right\} \times \left(\frac{Z}{a_0}\right)^2 R_{2s}$$

$$= \left(-\frac{\hbar^2}{2\mu}\right) \times \left(\frac{\rho-8}{4\rho}\right) \times \left(\frac{Z}{a_0}\right)^2 R_{2s}$$

$$V_{\text{eff}}R_{2s} = -\frac{Z\hbar^2}{\mu a_0 r}R_{2s} = -\left(\frac{Z}{a_0}\right)^2 \times \left(\frac{\hbar^2}{\mu}\right)\frac{1}{\rho}R_{2s}$$

$$\left[-\frac{\hbar^2}{2\mu}D_{\text{op}} + V_{\text{eff}}\right]R_{2s} = \left(\frac{Z}{a_0}\right)^2 \times \left(-\frac{\hbar^2}{2\mu}\right) \times \left\{\frac{\rho-8}{4\rho} + \frac{2}{\rho}\right\}R_{2s}$$

$$= -\frac{Z^2\hbar^2}{2\mu a_0^2}\left(\frac{1}{4}\right)R_{2s}$$

Therefore $\boxed{E_{2s} = -\tfrac{1}{4}\left(\dfrac{Z^2\hbar^2}{2\mu a_0^2}\right)}$ (3)

$2p$ orbital. $R_{2p} = N_{2p}\rho \mathrm{e}^{-\rho/2}$ where $\rho \equiv Zr/a_0$ here

$$\frac{\mathrm{d}R_{2p}}{\mathrm{d}\rho} = N_{2p}\left\{1 - \frac{\rho}{2}\right\}\mathrm{e}^{-\rho/2} = \frac{2-\rho}{2\rho}R_{2p}$$

$$\frac{\mathrm{d}^2R_{2p}}{\mathrm{d}\rho^2} = N_{2p}\left\{-\tfrac{1}{2} - \tfrac{1}{2}\left(1 - \frac{\rho}{2}\right)\right\}\mathrm{e}^{-\rho/2} = \frac{\rho-4}{4\rho}R_{2p}$$

$$-\frac{\hbar^2}{2\mu}D_{\text{op}}R_{2p} = -\frac{\hbar^2}{2\mu}\left\{\frac{\rho-4}{4\rho} + \frac{4-2\rho}{2\rho^2}\right\} \times \left(\frac{Z}{a_0}\right)^2 R_{2p}$$

$$= -\frac{\hbar^2}{2\mu}\left\{\frac{\rho^2-8\rho+8}{4\rho^2}\right\} \times \left(\frac{Z}{a_0}\right)^2 R_{2p}$$

$$V_{\text{eff}}R_{2p} = \left[-\frac{Z\hbar^2}{\mu a_0 r} + \frac{\hbar^2}{\mu r^2}\right]R_{2p} = \left[-\left(\frac{Z}{a_0}\right)^2 \times \left(\frac{\hbar^2}{\mu}\right)\frac{1}{\rho} + \left(\frac{Z}{a_0}\right)^2 \times \left(\frac{\hbar^2}{\mu}\right)\frac{1}{\rho^2}\right]R_{2p}$$

$$= \left(\frac{Z}{a_0}\right)^2 \times \left(-\frac{\hbar^2}{2\mu}\right) \times \left[\frac{2(\rho-1)}{\rho^2}\right]R_{2p}$$

$$\left[-\frac{\hbar^2}{2\mu}D_{\text{op}} + V_{\text{eff}}\right]R_{2p} = \left(\frac{Z}{a_0}\right)^2 \times \left(-\frac{\hbar^2}{2\mu}\right) \times \left\{\frac{\rho^2-8\rho+8}{4\rho^2} + \frac{2(\rho-1)}{\rho^2}\right\}R_{2p}$$

$$= -\frac{Z^2\hbar^2}{2\mu a_0^2}\left(\frac{\rho^2}{4\rho^2}\right)R_{2p} = -\frac{Z^2\hbar^2}{2\mu a_0^2}\left(\frac{1}{4}\right)R_{2p}$$

Therefore $\boxed{E_{2p} = -\tfrac{1}{4}\left(\dfrac{Z^2\hbar^2}{2\mu a_0^2}\right)}$ (4)

Comparison of eqns (3) and (4) reveals that $E_{2s} = E_{2p}$.

P13.15 **(a)** We must show that $\int |\psi_{3p_x}|^2\,\mathrm{d}\tau = 1$. The integrations are most easily performed in spherical coordinate (Fig. 11).

$$\begin{aligned}
\int |\psi_{3p_x}|^2\,\mathrm{d}\tau &= \int\limits_0^{2\pi}\int\limits_0^{\pi}\int\limits_0^{\infty} |\psi_{3p_x}|^2\, r^2\sin(\theta)\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi \\
&= \int\limits_0^{2\pi}\int\limits_0^{\pi}\int\limits_0^{\infty} \left| R_{31}(\rho)\left\{\frac{Y_{1-1}-Y_{11}}{\sqrt{2}}\right\}\right|^2 r^2\sin(\theta)\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi \text{ (Table 13.1, eqn 13.25)}
\end{aligned}$$

where $\rho = 2r/a_0, r = \rho a_0/2, \mathrm{d}r = (a_0/2)\,\mathrm{d}\rho$.

$$\begin{aligned}
&= \frac{1}{2}\int\limits_0^{2\pi}\int\limits_0^{\pi}\int\limits_0^{\infty}\left(\frac{a_0}{2}\right)^3 \left|\left[\left(\frac{1}{27(6)^{1/2}}\right)\left(\frac{1}{a_0}\right)^{3/2}\left(4-\frac{1}{3}\rho\right)\rho\mathrm{e}^{-\rho/6}\right]\right. \\
&\quad \times \left.\left[\left(\frac{3}{8\pi}\right)^{1/2} 2\sin(\theta)\cos(\phi)\right]\right|^2 \rho^2\sin(\theta)\,\mathrm{d}\rho\,\mathrm{d}\theta\,\mathrm{d}\phi \\
&= \frac{1}{46\,656\pi}\int\limits_0^{2\pi}\int\limits_0^{\pi}\int\limits_0^{\infty}\left|\left(4-\frac{1}{3}\rho\right)\rho\mathrm{e}^{-\rho/6}\sin(\theta)\cos(\phi)\right|^2 \rho^2\,\sin(\theta)\,\mathrm{d}\rho\,\mathrm{d}\theta\,\mathrm{d}\phi \\
&= \frac{1}{46\,656\pi}\underbrace{\int\limits_0^{2\pi}\cos^2(\phi)\,\mathrm{d}\phi}_{\pi}\underbrace{\int\limits_0^{\pi}\sin^3(\theta)\,\mathrm{d}\theta}_{4/3}\underbrace{\int\limits_0^{\infty}\left(4-\frac{1}{3}\rho\right)^2\rho^4\mathrm{e}^{-\rho/3}\,\mathrm{d}\rho}_{34992} \\
&= 1 \quad \text{Thus, } \psi_{3p_x} \text{ is normalized to 1.}
\end{aligned}$$

We must also show that $\int \psi_{3p_x}\psi_{3d_{xy}}\,\mathrm{d}\tau = 0$

Using Tables 12.3 and 13.1, we find that

$$\begin{aligned}
\psi_{3p_x} &= \frac{1}{54(2\pi)^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\left(4-\frac{1}{3}\rho\right)\rho\mathrm{e}^{-\rho/6}\sin(\theta)\cos(\phi) \\
\psi_{3d_{xy}} &= R_{32}\left\{\frac{Y_{22}-Y_{2-2}}{\sqrt{2}\mathrm{i}}\right\} \\
&= \frac{1}{32(2\pi)^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\rho^2\mathrm{e}^{-\rho/6}\sin^2(\theta)\sin(2\phi)
\end{aligned}$$

where $\rho = 2r/\mathrm{a}_0, r = \rho a_0/2, \mathrm{d}r = (a_0/2)\mathrm{d}\rho$.

$$\int \psi_{3p_x}\psi_{3d_{xy}}\mathrm{d}\tau = \text{constant} \times \int\limits_0^{\infty}\rho^5\mathrm{e}^{-\rho/3}\mathrm{d}\rho\underbrace{\int\limits_0^{2\pi}\cos(\phi)\sin(2\phi)\mathrm{d}\phi\int\limits_0^{\pi}\sin^4(\theta)\mathrm{d}\theta}_{0}$$

Since the integral equals zero, ψ_{3p_x} and $\psi_{3d_{xy}}$ are orthogonal.

(b) Radial nodes are determined by finding the ρ values ($\rho = 2r/a_0$) for which the radial wavefunction equals zero. These values are the roots of the polynomial portion of the wavefunction.

For the 3s orbital $6 - 6\rho + \rho^2 = 0$ when $\boxed{\rho_{\text{node}} = 3 + \sqrt{3} \quad \text{and} \quad \rho_{\text{node}} = 3 - \sqrt{3}}$.

The 3s orbital has these two spherically symmetrical modes. There is no node at $\rho = 0$ so we conclude that there is a finite probability of finding a 3s electron at the nucleus.

For the $3p_x$ orbital $(4 - \rho)(\rho) = 0$ when $\boxed{\rho_{\text{node}} = 0 \quad \text{and} \quad \rho_{\text{node}} = 4}$.

There is a zero probability of finding a $3p_x$ electron at the nucleus.

For the $3d_{xy}$ orbital $\boxed{\rho_{\text{node}} = 0}$ is the only radial node.

(c)
$$\langle r\rangle_{3s} = \int |R_{10}Y_{00}|^2\, r\, \mathrm{d}\tau = \int |R_{10}Y_{00}|^2\, r^3 \sin(\theta)\, \mathrm{d}r\, \mathrm{d}\theta\, \mathrm{d}\phi$$
$$= \int_0^{\infty} R_{10}^2 r^3 \mathrm{d}r \underbrace{\int_0^{2\pi}\int_0^{\pi} |Y_{00}|^2 \sin(\theta)\, \mathrm{d}\theta\, \mathrm{d}\phi}_{1}$$
$$= \frac{a_0}{3\,888} \underbrace{\int_0^{\infty} \left(6 - 2\rho + \rho^2/9\right)^2 \rho^3 \mathrm{e}^{-\rho/3}\, \mathrm{d}\rho}_{52488}$$

$$\boxed{\langle r\rangle_{3s} = \frac{27a_0}{2}}$$

(d)

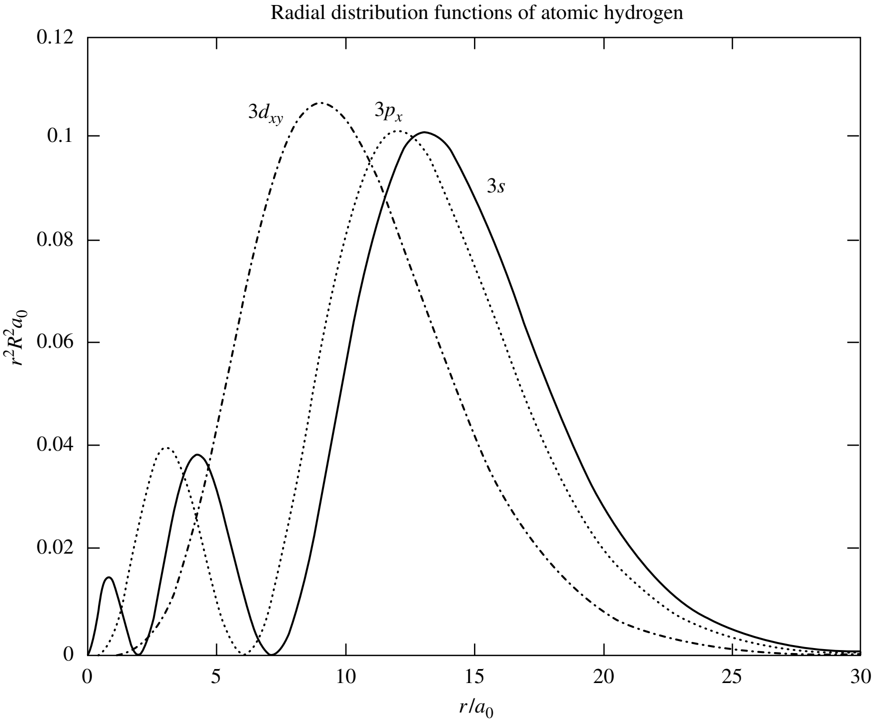


Figure 13.3(a)

The plot shows that the 3s orbital has larger values of the radial distribution function for $r < a_0$. This penetration of inner core electrons of multi-electron atoms means that a 3s electron experiences a larger effective nuclear charge and, consequently, has a lower energy than either a $3p_x$ or $3d_{xy}$ electron. This reasoning also lead us to conclude that a $3p_x$ electron has less energy than a $3d_{xy}$ electron.

$$E_{3s} < E_{3p_x} < E_{3d_{xy}}.$$

(e) Polar plots with $\theta = 90^\circ$

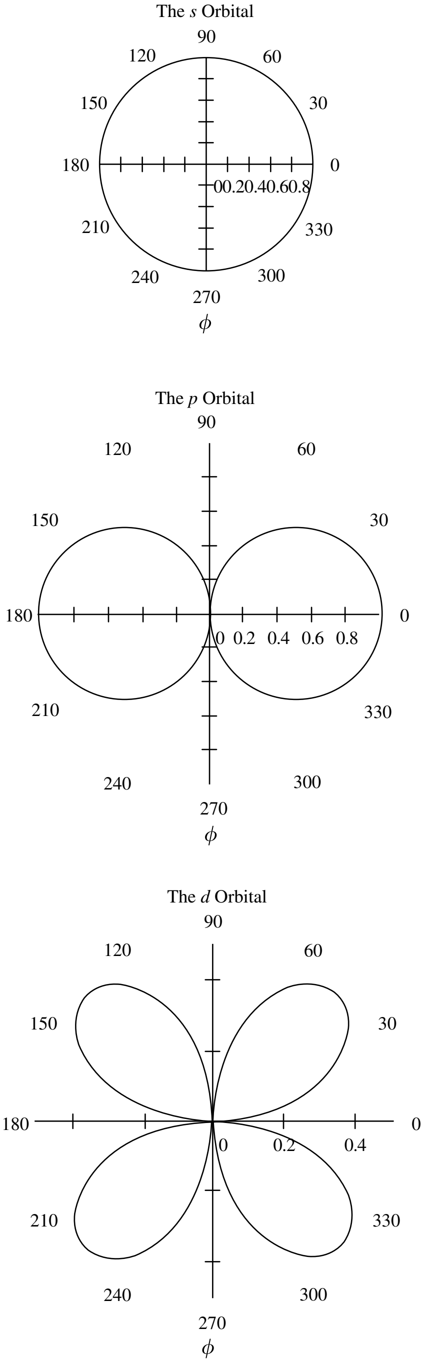
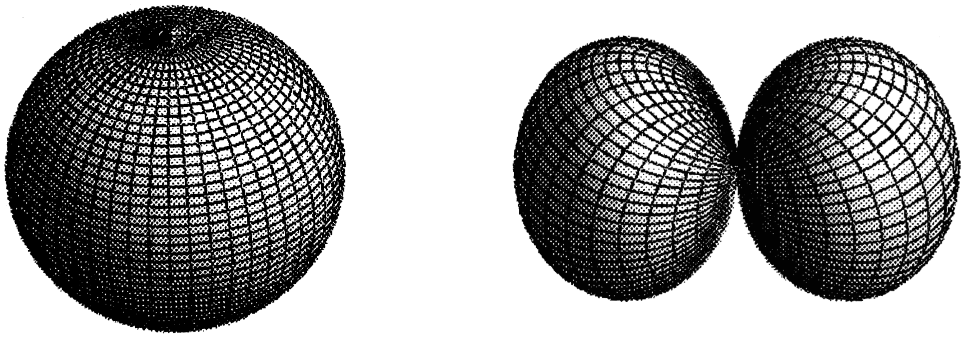


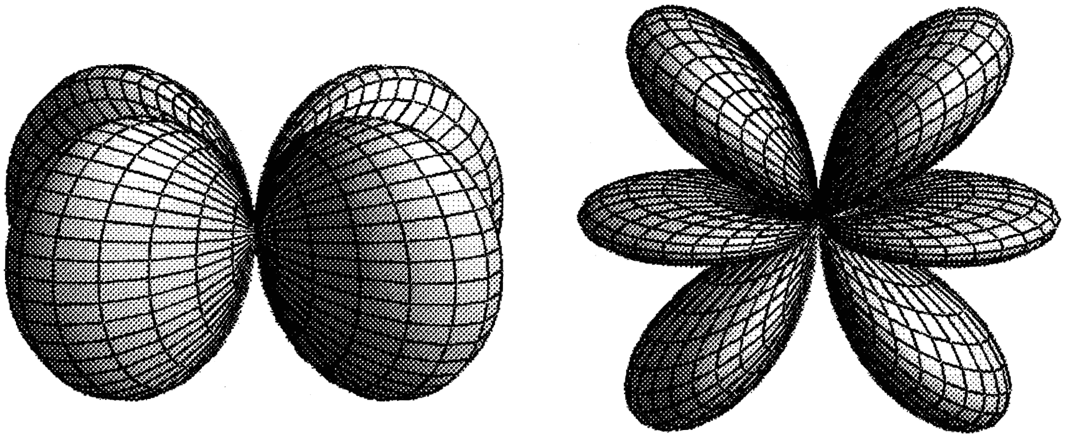
Figure 13.3(b)

Boundary surface plots



s-Orbital boundary surface

p-Orbital boundary surface



d-Orbital boundary surface

f-Orbital boundary surface

Figure 13.3(c)

P13.20 The attractive Coulomb force $= \dfrac{Ze^2}{4\pi\varepsilon_0} \cdot \dfrac{1}{r^2}$

The repulsive centrifugal force $= \dfrac{(\text{angular momentum})^2}{m_e r^3} = \dfrac{(n\hbar)^2}{m_e r^3}$ [postulated]

The two forces balance when

$$\frac{Ze^2}{4\pi\varepsilon_0} \times \frac{1}{r^2} = \frac{n^2\hbar^2}{m_e r^3}, \quad \text{implying that} \quad r = \frac{4\pi n^2\hbar^2\varepsilon_0}{Ze^2 m_e}$$

The total energy is

$$E = E_K + V = \frac{(\text{angular momentum})^2}{2I} - \frac{Ze^2}{4\pi\varepsilon_0} \times \frac{1}{r} = \frac{n^2\hbar^2}{2m_e r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r} \text{ [postulated]}$$

$$= \left(\frac{n^2\hbar^2}{2m_e}\right) \times \left(\frac{Ze^2 m_e}{4\pi n^2\hbar^2\varepsilon_0}\right)^2 - \left(\frac{Ze^2}{4\pi\varepsilon_0}\right) \times \left(\frac{Ze^2 m_e}{4\pi n^2\hbar^2\varepsilon_0}\right) = \boxed{-\frac{Z^2 e^4 m_e}{32\pi^2\varepsilon_0^2\hbar^2} \times \frac{1}{n^2}}$$

P13.21 **(a)** The trajectory is defined, which is not allowed according to quantum mechanics.

(b) The angular momentum of a three-dimensional system is given by $\{l(l+1)\}^{1/2}\hbar$, not by $n\hbar$. In the Bohr model, the ground state possesses orbital angular momentum ($n\hbar$, with $n = 1$), but the actual ground state has no angular momentum ($l = 0$). Moreover, the distribution of the electron is quite different in the two cases. The two models can be distinguished experimentally by (a) showing that there is zero orbital angular momentum in the ground state (by examining its magnetic properties) and (b) examining the electron distribution (such as by showing that the electron and the nucleus do come into contact, Chapter 18).

P13.25 *Justification* 13.5 noted that the transition dipole moment, μ_{fi} had to be non-zero for a transition to be allowed. The Justification examined conditions that allowed the z component of this quantity to be non-zero; now examine the x and y components.

$$\mu_{x,\mathrm{fi}} = -e\int \Psi\mathrm{f}^* x\Psi_{\mathrm{i}}\,\mathrm{d}\tau \quad \text{and} \quad \mu_{y,\mathrm{fi}} = -e\int \Psi\mathrm{f}^* y\Psi_{\mathrm{i}}\,\mathrm{d}\tau$$

As in the Justification, express the relevant Cartesian variables in terms of the spherical harmonics, $Y_{l,m}$. Start by expressing them in spherical polar coordinates:

$$x = r\sin\theta\cos\phi \quad \text{and} \quad y = r\sin\theta\sin\phi.$$

Note that $Y_{1,1}$ and $Y_{1,-1}$ have factors of $\sin\theta$. They also contain complex exponentials that can be related to the sine and cosine of ϕ through the identities (eqns FI1.20 and FI1.21)

$$\cos\phi = 1/2(\mathrm{e}^{\mathrm{i}\phi} + \mathrm{e}^{-\mathrm{i}\phi}) \quad \text{and} \quad \sin\phi = 1/2\mathrm{i}(\mathrm{e}^{\mathrm{i}\phi} - \mathrm{e}^{-\mathrm{i}\phi}).$$

These relations motivate us to try linear combinations $Y_{1,1}+Y_{1,-1}$ and $Y_{1,1}+Y_{1,-1}$ (form Table 12.3; note c here corresponds to the normalization constant in the table):

$$Y_{1,1} + Y_{1,-1} = -c\sin\theta(\mathrm{e}^{\mathrm{i}\phi} + \mathrm{e}^{-\mathrm{i}\phi}) = -2c\sin\theta\cos\phi = -2cx/r,$$

so $x = -(Y_{1,1} + Y_{1,-1})r/2c$;

$$Y_{1,1} - Y_{1,-1} = c\sin\theta(\mathrm{e}^{\mathrm{i}\phi} - \mathrm{e}^{-\mathrm{i}\phi}) = 2\mathrm{i}c\sin\theta\sin\phi = 2\mathrm{i}cy/r,$$

so $y = (Y_{1,1} - Y_{1,-1})r/2\mathrm{i}c$.

Now we can express the integrals in terms of radial wavefunctions $R_{n,l}$ and spherical harmonics Y_{l,m_l}

$$\mu_{x,\mathrm{fi}} = \frac{e}{2c}\int_0^\infty R_{n_\mathrm{f},l_\mathrm{f}} r R_{n_\mathrm{i},l_\mathrm{i}} r^2\,dr \int_0^\pi\int_0^{2\pi} Y^*{}_{l_\mathrm{f},m_{l_\mathrm{f}}}(Y_{1,1} + Y_{1,-1})Y_{l_\mathrm{i},m_{l_\mathrm{i}}}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi.$$

The angular integral can be broken into two, one of which contains $Y_{1,1}$ and the other $Y_{1,-1}$. According to the "triple integral" relation below Table 12.3, the integral

$$\int_0^\pi\int_0^{2\pi} Y^*{}_{l_\mathrm{f},m_{l_\mathrm{f}}} Y_{1,1} Y_{l_\mathrm{i},m_{l_\mathrm{i}}}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$

vanishes unless $l_\mathrm{f} = l_\mathrm{i} \pm 1$ and $m_\mathrm{f} = m_\mathrm{i} \pm 1$. The integral that contains $Y_{1,-1}$ introduces no further constraints; it vanishes unless $l_\mathrm{f} = l_\mathrm{i} \pm 1$ and $m_{l_\mathrm{f}} = m_{l_\mathrm{i}} \pm 1$. Similarly, the y component introduces no further constraints, for it involves the same spherical harmonics as the x component. The whole set of selection rules, then, is that transitions are allowed only if

$$\boxed{\Delta l = \pm 1 \text{ and } \Delta m_l = 0 \text{ or } \pm 1}.$$

P13.26 **(a)** The speed distribution in the molecular beam is related to the speed distribution within the chamber by a factor of $v\cos\theta$ as shown in Fig. 13.4. Since an integration over all possible θ must be performed, the $\cos\theta$ factor may be absorbed into the constant of proportionality.

$$f_{\text{beam}}(v) = Cvf_{\text{chamber}}(v) \quad \text{where } C \text{ is to be determined}$$

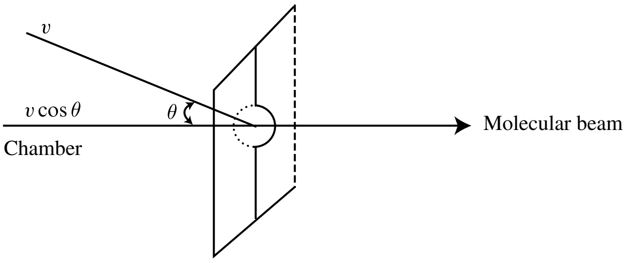


Figure 13.4

By normalization over the possible beam speeds ($0 < v_{\text{beam}} < \infty$)

$$f_{\text{beam}} = Cv\left(v^2 e^{-(mv^2/2kT)}\right)$$
$$= Cv^3 e^{-(mv^2/2kT)}$$
$$\int_{v=0}^{\infty} f_{\text{beam}} dv = 1 = C\int_{v=0}^{\infty} v^3 e^{-(mv^2/2kT)} dv = C\left\{\frac{1}{2(m/2kT)^2}\right\}$$
$$C = 2(m/2kT)^2$$
$$\langle v^2\rangle = \int_{v=0}^{\infty} v^2 f_{\text{beam}}(v)\,dv = C\int v^5 e^{-(mv^2/2kT)}\,dv$$
$$= C\left\{\frac{1}{(m/2kT)^3}\right\} = 2\frac{(m/2kT)^2}{(m/2kT)^3}$$
$$= \frac{4kT}{m}$$
$$\langle E_K\rangle = \frac{m}{2}\langle v^2\rangle = \frac{m}{2}\left(\frac{4kT}{m}\right) = \boxed{2kT}$$

(b) $$\Delta x = \left(\frac{2\mu_B L^2}{4E_K}\right)\frac{dB}{dz}$$

or $$\frac{dB}{dz} = \frac{4E_K\Delta x}{2\mu_B L^2} = \frac{4(2kT)\Delta x}{2\mu_B L^2}$$
$$= \frac{4kT\Delta x}{\mu_B L^2}$$
$$= \frac{4(1.3807\times10^{-23}\,\text{J K}^{-1})\times(1000\,\text{K})\times(1.00\times10^{-3}\,\text{m})}{(9.27402\times10^{-24}\,\text{J T}^{-1})\times(50\times10^{-2}\,\text{m})^2}$$
$$\frac{dB}{dz} = \boxed{23.8\,\text{T m}^{-1}}$$

14 Molecular structure

Solutions to exercises

Discussion questions

E14.1(b) Consider the case of the carbon atom. Mentally we break the process of hybridization into two major steps. The first is promotion, in which we imagine that one of the electrons in the $2s$ orbital of carbon ($2s^2 2p^2$) is promoted to the empty $2p$ orbital giving the configuration $2s2p^3$. In the second step we mathematically mix the four orbitals by way of the specific linear combinations in eqn 14.3 corresponding to the sp^3 hybrid orbitals. There is a principle of conservation of orbitals that enters here. If we mix four unhybridized atomic orbitals we must end up four hybrid orbitals. In the construction of the sp^2 hybrids we start with the $2s$ orbital and two of the $2p$ orbitals, and after mixing we end up with three sp^2 hybrid orbitals. In the sp case we start with the $2s$ orbital and one of the $2p$ orbitals. The justification for all of this is in a sense the first law of thermodynamics. Energy is a property and therefore its value is determined only by the final state of the system, not by the path taken to achieve that state, and the path can even be imaginary.

E14.2(b) It can be proven that if an arbitrary wavefunction is used to calculate the energy of a system, the value calculated is never less than the true energy. This is the variation principle. This principle allows us an enormous amount of latitude in constructing wavefunctions. We can continue modifying the wavefunctions in any arbitrary manner until we find a set that we feel provide an energy close to the true minimum in energy. Thus we can construct wavefunctions containing many parameters and then minimize the energy with respect to those parameters. These parameters may or may not have some chemical or physical significance. Of course, we might strive to construct trial wavefunctions that provide some chemical and physical insight and interpretation that we can perhaps visualize, but that is not essential. Examples of the mathematical steps involved are illustrated in Sections 14.6(c) and (d), *Justification* 14.3, and Section 14.7.

E14.3(b) These are all terms originally associated with the Huckel approximation used in the treatment of conjugated π-electron molecules, in which the π-electrons are considered independent of the σ-electrons. π-electron binding energy is the sum the energies of each π-electron in the molecule. The delocalization energy is the difference in energy between the conjugated molecule with n double bonds and the energy of n ethene molecules, each of which has one double bond. The π-bond formation energy is the energy released when a π bond is formed. It is obtained from the total π-electron binding energy by subtracting the contribution from the Coulomb integrals, α.

E14.4(b) In *ab initio* methods an attempt is made to evaluate all integrals that appear in the secular determinant. Approximations are still employed, but these are mainly associated with the construction of the wavefunctions involved in the integrals. In semi-empirical methods, many of the integrals are expressed in terms of spectroscopic data or physical properties. Semi-empirical methods exist at several levels. At some levels, in order to simplify the calculations, many of the integrals are set equal to zero.

The Hartree-Fock and DFT methods are similar in that they are both regarded as *ab initio* methods. In HF the central focus is the wavefunction whereas in DFT it is the electron density. They are both iterative self consistent methods in that the process are repeated until the energy and wavefunctions (HF) or energy and electron density (DFT) are unchanged to within some acceptable tolerance.

Numerical exercises

E14.5(b) Use Fig. 14.23 for H_2^-, 14.30 for N_2, and 14.28 for O_2.

(a) H_2^- (3 electrons): $\boxed{1\sigma^2 2\sigma^{*1}}$ $b = 0.5$

(b) N_2 (10 electrons): $\boxed{1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2}$ $b = 3$

(c) O_2 (12 electrons): $\boxed{1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*2}}$ $b = 2$

E14.6(b) ClF is isoelectronic with F_2, CS with N_2.

(a) ClF (14 electrons): $\boxed{1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*4}}$ $b = 1$

(b) CS (10 electrons): $\boxed{1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2}$ $b = 3$

(c) O_2^- (13 electrons): $\boxed{1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*3}}$ $b = 1.5$

E14.7(b) Decide whether the electron added or removed increases or decreases the bond order. The simplest procedure is to decide whether the electron occupies or is removed from a bonding or antibonding orbital. We can draw up the following table, which denotes the orbital involved

	N_2	NO	O_2	C_2	F_2	CN
(a) AB^-	$2\pi^*$	$2\pi^*$	$2\pi^*$	3σ	$4\sigma^*$	3σ
Change in bond order	$-1/2$	$-1/2$	$-1/2$	$+1/2$	$-1/2$	$+1/2$
(b) AB^+	3σ	$2\pi^*$	$2\pi^*$	1π	$2\pi^*$	3σ
Change in bond order	$-1/2$	$+1/2$	$+1/2$	$-1/2$	$+1/2$	$-1/2$

(a) Therefore, $\boxed{C_2 \text{ and CN}}$ are stabilized (have lower energy) by anion formation.

(b) $\boxed{\text{NO, } O_2 \text{ and } F_2}$ are stabilized by cation formation; in each of these cases the bond order increases.

E14.8(b) Figure 14.1 is based on Fig. 14.28 of the text but with Cl orbitals lower than Br orbitals. BrCl is likely to have a shorter bond length than $BrCl^-$; it has a bond order of 1, while $BrCl^-$ has a bond order of $\frac{1}{2}$.

E14.9(b)

O_2^+ (11 electrons) : $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*1}$ $b = 5/2$

O_2 (12 electrons) : $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*2}$ $b = 2$

O_2^- (13 electrons) : $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*3}$ $b = 3/2$

O_2^{2-} (14 electrons) : $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*4}$ $b = 1$

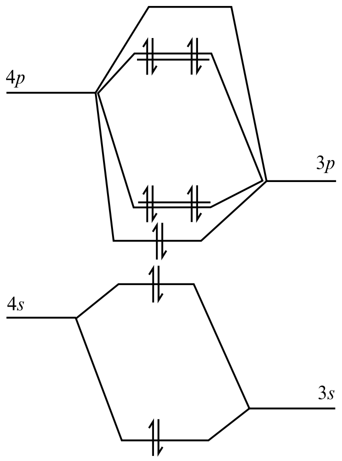


Figure 14.1

Each electron added to O_2^+ is added to an antibonding orbital, thus increasing the length. So the sequence $\boxed{O_2^+, O_2, O_2^-, O_2^{2-}}$ has progressively longer bonds.

E14.10(b) $$\int \psi^2\,d\tau = N^2 \int (\psi_A + \lambda\psi_B)^2\,d\tau = 1 = N^2 \int (\psi_A^2 + \lambda^2\psi_B^2 + 2\lambda\psi_A\psi_B)\,d\tau = 1$$

$$= N^2(1 + \lambda^2 + 2\lambda S) \quad \left[\int \psi_A\psi_B d\tau = S\right]$$

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

E14.11(b) We seek an orbital of the form $aA + bB$, where a and b are constants, which is orthogonal to the orbital $N(0.145A + 0.844B)$. Orthogonality implies

$$\int (aA + bB)N(0.145A + 0.844B)\,d\tau = 0$$

$$0 = N\int [0.145aA^2 + (0.145b + 0.844a)AB + 0.844bB^2]\,d\tau$$

The integrals of squares of orbitals are 1 and the integral $\int AB\,d\tau$ is the overlap integral S, so

$$0 = (0.145 + 0.844S)a + (0.145S + 0.844)b \quad \text{so} \quad a = \boxed{-\frac{0.145S + 0.844}{0.145 + 0.844S}b}$$

This would make the orbitals orthogonal, but not necessarily normalized. If $S = 0$, the expression simplifies to

$$a = -\frac{0.844}{0.145}b$$

and the new orbital would be normalized if $a = 0.844N$ and $b = -0.145N$. That is

$$\boxed{N(0.844A - 0.145B)}$$

E14.12(b) The trial function $\psi = x^2(L - 2x)$ does not obey the boundary conditions of a particle in a box, so it is $\boxed{\text{not appropriate}}$. In particular, the function does not vanish at $x = L$.

E14.13(b) The variational principle says that the minimum energy is obtained by taking the derivate of the trial energy with respect to adjustable parameters, setting it equal to zero, and solving for the parameters:

$$E_{\text{trial}} = \frac{3a\hbar^2}{2\mu} - \frac{e^2}{\varepsilon_0}\left(\frac{a}{2\pi^3}\right)^{1/2} \quad \text{so} \quad \frac{dE_{\text{trial}}}{da} = \frac{3\hbar^2}{2\mu} - \frac{e^2}{2\varepsilon_0}\left(\frac{1}{2\pi^3 a}\right)^{1/2} = 0.$$

Solving for a yields:

$$\frac{3\hbar^2}{2\mu} = \frac{e^2}{2\varepsilon_0}\left(\frac{1}{2\pi^3 a}\right)^{1/2} \quad \text{so} \quad a = \left(\frac{\mu e^2}{3\hbar^2\varepsilon_0}\right)^2\left(\frac{1}{2\pi^3}\right) = \frac{\mu^2 e^4}{18\pi^3\hbar^4 e_{0^2}}.$$

Substituting this back into the trial energy yields the minium energy:

$$E_{\text{trial}} = \frac{3\hbar^2}{2\mu}\left(\frac{\mu^2 e^4}{18\pi^3\hbar^4 e_0^2}\right) - \frac{e^2}{\varepsilon_0}\left(\frac{\mu^2 e^4}{18\pi^3\hbar^4 e_0^2 \cdot 2\pi^3}\right)^{1/2} = \boxed{\frac{-\mu e^4}{12\pi^3\varepsilon_0^2\hbar^2}}.$$

E14.14(b) The molecular orbitals of the fragments and the molecular oribitals that they form are shown in Fig. 14.2.

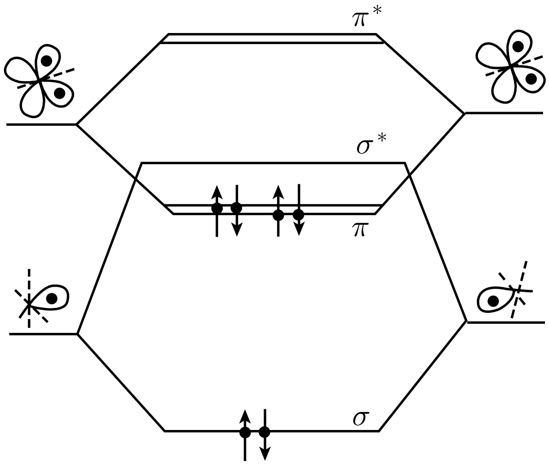


Figure 14.2

E14.15(b) We use the molecular orbital energy level diagram in Fig. 14.38. As usual, we fill the orbitals starting with the lowest energy orbital, obeying the Pauli principle and Hund's rule. We then write

(a) $C_6H_6^-$ (7 electrons): $\boxed{a_{2u}^2 e_{1g}^4 e_{2u}^1}$

$$E = 2(\alpha + 2\beta) + 4(\alpha + \beta) + (\alpha - \beta) = \boxed{7\alpha + 7\beta}$$

(b) $C_6H_6^+$ (5 electrons): $\boxed{a_{2u}^2 e_{1g}^3}$

$$E = 2(\alpha + 2\beta) + 3(\alpha + \beta) = \boxed{5\alpha + 7\beta}$$

E14.16(b) The secular determinants from E14.16(a) can be diagonalized with the assistance of general-purpose mathematical software. Alternatively, programs specifically designed of Hückel calculations (such as the one at Austrialia's Northern Territory University, http://www.smps.ntu.edu.au/modules/mod3/interface.html) can be used. In both molecules, 14 π-electrons fill seven orbitals.

(a) In anthracene, the energies of the filled orbitals are $\alpha + 2.41421\beta$, $\alpha + 2.00000\beta$, $\alpha + 1.41421\beta$ (doubly degenerate), $\alpha + 1.00000\beta$ (doubly degenerate), and $\alpha + 0.41421\beta$, so the total energy is $14\alpha + 19.31368\beta$ and the π energy is $\boxed{19.31368\beta}$.

(b) For phenanthrene, the energies of the filled orbitals are $\alpha + 2.43476\beta$, $\alpha + 1.95063\beta$, $\alpha + 1.51627\beta$, $\alpha + 1.30580\beta$, $\alpha + 1.14238\beta$, $\alpha + 0.76905\beta$, $\alpha + 0.60523$, so the total energy is $14\alpha + 19.44824\beta$ and the π energy is $\boxed{19.44824\beta}$.

Solutions to problems

Solutions to numerical problems

P14.1 $\psi_A = \cos kx$ measured from A, $\psi_B = \cos k'(x - R)$ measuring x from A.

Then, with $\psi = \psi_A + \psi_B$

$$\psi = \cos kx + \cos k'(x - R) = \cos kx + \cos k'R \cos k'x + \sin k'R \sin k'x$$

$$[\cos(a - b) = \cos a \cos b + \sin a \sin b]$$

(a) $k = k' = \dfrac{\pi}{2R}$; $\quad \cos k'R = \cos \dfrac{\pi}{2} = 0$; $\quad \sin k'R = \sin \dfrac{\pi}{2} = 1$

$$\psi = \cos \frac{\pi x}{2R} + \sin \frac{\pi x}{2R}$$

For the midpoint, $x = \frac{1}{2}R$, so $\psi\left(\frac{1}{2}R\right) = \cos \frac{1}{4}\pi + \sin \frac{1}{4}\pi = 2^{1/2}$ and there is constructive interference ($\psi > \psi_A, \psi_B$).

(b) $k = \dfrac{\pi}{2R}$, $\quad k' = \dfrac{3\pi}{2R}$; $\quad \cos k'R = \cos \dfrac{3\pi}{2} = 0$, $\quad \sin k'R = -1$.

$$\psi = \cos \frac{\pi x}{2R} - \sin \frac{3\pi x}{2R}$$

For the midpoint, $x = \frac{1}{2}R$, so $\psi\left(\frac{1}{2}R\right) = \cos \frac{1}{4}\pi - \sin \frac{3}{4}\pi = 0$ and there is destructive interference ($\psi < \psi_A, \psi_B$).

P14.5 We obtain the electron densities from $\rho_+ = \psi_+^2$ and $\rho_- = \psi_-^2$ with ψ_+ and ψ_- as given in Problem 14.4

$$\rho_\pm = N_\pm^2 \left(\frac{1}{\pi a_0^3}\right) \{e^{-|z|/a_0} \pm e^{-|z-R|/a_0}\}^2$$

We evaluate the factors preceding the exponentials in ψ_+ and ψ_-

$$N_+ \left(\frac{1}{\pi a_0^3}\right)^{1/2} = 0.561 \times \left(\frac{1}{\pi \times (52.9\,\text{pm})^3}\right)^{1/2} = \frac{1}{1216\,\text{pm}^{3/2}}$$

Likewise, $N_- \left(\dfrac{1}{\pi a_0^3}\right)^{1/2} = \dfrac{1}{621\,\text{pm}^{3/2}}$

Then $\rho_+ = \dfrac{1}{(1216)^2\,\text{pm}^3} \{e^{-|z|/a_0} + e^{-|z-R|/a_0}\}^2$

and $\rho_- = \dfrac{1}{(622)^2\,\text{pm}^3} \{e^{-|z|/a_0} + e^{-|z-R|/a_0}\}^2$

The "atomic" density is

$$\rho = \tfrac{1}{2}\{\psi_{1s}(A)^2 + \psi_{1s}(B)^2\} = \tfrac{1}{2} \times \left(\frac{1}{\pi a_0^3}\right) \{e^{-2r_A/a_0} + e^{-2r_B/a_0}\}$$

$$= \frac{e^{-(2r_A/a_0)} + e^{-(2r_B/a_0)}}{9.30 \times 10^5\,\text{pm}^3} = \frac{e^{-(2|z|/a_0)} + e^{-(2|z-R|/a_0)}}{9.30 \times 10^5\,\text{pm}^3}$$

The difference density is $\delta\rho_\pm = \rho_\pm - \rho$

Draw up the following table using the information in Problem 14.4

z/pm	−100	−80	−60	−40	−20	0	20	40	60	80	100	120	140	160	180	200
$\rho_+ \times 10^7/\text{pm}^{-3}$	0.20	0.42	0.90	1.92	4.09	8.72	5.27	3.88	3.73	4.71	7.42	5.10	2.39	1.12	0.53	0.25
$\rho_- \times 10^7/\text{pm}^{-3}$	0.44	0.94	2.01	4.27	9.11	19.40	6.17	0.85	0.25	4.02	14.41	11.34	5.32	2.50	1.17	0.55
$\rho \times 10^7/\text{pm}^{-3}$	0.25	0.53	1.13	2.41	5.15	10.93	5.47	3.26	3.01	4.58	8.88	6.40	3.00	1.41	0.66	0.31
$\delta\rho_+ \times 10^7/\text{pm}^{-3}$	−0.05	−0.11	−0.23	−0.49	−1.05	−2.20	−0.20	0.62	0.71	0.13	−1.46	−1.29	−0.61	−0.29	−0.14	−0.06
$\delta\rho_- \times 10^7/\text{pm}^{-3}$	0.19	0.41	0.87	1.86	3.96	8.47	0.70	−2.40	−2.76	−0.56	5.54	4.95	2.33	1.09	0.51	0.24

The densities are plotted in Fig. 14.3(a) and the difference densities are plotted in Fig. 14.3(b).

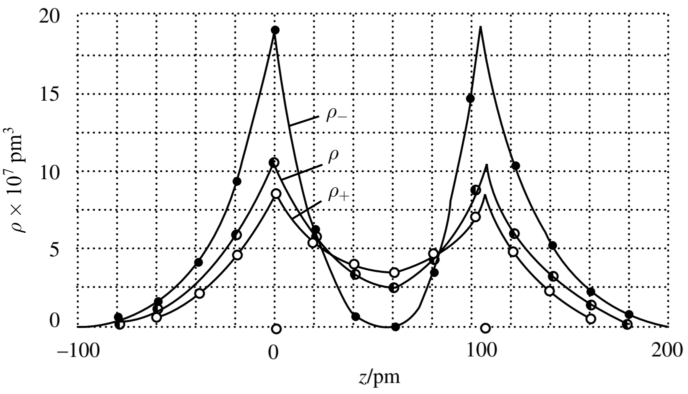


Figure 14.3(a)

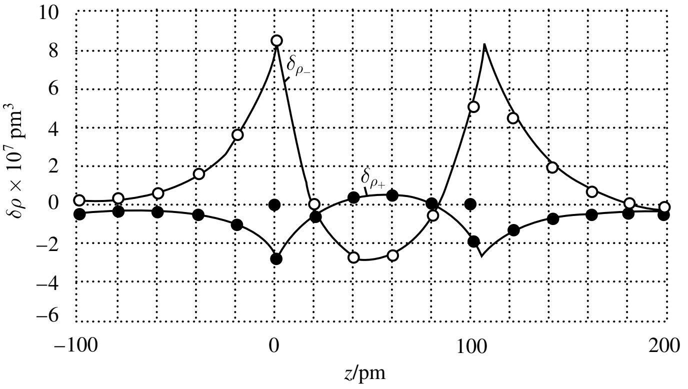
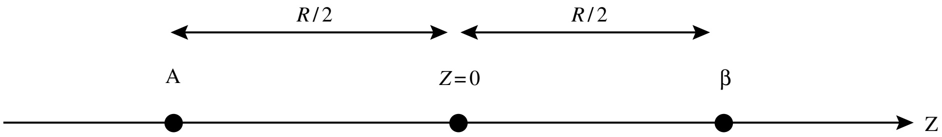


Figure 14.3(b)



P14.6 **(a)** With spatial dimensions in units (multiples) of a_0, the atomic arbitals of atom A and atom B may be written in the form (eqn 13.24):

$$p_{z,\mathrm{A}} = \frac{1}{4\sqrt{2\pi}}(z + R/2)\,\mathrm{e}^{-\left[x^2+y^2+(z+R/2)^2\right]^{1/2}/2}$$

$$p_{z,\mathrm{B}} = \frac{1}{4\sqrt{2\pi}}(z - R/2)\,\mathrm{e}^{-\left[x^2+y^2+(z-R/2)^2\right]^{1/2}/2}$$

according to eqn 14.98, the LCAO-MO's have the form:

$$\psi_{\sigma_\mathrm{u}} = \frac{p_{z,\mathrm{A}} + p_{z,\mathrm{B}}}{\sqrt{2(1+s)}} \quad \text{and} \quad \psi_{\sigma_\mathrm{g}} = \frac{p_{z,\mathrm{A}} + p_{z,\mathrm{B}}}{\sqrt{2(1-s)}}$$

$$\text{where} \quad s = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p_{z,\mathrm{A}}\,p_{z,\mathrm{B}}\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \quad \text{(eqn14.17)}$$

computations and plots are readily prepared with mathematical software such as mathcad.

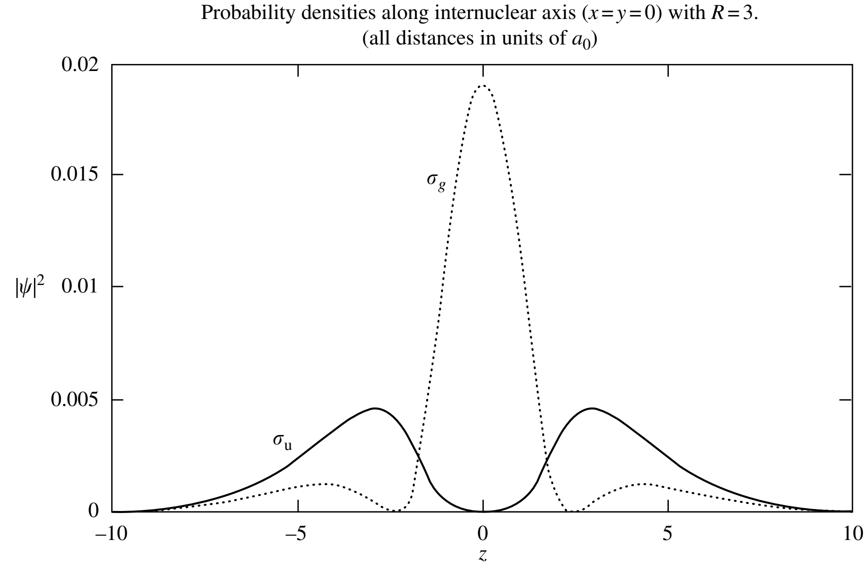
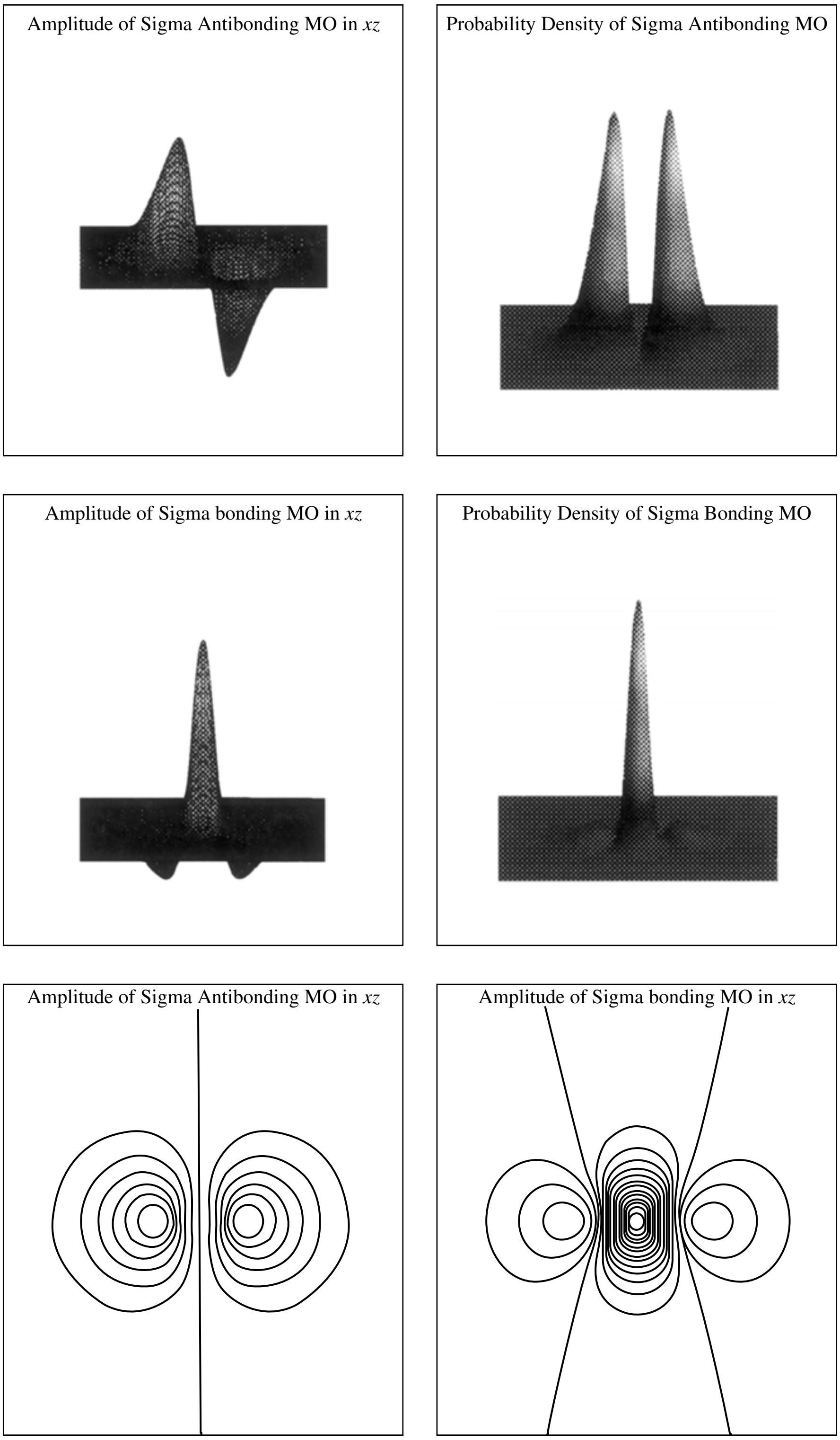


Figure 14.4(a)

(b) With spatial dimensions in units of a_0, the atomic orbitals for the construction of π molecular orbitals are:

$$p_{x,\mathrm{A}} = \frac{1}{4\sqrt{2\pi}}\quad x\mathrm{e}^{-\left[x^2+y^2+(z+R/2)^2\right]^{1/2}/2}$$

$R = 3$



Amplitude of Sigma Antibonding MO in *xz*

Probability Density of Sigma Antibonding MO

Amplitude of Sigma bonding MO in *xz*

Probability Density of Sigma Bonding MO

Amplitude of Sigma Antibonding MO in *xz*

Amplitude of Sigma bonding MO in *xz*

Figure 14.4(b)

$R = 3$

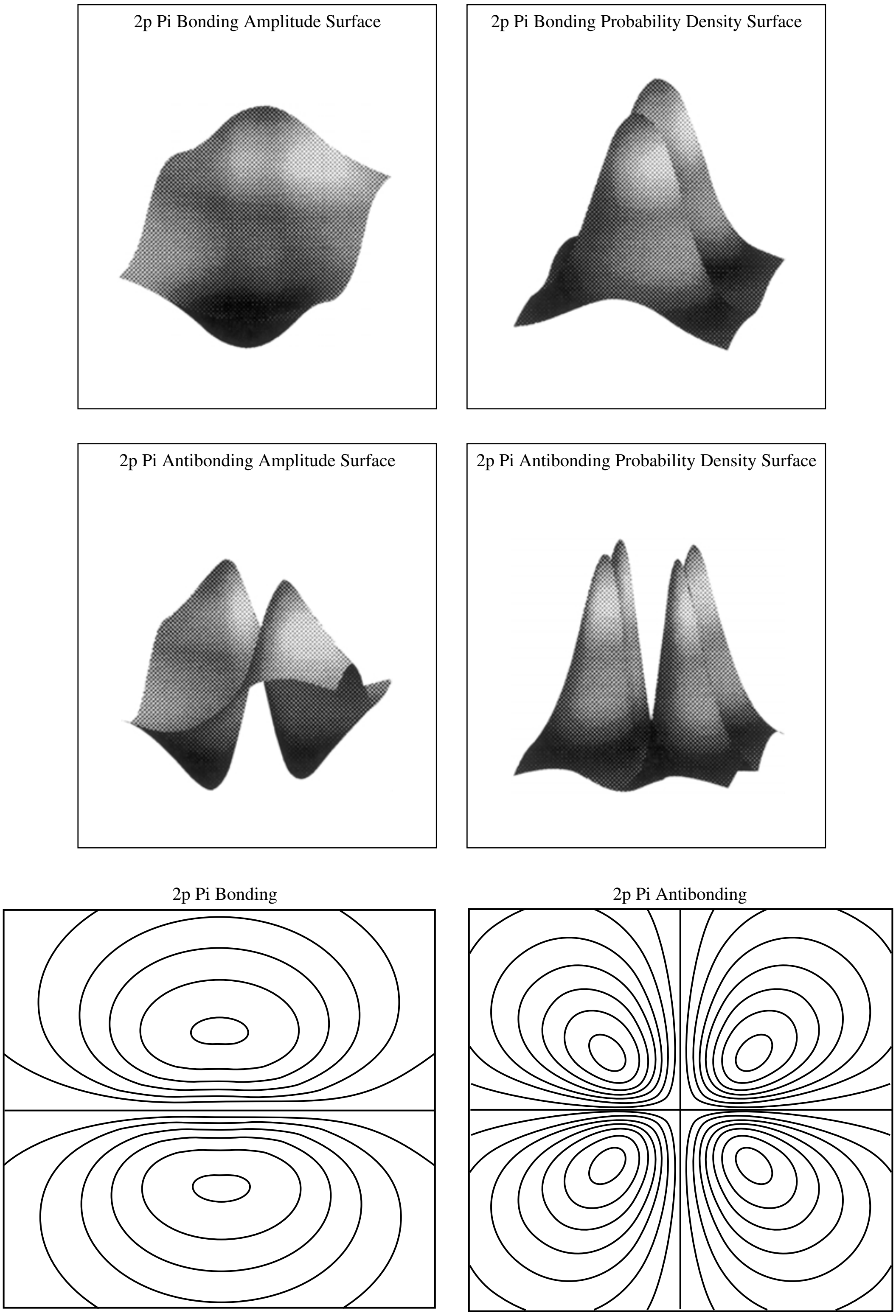


Figure 14.4(c)

$$p_x,\mathrm{B} = \frac{1}{4\sqrt{2\pi}} x\ \mathrm{e}^{-\left[x^2+y^2+(z-R/2)^2\right]^{1/2}\big/2}$$

The π-MO's are:

$$\psi_{\pi_\mathrm{u}} = \frac{p_{x,\mathrm{A}} + p_{x,\mathrm{B}}}{\sqrt{2(1+s)}} \quad \text{and} \quad \psi_{\pi_\mathrm{g}} = \frac{p_{x,\mathrm{A}} - p_{x,\mathrm{B}}}{\sqrt{2(1-s)}}$$

$$\text{where} \quad s = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p_{x,\mathrm{A}}\, p_{x,\mathrm{B}}\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z$$

The various plot clearly show the constructive interference that makes a bonding molecular orbital. Nodal planes created by destructive interference are clearly seen in the antibonding molecular orbitals. When calculations and plots are produced for the $R = 10$ case, constructive and destructive interference is seen to be much weaker because of the weak atomic orbital overlap.

P14.7 $P = |\psi|^2\,\mathrm{d}\tau \approx |\psi|^2\delta\tau, \quad \delta\tau = 1.00\,\mathrm{pm}^3$

(a) From Problem 14.5

$$\psi_+^2(z=0) = \rho_+(z=0) = 8.7 \times 10^{-7}\,\mathrm{pm}^{-3}$$

Therefore, the probability of finding the electron in the volume $\delta\tau$ at nucleus A is

$$P = 8.6 \times 10^{-7}\,\mathrm{pm}^{-3} \times 1.00\,\mathrm{pm}^3 = \boxed{8.6 \times 10^{-7}}$$

(b) By symmetry (or by taking $z = 106\,\mathrm{pm}$) $P = \boxed{8.6 \times 10^{-7}}$

(c) From Fig. 14.4(a), $\psi_+^2\left(\frac{1}{2}R\right) = 3.7 \times 10^{-7}\,\mathrm{pm}^{-3}$, so $P = \boxed{3.7 \times 10^{-7}}$

(d) From Fig. 14.5, the point referred to lies at 22.4 pm from A and 86.6 pm from B.

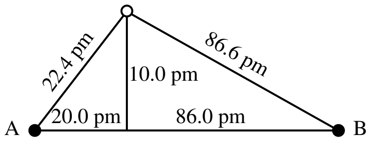


Figure 14.5

$$\text{Therefore, } \psi = \frac{\mathrm{e}^{-22.4/52.9} + \mathrm{e}^{-86.6/52.9}}{1216\,\mathrm{pm}^{3/2}} = \frac{0.65 + 0.19}{1216\,\mathrm{pm}^{3/2}} = 6.98 \times 10^{-4}\,\mathrm{pm}^{-3/2}$$

$$\psi^2 = 4.9 \times 10^{-7}\,\mathrm{pm}^{-3}, \quad \text{so} \quad P = \boxed{4.9 \times 10^{-7}}$$

For the antibonding orbital, we proceed similarly.

(a) $\psi_-^2(z=0) = 19.6 \times 10^{-7}\,\mathrm{pm}^{-3}$ [Problem 14.5], so $P = \boxed{2.0 \times 10^{-6}}$

(b) By symmetry, $P = \boxed{2.0 \times 10^{-6}}$

(c) $\psi_-^2\left(\frac{1}{2}R\right) = 0, \quad \text{so} \quad P = \boxed{0}$

(d) We evaluate ψ_- at the point specified in Fig. 14.5

$$\psi_- = \frac{0.65 - 0.19}{621\,\mathrm{pm}^{3/2}} = 7.41 \times 10^{-4}\,\mathrm{pm}^{-3/2}$$

$$\psi_-^2 = 5.49 \times 10^{-7}\,\mathrm{pm}^{-3}, \quad \text{so} \quad P = \boxed{5.5 \times 10^{-7}}$$

P14.10 **(a)** To simplify the mathematical expressions, atomic units (a.u.) are used for which all distances are in units of a_0 and $e^2/(4\pi\varepsilon_0 a_0)$ is the energy unit.

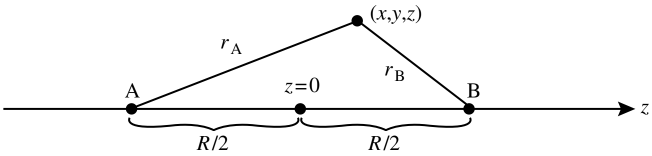


Figure 14.6(a)

$$A = \frac{1}{\sqrt{\pi}}\,\mathrm{e}^{-r_A} = \frac{1}{\sqrt{\pi}}\,\mathrm{e}^{-\sqrt{x^2+y^2+(z+R/2)^2}} \quad \text{(eqn 14.8)}$$

$$B = \frac{1}{\sqrt{\pi}}\,\mathrm{e}^{-r_B} = \frac{1}{\sqrt{\pi}}\,\mathrm{e}^{-\sqrt{x^2+y^2+(z-R/2)^2}}$$

$$H = -\frac{\nabla^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \quad \text{(eqn 14.6)}$$

$$\begin{aligned}
\alpha &= \int AHA\,\mathrm{d}\tau \quad \text{(coulomb integral, eqn 14.24)} \\
&= \int A\left(-\frac{\nabla^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}\right) A\,\mathrm{d}\tau \\
&= \underbrace{\int A\left(-\frac{\nabla^2}{2} - \frac{1}{r_A}\right) A\,\mathrm{d}\tau}_{\substack{E_{1s}=-1/2 \\ \text{(eqns 13.13,13.15)}}} - \underbrace{\int \frac{A^2}{r_B}\,\mathrm{d}\tau}_{j} + \underbrace{\frac{1}{R}\int A^2\,\mathrm{d}\tau}_{\substack{1/R \\ \text{(Born−Oppenheimer approx.)}}}
\end{aligned}$$

$$\boxed{\alpha = -\frac{1}{2} - j + \frac{1}{R}}$$

$$\begin{aligned}
\beta &= \int AHB\,\mathrm{d}\tau \quad \text{(Resonance integral, eqn 14.24)} \\
&= \int A\left(-\frac{\nabla^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}\right) B\,\mathrm{d}\tau
\end{aligned}$$

$$= \int A \underbrace{\left(-\frac{\nabla^2}{2} - \frac{1}{r_{\mathrm{B}}}\right) - B}_{E_{1s}B = -\frac{1}{2}B} \, \mathrm{d}\tau - \underbrace{\int \frac{AB}{r_{\mathrm{A}}}}_{k} \mathrm{d}\tau + \frac{1}{R} \underbrace{\int AB \, \mathrm{d}\tau}_{S}$$

$$= -\frac{1}{2} \underbrace{\int AB \, \mathrm{d}\tau}_{S} - k + \frac{S}{R}$$

$$\boxed{\beta = \left(\frac{1}{R} - \frac{1}{2}\right) S - k}$$

according to eqn 14.28, $E_{1\sigma_{\mathrm{g}}} = \dfrac{\alpha + \beta}{1 + S}$. In order to numerically calculate E as a function of R we must devise a method by which S, j, and k are evaluated with numerical integrations at specified R values. In the cartesian coordinate system drawn above, $\mathrm{d}\tau = \mathrm{d}x \, \mathrm{d}y \, \mathrm{d}z$ and triple integrals are required. Numerical integration may proceed slowly with this coordinate system.

However, the symmetry of the wavefunction may be utilized to reduce the problem to double integrals by using the spherical coordinate system of Fig. 14.15 and eqn 14.9. The numerical integration will proceed more rapidly.

$$A = \frac{1}{\sqrt{\pi}} \, \mathrm{e}^{-r} \quad \text{and} \quad B = \frac{1}{\sqrt{\pi}} \, \mathrm{e}^{-r_B} = \frac{1}{\sqrt{\pi}} \, \mathrm{e}^{-\sqrt{r^2 + R^2 - 2rR\cos\theta}} \qquad \text{(eqn 14.9)}$$

$$S(R) = \int AB \, \mathrm{d}\tau = \int_0^{2\pi} \int_{-\infty}^{\infty} \int_0^{\pi} A(r) B(r, \theta, R) r^2 \sin(\theta) \, \mathrm{d}\theta \, \mathrm{d}r \, \mathrm{d}\phi$$

$$= 2\pi \int_{-\infty}^{\infty} \int_0^{\pi} A(r) B(r, \theta, R) r^2 \sin(\theta) \, \mathrm{d}\theta \, \mathrm{d}r$$

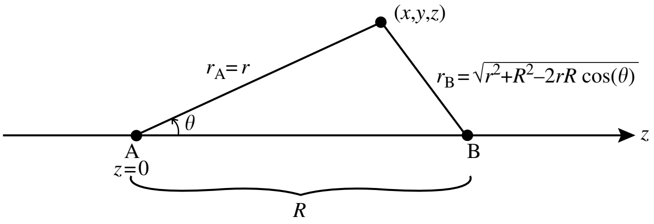


Figure 14.6(b)

The numerical integration, $S_{\mathrm{numerical}}(R)$, may be performed with mathematical software (mathcad, TOL = 0.001) and compared with the exact analytic solution (eqn 14.12), $S_{\mathrm{exact}}(R)$. As shown in the following plot, the percentage deviation of the numerical integration is never more than 0.01% below $R = \mathrm{L}/a_{\mathrm{o}}$. This is satisfactory.

The numerical integrals of j and k are setup in the same way.

$$j(R) = 2\pi \int_{-\infty}^{\infty} \int_0^{\pi} \frac{A(r)^2 r^2 \sin(\theta)}{r_{\mathrm{B}}(r, \theta, R)} \, \mathrm{d}\theta \, \mathrm{d}r$$

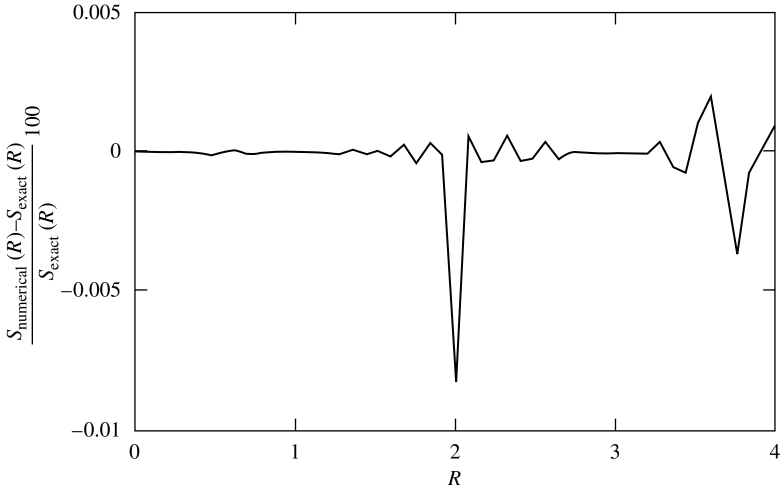


Figure 14.7(a)

$$k(R) = 2\pi \int_{-\infty}^{\infty} \int_{0}^{\pi} A(r)B(r,\theta,R)r\sin(\theta)\,\mathrm{d}\theta\,\mathrm{d}r$$

The coulomb and resonance integrals are:

$$\alpha(R) = -\frac{1}{2} - j(R) + \frac{1}{R} \quad \text{and} \quad \beta(R) = \left(\frac{1}{R} - \frac{1}{2}\right)S(R) - k(R)$$

This orbital energy is: $E_{1\sigma_g}(R) = \dfrac{\alpha(R)+\beta(R)}{1+S(R)}$

This numerical calculation of the energy, $E_{\text{numerical}}(R)$, may be performed and compared with the exact analytic solution (eqns 14.11 and 14.12), $E_{\text{exact}}(R)$. The following plot shows that the numerical integration method correctly gives energy values within about 0.06% of the exact value in the range $a_0 \le R \le 4a_0$.

(b) The minimum energy, as determined by a numerical computation, may be evaluated with several techniques. When the computations do not consume excessive lengths of time, $E(R)$

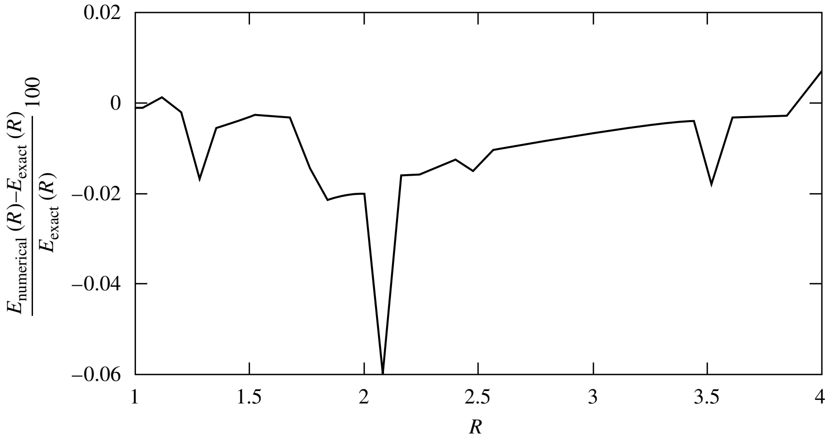


Figure 14.7(b)

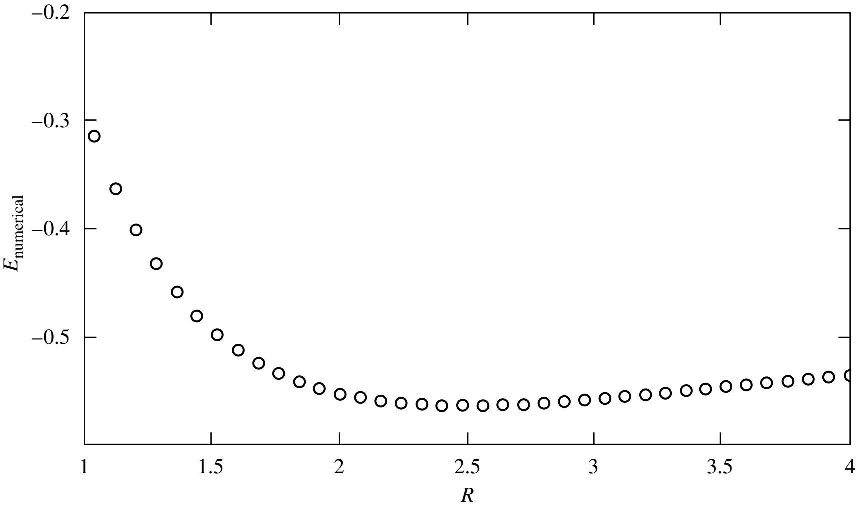


Figure 14.7(c)

may be calculated at many R values as is done in the above figure. The minimum energy and corresponding R may be read from a table of calculated values. Values of the figure give: $\boxed{E_{\min} = -0.5647(\text{a.u.}) = -15.367\text{e}}$ and $\boxed{R_{\text{e}} = 2.4801(\text{a.u.}) = 131.24 \text{ pm}}$. Alternatively, lengthy computations necessitate a small number of numerical calculations near the minimum after which an interpolation equation is devised for calculating E at any value of R. The minimum is determined by the criteria that $\frac{\text{d}}{\text{d}R}E_{\text{interpolation}}(R) = 0$.

The spectroscopic dissociation constant, D_{e}, for H_2^+ is referenced to a zero electronic energy when a hydrogen atom and a proton are at infinite separation.

$$D_{\text{e}} = E_{\min} - \left(E_{\text{H}} + E_{\text{proton}}\right) = \left[-0.5647 - \left(-\frac{1}{2} + 0\right)\right] (\text{a.u.})$$

$$\boxed{D_{\text{e}} = -0.0647 \text{ (a.u.)} = 1.76 \text{ eV}}$$

P14.12 The internuclear distance $\langle r \rangle_n \approx n^2 a_0$, would be about twice the average distance ($\approx 1.06 \times 10^6$ pm) of a hydrogenic electron from the nucleus when in the state $n = 100$. This distance is so large that each of the following estimates are applicable.

Resonance integral, $\beta \approx -\delta$ (where $\delta \approx 0$)

Overlap integral, $S \approx \varepsilon$ (where $\varepsilon \approx 0$)

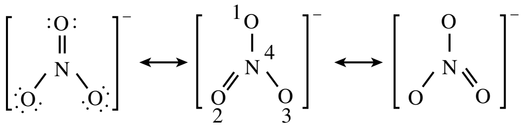
Coulomb integral, $\alpha \approx E_{n=100}$ for atomic hydrogen

$$\begin{aligned} \text{Binding energy} &= 2\{E_+ - E_{n=100}\} \\ &= 2\left\{\frac{\alpha + \beta}{1 - S} - E_{n=100}\right\} \\ &= 2\{\alpha - E_{n=100}\} \\ &\approx 0 \end{aligned}$$

Vibrational force constant, $k \approx 0$ because of the weak binding energy. Rotational constant, $B = \dfrac{\hbar^2}{2hcI} = \dfrac{\hbar^2}{2hc\mu r_{\text{AB}}^2} \approx 0$ because r_{AB}^2 is so large.

The binding energy is so small that thermal energies would easily cause the Rydberg molecule to break apart. It is not likely to exist for much longer than a vibrational period.

P14.13 In the simple Hückel approximation



$$\begin{vmatrix} \alpha_O - E & 0 & 0 & \beta \\ 0 & \alpha_O - E & 0 & \beta \\ 0 & 0 & \alpha_O - E & \beta \\ \beta & \beta & \beta & \alpha_N - E \end{vmatrix} = 0$$

$$(E - \alpha_O)^2 \times \left\{(E - \alpha_O) \times (E - \alpha_N) - 3\beta^2\right\} = 0$$

Therefore, the roots are

$$E - \alpha_O = 0 \text{ (twice)} \quad \text{and} \quad (E - \alpha_O) \times (E - \alpha_N) - 3\beta^2 = 0$$

Each equation is easily solved (Fig. 14.8(a)) for the permitted values of E in terms of α_O, α_N, and β. The quadratic equation is applicable in the second case.

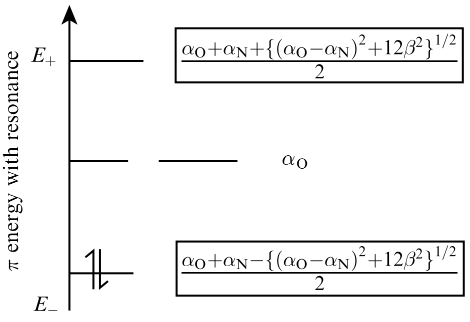


Figure 14.8(a)

In contrast, the π energies in the absence of resonance are derived for N═O, that is, just one of the three

$$\begin{vmatrix} \alpha_O - E & \beta \\ \beta & \alpha_N - E \end{vmatrix} = 0$$

Expanding the determinant and solving for E gives the result in Fig.14.8(b).

$$\text{Delocalization energy} = 2\{E_-(\text{with resonance}) - E_-(\text{without resonance})\}$$

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

If $\beta^2 \ll (\alpha_O - \alpha_N)^2$, then

$$\text{Delocalization energy} \approx \frac{4\beta^2}{(\alpha_O - \alpha_N)}.$$

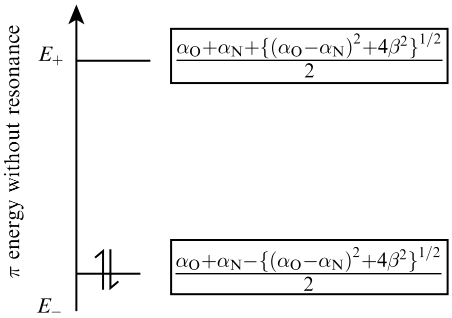


Figure 14.8(b)

P14.17 In all of the molecules considered in P14.16, the HOMO was bonding with respect to the carbon atoms connected by double bonds, but antibonding with respect to the carbon atoms connected by single bonds. (The bond lengths returned by the modeling software suggest that it makes sense to talk about double bonds and single bonds. Despite the electron delocalization, the nominal double bonds are consistently shorter than the nominal single bonds.) The LUMO had just the opposite character, tending to weaken the C═C bonds but strengthen the C—C bonds. To arrive at this conclusion, examine the nodal surfaces of the orbitals. An orbital has an antibonding effect on atoms between which nodes occur, and it has a binding effect on atoms that lie within regions in which the orbital does not change sign. The $\pi^* \leftarrow \pi$ transition, then, would lengthen and weaken the double bonds and shorten and strengthen the single bonds, bringing the different kinds of polyene bonds closer to each other in length and strength. Since each molecule has more double bonds than single bonds, there is an overall weakening of bonds.

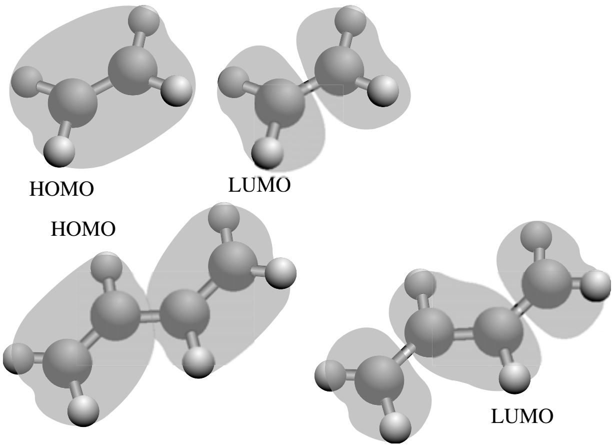


Figure 14.9(a)

Solutions to theoretical problems

P14.19 Since

$$\psi_{2s} = R_{20}Y_{00} = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2} \times \left(2-\frac{\rho}{2}\right)\mathrm{e}^{-\rho/4} \times \left(\frac{1}{4\pi}\right)^{1/2} \quad \text{[Tables 13.1, 12.3]}$$

$$= \tfrac{1}{4}\left(\frac{1}{2\pi}\right)^{1/2} \times \left(\frac{Z}{a_0}\right)^{3/2} \times \left(2-\frac{\rho}{2}\right)\mathrm{e}^{-\rho/4}$$

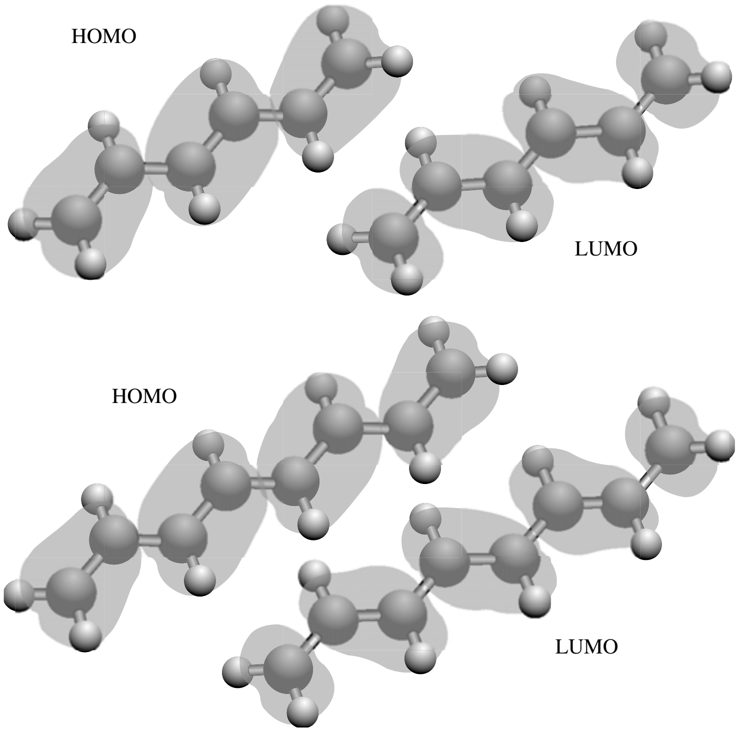


Figure 14.9(b)

$$
\begin{aligned}
\psi_{2p_x} &= \frac{1}{\sqrt{2}} R_{21}(Y_{1,1} - Y_{1-1}) \text{ [Section 13.2]} \\
&= \frac{1}{\sqrt{12}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{\rho}{2} \mathrm{e}^{-\rho/4} \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta \, (\mathrm{e}^{i\phi} + \mathrm{e}^{-i\phi}) \text{ [Tables 13.1, 12.3]} \\
&= \frac{1}{\sqrt{12}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{\rho}{2} \mathrm{e}^{-\rho/4} \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta \cos\phi \\
&= \frac{1}{4} \left(\frac{1}{2\pi}\right)^{1/2} \times \left(\frac{Z}{a_0}\right)^{3/2} \frac{\rho}{2} \mathrm{e}^{-\rho/4} \sin\theta \cos\phi \\
\psi_{2p_y} &= \frac{1}{2i} R_{21}(Y_{1,1} + Y_{1-1}) \text{ [Section 13.2]} \\
&= \frac{1}{4} \left(\frac{1}{2\pi}\right)^{1/2} \times \left(\frac{Z}{a_0}\right)^{3/2} \frac{\rho}{2} \mathrm{e}^{-\rho/4} \sin\theta \sin\phi \text{ [Tables 13.1, 12.3]}
\end{aligned}
$$

Therefore,

$$
\begin{aligned}
\psi &= \frac{1}{\sqrt{3}} \times \frac{1}{4} \times \left(\frac{1}{\pi}\right)^{1/2} \times \left(\frac{Z}{a_0}\right)^{3/2} \\
&\quad \times \left(\frac{1}{\sqrt{2}} \left(2 - \frac{\rho}{2}\right) - \frac{1}{2}\frac{\rho}{2} \sin\theta \cos\phi + \frac{\sqrt{3}}{2}\frac{\rho}{2} \sin\theta \sin\phi \right) \mathrm{e}^{-\rho/4} \\
&= \frac{1}{4} \left(\frac{1}{6\pi}\right)^{1/2} \times \left(\frac{Z}{a_0}\right)^{3/2} \times \left\{ 2 - \frac{\rho}{2} - \frac{1}{\sqrt{2}}\frac{\rho}{2} \sin\theta \cos\phi + \sqrt{\frac{3}{2}}\frac{\rho}{2} \sin\theta \sin\phi \right\} \mathrm{e}^{-\rho/4}
\end{aligned}
$$

$$= \frac{1}{4}\left(\frac{1}{6\pi}\right)^{1/2} \times \left(\frac{Z}{a_0}\right)^{3/2} \times \left\{2 - \frac{\rho}{2}\left(1 + \frac{1}{\sqrt{2}}\sin\theta\cos\phi - \sqrt{\frac{3}{2}}\sin\theta\sin\phi\right)\right\} \mathrm{e}^{-\rho/4}$$

$$= \frac{1}{4}\left(\frac{1}{6\pi}\right)^{1/2} \times \left(\frac{Z}{a_0}\right)^{3/2} \times \left\{2 - \frac{\rho}{2}\left(1 + \frac{[\cos\phi - \sqrt{3}\sin\phi]}{\sqrt{2}}\sin\theta\right)\right\} \mathrm{e}^{-\rho/4}$$

The maximum value of ψ occurs when $\sin\theta$ has its maximum value $(+1)$, and the term multiplying $\rho/2$ has its maximum negative value, which is -1, when $\phi = 120°$.

P14.21 The normalization constants are obtained from

$$\int \psi^2\,\mathrm{d}\tau = 1, \quad \psi = N(\psi_\mathrm{A} \pm \psi_\mathrm{B})$$

$$N^2 \int (\psi_\mathrm{A} \pm \psi_\mathrm{B})^2\,\mathrm{d}\tau = N^2 \int (\psi_\mathrm{A}^2 + \psi_\mathrm{B}^2 \pm 2\psi_\mathrm{A}\psi_\mathrm{B})\,\mathrm{d}\tau = N^2(1 + 1 \pm 2S) = 1$$

Therefore, $N^2 = \dfrac{1}{2(1 \pm S)}$

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{r_\mathrm{A}} - \frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{r_\mathrm{B}} + \frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{R}$$

$H\psi = E\psi$ implies that

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{r_\mathrm{A}}\psi - \frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{r_\mathrm{B}}\psi + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{R}\psi = E\psi$$

Multiply through by $\psi^*(= \psi)$ and integrate using

$$-\frac{\hbar^2}{2m}\nabla^2\psi_\mathrm{A} - \frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{r_\mathrm{A}}\psi_\mathrm{A} = E_\mathrm{H}\psi_\mathrm{A}$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_\mathrm{B} - \frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{r_\mathrm{B}}\psi_\mathrm{B} = E_\mathrm{H}\psi_\mathrm{B}$$

Then for $\psi = N(\psi_\mathrm{A} + \psi_\mathrm{B})$

$$N\int \psi\left(E_\mathrm{H}\psi_\mathrm{A} + E_\mathrm{H}\psi_\mathrm{B} - \frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{r_\mathrm{A}}\psi_\mathrm{B} - \frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{r_\mathrm{B}}\psi_\mathrm{A} + \frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{R}(\psi_\mathrm{A} + \psi_\mathrm{B})\right)\mathrm{d}\tau = E$$

hence $E_\mathrm{H}\displaystyle\int \psi^2\,\mathrm{d}\tau + \frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{R}\int \psi^2\,\mathrm{d}\tau - \frac{e^2}{4\pi\varepsilon_0}N\int \psi\left(\frac{\psi_\mathrm{B}}{r_\mathrm{A}} + \frac{\psi_\mathrm{A}}{r_\mathrm{B}}\right)\mathrm{d}\tau = E$

and so $E_\mathrm{H} + \dfrac{e^2}{4\pi\varepsilon_0}\cdot\dfrac{1}{R} - \dfrac{e^2}{4\pi\varepsilon_0}N^2\displaystyle\int\left(\psi_\mathrm{A}\frac{1}{r_\mathrm{A}}\psi_\mathrm{B} + \psi_\mathrm{B}\frac{1}{r_\mathrm{A}}\psi_\mathrm{B} + \psi_\mathrm{A}\frac{1}{r_\mathrm{B}}\psi_\mathrm{A} + \psi_\mathrm{B}\frac{1}{r_\mathrm{A}}\psi_\mathrm{A}\right)\mathrm{d}\tau = E$

Then use $\displaystyle\int \psi_\mathrm{A}\frac{1}{r_\mathrm{A}}\psi_\mathrm{B}\,\mathrm{d}\tau = \int \psi_\mathrm{B}\frac{1}{r_\mathrm{B}}\psi_\mathrm{A}\,\mathrm{d}\tau$ [by symmetry] $= V_2/(e^2/4\pi\varepsilon_0)$

$$\int \psi_\mathrm{A}\frac{1}{r_\mathrm{B}}\psi_\mathrm{A}\,\mathrm{d}\tau = \int \psi_\mathrm{B}\frac{1}{r_\mathrm{A}}\psi_\mathrm{B}\,\mathrm{d}\tau \text{ [by symmetry]} = V_1/(e^2/4\pi\varepsilon_0)$$

which gives $E_\mathrm{H} + \dfrac{e^2}{4\pi\varepsilon_0}\cdot\dfrac{1}{R} - \left(\dfrac{1}{1+S}\right) \times (V_1 + V_2) = E$

or $E = \boxed{E_{\mathrm{H}} - \dfrac{V_1 + V_2}{1+S} + \dfrac{e^2}{4\pi\varepsilon_0} \cdot \dfrac{1}{R}} = E_+$

as in Problem 14.8.

The analogous expression for E_- is obtained by starting from

$$\psi = N(\psi_{\mathrm{A}} - \psi_{\mathrm{B}})$$

with $N^2 = \dfrac{1}{2(1-S)}$

and the following through the step-wise procedure above. The result is

$$E = E_{\mathrm{H}} - \frac{V_1 - V_2}{1-S} + \frac{e^2}{4\pi\varepsilon_0 R} = E_-$$

as in Problem 14.9.

P14.22 **(a)** $\psi = \mathrm{e}^{-kr} \qquad H = -\dfrac{\hbar^2}{2\mu}\nabla^2 - \dfrac{e^2}{4\pi\varepsilon_0 r}$

$$\int \psi^2\,\mathrm{d}\tau = \int_0^\infty r^2\mathrm{e}^{-2kr}\,\mathrm{d}r \int_0^\pi \sin\theta\,\mathrm{d}\theta \int_0^{2\pi}\mathrm{d}\phi = \frac{\pi}{k^3}$$

$$\int \psi\frac{1}{r}\psi\,\mathrm{d}\tau = \int_0^\infty r\mathrm{e}^{-2kr}\,\mathrm{d}r \int_0^\pi \sin\theta\,\mathrm{d}\theta \int_0^{2\pi}\mathrm{d}\phi = \frac{\pi}{k^2}$$

$$\int \psi\nabla^2\psi\,\mathrm{d}\tau = \int \psi\frac{1}{r}\frac{\mathrm{d}^2}{\mathrm{d}r^2}(r\mathrm{e}^{-kr})\,\mathrm{d}\tau = \int \psi\left(k^2 - \frac{2k}{r}\right)\psi\,\mathrm{d}\tau$$
$$= \frac{\pi}{k} - \frac{2\pi}{k} = -\frac{\pi}{k}$$

Therefore

$$\int \psi H\psi\,\mathrm{d}\tau = \frac{\hbar^2}{2\mu} \times \frac{\pi}{k} - \frac{e^2}{4\pi\varepsilon_0} \times \frac{\pi}{k^2}$$

and

$$E = \frac{\left(\frac{\hbar^2\pi}{2\mu k}\right) - \left(\frac{e^2\pi}{4\pi\varepsilon_0 k^2}\right)}{\pi/k^3} = \frac{\hbar^2k^2}{2\mu} - \frac{e^2k}{4\pi\varepsilon_0}$$

$$\frac{\mathrm{d}E}{\mathrm{d}k} = 2\left(\frac{\hbar^2}{2\mu}\right)k - \frac{e^2}{4\pi\varepsilon_0} = 0 \quad \text{when} \quad k = \frac{e^2\mu}{4\pi\varepsilon_0\hbar^2}$$

The optimum energy is therefore

$E = -\dfrac{e^4\mu}{32\pi^2\varepsilon_0^2\hbar^2} = \boxed{-hc\mathcal{R}_{\mathrm{H}}}$ the exact value

(b) $\psi = \mathrm{e}^{-kr^2}$, H as before.

$$\int \psi^2\,\mathrm{d}\tau = \int_0^\infty \mathrm{e}^{-2kr^2}r^2\,\mathrm{d}r \int_0^\pi \sin\theta\,\mathrm{d}\theta \int_0^{2\pi}\mathrm{d}\phi = \frac{\pi}{2}\left(\frac{\pi}{2k^3}\right)^{1/2}$$

$$\psi\frac{1}{r}\psi\,\mathrm{d}\tau = \int_0^\infty r\mathrm{e}^{-2kr^2}\,\mathrm{d}r \int_0^\pi \sin\theta\,\mathrm{d}\theta \int_0^{2\pi}\mathrm{d}\phi = \frac{\pi}{k}$$

$$\begin{aligned}\int \psi \nabla^2 \psi \,\mathrm{d}\tau &= -2\int \psi(3k - 2k^2r^2)\psi \,\mathrm{d}\tau \\ &= -2\int_0^{\infty} (3kr^2 - 2k^2r^4)\mathrm{e}^{-2kr^2}\,\mathrm{d}r \int_0^{\pi} \sin\theta \,\mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi \\ &= -8\pi\left\{\left(\frac{3k}{8}\right)\times\left(\frac{\pi}{2k^3}\right)^{1/2} - \frac{3k^2}{16}\left(\frac{\pi}{2k^5}\right)^{1/2}\right\}\end{aligned}$$

Therefore

$$E = \frac{3\hbar^2 k}{2\mu} - \frac{e^2 k^{1/2}}{\varepsilon_0(2\pi)^{1/2}}$$

$$\frac{\mathrm{d}E}{\mathrm{d}k} = 0 \quad \text{when} \quad k = \frac{e^4\mu^2}{18\pi^3\varepsilon_0^2\hbar^4}$$

and the optimum energy is therefore

$$E = -\frac{e^4\mu}{12\pi^3\varepsilon_0^2\hbar^2} = \boxed{-\frac{8}{3\pi}\times hc\mathcal{R}_\mathrm{H}}$$

Since $8/3\pi < 1$, the energy in (**a**) is lower than in (**b**), and so the exponential wavefunction is better than the Gaussian.

P14.23 (**a**) The variation principle selects parameters so that energy is minimized. We begin by finding the cirteria for selecting η_best at constant $R(\omega = \eta R)$

$$\begin{aligned}\frac{\mathrm{d}E_\mathrm{el}(\eta_\mathrm{best})}{\mathrm{d}\eta} &= 0 \\ &= 2\eta F_1 + \eta^2\frac{\mathrm{d}\omega}{d\eta}\frac{\mathrm{d}F_1}{\mathrm{d}\omega} + F_2 + \eta\frac{\mathrm{d}\omega}{\mathrm{d}\eta}\frac{\mathrm{d}F_2}{\mathrm{d}\omega} \\ &= 2\eta F_1 + \eta^2 R\frac{\mathrm{d}F_1}{\mathrm{d}\omega} + F_2 + \eta R\frac{\mathrm{d}F_2}{\mathrm{d}\omega} \\ \eta_\mathrm{best}(\omega) &= \frac{-F_2(\omega) - \omega\frac{\mathrm{d}F_2(\omega)}{\mathrm{d}\omega}}{2F_1(\omega) - \omega\frac{\mathrm{d}F_1(\omega)}{\mathrm{d}\omega}}\end{aligned}$$

We must now select R so as to minimize the total energy, E. Using Hartree atomic units for which length is in units of a_0 and energy is in units of $e^2/4\pi\varepsilon_0 a_0$, the total energy equation is:

$$E(\omega) = E_\mathrm{el}(\omega) + \frac{1}{R(\omega)} = \eta_\mathrm{best}^2 F_1(\omega) + \eta_\mathrm{best}(\omega)F_2(\omega) + \frac{\eta_\mathrm{best}(\omega)}{\omega}$$

where $R(\omega) = \omega/\eta_\mathrm{best}(\omega)$. Mathematical software provides numerical methods for easy evaluation of derivatives within $\eta_\mathrm{best}(\omega)$. We need only setup the software to calculate $E(\omega)$ and $R(\omega)$ over a range of ω values. The value of R for which E is a minimum is the solution.

The following plot is generated with $1.5 \le \omega \le 8.0$

The plots indicates an energy minimum at about -0.58 au and an R_e value of about 2.0 au. More precise values can be determined by generating a plot over a more restricted ω range, say, $2.478 \le \omega \le 2.481$. A table of ω, $R(\omega)$, and $E(\omega)$ may be examined for the minimum energy and corresponding ω and R values.

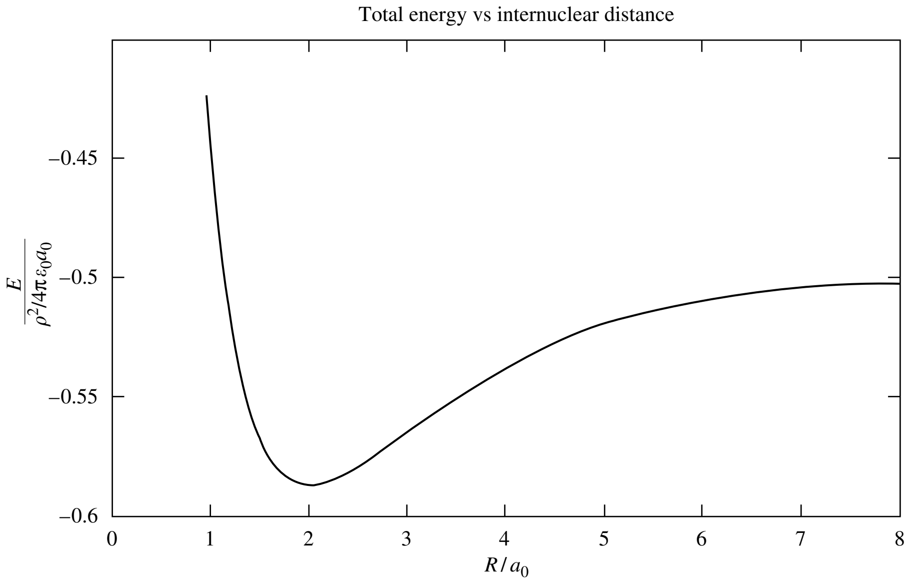


Figure 14.10

$$\omega_{\text{best}} = 2.4802a_0$$

$$\boxed{\begin{aligned}&R_e = 2.0033a_0 = 106.011\,\text{pm}\\&E(R_e) = -0.5865\,\text{au} = -15.960\,\text{eV}\\&\eta_{\text{best}} = 1.2380\end{aligned}}$$

D_e for H^+ is referenced to a zero electronic energy when a hydrogen atom and a proton are at rest at infinite separation.

$$\begin{aligned}D_e &= -\left[E(R_e) - E_H^+ - E_{\text{proton}}\right]\\&= -\left[-0.5865\,\text{au} + 0.5\,\text{au} - 0\,\text{au}\right]\\\boxed{D_e} &\boxed{= 0.0865\,\text{au} = 2.35\,\text{eV}}\end{aligned}$$

The experimental value of D_e is 2.78 eV and that of R_e is $2.00a_0$. The equilibrium internuclear distance is in excellent agreement with the experimental value but the spectroscopic dissociation energy is off by 15.3%.

(b) The virial theorem (Atkins Eq. 12.46) states that the potential energy is twice the negative of the kinetic energy. In the electronic energy equation,

$$E_{\text{el}} = \eta^2 F_1(\omega) + \eta F_2(\omega)$$

the term $\eta^2 F_1(\omega)$ is the electron kinetic energy and, consequently, the total kinetic energy because the nuclei do not move the Born-Oppenheimer approximation. The term $\eta F_2(\omega)$ is the electron potential energy only so the nuclear potential ($1/R_e$ in au) must be added to get the total potential energy. The wavefunction approximation satisfies the virial theorem when

$$f = \eta_{\text{best}} F_2(\omega_{\text{best}}) + 1/R_e + 2\eta_{\text{best}}^2 F_1(\omega_{\text{best}}) = 0$$

Since numerology has been used, we will calculate the fraction $|f/E(R_e)|$. If the fraction is very small the virial theorem is satisfied.

$$\left|\frac{2\eta_{\text{best}}^2 F_1\,(\omega_{\text{best}}) + \eta_{\text{best}} F_2\,(\omega_{\text{best}}) + \frac{1}{R_e}}{E(R_e)}\right| = 4.996 \times 10^{-6}$$

The fraction is so small that we conclude that the virial theorem is satisfied.

(c) $$\psi_A = \sqrt{\frac{\eta^3}{\pi a_0^3}}\,\mathrm{e}^{-\eta r_A/a_0}; \quad \psi_B = \sqrt{\frac{\eta^2}{\pi a_0^3}}\,\mathrm{e}^{-\eta r_B/a_0}$$

$$S = \int \psi_A \psi_B \, \mathrm{d}\tau = \frac{\eta^3}{\pi a_0^3} \int \mathrm{e}^{-\eta(r_A + r_B)/a_0}\,\mathrm{d}\tau$$

$$= \frac{\eta^3}{\pi a_0^3} \int_0^{2\pi} \int_{-1}^{1} \int_1^{\infty} \mathrm{e}^{-\eta R \mu/a_0} \left\{ \frac{R^3}{8}(\mu^2 - \nu^2) \right\} \mathrm{d}\mu\,\mathrm{d}\nu\,\mathrm{d}\phi$$

$$= \frac{1}{\pi}\left(\frac{\eta R}{2a_0}\right)^3 \left\{ \begin{array}{l} \displaystyle\int_0^{2\pi} \mathrm{d}\phi \int_{-1}^{1} \mathrm{d}\nu \int_1^{\infty} \mu^2 \mathrm{e}^{-\eta R\mu/a_0}\,\mathrm{d}\mu \\ \displaystyle -\int_0^{2\pi} \mathrm{d}\phi \int_{-1}^{1} \nu^2\,\mathrm{d}\nu \int_1^{\infty} \mathrm{e}^{-\eta R\mu/a_0}\,\mathrm{d}\mu \end{array} \right\}$$

$$= \frac{1}{\pi}\left(\frac{\eta R}{2a_0}\right)^3 \left\{ \begin{array}{c} \left(\dfrac{4\pi a_0}{\eta^3 R^3}\right)\left(2a_0^2 + 2\eta R\, a_0 + \eta^2 R^2\right)\mathrm{e}^{-\eta R/a_0} \\ -2\pi\left(\dfrac{2}{3}\right)\left(\dfrac{a_0}{\eta R}\right)\mathrm{e}^{-\eta R/a_0} \end{array} \right\}$$

$$= \frac{1}{\pi}\left(\frac{\eta R}{2a_0}\right)^3 \left(\frac{2\pi a_0^3}{\eta^3 R^3}\right) \left\{ \begin{array}{c} \left(4 + \dfrac{4\eta R}{a_0} + \dfrac{\eta^2 R^2}{a_0^2}\right)\mathrm{e}^{-\eta R/a_0} \\ -\dfrac{2}{3}\left(\dfrac{\eta^2 R^2}{a_0^2}\right)\mathrm{e}^{-\eta R/a_0} \end{array} \right\}$$

$$= \tfrac{1}{4}\left(4 + 4\omega + \tfrac{4}{3}\omega^2\right)\mathrm{e}^{-\omega} \quad \text{where} \quad \omega = \eta R/a_0$$

$$S = \left(1 + \omega + \tfrac{1}{3}\omega^2\right)\mathrm{e}^{-\omega}$$

P14.25 The secular determinant for a cyclic species H_N^m has the form

$$\begin{array}{cccccccc} 1 & 2 & 3 & \dots & \dots & \dots & N-1 & N \\ \hline x & 1 & 0 & \dots & \dots & \dots & 0 & 1 \\ 1 & x & 1 & \dots & \dots & \dots & 0 & 0 \\ 0 & 1 & x & 1 & \dots & \dots & 0 & 0 \\ 0 & 0 & 1 & x & 1 & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & 1 \\ 1 & 0 & 0 & 0 & 0 & \dots & 1 & x \end{array}$$

where $x = \dfrac{\alpha - E}{\beta}$ or $E = \alpha - \beta x$

Expanding the determinant, finding the roots of the polynomial, and solving for the total binding energy yields the following table. Note that $\alpha < 0$ and $\beta < 0$.

Species	Number of e^-	Permitted x	Total binding energy
H_4	4	$-2,0,0,2$	$4\alpha + 4\beta$
H_5^+	4	$-2, \frac{1}{2}\left(1-\sqrt{5}\right), \frac{1}{2}\left(1-\sqrt{5}\right), \frac{1}{2}\left(1+\sqrt{5}\right), \frac{1}{2}\left(1+\sqrt{5}\right)$	$4\alpha + \left(3+\sqrt{5}\right)\beta$
H_5	5	$-2, \frac{1}{2}\left(1-\sqrt{5}\right), \frac{1}{2}\left(1-\sqrt{5}\right), \frac{1}{2}\left(1+\sqrt{5}\right), \frac{1}{2}\left(1+\sqrt{5}\right)$	$5\alpha + \frac{1}{2}\left(5+3\sqrt{5}\right)\beta$
H_5^-	6	$-2, \frac{1}{2}\left(1-\sqrt{5}\right), \frac{1}{2}\left(1-\sqrt{5}\right), \frac{1}{2}\left(1+\sqrt{5}\right), \frac{1}{2}\left(1+\sqrt{5}\right)$	$6\alpha + \left(2+2\sqrt{5}\right)\beta$
H_6	6	$-2,-1,-1,1,1,2$	$6\alpha + 8\beta$
H_7^+	6	$-2,-1.248,-1.248,-1.248,-1.248,0.445,0.445,0.445$	$6\alpha + 8.992\beta$

$$
\begin{aligned}
H_4 \to 2H_2 \qquad \Delta_r U &= 4(\alpha+\beta) - (4\alpha+4\beta) = 0 \\
H_5^+ \to H_2H_3^+ \qquad \Delta_r U &= 2(\alpha+\beta) + (2\alpha+4\beta) - (4\alpha+5.236\beta) \\
&= 0.764\beta < 0
\end{aligned}
$$

The above $\Delta_r U$ values indicate that H_4 and H_5^+ are unstable.

$$
\begin{aligned}
H_5^- \to H_2 + H_3^- \qquad \Delta_r U &= 2(\alpha+\beta) - (4\alpha+2\beta) - (6\alpha+6.472\beta) \\
&= -2.472\beta > 0 \\
H_6 \to 3H_2 \qquad \Delta_r U &= 6(\alpha+\beta) - (6\alpha+8\beta) \\
&= -2\beta > 0 \\
H_7^+ \to 2H_2 + H_3^+ \qquad \Delta_r U &= 4(\alpha+\beta) + (2\alpha+4\beta) - (6\alpha+8.992\beta) \\
&= -0.992\beta > 0
\end{aligned}
$$

The $\Delta_r U$ values for H_5^-, H_6, and H_7^+ indicate that they are stable.

	Statisfies Hückel's $4n+2$ low energy rule	
Species	Correct number of e^-	Stable
H_4, $4e^-$	No	No
H_5^+, $4e^-$	No	No
H_5^-, $6e^-$	Yes	Yes
H_6, $6e^-$	Yes	Yes
H_7^+, $6e^-$	Yes	Yes

Hückel's $4n+2$ rule successfully predicts the stability of hydrogen rings.

15 Molecular symmetry

Solutions to exercises

Discussion questions

E15.1(b)

Symmetry operations	Symmetry elements
1. Identity, E	1. The entire object
2. n-fold rotation	2. n-fold axis of symmetry, C_n
3. Reflection	3. Mirror plane, σ
4. Inversion	4. Centre of symmetry, i
5. n-fold improper rotation	5. n-fold improper rotation axis, S_n

E15.2(b) A molecule may be chiral, and therefore optically active, only if it does not posses an axis of improper rotation, S_n. An improper rotation is a rotation followed by a reflection and this combination of operations always converts a right-handed object into a left-handed object and *vice-versa*; hence an S_n axis guarantees that a molecule cannot exist in chiral forms.

E15.3(b) See Sections 15.4(a) and (b).

E15.4(b) The direct sum is the decomposition of the direct product. The procedure for the decomposition is the set of steps outlined in Section 15.5(a) on p. 471 and demonstrated in *Illustration* 15.1.

Numerical exercises

E15.5(b) CCl_4 has $\boxed{4\,C_3 \text{ axes}}$ (each C–Cl axis), $\boxed{3\,C_2 \text{ axes}}$ (bisecting Cl–C–Cl angles), $\boxed{3\,S_4 \text{ axes}}$ (the same as the C_2 axes), and $\boxed{\text{6 dihedral mirror planes}}$ (each Cl–C–Cl plane).

E15.6(b) Only molecules belonging to C_s, C_n, and C_{nv} groups may be polar, so . . .

(a) CH_3Cl (C_{3v}) $\boxed{\text{may be polar}}$ along the C–Cl bond;

(b) $HW_2(CO)_{10}$ (D_{4h}) $\boxed{\text{may not be polar}}$

(c) $SnCl_4(T_d)$ $\boxed{\text{may not be polar}}$

E15.7(b) The factors of the integrand have the following characters under the operations of D_{6h}

	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
p_x	2	1	−1	−2	0	0	−2	−1	1	2	0	0
z	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1
p_z	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1
Integrand	2	1	−1	−2	0	0	−2	−1	1	2	0	0

The integrand has the same set of characters as species E_{1u}, so it does not include A_{1g}; therefore the integral $\boxed{\text{vanishes}}$

E15.8(b) We need to evaluate the character sets for the product $A_{1g}E_{2u}q$, where $q = x,\ y$, or z

	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1
E_{2u}	2	−1	−1	2	0	0	−2	1	1	−2	0	0
$(x,\ y)$	2	1	−1	−2	0	0	−2	−1	1	2	0	0
Integrand	4	−1	1	−4	0	0	4	−1	1	−4	0	0

To see whether the totally symmetric species A_{1g} is present, we form the sum over classes of the number of operations times the character of the integrand

$$\begin{aligned} c(A_{1g}) &= (4) + 2(-1) + 2(1) + (-4) + 3(0) + 3(0) + (4) \\ &\quad +2(-1) + 2(1) + (-4) + 3(0) + 3(0) = 0 \end{aligned}$$

Since the species A_{1g} is absent, the transition is $\boxed{\text{forbidden}}$ for x- or y-polarized light. A similar analysis leads to the conclusion that A_{1g} is absent from the product $A_{1g}E_{2u}z$; therefore the transition is forbidden.

E15.9(b) The classes of operations for D_2 are: E, $C_2(x)$, $C_2(y)$, and $C_2(z)$. How does the function xyz behave under each kind of operation? E leaves it unchanged. $C_2(x)$ leaves x unchanged and takes y to $-y$ and z to $-z$, leaving the product xyz unchanged. $C_2(y)$ and $C_2(z)$ have similar effects, leaving one axis unchanged and taking the other two into their negatives. These observations are summarized as follows

	E	$C_2(x)$	$C_2(y)$	$C_2(z)$
xyz	1	1	1	1

A look at the character table shows that this set of characters belong to symmetry species $\boxed{A_1}$

E15.10(b) A molecule cannot be chiral if it has an axis of improper rotation. The point group T_d has $\boxed{S_4 \text{ axes}}$ and $\boxed{\text{mirror planes } (= S_1)}$, which preclude chirality. The T_h group has, in addition, a $\boxed{\text{centre of inversion } (= S_2)}$.

E15.11(b) The group multiplication table of group C_{4v} is

	E	C_4^+	C_4^-	C_2	$\sigma_v(x)$	$\sigma_v(y)$	$\sigma_d(xy)$	$\sigma_d(-xy)$
E	E	C_4^+	C_4^-	C_2	$\sigma_v(x)$	$\sigma_v(y)$	$\sigma_d(xy)$	$\sigma_d(-xy)$
C_4^+	C_4^+	C_2	E	C_4^-	$\sigma_d(xy)$	$\sigma(-xy)$	$\sigma_v(y)$	$\sigma_v(x)$
C_4^-	C_4^-	E	C_2	C_4^+	$\sigma_d(-xy)$	$\sigma(xy)$	$\sigma_v(x)$	$\sigma_v(y)$
C_2	C_2	C_4^-	C_4^+	E	$\sigma_v(y)$	$\sigma_v(x)$	$\sigma_d(-xy)$	$\sigma_d(xy)$
$\sigma_v(x)$	$\sigma_v(x)$	$\sigma_d(-xy)$	$\sigma_d(xy)$	$\sigma_v(y)$	E	C_2	C_4^-	C_4^+
$\sigma_v(y)$	$\sigma_v(y)$	$\sigma_d(xy)$	$\sigma_d(-xy)$	$\sigma_v(x)$	C_2	E	C_4^+	C_4^-
$\sigma_d(xy)$	$\sigma_d(xy)$	$\sigma_v(x)$	$\sigma_v(y)$	$\sigma_d(-xy)$	C_4^+	C_4^-	E	C_2
$\sigma_d(-xy)$	$\sigma_d(-xy)$	$\sigma_v(y)$	$\sigma_v(x)$	$\sigma_d(xy)$	C_4^-	C_4^+	C_2	E

E15.12(b) See Fig. 15.1.

(a) Sharpened pencil: E, C_∞, σ_v; therefore $\boxed{C_{\infty v}}$

(b) Propellor: E, C_3, $3C_2$; therefore $\boxed{D_3}$

(c) Square table: E, C_4, $4\sigma_v$; therefore $\boxed{C_{4v}}$; Rectangular table: E, C_2, $2\sigma_v$; therefore C_{2v}

(d) Person: E, σ_v (approximately); therefore $\boxed{C_s}$

E15.13(b) We follow the flow chart in the text (Fig. 15.14). The symmetry elements found in order as we proceed down the chart and the point groups are

(a) Naphthalene: E, C_2, C_2', C_2'', $3\sigma_h$, i; $\boxed{D_{2h}}$

(b) Anthracene: E, C_2, C_2', C_2'', $3\sigma_h$, i; $\boxed{D_{2h}}$

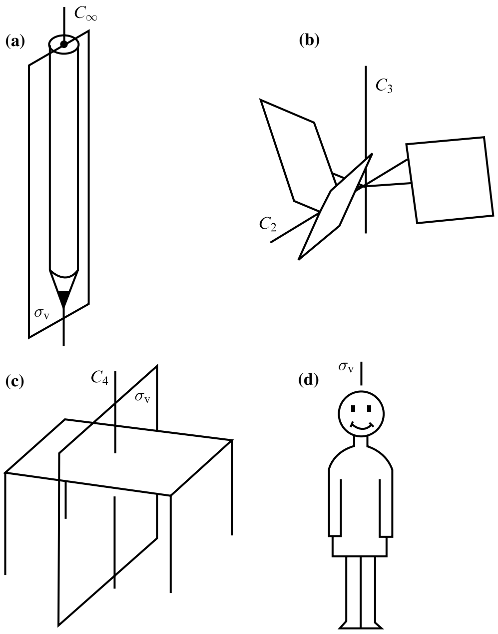


Figure 15.1

(c) Dichlorobenzenes:

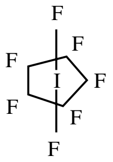
(i) 1,2-dichlorobenzene: $E,\ C_2,\ \sigma_v,\ \sigma_v'$; $\boxed{C_{2v}}$

(ii) 1,3-dichlorobenzene: $E,\ C_2,\ \sigma_v,\ \sigma_v'$; $\boxed{C_{2v}}$

(iii) 1,4-dichlorobenzene: $E,\ C_2,\ C_2',\ C_2'',\ 3\sigma_h, i$; $\boxed{D_{2h}}$

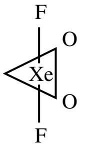
E15.14(b) **(a)** H–F $C_{\infty v}$

(b)



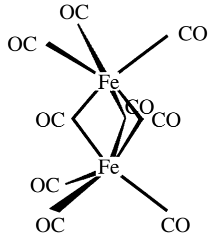
D_{5h}

(c)

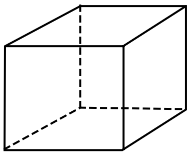


C_{2v}

(d) D_{3h}

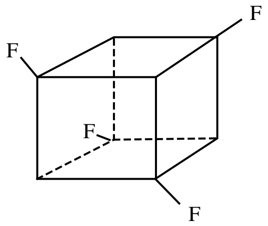


(e)



O_h

(f) T_d



The following responses refer to the text flow chart (Fig. 15.14) for assigning point groups.

(a) HF: linear, no i, so $\boxed{C_{\infty v}}$

(b) IF_7: nonlinear, fewer than $2C_n$ with $n > 2$, C_5, $5C_2'$ perpendicular to C_5, σ_h, so $\boxed{D_{5h}}$

(c) XeO_2F_2: nonlinear, fewer than $2C_n$ with $n > 2$, C_2, no C_2' perpendicular to C_2, no σ_h, $2\sigma_v$, so $\boxed{C_{2v}}$

(d) $Fe_2(CO)_9$: nonlinear, fewer than $2C_n$ with $n > 2$, C_3, $3C_2$ perpendicular to C_3, σ_h, so $\boxed{D_{3h}}$

(e) cubane (C_8H_8): nonlinear, more than $2C_n$ with $n > 2$, i, no C_5, so $\boxed{O_h}$

(f) tetrafluorocubane (**23**): nonlinear, more than $2C_n$ with $n > 2$, no i, so $\boxed{T_d}$

E15.15(b) **(a)** Only molecules belonging to C_s, C_n, and C_{nv} groups may be polar. In Exercise 15.13b $\boxed{\textit{ortho}\text{-dichlorobenzene}}$ and $\boxed{\textit{meta}\text{-dichlorobenzene}}$ belong to C_{2v} and so may be polar; in Exercise 15.10b, $\boxed{\text{HF and } XeO_2F_2}$ belong to C_{nv} groups, so they may be polar.

(b) A molecule cannot be chiral if it has an axis of improper rotation—including disguised or degenerate axes such as an inversion centre (S_2) or a mirror plane (S_1). In Exercises 15.9b and 15.10b, all the molecules have mirror planes, so $\boxed{\text{none}}$ can be chiral.

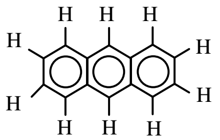
E15.16(b) In order to have nonzero overlap with a combination of orbitals that spans E, an orbital on the central atom must itself have some E character, for only E can multiply E to give an overlap integral with a totally symmetric part. A glance at the character table shows that $\boxed{p_x \text{ and } p_y}$ orbitals available to a bonding N atom have the proper symmetry. If d orbitals are available (as in SO_3), $\boxed{\text{all } d \text{ orbitals except } d_z^2}$ could have nonzero overlap.

E15.17(b) The product $\Gamma_f \times \Gamma(\mu) \times \Gamma_i$ must contain A_1 (Example 15.7). Then, since $\Gamma_i = B_1$, $\Gamma(\mu) = \Gamma(y) = B_2$ (C_{2v} character table), we can draw up the following table of characters

	E	C_2	σ_v	σ_v'	
B_2	1	−1	−1	1	
B_1	1	−1	1	−1	
B_1B_2	1	1	−1	−1	$= A_2$

Hence, the upper state is $\boxed{A_2}$, because $A_2 \times A_2 = A_1$.

E15.18(b) **(a)** Anthracene



D_{2h}

The components of μ span $B_{3u}(x)$, $B_{2u}(y)$, and $B_{1u}(z)$. The totally symmetric ground state is A_g.

Since $A_g \times \Gamma = \Gamma$ in this group, the accessible upper terms are $\boxed{B_{3u}}$ (x-polarized), $\boxed{B_{2u}}$ (y-polarized), and $\boxed{B_{1u}}$ (z-polarized).

(b) Coronene, like benzene, belongs to the D_{6h} group. The integrand of the transition dipole moment must be or contain the A_{1g} symmetry species. That integrand for transitions from the ground state is $A_{1g}qf$, where q is x, y, or z and f is the symmetry species of the upper state. Since the ground state is already totally symmetric, the product qf must also have A_{1g} symmetry for the entire integrand to have A_{1g} symmetry. Since the different symmetry species are orthogonal, the only way qf can have A_{1g} symmetry is if q and f have the same symmetry. Such combinations include zA_{2u}, xE_{1u}, and yE_{1u}. Therefore, we conclude that transitions are allowed to states with $\boxed{A_{2u} \text{ or } E_{1u}}$ symmetry.

E15.19(b)

	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0
sin θ	1	Linear combinations of sin θ and cos θ	1
cos θ	1		−1
Product	1	1	−1

The product does not contain A_1, so $\boxed{\text{yes}}$ the integral vanishes.

Solutions to problems

P15.3 Consider Fig. 15.2. The effect of σ_h on a point P is to generate $\sigma_h P$, and the effect of C_2 on $\sigma_h P$ is to generate the point $C_2\sigma_h P$. The same point is generated from P by the inversion i, so $C_2\sigma_h P = iP$ for all points P. Hence, $\boxed{C_2\sigma_h = i}$, and i must be a member of the group.

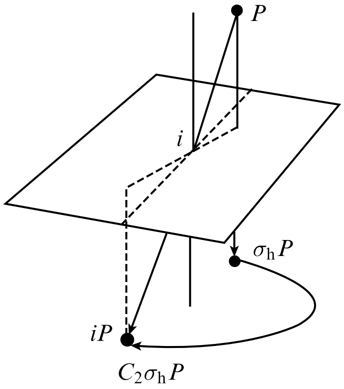


Figure 15.2

P15.6 *Representation 1*

$$\mathbf{D}(C_3)\mathbf{D}(C_2) = 1 \times 1 = 1 = \mathbf{D}(C_6)$$

and from the character table is either A_1 or A_2. Hence, either $\mathbf{D}(\sigma_v) = \mathbf{D}(\sigma_d) = \boxed{+1 \text{ or } -1}$ respectively.

Representation 2

$$\mathbf{D}(C_3)\mathbf{D}(C_2) = 1 \times (-1) = -1 = \mathbf{D}(C_6)$$

and from the character table is either B_1 or B_2. Hence, either $\mathbf{D}(\sigma_v) = -\mathbf{D}(\sigma_d) = \boxed{1}$ or $\mathbf{D}(\sigma_v) = -\mathbf{D}(\sigma_d) = \boxed{-1}$ respectively.

P15.8 A quick rule for determining the character without first having to set up the matrix representation is to count 1 each time a basis function is left unchanged by the operation, because only these functions give a nonzero entry on the diagonal of the matrix representative. In some cases there is a sign change, $(\ldots -f \ldots) \leftarrow (\ldots f \ \ldots)$; then −1 occurs on the diagonal, and so count −1. The character of the identity is always equal to the dimension of the basis since each function contributes 1 to the trace.

E: all four orbitals are left unchanged; hence $\chi = 4$
C_3: One orbital is left unchanged; hence $\chi = 1$
C_2: No orbitals are left unchanged; hence $\chi = 0$
S_4: No orbitals are left unchanged; hence $\chi = 0$
σ_d: Two orbitals are left unchanged; hence $\chi = 2$

The character set 4, 1, 0, 0, 2 spans $\boxed{A_1 + T_2.}$ Inspection of the character table of the group T_d shows that s spans A_1 and that the three p orbitals on the C atom span T_2. Hence, the $\boxed{s \text{ and } p}$ orbitals of the C atom may form molecular orbitals with the four H1s orbitals. In T_d, the d orbitals of the central atom span $E + T_2$ (character table, final column), and so only the T_2 set $\boxed{(d_{xy}, d_{yz}, d_{zx})}$ may contribute to molecular orbital formation with the H orbitals.

P15.9 **(a)** In C_{3v} symmetry the H1s orbitals span the same irreducible representations as in NH_3, which is $A_1 + A_1 + E$. There is an additional A_1 orbital because a fourth H atom lies on the C_3 axis. In C_{3v}, the d orbitals span $A_1 + E + E$ [see the final column of the C_{3v} character table]. Therefore, $\boxed{\text{all five } d \text{ orbitals}}$ may contribute to the bonding.

(b) In C_{2v} symmetry the H1s orbitals span the same irreducible representations as in H_2O, but one "H_2O" fragment is rotated by 90° with respect to the other. Therefore, whereas in H_2O the H1s orbitals span $A_1 + B_2$ $[H_1 + H_2, H_1 - H_2]$, in the distorted CH_4 molecule they span $A_1 + B_2 + A_1 + B_1$ $[H_1 + H_2, H_1 - H_2, H_3 + H_4, H_3 - H_4]$. In C_{2v} the d orbitals span $2A_1 + B_1 + B_2 + A_2$ [C_{2v} character table]; therefore, $\boxed{\text{all except } A_2(d_{xy})}$ may participate in bonding.

P15.10 The most distinctive symmetry operation is the $\boxed{S_4}$ axis through the central atom and aromatic nitrogens on both ligands. That axis is also a $\boxed{C_2}$ axis. The group is $\boxed{S_4}$.

P15.12 **(a)** Working through the flow diagram (Fig. 15.14) in the text, we note that there are no C_n axes with $n > 2$ (for the C_3 axes present in a tetrahedron are not symmetry axes any longer), but it does have C_2 axes; in fact it has $2C_2$ axes perpendicular to whichever C_2 we call principal; it has no σ_h, but it has $2\sigma_d$. So the point group is $\boxed{D_{2d}}$.

(b) Within this point group, the distortion belongs to the fully symmetric species $\boxed{A_1}$, for its motion is unchanged by the S_4 operation, either class of C_2, or σ_d.

(c) The resulting structure is a square bipyramid, but with one pyramid's apex farther from the base than the other's. Working through the flow diagram in Fig. 15.14, we note that there is only one C_n axis with $n > 2$, namely a C_4 axis; it has no C_2 axes perpendicular to the C_4, and it has no σ_h, but it has $4\sigma_v$. So the point group is $\boxed{C_{4v}}$.

(d) Within this point group, the distortion belongs to the fully symmetric species $\boxed{A_1}$. The translation of atoms along the given axis is unchanged by any symmetry operation for the motion is contained within each of the group's symmetry elements.

P15.14 **(a)** xyz changes sign under the inversion operation (one of the symmetry elements of a cube); hence it does not span A_{1g} and its integral $\boxed{\text{must be zero}}$

(b) xyz spans A_1 in T_d [Problem 15.13] and so its integral $\boxed{\text{need not be zero}}$

(c) $xyz \to -xyz$ under $z \to -z$ (the σ_h operation in D_{6h}), and so its integral $\boxed{\text{must be zero}}$

P15.16 We shall adapt the simpler subgroup C_{6v} of the full D_{6h} point group. The six π-orbitals span $A_1 + B_1 + E_1 + E_2$, and are

$$a_1 = \frac{1}{\sqrt{6}}(\pi_1 + \pi_2 + \pi_3 + \pi_4 + \pi_5 + \pi_6)$$
$$b_1 = \frac{1}{\sqrt{6}}(\pi_1 - \pi_2 + \pi_3 - \pi_4 + \pi_5 - \pi_6)$$
$$e_2 = \begin{cases} \dfrac{1}{\sqrt{12}}(2\pi_1 - \pi_2 - \pi_3 + 2\pi_4 - \pi_5 - \pi_6) \\ \tfrac{1}{2}(\pi_2 - \pi_3 + \pi_5 - \pi_6) \end{cases}$$
$$e_1 = \begin{cases} \dfrac{1}{\sqrt{12}}(2\pi_1 + \pi_2 - \pi_3 - 2\pi_4 - \pi_5 + \pi_6) \\ \tfrac{1}{2}(\pi_2 + \pi_3 - \pi_5 - \pi_6) \end{cases}$$

The hamiltonian transforms as A_1; therefore all integrals of the form $\int \psi' H \psi \, d\tau$ vanish unless ψ' and ψ belong to the same symmetry species. It follows that the secular determinant factorizes into four determinants

$$A_1\!: \quad H_{a_1a_1} = \tfrac{1}{6}\int (\pi_1 + \cdots + \pi_6) H (\pi_1 + \cdots + \pi_6)\, d\tau = \alpha + 2\beta$$

$$B_1\!: \quad H_{b_1b_1} = \tfrac{1}{6}\int (\pi_1 - \pi_2 + \cdots) H (\pi_1 - \pi_2 + \cdots)\, d\tau = \alpha - 2\beta$$

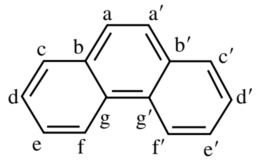
$$E_1\!: \quad H_{e_1(a)e_1(a)} = \alpha - \beta, \quad H_{e_1(b)e_1(b)} = \alpha - \beta, \quad H_{e_1(a)e_1(b)} = 0$$

$$\text{Hence} \begin{vmatrix} \alpha - \beta - \varepsilon & 0 \\ 0 & \alpha - \beta - \varepsilon \end{vmatrix} = 0 \text{ solves to } \varepsilon = \alpha - \beta \text{ (twice)}$$

$$E_2\!: \quad H_{e_2(a)e_2(a)} = \alpha + \beta, \quad H_{e_2(b)e_2(b)} = \alpha + \beta, \quad H_{e_2(a)e_2(b)} = 0$$

$$\text{Hence} \begin{vmatrix} \alpha + \beta - \varepsilon & 0 \\ 0 & \alpha + \beta - \varepsilon \end{vmatrix} = 0 \text{ solves to } \varepsilon = \alpha + \beta \text{ (twice)}$$

P15.17 Consider phenanthrene with carbon atoms as labeled in the figure below



(**a**) The $2p$ orbitals involved in the π system are the basis we are interested in. To find the irreproducible representations spanned by this basis, consider how each basis is transformed under the symmetry operations of the C_{2v} group. To find the character of an operation in this basis, sum the coefficients of the basis terms that are unchanged by the operation.

	a	a′	b	b′	c	c′	d	d′	e	e′	f	f′	g	g′	χ
E	a	a′	b	b′	c	c′	d	d′	e	e′	f	f′	g	g′	14
C_2	−a′	−a	−b′	−b	−c′	−c	−d′	−d	−e′	−e	−f′	−f	−g′	−g	0
σ_v	a′	a	b′	b	c′	c	d′	d	e′	e	f′	f	g′	g	0
σ_v'	−a	−a′	−b	−b′	−c	−c′	−d	−d′	−e	−e′	−f	−f′	−g	−g′	−14

To find the irreproducible representations that these orbitals span, multiply the characters in the representation of the orbitals by the characters of the irreproducible representations, sum those products, and divide the sum by the order h of the group (as in Section 15.5(a)). The table below illustrates the procedure, beginning at left with the C_{2v} character table.

	E	C_2	σ_v	σ'_v	product	E	C_2	σ_v	σ'_v	sum/h
A_1	1	1	1	1		14	0	0	−14	0
A_2	1	1	−1	−1		14	0	0	14	7
B_1	1	−1	1	−1		14	0	0	14	7
B_2	1	−1	−1	1		14	0	0	−14	0

The orbitals span $\boxed{7A_2 + B_2}$.

To find symmetry-adapted linear combinations (SALCs), follow the procedure described in Section 15.5(c). Refer to the table above that displays the transformations of the original basis orbitals. To find SALCs of a given symmetry species, take a column of the table, multiply each entry by the character of the species' irreproducible representation, sum the terms in the column, and divide by the order of the group. For example, the characters of species A_1 are 1, 1, 1, 1, so the columns to be summed are identical to the columns in the table above. Each column sums to zero, so we conclude that there are no SALCs of A_1 symmetry. (No surprise here: the orbitals span only A_2 and B_1.) An A_2 SALC is obtained by multiplying the characters 1, 1, −1, −1 by the first column:

$$\tfrac{1}{4}(\mathrm{a} - \mathrm{a}' - \mathrm{a}' + \mathrm{a}) = \tfrac{1}{2}(\mathrm{a} - \mathrm{a}').$$

The A_2 combination from the second column is the same. There are seven distinct A_2 combinations in all: $\boxed{1/2(\mathrm{a}-\mathrm{a}'),\ 1/2(\mathrm{b}-\mathrm{b}'),\ \ldots,\ 1/2(\mathrm{g}-\mathrm{g}')}$. The B_1 combination from the first column is:

$$\tfrac{1}{4}(\mathrm{a} + \mathrm{a}' + \mathrm{a}' + \mathrm{a}) = \tfrac{1}{2}(\mathrm{a} + \mathrm{a}').$$

The B_1 combination from the second column is the same. There are seven distinct B_1 combinations in all: $\boxed{\tfrac{1}{2}(\mathrm{a}+\mathrm{a}'),\ \tfrac{1}{2}(\mathrm{b}+\mathrm{b}'),\ \ldots,\ \tfrac{1}{2}(\mathrm{g}+\mathrm{g}')}$. There are no B_2 combinations, as the columns sum to zero.

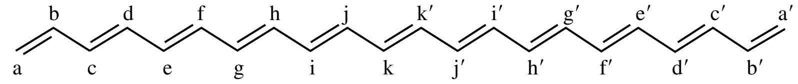
(b) The structure is labeled to match the row and column numbers shown in the determinant. The Hückel secular determinant of phenanthrene is:

$$\begin{array}{c|cccccccccccccc|}
 & \mathrm{a} & \mathrm{b} & \mathrm{c} & \mathrm{d} & \mathrm{e} & \mathrm{f} & \mathrm{g} & \mathrm{g}' & \mathrm{f}' & \mathrm{e}' & \mathrm{d}' & \mathrm{c}' & \mathrm{b}' & \mathrm{a}' \\
\mathrm{a} & \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta \\
\mathrm{b} & \beta & \alpha-E & \beta & 0 & 0 & 0 & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\mathrm{c} & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\mathrm{d} & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\mathrm{e} & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\mathrm{f} & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\mathrm{g} & 0 & \beta & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 & 0 & 0 \\
\mathrm{g}' & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & \beta & 0 \\
\mathrm{f}' & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 & 0 \\
\mathrm{e}' & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 & 0 \\
\mathrm{d}' & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 & 0 \\
\mathrm{c}' & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E & \beta & 0 \\
\mathrm{b}' & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & 0 & 0 & 0 & \beta & \alpha-E & \beta \\
\mathrm{a}' & \beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha-E
\end{array}$$

This determinant has the same eigenvalues as as in exercise 14.16(b)b.

(**c**) The ground state of the molecule has A_1 symmetry by virtue of the fact that its wavefunction is the product of doubly occupied orbitals, and the product of any two orbitals of the same symmetry has A_1 character. If a transition is to be allowed, the transition dipole must be non-zero, which in turn can only happen if the representation of the product $\Psi_f^* \boldsymbol{\mu} \Psi_i$ includes the totally symmetric species A_1. Consider first transitions to another A_1 wavefunction, in which case we need the product $A_1 \boldsymbol{\mu} A_1$. Now $A_1 A_1 = A_1$, and the only character that returns A_1 when multiplied by A_1 is A_1 itself. The z component of the dipole operator belongs to species A_1, so z-polarized $A_1 \leftarrow A_1$ transitions are allowed. (Note: transitions from the A_1 ground state to an A_1 excited state are transitions from an orbital occupied in the ground state to an excited-state orbital of the same symmetry.) The other possibility is a transition from an orbital of one symmetry (A_2 or B_1) to the other; in that case, the excited-state wavefunction will have symmetry of $A_1 B_1 = B_2$ from the two singly occupied orbitals in the excited state. The symmetry of the transition dipole, then, is $A_1 \boldsymbol{\mu} B_2 = \boldsymbol{\mu} B_2$, and the only species that yields A_1 when multiplied by B_2 is B_2 itself. Now the y component of the dipole operator belongs to species B_2, so these transitions are also allowed (y-polarized).

P15.21 (a) Following the flow chart in Fig. 15.14, not that the molecule is not linear (at least not in the mathematical sense); there is only one C_n axis (a C_2), and there is a σ_h. The point group, then, is $\boxed{C_{2h}}$.



(b) The $2p_z$ orbitals are transformed under the symmetry operations of the C_{2h} group as follows.

	a	a′	b	b′	c	c′	…	j	j′	k	k′	χ
E	a	a′	b	b′	c	c′	…	j	j′	k	k′	22
C_2	a′	a	b′	b	c′	c	…	j′	j	k′	k	0
i	−a′	−a	−b′	−b	−c′	−c	…	−j′	−j	−k′	−k	0
σ_h	−a	−a′	−b	−b′	−c	−c′	…	−j	−j′	−k	−k′	−22

To find the irreproducible representations that these orbitals span, we multiply the characters of orbitals by the characters of the irreproducible representations, sum those products, and divide the sum by the order h of the group (as in Section 15.5(a)). The table below illustrates the procedure, beginning at left with the C_{2h} character table.

	E	C_2	i	σ_h	product	E	C_2	i	σ_h	sum/h
A_g	1	1	1	1		22	0	0	−22	0
A_u	1	1	−1	−1		22	0	0	22	11
B_g	1	−1	1	−1		22	0	0	22	11
B_u	1	−1	−1	1		22	0	0	−22	0

The orbitals span $\boxed{11A_u + 11B_g}$.

To find symmetry-adapted linear combinations (SALCs), follow the procedure described in Section 15.5(c). Refer to the above that displays the transformations of the original basis orbitals. To find SALCs of a given symmetry species, take a column of the table, multiply each entry by the character of the species' irreproducible representation, sum the terms in the column, and divide by the order of the group. For example, the characters of species A_u are 1, 1, 1, 1, so the columns to be summed are identical to the columns in the table above. Each column sums to zero, so we conclude that there are no SALCs of A_g symmetry. (No surprise: the orbitals span only A_u and B_g). An A_u SALC is obtained by multiplying the characters 1, 1, −1, −1 by the first column:

$$\tfrac{1}{4}(\mathrm{a}+\mathrm{a}'+\mathrm{a}'+\mathrm{a})=\tfrac{1}{2}(\mathrm{a}+\mathrm{a}').$$

The A_u combination from the second column is the same. There are 11 distinct A_u combinations in all: $\boxed{1/2(\mathrm{a}+\mathrm{a}'),\ 1/2(\mathrm{b}+\mathrm{b}'),\ \ldots\ 1/2(\mathrm{k}+\mathrm{k}')}$. The B_g combination from the first column is:

$$\tfrac{1}{4}(\mathrm{a}-\mathrm{a}'-\mathrm{a}'+\mathrm{a})=\tfrac{1}{2}(\mathrm{a}-\mathrm{a}').$$

The B_g combination from the second column is the same. There are 11 distinct B_g combinations in all: $\boxed{1/2(\mathrm{a}-\mathrm{a}'),\ 1/2(\mathrm{b}-\mathrm{b}'),\ \ldots\ 1/2(\mathrm{k}-\mathrm{k}')}$. There are no B_u combinations, as the columns sum to zero.

(c) The structure is labeled to match the row and column numbers shown in the determinant. The Hückel secular determinant is:

$$\begin{array}{c|cccccccccccccc|}
 & \mathrm{a} & \mathrm{b} & \mathrm{c} & \ldots & \mathrm{i} & \mathrm{j} & \mathrm{k} & \mathrm{k}' & \mathrm{j}' & \mathrm{i}' & \ldots & \mathrm{c}' & \mathrm{b}' & \mathrm{a}' \\
\mathrm{a} & \alpha-E & \beta & 0 & \ldots & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & 0 & 0 & 0 \\
\mathrm{b} & \beta & \alpha-E & \beta & \ldots & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & 0 & 0 & 0 \\
\mathrm{c} & 0 & \beta & \alpha-E & \ldots & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & 0 & 0 & 0 \\
\ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\
\mathrm{i} & 0 & 0 & 0 & \ldots & \alpha-E & \beta & 0 & 0 & 0 & 0 & \ldots & 0 & 0 & 0 \\
\mathrm{j} & 0 & 0 & 0 & \ldots & \beta & \alpha-E & \beta & 0 & 0 & 0 & \ldots & 0 & 0 & 0 \\
\mathrm{k} & 0 & 0 & 0 & \ldots & 0 & \beta & \alpha-E & \beta & 0 & 0 & \ldots & 0 & 0 & 0 \\
\mathrm{k}' & 0 & 0 & 0 & \ldots & 0 & 0 & \beta & \alpha-E & \beta & 0 & \ldots & 0 & 0 & 0 \\
\mathrm{j}' & 0 & 0 & 0 & \ldots & 0 & 0 & 0 & \beta & \alpha-E & \beta & \ldots & 0 & 0 & 0 \\
\mathrm{i}' & 0 & 0 & 0 & \ldots & 0 & 0 & 0 & 0 & \beta & \alpha-E & \ldots & 0 & 0 & 0 \\
\ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\
\mathrm{c}' & 0 & 0 & 0 & \ldots & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & \alpha-E & \beta & 0 \\
\mathrm{b}' & 0 & 0 & 0 & \ldots & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & \beta & \alpha-E & \beta \\
\mathrm{a}' & 0 & 0 & 0 & \ldots & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & 0 & \beta & \alpha-E
\end{array}$$

The energies of the filled orbitals are $\alpha+1.98137\beta$, $\alpha+1.92583\beta$, $\alpha+1.83442\beta$, $\alpha+1.70884\beta$, $\alpha+1.55142\beta$, $\alpha+1.36511\beta$, $\alpha+1.15336\beta$, $\alpha+0.92013\beta$, $\alpha+0.66976\beta$, $\alpha+0.40691\beta$, and $\alpha+0.13648\beta$. The π energy is 27.30729β.

(d) The ground state of the molecule has A_g symmetry by virtue of the fact that its wavefunction is the product of doubly occupied orbitals, and the product of any two orbitals of the same symmetry has A_g character. If a transition is to be allowed, the transition dipole must be nonzero, which in turn can only happen if the representation of the product $\Psi f^{*}\boldsymbol{\mu}\Psi_i$ includes the totally symmetric species A_g. Consider first transitions to another A_g wavefunction, in which case we need the product $A_g\boldsymbol{\mu}A_g$. Now $A_gA_g = A_g$, and the only character that returns A_g when multiplied by A_g is A_g itself. No component of the dipole operator belongs to species A_g, so no $A_g \leftarrow A_g$ transitions are allowed. (Note: such transitions are transitions from an orbital occupied in the ground state to an excited-state orbital of the same symmetry.) The other possibility is a transition from an orbital of one symmetry (A_u or B_g) to the other; in that case, the excited-state wavefunction will have symmetry of $A_uB_g = B_u$ from the two singly occupied orbitals in the excited state. The symmetry of the transition dipole, then, is $A_g\boldsymbol{\mu}B_u = \boldsymbol{\mu}B_u$, and the only species that yields A_g when multiplied by B_u is B_u itself. The x and y components of the dipole operator belongs to species B_u, so these transitions are allowed.

16 Spectroscopy 1: rotational and vibrational spectroscopy

Solutions to exercises

Discussion questions

E16.1(b) (1) *Doppler broadening*. This contribution to the linewidth is due to the Doppler effect which shifts the frequency of the radiation emitted or absorbed when the atoms or molecules involved are moving towards or away from the detecting device. Molecules have a wide range of speeds in all directions in a gas and the detected spectral line is the absorption or emission profile arising from all the resulting Doppler shifts. As shown in *Justification* 16.3, the profile reflects the distribution of molecular velocities parallel to the line of sight which is a bell-shaped Gaussian curve.

(2) *Lifetime broadening*. The Doppler broadening is significant in gas phase samples, but lifetime broadening occurs in all states of matter. This kind of broadening is a quantum mechanical effect related to the uncertainty principle in the form of eqn 16.25 and is due to the finite lifetimes of the states involved in the transition. When τ is finite, the energy of the states is smeared out and hence the transition frequency is broadened as shown in eqn 16.26.

(3) *Pressure broadening or collisional broadening*. The actual mechanism affecting the lifetime of energy states depends on various processes one of which is collisional deactivation and another is spontaneous emission. The first of these contributions can be reduced by lowering the pressure, the second cannot be changed and results in a natural linewidth.

E16.2(b) (1) *Rotational Raman spectroscopy*. The gross selection rule is that the molecule must be anisotropically polarizable, which is to say that its polarizability, α, depends upon the direction of the electric field relative to the molecule. Non-spherical rotors satisfy this condition. Therefore, linear and symmetric rotors are rotationally Raman active.

(2) *Vibrational Raman spectroscopy*. The gross selection rule is that the polarizability of the molecule must change as the molecule vibrates. All diatomic molecules satisfy this condition as the molecules swell and contract during a vibration, the control of the nuclei over the electrons varies, and the molecular polarizability changes. Hence both homonuclear and heteronuclear diatomics are vibrationally Raman active. In polyatomic molecules it is usually quite difficult to judge by inspection whether or not the molecule is anisotropically polarizable; hence group theoretical methods are relied on for judging the Raman activity of the various normal modes of vibration. The procedure is discussed in Section 16.17(b) and demonstrated in *Illustration* 16.7.

E16.3(b) The exclusion rule applies to the benzene molecule because it has a center of symmetry. Consequently, none of the normal modes of vibration of benzene can be both infrared and Raman active. If we wish to characterize all the normal modes we must obtain both kinds of spectra. See the solutions to Exercises 16.29(a) and 16.29(b) for specified illustrations of which modes are IR active and which are Raman active.

Numerical exercises

E16.4(b) The ratio of coefficients A/B is

(a) $$\frac{A}{B} = \frac{8\pi h\nu^3}{c^3} = \frac{8\pi(6.626\times10^{-34}\,\mathrm{J\,s})\times(500\times10^{6}\,\mathrm{s^{-1}})^3}{(2.998\times10^{8}\,\mathrm{m\,s^{-1}})^3} = \boxed{7.73\times10^{-32}\,\mathrm{J\,m^{-3}\,s}}$$

(b) The frequency is

$$\nu = \frac{c}{\lambda} \quad \text{so} \quad \frac{A}{B} = \frac{8\pi h}{\lambda^3} = \frac{8\pi(6.626 \times 10^{-34}\,\text{J s})}{(3.0 \times 10^{-2}\,\text{m})^3} = \boxed{6.2 \times 10^{-28}\,\text{J m}^{-3}\,\text{s}}$$

E16.5(b) A source approaching an observer appears to be emitting light of frequency

$$\nu_{\text{approaching}} = \frac{\nu}{1 - \frac{s}{c}} \text{ [16.22, Section 16.3]}$$

Since $\nu \propto \dfrac{1}{\lambda}$, $\quad \lambda_{\text{obs}} = \left(1 - \dfrac{s}{c}\right)\lambda$

For the light to appear green the speed would have to be

$$s = \left(1 - \frac{\lambda_{\text{obs}}}{\lambda}\right) c = (2.998 \times 10^8\,\text{m s}^{-1}) \times \left(1 - \frac{520\,\text{nm}}{660\,\text{nm}}\right) = \boxed{6.36 \times 10^7\,\text{m s}^{-1}}$$

or about 1.4×10^8 m.p.h.

(Since $s \approx c$, the relativistic expression

$$\nu_{\text{obs}} = \left(\frac{1 + \frac{s}{c}}{1 - \frac{s}{c}}\right)^{1/2} \nu$$

should really be used. It gives $s = 7.02 \times 10^7\,\text{m s}^{-1}$.)

E16.6(b) The linewidth is related to the lifetime τ by

$$\delta\tilde{\nu} = \frac{5.31\,\text{cm}^{-1}}{\tau/\text{ps}} \text{ [16.26]} \quad \text{so} \quad \tau = \frac{5.31\,\text{cm}^{-1}}{\delta\tilde{\nu}}\,\text{ps}$$

(a) We are given a frequency rather than a wavenumber

$$\tilde{\nu} = \nu/c \quad \text{so} \quad \tau = \frac{(5.31\,\text{cm}^{-1}) \times (2.998 \times 10^{10}\,\text{cm s}^{-1})}{100 \times 10^6\,\text{s}^{-1}}\,\text{ps} = 1.59 \times 10^3\,\text{ps}$$

or $\boxed{1.59\,\text{ns}}$

(b) $\quad \tau = \dfrac{5.31\,\text{cm}^{-1}}{2.14\,\text{cm}^{-1}}\,\text{ps} = \boxed{2.48\,\text{ps}}$

E16.7(b) The linewidth is related to the lifetime τ by

$$\delta\tilde{\nu} = \frac{5.31\,\text{cm}^{-1}}{\tau/\text{ps}} \quad \text{so} \quad \delta\nu = \frac{(5.31\,\text{cm}^{-1})c}{\tau/\text{ps}}$$

(a) If every collision is effective, then the lifetime is $1/(1.0 \times 10^9\,\text{s}^{-1}) = 1.0 \times 10^{-9}\,\text{s} = 1.0 \times 10^3\,\text{ps}$

$$\delta\tilde{\nu} = \frac{(5.31\,\text{cm}^{-1}) \times (2.998 \times 10^{10}\,\text{cm s}^{-1})}{1.0 \times 10^3} = 1.6 \times 10^8\,\text{s}^{-1} = \boxed{160\,\text{MHz}}$$

(b) If only one collision in 10 is effective, then the lifetime is a factor of 10 greater, 1.0×10^4 ps

$$\delta\tilde{\nu} = \frac{(5.31\,\text{cm}^{-1}) \times (2.998 \times 10^{10}\,\text{cm s}^{-1})}{1.0 \times 10^4} = 1.6 \times 10^7\,\text{s}^{-1} = \boxed{16\,\text{MHz}}$$

E16.8(b) The frequency of the transition is related to the rotational constant by

$$h\nu = \Delta E = hc\Delta F = hcB[J(J+1)-(J-1)J] = 2hcBJ$$

where J refers to the upper state ($J=3$). The rotational constant is related to molecular structure by

$$B = \frac{\hbar}{4\pi cI} = \frac{\hbar}{4\pi c m_{\text{eff}} R^2}$$

where I is moment of inertia, m_{eff} is effective mass, and R is the bond length. Putting these expressions together yields

$$\nu = 2cBJ = \frac{\hbar J}{2\pi m_{\text{eff}} R^2}$$

The reciprocal of the effective mass is

$$m_{\text{eff}}^{-1} = m_{\text{C}}^{-1} + m_{\text{O}}^{-1} = \frac{(12\,\text{u})^{-1} + (15.9949\,\text{u})^{-1}}{1.66054\times10^{-27}\,\text{kg u}^{-1}} = 8.78348\times10^{25}\,\text{kg}^{-1}$$

$$\text{So } \nu = \frac{(8.78348\times10^{25}\,\text{kg}^{-1})\times(1.0546\times10^{-34}\,\text{J s})\times(3)}{2\pi(112.81\times10^{-12}\,\text{m})^2} = \boxed{3.4754\times10^{11}\,\text{s}^{-1}}$$

E16.9(b) **(a)** The wavenumber of the transition is related to the rotational constant by

$$hc\tilde{\nu} = \Delta E = hc\Delta F = hcB[J(J+1)-(J-1)J] = 2hcBJ$$

where J refers to the upper state ($J=1$). The rotational constant is related to molecular structure by

$$B = \frac{\hbar}{4\pi cI}$$

where I is moment of inertia. Putting these expressions together yields

$$\tilde{\nu} = 2BJ = \frac{\hbar J}{2\pi cI} \quad \text{so} \quad I = \frac{hJ}{c\tilde{\nu}} = \frac{(1.0546\times10^{-34}\,\text{J s})\times(1)}{2\pi(2.998\times10^{10}\,\text{cm s}^{-1})\times(16.93\,\text{cm}^{-1})}$$

$$I = \boxed{3.307\times10^{-47}\,\text{kg m}^2}$$

(b) The moment of inertia is related to the bond length by

$$I = m_{\text{eff}}R^2 \quad \text{so} \quad R = \left(\frac{I}{m_{\text{eff}}}\right)^{1/2}$$

$$m_{\text{eff}}^{-1} = m_{\text{H}}^{-1} + m_{\text{Br}}^{-1} = \frac{(1.0078\,\text{u})^{-1} + (80.9163\,\text{u})^{-1}}{1.66054\times10^{-27}\,\text{kg u}^{-1}} = 6.0494\times10^{26}\,\text{kg}^{-1}$$

$$\text{and } R = \left\{(6.0494\times10^{26}\,\text{kg}^{-1})\times(3.307\times10^{-47}\,\text{kg m}^2)\right\}^{1/2}$$
$$= 1.414\times10^{-10}\,\text{m} = \boxed{141.4\,\text{pm}}$$

E16.10(b) The wavenumber of the transition is related to the rotational constant by

$$hc\tilde{\nu} = \Delta E = hc\Delta F = hcB[J(J+1) - (J-1)J] = 2hcBJ$$

where J refers to the upper state. So wavenumbers of adjacent transitions (transitions whose upper states differ by 1) differ by

$$\Delta\tilde{\nu} = 2B = \frac{\hbar}{2\pi cI} \quad \text{so} \quad I = \frac{\hbar}{2\pi c\Delta\tilde{\nu}}$$

where I is moment of inertia, m_{eff} is effective mass, and R is the bond length.

So $I = \dfrac{(1.0546 \times 10^{-34}\,\text{J s})}{2\pi(2.9979 \times 10^{10}\,\text{cm s}^{-1}) \times (1.033\,\text{cm}^{-1})} = \boxed{5.420 \times 10^{-46}\,\text{kg m}^2}$

The moment of inertia is related to the bond length by

$$I = m_{\text{eff}}R^2 \quad \text{so} \quad R = \left(\frac{I}{m_{\text{eff}}}\right)^{1/2}$$

$$m_{\text{eff}}^{-1} = m_{\text{F}}^{-1} + m_{\text{Cl}}^{-1} = \frac{(18.9984\,\text{u})^{-1} + (34.9688\,\text{u})^{-1}}{1.66054 \times 10^{-27}\,\text{kg u}^{-1}} = 4.89196 \times 10^{25}\,\text{kg}^{-1}$$

and $R = \left\{(4.89196 \times 10^{25}\,\text{kg}^{-1}) \times (5.420 \times 10^{-46}\,\text{kg m}^2)\right\}^{1/2}$

$$= 1.628 \times 10^{-10}\,\text{m} = \boxed{162.8\,\text{pm}}$$

E16.11(b) The rotational constant is

$$B = \frac{\hbar}{4\pi cI} = \frac{\hbar}{4\pi c(2m_{\text{O}}R^2)} \quad \text{so} \quad R = \left(\frac{\hbar}{8\pi cm_{\text{O}}B}\right)^{1/2}$$

where I is moment of inertia, m_{eff} is effective mass, and R is the bond length.

$$R = \left(\frac{(1.0546 \times 10^{-34}\,\text{J s})}{8\pi(2.9979 \times 10^{10}\,\text{cm s}^{-1}) \times (15.9949\,\text{u}) \times (1.66054 \times 10^{-27}\,\text{kg u}^{-1}) \times (0.39021)}\right)^{1/2}$$

$$= 1.1621 \times 10^{-10}\,\text{m} = \boxed{116.21\,\text{pm}}$$

E16.12(b) This exercise is analogous to Exercise 16.12(a), but here our solution will employ a slightly different algebraic technique. Let $R = R_{\text{OC}}$, $R' = R_{\text{CS}}$, $\text{O} = {}^{16}\text{O}$, $\text{C} = {}^{12}\text{C}$.

$$I = \frac{\hbar}{4\pi B} \text{ [Footnote 6, p. 466]}$$

$$I(\text{OC}^{32}\text{S}) = \frac{1.05457 \times 10^{-34}\,\text{J s}}{(4\pi) \times (6.0815 \times 10^{9}\,\text{s}^{-1})} = 1.3799 \times 10^{-45}\,\text{kg m}^2 = 8.3101 \times 10^{-19}\,\text{u m}^2$$

$$I(\text{OC}^{34}\text{S}) = \frac{1.05457 \times 10^{-34}\,\text{J s}}{(4\pi) \times (5.9328 \times 10^{9}\,\text{s}^{-1})} = 1.4145 \times 10^{-45}\,\text{kg m}^2 = 8.5184 \times 10^{-19}\,\text{u m}^2$$

The expression for the moment of inertia given in Table 16.1 may be rearranged as follows.

$$\begin{aligned} Im &= m_{\text{A}}mR^2 + m_{\text{C}}mR'^2 - (m_{\text{A}}R - m_{\text{C}}R')^2 \\ &= m_{\text{A}}mR^2 + m_{\text{C}}mR'^2 - m_{\text{A}}^2R^2 + 2m_{\text{A}}m_{\text{C}}RR' - m_{\text{C}}^2R'^2 \\ &= m_{\text{A}}(m_{\text{B}} + m_{\text{C}})R^2 + m_{\text{C}}(m_{\text{A}} + m_{\text{B}})R'^2 + 2m_{\text{A}}m_{\text{C}}RR' \end{aligned}$$

Let $m_{\mathrm{C}} = m_{^{32}\mathrm{S}}$ and $m'_{\mathrm{C}} = m_{^{34}\mathrm{S}}$

$$\frac{Im}{m_{\mathrm{C}}} = \frac{m_{\mathrm{A}}}{m_{\mathrm{C}}}(m_{\mathrm{B}} + m_{\mathrm{C}})R^2 + (m_{\mathrm{A}} + m_{\mathrm{B}})R'^2 + 2m_{\mathrm{A}}RR' \qquad \text{(a)}$$

$$\frac{I'm'}{m'_{\mathrm{C}}} = \frac{m_{\mathrm{A}}}{m'_{\mathrm{C}}}(m_{\mathrm{B}} + m'_{\mathrm{C}})R^2 + (m_{\mathrm{A}} + m_{\mathrm{B}})R'^2 + 2m_{\mathrm{A}}RR' \qquad \text{(b)}$$

Subtracting

$$\frac{Im}{m_{\mathrm{C}}} - \frac{I'm'}{m'_{\mathrm{C}}} = \left[\left(\frac{m_{\mathrm{A}}}{m_{\mathrm{C}}}\right)(m_{\mathrm{B}} + m_{\mathrm{C}}) - \left(\frac{m_{\mathrm{A}}}{m'_{\mathrm{C}}}\right)(m_{\mathrm{B}} + m'_{\mathrm{C}})\right]R^2$$

Solving for R^2

$$R^2 = \frac{\left(\frac{Im}{m_{\mathrm{C}}} - \frac{I'm'}{m'_{\mathrm{C}}}\right)}{\left[\left(\frac{m_{\mathrm{A}}}{m_{\mathrm{C}}}\right)(m_{\mathrm{B}} + m_{\mathrm{C}}) - \left(\frac{m_{\mathrm{A}}}{m'_{\mathrm{C}}}\right)(m_{\mathrm{B}} + m'_{\mathrm{C}})\right]} = \frac{m'_{\mathrm{C}}Im - m_{\mathrm{C}}I'm'}{m_{\mathrm{B}}m_{\mathrm{A}}(m'_{\mathrm{C}} - m_{\mathrm{C}})}$$

Substituting the masses, with $m_{\mathrm{A}} = m_{\mathrm{O}}$, $m_{\mathrm{B}} = m_{\mathrm{C}}$, $m_{\mathrm{C}} = m_{^{32}\mathrm{S}}$, and $m'_{\mathrm{C}} = m_{^{34}\mathrm{S}}$

$$m = (15.9949 + 12.0000 + 31.9721)\,\mathrm{u} = 59.9670\,\mathrm{u}$$

$$m' = (15.9949 + 12.0000 + 33.9679)\,\mathrm{u} = 61.9628\,\mathrm{u}$$

$$\begin{aligned} R^2 &= \frac{(33.9679\,\mathrm{u}) \times (8.3101 \times 10^{-19}\,\mathrm{u\,m^2}) \times (59.9670\,\mathrm{u})}{(12.000\,\mathrm{u}) \times (15.9949\,\mathrm{u}) \times (33.9679\,\mathrm{u} - 31.9721\,\mathrm{u})} \\ &\quad - \frac{(31.9721\,\mathrm{u}) \times (8.5184 \times 10^{-19}\,\mathrm{u\,m^2}) \times (61.9628\,\mathrm{u})}{(12.000\,\mathrm{u}) \times (15.9949\,\mathrm{u}) \times (33.9679\,\mathrm{u} - 31.9721\,\mathrm{u})} \\ &= \frac{51.6446 \times 10^{-19}\,\mathrm{m^2}}{383.071} = 1.3482 \times 10^{-20}\,\mathrm{m^2} \end{aligned}$$

$$R = 1.161\bar{1} \times 10^{-10}\,\mathrm{m} = \boxed{116.1\,\mathrm{pm}} = R_{\mathrm{OC}}$$

Because the numerator of the expression for R^2 involves the difference between two rather large numbers of nearly the same magnitude, the number of significant figures in the answer for R is certainly no greater than 4. Having solved for R, either equation (a) or (b) above can be solved for R'. The result is

$$R' = 1.559 \times 10^{-10}\,\mathrm{m} = \boxed{155.9\,\mathrm{pm}} = R_{\mathrm{CS}}$$

E16.13(b) The wavenumber of a Stokes line in rotational Raman is

$$\tilde{\nu}_{\mathrm{Stokes}} = \tilde{\nu}_{\mathrm{i}} - 2B(2J + 3)\ [16.49a]$$

where J is the initial (lower) rotational state. So

$$\tilde{\nu}_{\mathrm{Stokes}} = 20\,623\,\mathrm{cm^{-1}} - 2(1.4457\,\mathrm{cm^{-1}}) \times [2(2) + 3] = \boxed{20\,603\,\mathrm{cm^{-1}}}$$

E16.14(b) The separation of lines is $4B$, so $B = \frac{1}{4} \times (3.5312\,\mathrm{cm^{-1}}) = 0.88280\,\mathrm{cm^{-1}}$

Then we use $R = \left(\dfrac{\hbar}{4\pi m_{\mathrm{eff}}cB}\right)^{1/2}$ [Exercise16.11(a)] with $m_{\text{eff}} = \frac{1}{2}m(^{19}\text{F}) = \frac{1}{2} \times (18.9984\,\text{u}) \times (1.6605 \times 10^{-27}\,\text{kg}\,\text{u}^{-1}) = 1.577\,34\overline{2} \times 10^{-26}\,\text{kg}$

$$R = \left(\frac{1.0546 \times 10^{-34}\,\text{J s}}{4\pi(1.577\,342 \times 10^{-26}\,\text{kg}) \times (2.998 \times 10^{10}\,\text{cm s}^{-1}) \times (0.88280\,\text{cm}^{-1})}\right)^{1/2}$$

$$= 1.4178\overline{5} \times 10^{-10}\,\text{m} = \boxed{141.78\,\text{pm}}$$

E16.15(b) Polar molecules show a pure rotational absorption spectrum. Therefore, select the polar molecules based on their well-known structures. Alternatively, determine the point groups of the molecules and use the rule that only molecules belonging to C_n, $C_{n\text{v}}$, and C_s may be polar, and in the case of C_n and $C_{n\text{v}}$, that dipole must lie along the rotation axis. Hence all are polar molecules.

Their point group symmetries are

(a) $H_2O,\ C_{2\text{v}}$, **(b)** $H_2O_2,\ C_2$, **(c)** $NH_3,\ C_{3\text{v}}$, **(d)** $N_2O,\ C_{\infty\text{v}}$

$\boxed{\text{All}}$ show a pure rotational spectrum.

E16.16(b) A molecule must be anisotropically polarizable to show a rotational Raman spectrum; all molecules except spherical rotors have this property. So $\boxed{CH_2Cl_2}$, $\boxed{CH_3CH_3}$, and $\boxed{N_2O}$ can display rotational Raman spectra; SF_6 cannot.

E16.17(b) The angular frequency is

$$\omega = \left(\frac{k}{m}\right)^{1/2} = 2\pi\nu \quad \text{so} \quad k = (2\pi\nu)^2 m = (2\pi)^2 \times (3.0\,\text{s}^{-1})^2 \times (2.0 \times 10^{-3}\,\text{kg})$$

$$k = \boxed{0.71\,\text{N m}^{-1}}$$

E16.18(b) $\omega = \left(\dfrac{k}{m_{\text{eff}}}\right)^{1/2} \qquad \omega' = \left(\dfrac{k}{m'_{\text{eff}}}\right)^{1/2}$ [prime $= {}^2\text{H}^{37}\text{Cl}$]

The force constant, k, is assumed to be the same for both molecules. The fractional difference is

$$\frac{\omega' - \omega}{\omega} = \frac{\left(\frac{k}{m'_{\text{eff}}}\right)^{1/2} - \left(\frac{k}{m_{\text{eff}}}\right)^{1/2}}{\left(\frac{k}{m_{\text{eff}}}\right)^{1/2}} = \frac{\left(\frac{1}{m'_{\text{eff}}}\right)^{1/2} - \left(\frac{1}{m_{\text{eff}}}\right)^{1/2}}{\left(\frac{1}{m_{\text{eff}}}\right)^{1/2}} = \left(\frac{m_{\text{eff}}}{m'_{\text{eff}}}\right)^{1/2} - 1$$

$$\frac{\omega' - \omega}{\omega} = \left(\frac{m_{\text{eff}}}{m'_{\text{eff}}}\right)^{1/2} - 1 = \left\{\frac{m_\text{H} m_\text{Cl}}{m_\text{H} + m_\text{Cl}} \times \frac{(m_{^2\text{H}} + m_{^{37}\text{Cl}})}{(m_{^2\text{H}} \cdot m_{^{37}\text{Cl}})}\right\}^{1/2} - 1$$

$$= \left\{\frac{(1.0078\,\text{u}) \times (34.9688\,\text{u})}{(1.0078\,\text{u}) + (34.9688\,\text{u})} \times \frac{(2.0140\,\text{u}) + (36.9651\,\text{u})}{(2.0140\,\text{u}) \times (36.9651\,\text{u})}\right\}^{1/2} - 1$$

$$= -0.284$$

Thus the difference is $\boxed{28.4 \text{ per cent}}$

E16.19(b) The fundamental vibrational frequency is

$$\omega = \left(\frac{k}{m_{\text{eff}}}\right)^{1/2} = 2\pi\nu = 2\pi c\tilde{\nu} \quad \text{so} \quad k = (2\pi c\tilde{\nu})^2 m_{\text{eff}}$$

We need the effective mass

$$m_{\text{eff}}^{-1} = m_1^{-1} + m_2^{-1} = (78.9183\,\text{u})^{-1} + (80.9163\,\text{u})^{-1} = 0.025\,029\,8\,\text{u}^{-1}$$

$$k = \frac{[2\pi(2.998 \times 10^{10}\,\text{cm s}^{-1}) \times (323.2\,\text{cm}^{-1})]^2 \times (1.66054 \times 10^{-27}\,\text{kg u}^{-1})}{0.025\,029\,8\,\text{u}^{-1}}$$

$$= \boxed{245.9\,\text{N m}^{-1}}$$

E16.20(b) The ratio of the population of the ground state (N_0) to the first excited state (N_1) is

$$\frac{N_0}{N_1} = \exp\left(\frac{-h\nu}{kT}\right) = \exp\left(\frac{-hc\tilde{\nu}}{kT}\right)$$

(a) $$\frac{N_0}{N_1} = \exp\left(\frac{-(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{10}\,\text{cm s}^{-1}) \times (321\,\text{cm}^{-1})}{(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (298\,\text{K})}\right) = \boxed{0.212}$$

(b) $$\frac{N_0}{N_1} = \exp\left(\frac{-(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^{10}\,\text{cm s}^{-1}) \times (321\,\text{cm}^{-1})}{(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (800\,\text{K})}\right) = \boxed{0.561}$$

E16.21(b) The relation between vibrational frequency and wavenumber is

$$\omega = \left(\frac{k}{m_{\text{eff}}}\right)^{1/2} = 2\pi\nu = 2\pi c\tilde{\nu} \quad \text{so} \quad \tilde{\nu} = \frac{1}{2\pi c}\left(\frac{k}{m_{\text{eff}}}\right)^{1/2} = \frac{\left(km_{\text{eff}}^{-1}\right)^{1/2}}{2\pi c}$$

The reduced masses of the hydrogen halides are very similar, but not identical

$$m_{\text{eff}}^{-1} = m_{\text{D}}^{-1} + m_{\text{X}}^{-1}$$

We assume that the force constants as calculated in Exercise 16.21(a) are identical for the deuterium halide and the hydrogen halide.

For DF

$$m_{\text{eff}}^{-1} = \frac{(2.0140\,\text{u})^{-1} + (18.9984\,\text{u})^{-1}}{1.66054 \times 10^{-27}\,\text{kg u}^{-1}} = 3.3071 \times 10^{26}\,\text{kg}^{-1}$$

$$\tilde{\nu} = \frac{\left\{(3.3071 \times 10^{26}\,\text{kg}^{-1}) \times (967.04\,\text{kg s}^{-2})\right\}^{1/2}}{2\pi(2.9979 \times 10^{10}\,\text{cm s}^{-1})} = \boxed{3002.3\,\text{cm}^{-1}}$$

For DCl

$$m_{\text{eff}}^{-1} = \frac{(2.0140\,\text{u})^{-1} + (34.9688\,\text{u})^{-1}}{1.66054 \times 10^{-27}\,\text{kg u}^{-1}} = 3.1624 \times 10^{26}\,\text{kg}^{-1}$$

$$\tilde{\nu} = \frac{\left\{(3.1624 \times 10^{26}\,\text{kg}^{-1}) \times (515.59\,\text{kg s}^{-2})\right\}^{1/2}}{2\pi(2.9979 \times 10^{10}\,\text{cm s}^{-1})} = \boxed{2143.7\,\text{cm}^{-1}}$$

For DBr

$$m_{\text{eff}}^{-1} = \frac{(2.0140\,\text{u})^{-1} + (80.9163\,\text{u})^{-1}}{1.66054 \times 10^{-27}\,\text{kg u}^{-1}} = 3.0646 \times 10^{26}\,\text{kg}^{-1}$$

$$\tilde{\nu} = \frac{\left\{(3.0646 \times 10^{26}\,\text{kg}^{-1}) \times (411.75\,\text{kg s}^{-2})\right\}^{1/2}}{2\pi(2.9979 \times 10^{10}\,\text{cm s}^{-1})} = \boxed{1885.8\,\text{cm}^{-1}}$$

For DI

$$m_{\text{eff}}^{-1} = \frac{(2.0140\,\text{u})^{-1} + (126.9045\,\text{u})^{-1}}{1.66054 \times 10^{-27}\,\text{kg u}^{-1}} = 3.0376 \times 10^{26}\,\text{kg}^{-1}$$

$$\tilde{\nu} = \frac{\left\{(3.0376 \times 10^{26}\,\text{kg}^{-1}) \times (314.21\,\text{kg s}^{-2})\right\}^{1/2}}{2\pi(2.9979 \times 10^{10}\,\text{cm s}^{-1})} = \boxed{1640.1\,\text{cm}^{-1}}$$

E16.22(b) Data on three transitions are provided. Only two are necessary to obtain the value of $\tilde{\nu}$ and x_e. The third datum can then be used to check the accuracy of the calculated values.

$$\Delta G(v = 1 \leftarrow 0) = \tilde{\nu} - 2\tilde{\nu}x_e = 2345.15\,\text{cm}^{-1} \;[16.64]$$

$$\Delta G(v = 2 \leftarrow 0) = 2\tilde{\nu} - 6\tilde{\nu}x_e = 4661.40\,\text{cm}^{-1} \;[16.65]$$

Multiply the first equation by 3, then subtract the second.

$$\tilde{\nu} = (3) \times (2345.15\,\text{cm}^{-1}) - (4661.40\,\text{cm}^{-1}) = \boxed{2374.05\,\text{cm}^{-1}}$$

Then from the first equation

$$x_e = \frac{\tilde{\nu} - 2345.15\,\text{cm}^{-1}}{2\tilde{\nu}} = \frac{(2374.05 - 2345.15)\,\text{cm}^{-1}}{(2) \times (2374.05\,\text{cm}^{-1})} = \boxed{6.087 \times 10^{-3}}$$

x_e data are usually reported as $x_e\tilde{\nu}$ which is

$$x_e\tilde{\nu} = 14.45\,\text{cm}^{-1}$$

$$\Delta G(v = 3 \leftarrow 0) = 3\tilde{\nu} - 12\nu x_e = (3) \times (2374.05\,\text{cm}^{-1}) - (12) \times (14.45\,\text{cm}^{-1})$$

$$= 6948.74\,\text{cm}^{-1}$$

which is close to the experimental value.

E16.23(b) $\Delta G_{v+1/2} = \tilde{\nu} - 2(v + 1)x_e\tilde{\nu}$ [16.64] where $\Delta G_{v+1/2} = G(v + 1) - G(v)$

Therefore, since

$$\Delta G_{v+1/2} = (1 - 2x_e)\tilde{\nu} - 2vx_e\tilde{\nu}$$

a plot of $\Delta G_{v+1/2}$ against v should give a straight line which gives $(1 - 2x_e)\tilde{\nu}$ from the intercept at $v = 0$ and $-2x_e\tilde{\nu}$ from the slope. We draw up the following table

v	0	1	2	3	4
$G(v)/\text{cm}^{-1}$	1144.83	3374.90	5525.51	7596.66	9588.35
$\Delta G_{v+1/2}/\text{cm}^{-1}$	2230.07	2150.61	2071.15	1991.69	

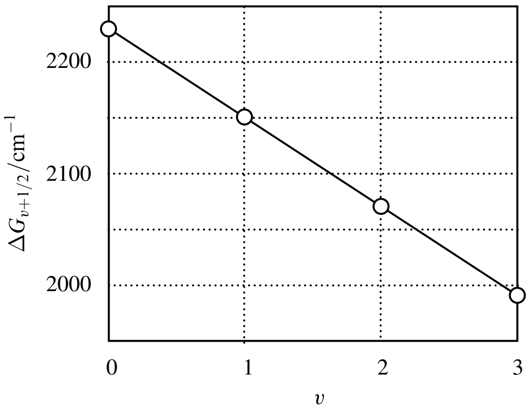


Figure 16.1

The points are plotted in Fig. 16.1.

The intercept lies at 2230.51 and the slope $= -79.65\,\mathrm{cm}^{-1}$; hence $x_e\tilde{\nu} = 39.83\,\mathrm{cm}^{-1}$.

Since $\tilde{\nu} - 2x_e\tilde{\nu} = 2230.51\,\mathrm{cm}^{-1}$, it follows that $\tilde{\nu} = 2310.16\,\mathrm{cm}^{-1}$.

The dissociation energy may be obtained by assuming that the molecule is described by a Morse potential and that the constant D_e in the expression for the potential is an adequate first approximation for it. Then

$$D_e = \frac{\tilde{\nu}}{4x_e}[16.62] = \frac{\tilde{\nu}^2}{4x_e\tilde{\nu}} = \frac{(2310.16\,\mathrm{cm}^{-1})^2}{(4)\times(39.83\,\mathrm{cm}^{-1})} = 33.50\times10^3\,\mathrm{cm}^{-1} = 4.15\,\mathrm{eV}$$

However, the depth of the potential well D_e differs from D_0, the dissociation energy of the bond, by the zero-point energy; hence

$$D_0 = D_e - \tfrac{1}{2}\tilde{\nu} = (33.50\times10^3\,\mathrm{cm}^{-1}) - \left(\tfrac{1}{2}\right)\times(2310.16\,\mathrm{cm}^{-1})$$

$$= \boxed{3.235\times10^4\,\mathrm{cm}^{-1}} = \boxed{4.01\,\mathrm{eV}}$$

E16.24(b) The wavenumber of an R-branch IR transition is

$$\tilde{\nu}_R = \tilde{\nu} + 2B(J+1)\ [16.69c]$$

where J is the initial (lower) rotational state. So

$$\tilde{\nu}_R = 2308.09\,\mathrm{cm}^{-1} + 2(6.511\,\mathrm{cm}^{-1})\times(2+1) = \boxed{2347.16\,\mathrm{cm}^{-1}}$$

E16.25(b) See Section 16.10. Select those molecules in which a vibration gives rise to a change in dipole moment. It is helpful to write down the structural formulas of the compounds. The infrared active compounds are

(a) CH_3CH_3 **(b)** $CH_4(g)$ **(c)** CH_3Cl

Comment. A more powerful method for determining infrared activity based on symmetry considerations is described in Section 16.15.

E16.26(b) A nonlinear molecule has $3N - 6$ normal modes of vibration, where N is the number of atoms in the molecule; a linear molecule has $3N - 5$.

(a) C_6H_6 has $3(12) - 6 = \boxed{30}$ normal modes.

(b) $C_6H_6CH_3$ has $3(16) - 6 = \boxed{42}$ normal modes.

(c) HC≡C—C≡CH is linear; it has $3(6) - 5 = \boxed{13}$ normal modes.

E16.27(b) **(a)** A planar AB_3 molecule belongs to the D_{3h} group. Its four atoms have a total of 12 displacements, of which 6 are vibrations. We determine the symmetry species of the vibrations by first determining the characters of the reducible representation of the molecule formed from all 12 displacements and then subtracting from these characters the characters corresponding to translation and rotation. This latter information is directly available in the character table for the group D_{3h}. The resulting set of characters are the characters of the reducible representation of the vibrations. This representation can be reduced to the symmetry species of the vibrations by inspection or by use of the little orthogonality theorem.

D_{3h}	E	σ_h	$2C_3$	$2S_3$	$3C_2'$	$3\sigma_v$
χ (translation)	3	1	0	−2	−1	1
Unmoved atoms	4	4	1	1	2	2
χ (total, product)	12	4	0	−2	−2	2
χ (rotation)	3	−1	0	2	−1	−1
χ (vibration)	6	4	0	−2	0	2

χ (vibration) corresponds to $A_1' + A_2'' + 2E'$.

Again referring to the character table of D_{3h}, we see that E' corresponds to x and y, A_2'' to z; hence $\boxed{A_2'' \text{ and } E' \text{ are IR active.}}$ We also see from the character table that E' and A_1' correspond to the quadratic terms; hence $\boxed{A_1' \text{ and } E' \text{ are Raman active}}$.

(b) A trigonal pyramidal AB_3 molecule belongs to the group C_{3v}. In a manner similar to the analysis in part (a) we obtain

C_{3v}	E	$2C_3$	$3\sigma_v$
χ (total)	12	0	2
χ (vibration)	6	−2	2

χ (vibration) corresponds to $2A_1 + 2E$. We see from the character table that $\boxed{A_1 \text{ and } E}$ are IR active and that $\boxed{A_1 + E}$ are also Raman active. Thus all modes are observable in both the IR and the Raman spectra.

E16.28(b) **(b)** The boat-like bending of a benzene ring clearly changes the dipole moment of the ring, for the moving of the C—H bonds out of the plane will give rise to a non-cancelling component of their dipole moments. So the vibration is $\boxed{\text{IR active}}$.

(a) Since benzene has a centre of inversion, the exclusion rule applies: a mode which is IR active (such as this one) must be $\boxed{\text{Raman inactive}}$.

E16.29(b) The displacements span $A_{1g} + A_{1u} + A_{2g} + 2E_{1u} + E_{1g}$. The rotations R_x and R_y span E_{1g}, and the translations span $E_{1u} + A_{1u}$. So the vibrations span $\boxed{A_{1g} + A_{2g} + E_{1u}}$

Solutions to problems

Solutions to numerical problems

P16.1 Use the energy density expression in terms of wavelengths (eqn 11.5)

$$E = \rho\, \mathrm{d}\lambda \quad \text{where } \rho = \frac{8\pi hc}{\lambda^5(\mathrm{e}^{hc/\lambda kT} - 1)}.$$

Evaluate

$$E = \int_{400\times 10^{-9}\,\mathrm{m}}^{700\times 10^{-9}\,\mathrm{m}} \frac{8\pi hc}{\lambda^5(\mathrm{e}^{hc/\lambda kT} - 1)}\mathrm{d}\lambda$$

at three different temperatures. Compare those results to the classical, Rayleigh–Jeans expression (eqn 11.3):

$$E_{\text{class}} = \rho_{\text{class}}\mathrm{d}\lambda \quad \text{where } \rho_{\text{class}} = \frac{8\pi kT}{\lambda^4},$$

$$\text{so} \quad E_{\text{class}} = \int_{400\times 10^{-9}\,\mathrm{m}}^{700\times 10^{-9}\,\mathrm{m}} \frac{8\pi kT}{\lambda^4}\mathrm{d}\lambda = -\frac{8\pi kT}{3\lambda^3}\bigg|_{400\times 10^{-9}\mathrm{m}}^{700\times 10^{-9}\mathrm{m}}.$$

T/K	$E/\mathrm{J\,m^{-3}}$	$E_{\text{class}}/\mathrm{J\,m^{-3}}$
(a) 1500	2.136×10^{-6}	2.206
(b) 2500	9.884×10^{-4}	3.676
(c) 5800	3.151×10^{-1}	8.528

The classical values are very different from the accurate Planck values! Try integrating the expressions over 400–700 μm or mm to see that the expressions agree reasonably well at longer wavelengths.

P16.3 On the assumption that every collision deactivates the molecule we may write

$$\tau = \frac{1}{z} = \boxed{\frac{kT}{4\sigma p}\left(\frac{\pi m}{kT}\right)^{1/2}}$$

For HCl, with $m \approx 36\,\mathrm{u}$,

$$\tau \approx \left(\frac{(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K})}{(4) \times (0.30 \times 10^{-18}\,\mathrm{m^2}) \times (1.013 \times 10^5\,\mathrm{Pa})}\right) \times \left(\frac{\pi \times (36) \times (1.661 \times 10^{-27}\,\mathrm{kg})}{(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K})}\right)^{1/2}$$

$$\approx 2.3 \times 10^{-10}\,\mathrm{s}$$

$$\delta E \approx h\delta\nu = \frac{\hbar}{\tau}\ [24]$$

The width of the collision-broadened line is therefore approximately

$$\delta\nu \approx \frac{1}{2\pi\tau} = \frac{1}{(2\pi)\times(2.3\times10^{-10}\,\mathrm{s})} \approx \boxed{700\,\mathrm{MHz}}$$

The Doppler width is approximately 1.3 MHz (Problem 16.2). Since the collision width is proportional to p [$\delta\nu \propto 1/\tau$ and $\tau \propto 1/p$], the pressure must be reduced by a factor of about $\frac{1.3}{700} = 0.002$ before Doppler broadening begins to dominate collision broadening. Hence, the pressure must be reduced to below $(0.002)\times(760\,\mathrm{Torr}) = \boxed{1\,\mathrm{Torr}}$

P16.5 $B = \dfrac{\hbar}{4\pi cI}$ [16.31]; $I = m_{\mathrm{eff}}R^2$; $R^2 = \dfrac{\hbar}{4\pi c m_{\mathrm{eff}}B}$

$$m_{\mathrm{eff}} = \frac{m_{\mathrm{C}}m_{\mathrm{O}}}{m_{\mathrm{C}}+m_{\mathrm{O}}} = \left(\frac{(12.0000\,\mathrm{u})\times(15.9949\,\mathrm{u})}{(12.0000\,\mathrm{u})+(15.9949\,\mathrm{u})}\right)\times(1.66054\times10^{-27}\,\mathrm{kg\,u^{-1}})$$
$$= 1.13852\times10^{-26}\,\mathrm{kg}$$

$$\frac{\hbar}{4\pi c} = 2.79932\times10^{-44}\,\mathrm{kg\,m}$$

$$R_0^2 = \frac{2.79932\times10^{-44}\,\mathrm{kg\,m}}{(1.13852\times10^{-26}\,\mathrm{kg})\times(1.9314\times10^{2}\,\mathrm{m^{-1}})} = 1.2730\overline{3}\times10^{-20}\,\mathrm{m^2}$$

$$R_0 = 1.1283\times10^{-10}\,\mathrm{m} = \boxed{112.83\,\mathrm{pm}}$$

$$R_1^2 = \frac{2.79932\times10^{-44}\,\mathrm{kg\,m}}{(1.13852\times10^{-26}\,\mathrm{kg})\times(1.6116\times10^{2}\,\mathrm{m^{-1}})} = 1.52565\times10^{-20}\,\mathrm{m^2}$$

$$R_1 = 1.2352\times10^{-10}\,\mathrm{m} = \boxed{123.52\,\mathrm{pm}}$$

Comment. The change in internuclear distance is roughly 10 per cent, indicating that the rotations and vibrations of molecules are strongly coupled and that it is an oversimplification to consider them independently of each other.

P16.8 $\tilde{\nu} = 2B(J+1)[16.44] = 2B$

Hence, $B(^1\mathrm{HCl}) = 10.4392\,\mathrm{cm^{-1}}$, $B(^2\mathrm{HCl}) = 5.3920\,\mathrm{cm^{-1}}$

$$B = \frac{\hbar}{4\pi cI}\ [30] \qquad I = m_{\mathrm{eff}}R^2\ [\text{Table 16.1}]$$

$$R^2 = \frac{\hbar}{4\pi c m_{\mathrm{eff}}B} \qquad \frac{\hbar}{4\pi c} = 2.79927\times10^{-44}\,\mathrm{kg\,m}$$

$$m_{\mathrm{eff}}(\mathrm{HCl}) = \left(\frac{(1.007825\,\mathrm{u})\times(34.96885\,\mathrm{u})}{(1.007825\,\mathrm{u})+(34.96885\,\mathrm{u})}\right)\times(1.66054\times10^{-27}\,\mathrm{kg\,u^{-1}})$$
$$= 1.62665\times10^{-27}\,\mathrm{kg}$$

$$m_{\mathrm{eff}}(\mathrm{DCl}) = \left(\frac{(2.0140\,\mathrm{u})\times(34.96885\,\mathrm{u})}{(2.0140\,\mathrm{u})+(34.96885\,\mathrm{u})}\right)\times(1.66054\times10^{-27}\,\mathrm{kg\,u^{-1}})$$
$$= 3.1622\times10^{-27}\,\mathrm{kg}$$

$$R^2(\mathrm{HCl}) = \frac{2.79927\times10^{-44}\,\mathrm{kg\,m}}{(1.62665\times10^{-27}\,\mathrm{kg})\times(1.04392\times10^{3}\,\mathrm{m^{-1}})} = 1.64848\times10^{-20}\,\mathrm{m^2}$$

$$R(\mathrm{HCl}) = 1.28393\times10^{-10}\,\mathrm{m} = \boxed{128.393\,\mathrm{pm}}$$

$$R^2(^2\mathrm{HCl}) = \frac{2.79927 \times 10^{-44}\,\mathrm{kg\,m}}{(3.1622 \times 10^{-27}\,\mathrm{kg}) \times (5.3920 \times 10^2\,\mathrm{m^{-1}})} = 1.6417 \times 10^{-20}\,\mathrm{m^2}$$

$$R(^2\mathrm{HCl}) = 1.2813 \times 10^{-10}\,\mathrm{m} = \boxed{128.13\,\mathrm{pm}}$$

The difference between these values of R is small but measurable.

Comment. Since the effects of centrifugal distortion have not been taken into account, the number of significant figures in the calculated values of R above should be no greater than 4, despite the fact that the data is precise to 6 figures.

P16.10 From the equation for a linear rotor in Table 16.1 it is possible to show that $I_\mathrm{m} = m_\mathrm{a}m_\mathrm{c}(R + R')^2 + m_\mathrm{a}m_\mathrm{b}R^2 + m_\mathrm{b}m_\mathrm{c}R'^2$.

Thus, $$I(^{16}\mathrm{O}^{12}\mathrm{C}^{32}\mathrm{S}) = \left(\frac{m(^{16}\mathrm{O})m(^{32}\mathrm{S})}{m(^{16}\mathrm{O}^{12}\mathrm{C}^{32}\mathrm{S}}\right) \times (R + R')^2 + \left(\frac{m(^{12}\mathrm{C})\{m(^{16}\mathrm{O})R^2 + m(^{32}\mathrm{S})R'^2\}}{m(^{16}\mathrm{O}^{12}\mathrm{C}^{32}\mathrm{S})}\right)$$

$$I(^{16}\mathrm{O}^{12}\mathrm{C}^{34}\mathrm{S}) = \left(\frac{m(^{16}\mathrm{O})m(^{34}\mathrm{S})}{m(^{16}\mathrm{O}^{12}\mathrm{C}^{34}\mathrm{S}}\right) \times (R + R')^2 + \left(\frac{m(^{12}\mathrm{C})\{m(^{16}\mathrm{O})R^2 + m(^{34}\mathrm{S})R'^2\}}{m(^{16}\mathrm{O}^{12}\mathrm{C}^{34}\mathrm{S})}\right)$$

$m(^{16}\mathrm{O}) = 15.9949\,\mathrm{u}$, $m(^{12}\mathrm{C}) = 12.0000\,\mathrm{u}$, $m(^{32}\mathrm{S}) = 31.9721\,\mathrm{u}$, and $m(^{34}\mathrm{S}) = 33.9679\,\mathrm{u}$. Hence,

$$\begin{aligned} I(^{16}\mathrm{O}^{12}\mathrm{C}^{32}\mathrm{S})/\mathrm{u} &= (8.5279) \times (R + R')^2 + (0.20011) \times (15.9949R^2 + 31.9721R'^2) \\ I(^{16}\mathrm{O}^{12}\mathrm{C}^{34}\mathrm{S})/\mathrm{u} &= (8.7684) \times (R + R')^2 + (0.19366) \times (15.9949R^2 + 33.9679R'^2) \end{aligned}$$

The spectral data provides the experimental values of the moments of inertia based on the relation $\nu = 2c\,B(J + 1)$ [16.44] with $B = \dfrac{\hbar}{4\pi cI}$ [16.31]. These values are set equal to the above equations which are then solved for R and R'. The mean values of I obtained from the data are

$$\begin{aligned} I(^{16}\mathrm{O}^{12}\mathrm{C}^{32}\mathrm{S}) &= 1.37998 \times 10^{-45}\,\mathrm{kg\,m^2} \\ I(^{16}\mathrm{O}^{12}\mathrm{C}^{34}\mathrm{S}) &= 1.41460 \times 10^{-45}\,\mathrm{kg\,m^2} \end{aligned}$$

Therefore, after conversion of the atomic mass units to kg, the equations we must solve are

$$\begin{aligned} 1.37998 \times 10^{-45}\,\mathrm{m^2} &= (1.4161 \times 10^{-26}) \times (R + R')^2 + (5.3150 \times 10^{-27}R^2) \\ &\quad + (1.0624 \times 10^{-26}R'^2) \\ 1.41460 \times 10^{-45}\,\mathrm{m^2} &= (1.4560 \times 10^{-26}) \times (R + R')^2 + (5.1437 \times 10^{-27}R^2) \\ &\quad + (1.0923 \times 10^{-26}R'^2) \end{aligned}$$

These two equations may be solved for R and R'. They are tedious to solve, but straightforward. Exercise 16.6(b) illustrates the details of the solution. The outcome is $R = \boxed{116.28\,\mathrm{pm}}$ and $R' = \boxed{155.97\,\mathrm{pm}}$. These values may be checked by direct substitution into the equations.

Comment. The starting point of this problem is the actual experimental data on spectral line positions. Exercise 16.12(b) is similar to this problem; its starting points is, however, given values of the rotational constants B, which were themselves obtained from the spectral line positions. So the results for R and R' are expected to be essentially identical and they are.

Question. What are the rotational constants calculated from the data on the positions of the absorption lines?

P16.12 The wavenumbers of the transitions with $\Delta v = +1$ are

$$\Delta G_{v+1/2} = \tilde{\nu} - 2(v+1)x_e\tilde{\nu} \text{ [16.64]} \quad \text{and} \quad D_e = \frac{\tilde{\nu}^2}{4x_e\tilde{\nu}} \text{ [16.62]}$$

A plot of $\Delta G_{v+1/2}$ against $v+1$ should give a straight line with intercept $\tilde{\nu}$ at $v+1=0$ and slope $-2x_e\tilde{\nu}$.

Draw up the following table

$v+1$	1	2	3
$\Delta G_{v+1/2}/\text{cm}^{-1}$	284.50	283.00	281.50

The points are plotted in Fig. 16.2.

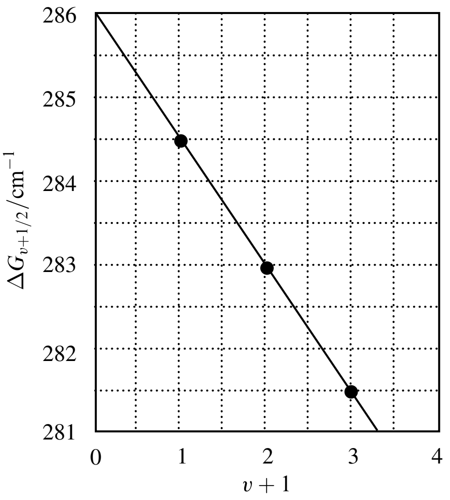


Figure 16.2

The intercept is at 286.0, so $\tilde{\nu} = 286\,\text{cm}^{-1}$. The slope is -1.50, so $x_e\tilde{\nu} = 0.750\,\text{cm}^{-1}$. It follows that

$$D_e = \frac{(286\,\text{cm}^{-1})^2}{(4)\times(0.750\,\text{cm}^{-1})} = 27300\,\text{cm}^{-1}, \quad \text{or} \quad 3.38\,\text{eV}$$

The zero-point level lies at $\boxed{142.81\,\text{cm}^{-1}}$ and so $D_0 = \boxed{3.36\,\text{eV}}$. Since

$$m_{\text{eff}} = \frac{(22.99)\times(126.90)}{(22.99)+(126.90)}\,\text{u} = 19.46\overline{4}\,\text{u}$$

the force constant of the molecule is

$$\begin{aligned} k &= 4\pi^2 m_{\text{eff}} c^2 \tilde{\nu}^2 \text{ [Exercise 16.19(a)]} \\ &= (4\pi^2)\times(19.46\overline{4})\times(1.6605\times10^{-27}\,\text{kg})\times[(2.998\times10^{10}\,\text{cm s}^{-1})\times(286\,\text{cm}^{-1})]^2 \\ &= \boxed{93.8\,\text{N m}^{-1}} \end{aligned}$$

P16.14 The set of peaks to the left of center are the P branch, those to the right are the R branch. Within the rigid rotor approximation the two sets are separated by $4B$. The effects of the interactions between vibration and rotation and of centrifugal distortion are least important for transitions with small J values hence the separation between the peaks immediately to the left and right of center will give good approximate values of B and bond length.

(a) $\tilde{\nu}_{\mathrm{Q}}(J) = \tilde{\nu}[46\text{ b}] = \boxed{2143.26\,\mathrm{cm}^{-1}}$

(b) The zero-point energy is $\frac{1}{2}\tilde{\nu} = 1071.63\,\mathrm{cm}^{-1}$. The molar zero-point energy in $\mathrm{J\,mol}^{-1}$ is

$$\begin{aligned} N_{\mathrm{A}}hc \times (1071.63\,\mathrm{cm}^{-1}) &= N_{\mathrm{A}}hc \times (1.07163 \times 10^{5}\,\mathrm{m}^{-1}) \\ &= 1.28195 \times 10^{4}\,\mathrm{J\,mol}^{-1} = \boxed{12.8195\,\mathrm{kJ\,mol}^{-1}} \end{aligned}$$

(c) $k = 4\pi^2\mu c^2\tilde{\nu}^2$

$$\begin{aligned} \mu(^{12}\mathrm{C}^{16}\mathrm{O}) &= \frac{m_{\mathrm{C}}m_{\mathrm{O}}}{m_{\mathrm{C}}+m_{\mathrm{O}}} = \left(\frac{(12.0000\,\mathrm{u}) \times (15.9949\,\mathrm{u})}{(12.0000\,\mathrm{u}) + (15.9949\,\mathrm{u})}\right) \times (1.66054 \times 10^{-27}\,\mathrm{kg\,u}^{-1}) \\ &= 1.13852 \times 10^{-26}\,\mathrm{kg} \end{aligned}$$

$$k = 4\pi^2c^2 \times (1.13852 \times 10^{-26}\,\mathrm{kg}) \times (2.14326 \times 10^{5}\,\mathrm{m}^{-1})^2 = \boxed{1.85563 \times 10^{3}\,\mathrm{N\,m}^{-1}}$$

(d) $4B \approx 7.655\,\mathrm{cm}^{-1}$

$B \approx \boxed{1.91\,\mathrm{cm}^{-1}}$ [4 significant figures not justified]

(e) $$B = \frac{\hbar}{4\pi cI}[16.31] = \frac{\hbar}{4\pi c\mu R^2}\ [\text{Table 16.1}]$$

$$R^2\frac{\hbar}{4\pi c\mu B} = \frac{\hbar}{(4\pi c) \times (1.13852 \times 10^{-26}\,\mathrm{kg}) \times (191\,\mathrm{m}^{-1})} = 1.28\bar{7} \times 10^{-20}\,\mathrm{m}^2$$

$R = 1.13 \times 10^{-10}\,\mathrm{m} = \boxed{113\,\mathrm{pm}}$

P16.15 $D_0 = D_{\mathrm{e}} - \tilde{\nu}'$ with $\tilde{\nu}' = \frac{1}{2}\tilde{\nu} - \frac{1}{4}x_{\mathrm{e}}\tilde{\nu}$ [Section 16.11]

(a) $$^{1}\mathrm{HCl}\text{: } \tilde{\nu}' = \left\{(1494.9) - \left(\tfrac{1}{4}\right) \times (52.05)\right\}\,\mathrm{cm}^{-1} = 1481.8\,\mathrm{cm}^{-1}, \quad \text{or} \quad 0.184\,\mathrm{eV}$$

Hence, $D_0 = 5.33 - 0.18 = \boxed{5.15\,\mathrm{eV}}$

(b) $^{2}\mathrm{HCl}$: $\dfrac{2m_{\mathrm{eff}}\omega x_{\mathrm{e}}}{\hbar} = a^2$ [16.62], so $\tilde{\nu}x_{\mathrm{e}} \propto \dfrac{1}{m_{\mathrm{eff}}}$ as a is a constant. We also have $D_{\mathrm{e}} = \dfrac{\tilde{\nu}^2}{4x_{\mathrm{e}}\tilde{\nu}}$ [Exercise 16.23(a)]; so $\tilde{\nu}^2 \propto \dfrac{1}{m_{\mathrm{eff}}}$, implying $\tilde{\nu} \propto \dfrac{1}{m_{\mathrm{eff}}^{1/2}}$. Reduced masses were calculated in Exercises 16.21(a) and 16.21(b), and we can write

$$\tilde{\nu}(^{2}\mathrm{HCl}) = \left(\frac{m_{\mathrm{eff}}(^{1}\mathrm{HCl})}{m_{\mathrm{eff}}(^{2}\mathrm{HCl})}\right)^{1/2} \times \tilde{\nu}(^{1}\mathrm{HCl}) = (0.7172) \times (2989.7\,\mathrm{cm}^{-1}) = 2144.2\,\mathrm{cm}^{-1}$$

$$x_{\mathrm{e}}\tilde{\nu}(^{2}\mathrm{HCl}) = \left(\frac{m_{\mathrm{eff}}(^{1}\mathrm{HCl})}{m_{\mathrm{eff}}(^{2}\mathrm{HCl})}\right) \times x_{\mathrm{e}}\tilde{\nu}(^{1}\mathrm{HCl}) = (0.5144) \times (52.05\,\mathrm{cm}^{-1}) = 26.77\,\mathrm{cm}^{-1}$$

$$\tilde{\nu}'(^{2}\mathrm{HCl}) = \left(\tfrac{1}{2}\right) \times (2144.2) - \left(\tfrac{1}{4}\right) \times (26.77\,\mathrm{cm}^{-1}) = 1065.4\,\mathrm{cm}^{-1}, \quad 0.132\,\mathrm{eV}$$

Hence, $D_0(^{2}\mathrm{HCl}) = (5.33 - 0.132)\,\mathrm{eV} = \boxed{5.20\,\mathrm{eV}}$

P16.19 **(a)** Vibrational wavenumbers ($\tilde{\nu}/\text{cm}^{-1}$) computed by PC Spartan Pro$^{\text{TM}}$ at several levels of theory are tabulated below, along with experimental values:

	A_1	A_1	B_2
Semi-empirical PM3	412	801	896
SCF 6-316G**	592	1359	1569
Density functional	502	1152	1359
Experimental	525	1151	1336

The vibrational modes are shown graphically below.

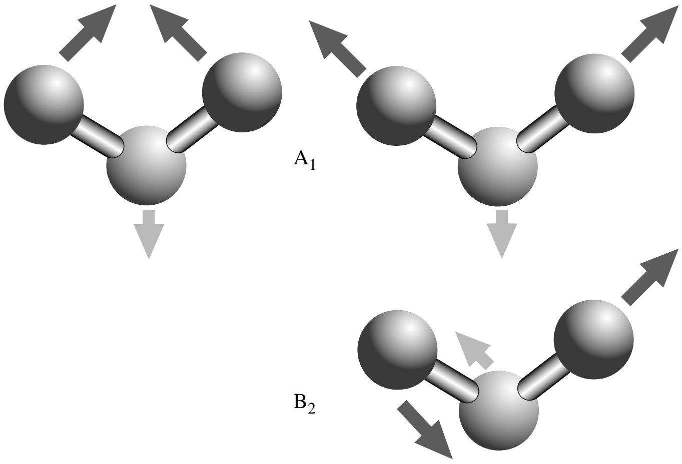


Figure 16.3

(b) The wavenumbers computed by density functional theory agree quite well with experiment. Agreement of the semi-empirical and SCF values with experiment is not so good. In this molecule, experimental wavenumbers can be correlated rather easily to computed vibrational modes even where the experimental and computed wavenumbers disagree substantially. Often, as in this case, computational methods that do a poor job of computing absolute transition wavenumbers still put transitions in proper order by wavenumber. That is, the modeling software systematically overestimates (as in this SCF computation) or underestimates (as in this semi-empirical computation) the wavenumbers, thus keeping them in the correct order. Group theory is another aid in the assignment of tansitions: it can classify modes as forbidden, allowed only in particular polarizations, etc. Also, visual examination of the modes of motion can help to classify many modes as predominantly bond-stretching, bond-bending, or internal rotation; these different modes of vibration can be correlated to quite different ranges of wavenumbers (stretches highest, especially stretches involving hydrogen atoms, and internal rotations lowest.).

P16.21 Summarize the six observed vibrations according to their wavenumbers ($\tilde{\nu}/\text{cm}^{-1}$):

IR	870	1370	2869	3417
Raman	877	1408	1435	3407.

(a) If H_2O_2 were linear, it would have $3N - 5 = \boxed{7}$ vibrational modes.

(b) Follow the flow chart in Fig. 15.14. Structure **2** is not linear, there is only one C_n axis (a C_2), and there is a σ_h; the point group is $\boxed{C_{2h}}$. Structure **3** is not linear, there is only one C_n axis (a C_2), no σ_h, but two σ_v; the point group is $\boxed{C_{2v}}$. Structure **4** is not linear, there is only one C_n axis (a C_2), no σ_h, no σ_v; the point group is $\boxed{C_2}$.

(c) The exclusion rule applies to structure **2** because it has a center of inversion: no vibrational modes can be both IR and Raman active. So structure **2** is inconsistent with observation. The vibrational modes of structure **3** span $3A_1 + A_2 + 2B_2$. (The full basis of 12 cartesian coordinates spans $4A_1 + 2A_2 + 2B_1 + 4B_2$; remove translations and rotations.) The C_{2v} character table says that five of these modes are IR active ($3A_1 + 2B_2$) and all are Raman active. All of the modes of structure **4** are both IR and Raman active. (A look at the character table shows that both symmetry species are IR and Raman active, so determining the symmetry species of the normal modes does not help here.) Both structures **3** and **4** have more active modes than were observed. This is consistent with the observations. After all, group theory can only tell us whether the transition moment *must* be zero by symmetry; it does not tell us whether the transition moment is sufficiently strong to be observed under experimental conditions.

Solutions to theoretical problems

P16.22 The centre of mass of a diatomic molecule lies at a distance x from atom A and is such that the masses on either side of it balance

$$m_A x = m_B(R - x)$$

and hence it is at

$$x = \frac{m_B}{m}R \quad m = m_A + m_B$$

The moment of inertia of the molecule is

$$I = m_A x^2 + m_B(R-x)^2[26] = \frac{m_A m_B^2 R^2}{m^2} + \frac{m_B m_A^2 R^2}{m^2} = \frac{m_A m_B}{m}R^2$$

$$= \boxed{m_{\text{eff}} R^2} \quad \text{since } m_{\text{eff}} = \frac{m_A m_B}{m_A + m_B}$$

P16.23 Because the centrifugal force and the restoring force balance,

$$k(r_c - r_e) = \mu\omega^2 r_c,$$

we can solve for the distorted bond length as a function of the equilibrium bond length:

$$r_c = \frac{r_e}{1 - \mu\omega^2/k}$$

Classically, then, the energy would be the rotational energy plus the energy of the stretched bond:

$$E = \frac{J^2}{2I} + \frac{k(r_c - r_e)^2}{2} = \frac{J^2}{2I} + \frac{k^2(r_c - r_e)^2}{2k} = \frac{J^2}{2I} + \frac{(\mu\omega^2 r_c)^2}{2k}.$$

How is the energy different form the rigid-rotor energy? Besides the energy of stretching of the bond, the larger moment of inertia alters the strictly rotational piece of the energy. Substitute μr_c^2 for I and substitute for r_c in terms of r_e throughtout:

So $$E = \frac{J^2(1 - \mu\omega^2/k)^2}{2\mu r_e{}^2} + \frac{\mu^2\omega^4 r_e{}^2}{2k(1 - \mu\omega^2/k)^2}.$$

Assuming that $\mu\omega^2/k$ is small (a reasonable assumption for most molecules), we can expand the expression and discard squares or higher powers of $\mu\omega^2/k$:

$$E \approx \frac{J^2(1-2\mu\omega^2/k)}{2\mu r_e{}^2} + \frac{\mu^2\omega^4 r_e^2}{2k}.$$

(Note that the entire second term has a factor of $\mu\omega^2/k$ even before squaring and expanding the denominator, so we discard all terms of that expansion after the first.) Begin to clean up the expression by using classical definitions of angular momentum:

$$J = I\omega = \mu r^2\omega \quad \text{so} \quad \omega = J/\mu r_e{}^2,$$

which allows us to substitute expressions involving J for all ωs:

$$E \approx \frac{J^2}{2\mu r_e{}^2} - \frac{J^4}{\mu^2 r_e{}^6 k} + \frac{J^4}{2\mu^2 r_e{}^6 k}.$$

(At the same time, we have expanded the first term, part of which we can now combine with the last term.) Continue to clean up the expression by substituting I/μ for r^2, and then carry the expression over to its quantum mechanical equivalent by substituting $J(J+1)\hbar^2$ for J^2:

$$E \approx \frac{J^2}{2I} - \frac{J^4\mu}{2I^3k} \quad \Rightarrow \quad E \approx \frac{J(J+1)\hbar^2}{2I} - \frac{J^2(J+1)^2\hbar^4\mu}{2I^3k}.$$

Dividing by hc gives the rotational term, $F(J)$:

$$F(J) \approx \frac{J(J+1)\hbar^2}{2hcI} - \frac{J^2(J+1)^2\hbar^4\mu}{2hcI^3k} = \frac{J(J+1)\hbar}{4\pi cI} - \frac{J^2(J+1)^2\hbar^3\mu}{4\pi cI^3k},$$

where we have used $\hbar = h/2\pi$ to eliminate a common divisor of h. Now use the definition of the rotational constant,

$$B = \frac{\hbar}{4\pi cI} \quad \Rightarrow \quad F(J) \approx J(J+1)B - J^2(J+1)^2B^3\frac{16\pi^2c^2\mu}{k}.$$

Finally, use the relationship between the force constant and vibrational wavenumber:

$$\left(\frac{k}{\mu}\right)^{1/2} = \omega_{\text{vib}} = 2\pi\nu = 2\pi c\tilde{\nu} \quad \text{so} \quad \frac{\mu}{k} = \frac{1}{4\pi^2c^2\tilde{\nu}^2}$$

leaving $F(J) \approx BJ(J+1) - \dfrac{4B^3}{\tilde{\nu}^2}J^2(J+1)^2 = BJ(J+1) - DJ^2(J+1)^2$ where $\boxed{D = \dfrac{4B^3}{\tilde{\nu}^2}}$.

P16.26 $S(v,J) = \left(v+\frac{1}{2}\right)\tilde{\nu} + BJ(J+1)$ [16.68]

$$\Delta S_J^{\text{O}} = \tilde{\nu} - 2B(2J-1) \quad [\Delta v = 1, \Delta J = -2]$$

$$\Delta S_J^{\text{S}} = \tilde{\nu} + 2B(2J+3) \quad [\Delta v = 1, \Delta J = +2]$$

The transition of maximum intensity corresponds, approximately, to the transition with the most probable value of J, which was calculated in Problem 16.25

$$J_{\max} = \left(\frac{kT}{2hcB}\right)^{1/2} - \frac{1}{2}$$

The peak-to-peak separation is then

$$\begin{aligned}\Delta S &= \Delta S^{\mathrm{S}}_{J_{\max}} - \Delta S^{\mathrm{O}}_{J_{\max}} = 2B(2J_{\max}+3) - \{-2B(2J_{\max}-1)\} = 8B\left(J_{\max}+\tfrac{1}{2}\right)\\ &= 8B\left(\frac{kT}{2hcB}\right)^{1/2} = \left(\frac{32BkT}{hc}\right)^{1/2}\end{aligned}$$

To analyse the data we rearrange the relation to

$$B = \frac{hc(\Delta S)^2}{32kT}$$

and convert to a bond length using $B = \dfrac{\hbar}{4\pi cI}$, with $I = 2m_x R^2$ (Table 16.1) for a linear rotor. This gives

$$R = \left(\frac{\hbar}{8\pi c m_x B}\right)^{1/2} = \left(\frac{1}{\pi c \Delta S}\right) \times \left(\frac{2kT}{m_x}\right)^{1/2}$$

We can now draw up the following table

	$HgCl_2$	$HgBr_2$	HgI_2
T/K	555	565	565
m_x/u	35.45	79.1	126.90
ΔS/cm^{-1}	23.8	15.2	11.4
R/pm	227.6	240.7	253.4

Hence, the three bond lengths are approximately $\boxed{230,\ 240,\ \text{and}\ 250\,\text{pm}}$

P16.28 The energy levels of a Morse oscillator, expressed as wavenumbers, are given by:

$$G(\nu) = \left(\nu+\tfrac{1}{2}\right)\tilde{\nu} - \left(\nu+\tfrac{1}{2}\right)^2 x_e\tilde{\nu} = \left(\nu+\tfrac{1}{2}\right)\tilde{\nu} - \left(\nu+\tfrac{1}{2}\right)^2 \tilde{\nu}2/4D_e.$$

States are bound only if the energy is less than the well depth, D_e, also expressed as a wavenumber:

$$G(\nu) < D_e \quad \text{or} \quad \left(\nu+\tfrac{1}{2}\right)\tilde{\nu} - \left(\nu+\tfrac{1}{2}\right)^2 \tilde{\nu}^2/4D_e < D_e.$$

Solve for the maximum value of ν by making the inequality into an equality:

$$\left(\nu+\tfrac{1}{2}\right)^2 \tilde{\nu}^2/4D_e - \left(\nu+\tfrac{1}{2}\right)\tilde{\nu} + D_e = 0.$$

Multiplying through by $4D_e$ results in an expression that can be factored by inspection into:

$$\left[\left(\nu+\tfrac{1}{2}\right)\tilde{\nu} - 2D_e\right]^2 = 0 \quad \text{so} \quad \nu+\tfrac{1}{2} = 2D_e/\tilde{\nu} \quad \text{and} \quad \nu = \boxed{2D_e/\tilde{\nu} - \tfrac{1}{2}}.$$

Of course, ν is an integer, so its maximum value is really the greatest integer less than this quantity.

Solutions to applications

P16.29 **(a)** Resonance Raman spectroscopy is preferable to vibrational spectroscopy for studying the O—O stretching mode because such a mode would be $\boxed{\text{infrared inactive}}$, or at best only weakly active. (The mode is sure to be inactive in free O_2, because it would not change the molecule's dipole moment. In a complex in which O_2 is bound, the O—O stretch may change the dipole moment, but it is not certain to do so at all, let alone strongly enough to provide a good signal.)

(b) The vibrational wavenumber is proportional to the frequency, and it depends on the effective mass as follows,

$$\tilde{\nu} \propto \left(\frac{k}{m_{\text{eff}}}\right)^{1/2}, \quad \text{so} \quad \frac{\tilde{\nu}(^{18}O_2)}{\tilde{\nu}(^{16}O_2)} = \left(\frac{m_{\text{eff}}(^{16}O_2)}{m_{\text{eff}}(^{18}O_2)}\right)^{1/2} = \left(\frac{16.0\,\text{u}}{18.0\,\text{u}}\right)^{1/2} = 0.943,$$

and $\tilde{\nu}(^{18}O_2) = (0.943)(844\,\text{cm}^{-1}) = \boxed{796\,\text{cm}^{-1}}$.

Note the assumption that the effective masses are proportional to the isotopic masses. This assumption is valid in the free molecule, where the effective mass of O_2 is equal to half the mass of the O atom; it is also valid if the O_2 is strongly bound at one end, such that one atom is free and the other is essentially fixed to a very massive unit.

(c) The vibrational wavenumber is proportional to the square root of the force constant. The force constant is itself a measure of the strength of the bond (technically of its stiffness, which correlates with strength), which in turn is characterized by bond order. Simple molecule orbital analysis of O_2, O_{2^-}, and ${O_2}^{2-}$ results in bond orders of $\boxed{\text{2, 1.5, and 1 respectively}}$. Given decreasing bond order, one would expect decreasing vibrational wavenumbers (and vice versa).

(d) The wavenumber of the O—O stretch is very similar to that of the peroxide anion, suggesting $\boxed{{Fe^{3+}}_2{O_2}^{2-}}$.

(e) The detection of two bands due to $^{16}O^{18}O$ implies that the two O atoms occupy non-equivalent positions in the complex. Structures **7** and **8** are consistent with this observation, but structures **5** and **6** are not.

P16.31 **(a)** The molar absorption coefficient $\varepsilon(\tilde{\nu})$ is given by

$$\varepsilon(\tilde{\nu}) = \frac{A(\tilde{\nu})}{l[CO_2]} = \frac{RTA(\tilde{\nu})}{lx_{CO_2}p} \quad \text{(eqns 16.11, 1.15, and 1.18)}$$

where $T = 298\,\text{K}$, $l = 10\,\text{cm}$, $p = 1\,\text{bar}$, and $x_{CO_2} = 0.021$.

The absorption band originates with the 001 ← 000 transition of the antisymmetric stretch vibrational mode at $2349\,\text{cm}^{-1}$ (Fig. 16.48). The band is very broad because of accompanying rotational transitions and lifetime broadening of each individual absorption (also called collisional broadening or pressure broadening, Section 16.3). The spectra reveals that the Q branch is missing so we conclude that the transition $\boxed{\Delta J = 0 \text{ is forbidden}}$ (Section 16.12) for the $D_{\infty h}$ point group of CO_2. The P-branch ($\Delta J = -1$) is evident at lower energies and the R-branch ($\Delta J = +1$) is evident at higher energies.

(b) ^{16}O—^{12}C—^{16}O has two identical nuclei of zero spin so the CO_2 wavefunction must be symmetric w/r/t nuclear interchange and it must obey Bose–Einstein nuclear statistics (Section 16.8). Consequently, J takes on even values only for the $\nu = 0$ vibrational state and odd values only for the $\nu = 1$ state. The (ν, J) states for this absorption band are $(1, J+1) \leftarrow (0, J)$ for $J = 0, 2, 4, \ldots$. According to eqn 16.68, the energy of the $(0, J)$ state is

$$S(0, J) = \tfrac{1}{2}\nu + BJ(J+1),$$

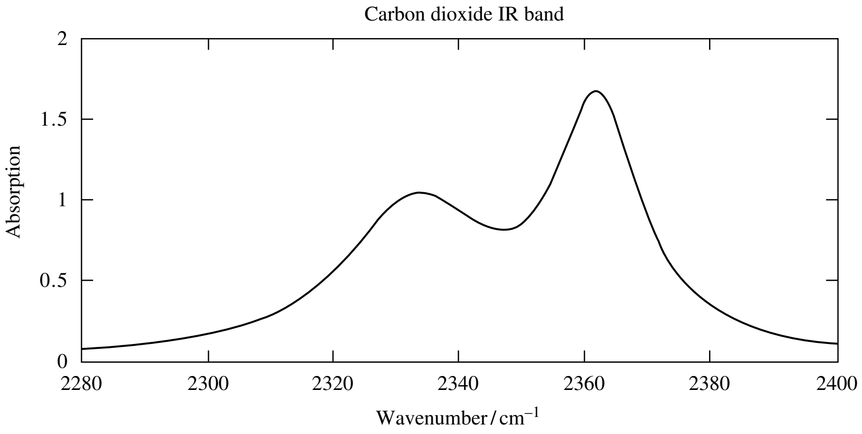


Figure 16.4(a)

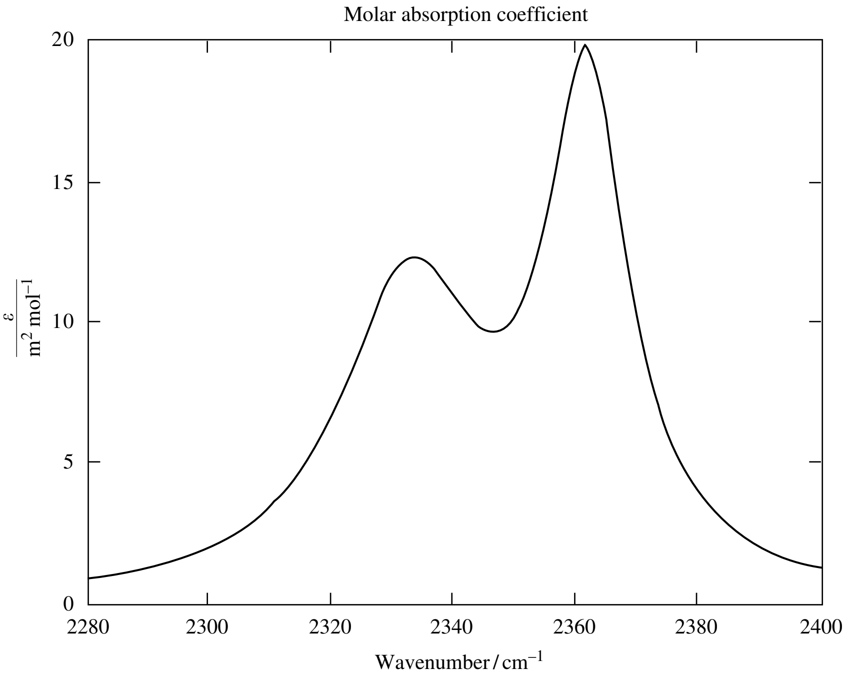


Figure 16.4(b)

where $\nu = 2349\,\mathrm{cm^{-1}}$

$$I = \frac{2m_{\mathrm{O}}R^2}{N_{\mathrm{A}}} = \frac{2(0.01600\,\mathrm{kg\,mol^{-1}})(116.2\times10^{-12}\,\mathrm{m})^2}{6.022\times10^{23}\,\mathrm{mol^{-1}}}$$

$$= 7.175\times10^{-46}\,\mathrm{kg\,m^2} \qquad \text{(Table 16.1)}$$

$$B = \frac{h}{8\pi^2 cI} \qquad \text{(eqn 16.31)}$$

$$= \frac{6.626\times10^{-34}\,\mathrm{J\,s}}{8\pi^2(2.998\times10^{8}\,\mathrm{m\,s^{-1}})(7.175\times10^{-46}\,\mathrm{kg\,m^2})}$$

$$= 39.02\,\mathrm{m^{-1}} = 0.3902\,\mathrm{cm^{-1}}$$

The transitions of the P and R branches occur at

$$\tilde{\nu}_{\mathrm{P}} = \tilde{\nu} - 2BJ \qquad [16.69\mathrm{b}]$$

and

$$\tilde{\nu}_R = \tilde{\nu} + 2B(J+1) \qquad [16.69c]$$

where $J = 0, 2, 4, 6 \ldots$

The highest energy transition of the P branch is at $\tilde{\nu} - 4B$; the lowest energy transition of the R branch is at $\tilde{\nu} + 2B$. Transitions are separated by $4B(1.5608\,\mathrm{cm}^{-1})$ within each branch. The probability of each transition is proportional to the lower state population, which we assume to be given by the Boltzman distribution with a degeneracy of $2J+1$. The transition probability is also proportional to both a nuclear degeneracy factor (eqn 16.50) and a transition dipole moment, which is approximately independent of J. The former factors are absorbed into the constant of proportionality.

$$\text{transition probability } \propto (2J+1)\mathrm{e}^{-S(0,J)hc/kT}$$

A plot of the right-hand-side of this equation, Fig. 16.4(c), against J at 298 K indicates a maximum transition probability at $J_{\max} = 16$. We "normalize" the maximum in the predicted structure, and eliminate the constant of proportionality by examining the transition probability ratio:

$$\frac{\text{transition probability for } J\text{th state}}{\text{transition probability for} J_{\max} \text{state}} = \frac{(2J+1)\mathrm{e}^{-S(0,J)hc/kT}}{33\mathrm{e}^{-S(0,16)hc/RT}}$$

$$= \left(\frac{2J+1}{33}\right)\mathrm{e}^{-(J^2+J-272)Bhc/kT}$$

A plot Fig. 16.4(c) of the above ratio against predicted wavenumbers can be compared to the ratio $A(\tilde{\nu})/A_{\max}$ where $A_{\max}$ is the observed spectrum maximum (1.677). It shows a fair degree of agreement between the experimental and simple theoretical band shapes.

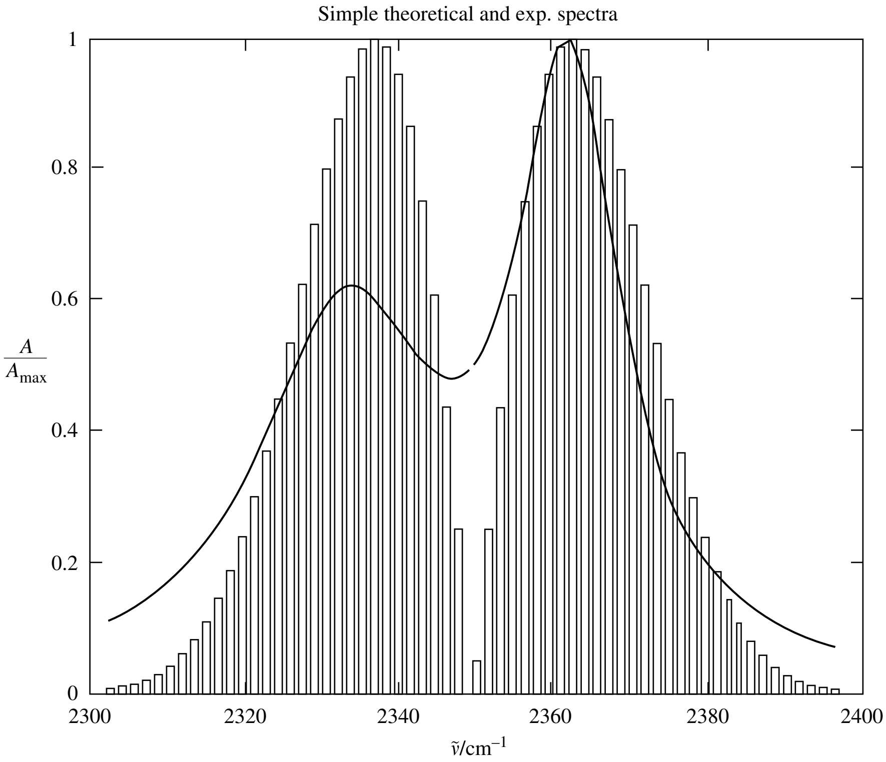


Figure 16.4(c)

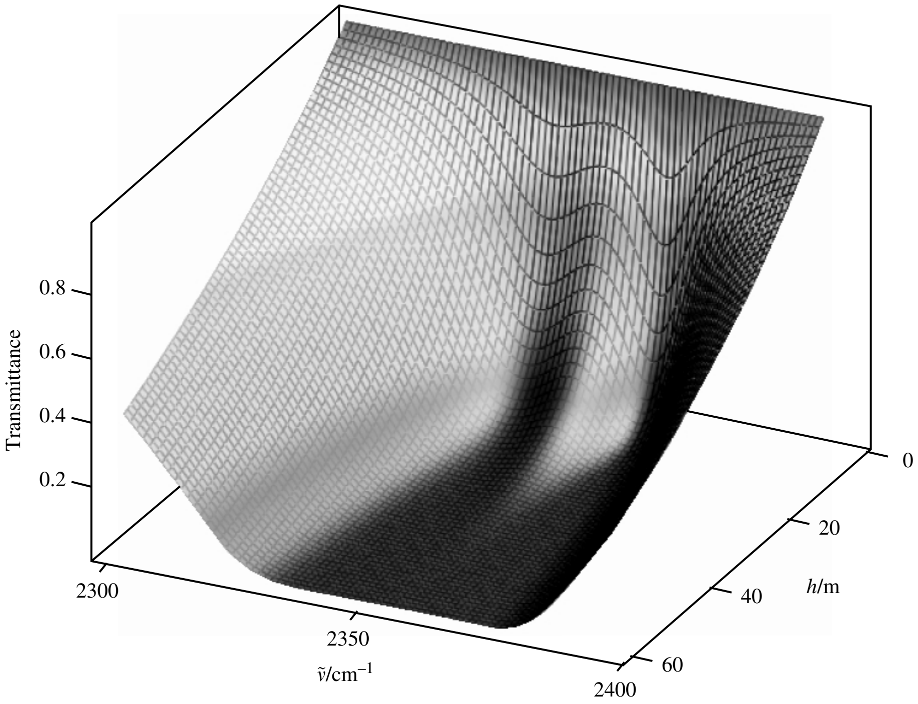


Figure 16.4(d)

(c) Using the equations of justificant 16.1, we may write the relationship

$$A = \varepsilon(\tilde{\nu}) \int_0^h [\mathrm{CO_2}]\, \mathrm{d}h$$

The strong absorption of the band suggests that h should not be a very great length and that $[\mathrm{CO_2}]$ should be constant between the Earth's surface and h. Consequently, the integration gives

$$\begin{aligned} A &= \varepsilon(\tilde{\nu})[\mathrm{CO_2}]h \\ &= \varepsilon(\tilde{\nu})h\left\{\frac{x_{\mathrm{CO_2}}p}{RT}\right\} \qquad \text{Dalton's law of partial pressures} \end{aligned}$$

p and T are not expected to change much for modest values of h so we estimate that $p = 1$ bar and $T = 288$ K.

$$\begin{aligned} A &= \varepsilon(\tilde{\nu})h\left\{\frac{(3.3 \times 10^{-4})\left(1 \times 10^5\,\mathrm{Pa}\right)}{\left(8.31451\,\mathrm{J}\,\cancel{\mathrm{K}^{-1}}\mathrm{mol}^{-1}\right)(288\,\cancel{\mathrm{K}})}\right\} \\ &= (0.0138\,\mathrm{m}^{-3}\,\mathrm{mol})\ \varepsilon(\tilde{\nu})h \end{aligned}$$

$$\text{Transmittance} = 10^{-\mathrm{A}} = 10^{-\left(0.0138\,\mathrm{m}^{-3}\,\mathrm{mol}\right)\varepsilon(\tilde{\nu})h} \qquad [16.10]$$

The transmittance surface plot clearly shows that before a height of about 30 m has been reached all of the Earth's IR radiation in the $2320\,\mathrm{cm}^{-1} - 2380\,\mathrm{cm}^{-1}$ range has been absorbed by atmospheric carbon dioxide.

See C.A. Meserole, F.M. Mulcalry, J. Lutz, and H.A. Yousif, *J. Chem. Ed.*, *74*, 316 (1997).

P16.34 **(a)** The H_3^+ molecule is held together by a two-electron, three-center bond, and hence its structure is expected to be an equilateral triangle. Looking at Fig. 16.5 and using the Law of cosines

$$\begin{aligned} R^2 &= 2R_C^2 - 2R_C^2\cos(180^\circ - 2\theta) \\ &= 2R_C^2(1-\cos(120^\circ)) = 3R_C^2 \end{aligned}$$

Therefore

$$R_C = R/\sqrt{3}$$
$$I_C = 3mR_C^2 = 3m(R/\sqrt{3})^2 = mR^2$$
$$I_B = 2mR_B = 2m(R/2)^2 = mR^2/2$$

Therefore

$$I_C = 2I_B$$

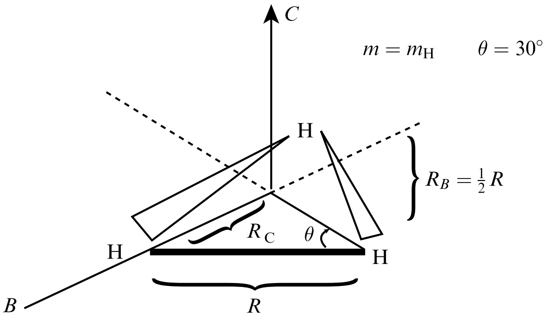


Figure 16.5

(b)
$$B = \frac{\hbar}{4\pi c I_B} = \frac{2\hbar}{4\pi c m R^2} = \frac{\hbar}{2\pi c m R^2}\ [16.37]$$

$$\begin{aligned} R &= \left(\frac{\hbar}{2\pi c m B}\right)^{1/2} = \left(\frac{\hbar N_A}{2\pi c M_H B}\right)^{1/2} \\ &= \left(\frac{(1.0546\times10^{-34}\,\mathrm{J\,s})\times(6.0221\times10^{23}\,\mathrm{mol^{-1}})\times\left(\frac{10^{-2}\,\mathrm{m}}{\mathrm{cm}}\right)}{2\pi(2.998\times10^{8}\,\mathrm{m\,s^{-1}})\times(0.001\,008\,\mathrm{kg\,mol^{-1}})\times(43.55\,\mathrm{cm^{-1}})}\right)^{1/2} \\ &= 8.764\times10^{-11}\,\mathrm{m} = \boxed{87.64\,\mathrm{pm}} \end{aligned}$$

Alternatively the rotational constant C can be used to calculate R.

$$C = \frac{\hbar}{4\pi c I_C} = \frac{\hbar}{4\pi c m R^2}\ [36]$$

$$\begin{aligned} R &= \left(\frac{\hbar}{4\pi c m C}\right)^{1/2} = \left(\frac{\hbar N_A}{4\pi c M_H C}\right)^{1/2} \\ &= \left(\frac{(1.0546\times10^{-34}\,\mathrm{J\,s})\times(6.0221\times10^{23}\,\mathrm{mol^{-1}})\times\left(\frac{10^{-2}\,\mathrm{m}}{\mathrm{cm}}\right)}{4\pi(2.998\times10^{8}\,\mathrm{m\,s^{-1}})\times(0.001\,008\,\mathrm{kg\,mol^{-1}})\times(20.71\,\mathrm{cm^{-1}})}\right)^{1/2} \\ &= 8.986\times10^{-11}\,\mathrm{m} = \boxed{89.86\,\mathrm{pm}} \end{aligned}$$

The values of R calculated with either the rotational constant C or the rotational constant B differ slightly. We approximate the bond length as the average of these two.

$$\langle R\rangle \approx \frac{(87.64 + 89.86)\,\text{pm}}{2} = \boxed{88.7\,\text{pm}}$$

(c)

$$B = \frac{\hbar}{2\pi c m R^2} = \frac{(1.0546\times10^{-34}\,\text{J s})\times(6.0221\times10^{23}\,\text{mol}^{-1})\times\left(\frac{10^{-2}\,\text{m}}{\text{cm}}\right)}{2\pi(2.998\times10^{8}\,\text{m s}^{-1})\times(0.001\,008\,\text{kg mol}^{-1})\times(87.32\times10^{-12}\,\text{m})^2}$$

$$= \boxed{43.87\,\text{cm}^{-1}}$$

$$C = \tfrac{1}{2}B = \boxed{21.93\,\text{cm}^{-1}}$$

(d)

$$\frac{1}{m_{\text{eff}}} = \frac{3}{m} \quad \text{or} \quad m_{\text{eff}} = \tfrac{1}{3}m$$

Since $m_{\text{D}} = 2m_{\text{H}}$, $m_{\text{eff,D}} = 2m_{\text{H}}/3$

$$\tilde{\nu}_2(\text{D}_3^+) = \left(\frac{m_{\text{eff}}(\text{H}_3)}{m_{\text{eff}}(\text{D}_3)}\right)^{1/2} \tilde{\nu}_2(\text{H}_3)\ [57]$$

$$= \left(\frac{m_{\text{H}}/3}{2m_{\text{H}}/3}\right)^{1/2} \tilde{\nu}_2(\text{H}_3) = \frac{\tilde{\nu}_2(\text{H}_2)}{2^{1/2}}$$

$$= \frac{2521.6\,\text{cm}^{-1}}{2^{1/2}} = \boxed{1783.0\,\text{cm}^{-1}}$$

Since B and $C \propto \dfrac{1}{m}$, where m = mass of H or D

$$B(\text{D}_3^+) = B(\text{H}_3^+) \times \frac{M_{\text{H}}}{M_{\text{D}}} = 43.55\,\text{cm}^{-1} \times \left(\frac{1.008}{2.014}\right) = \boxed{21.80\,\text{cm}^{-1}}$$

$$C(\text{D}_3^+) = C(\text{H}_3^+) \times \frac{M_{\text{H}}}{M_{\text{D}}} = 20.71\,\text{cm}^{-1} \times \left(\frac{1.008}{2.014}\right) = \boxed{10.37\,\text{cm}^{-1}}$$

17 Spectroscopy 2: electronic transitions

Solutions to exercises

Discussion questions

E17.1(b) The Franck–Condon principle states that because electrons are so much lighter than nuclei an electronic transition occurs so rapidly compared to vibrational motions that the internuclear distance is relatively unchanged as a result of the transition. This implies that the most probable transitions $\nu_f \leftarrow \nu_i$ are vertical. This vertical line will, however, intersect any number of vibrational levels ν_f in the upper electronic state. Hence transitions to many vibrational states of the excited state will occur with transition probabilities proportional to the Frank–Condon factors which are in turn proportional to the overlap integral of the wavefunctions of the initial and final vibrational states. A vibrational progression is observed, the shape of which is determined by the relative horizontal positions of the two electronic potential energy curves. The most probable transitions are those to excited vibrational states with wavefunctions having a large amplitude at the internuclear position R_e.

Question. You might check the validity of the assumption that electronic transitions are so much faster than vibrational transitions by calculating the time scale of the two kinds of transitions. How much faster is the electronic transition, and is the assumption behind the Franck–Condon principle justified?

E17.2(b) Color can arise by emission, absorption, or scattering of electromagnetic radiation by an object. Many molecules have electronic transitions that have wavelengths in the visible portion of the electromagnetic spectrum. When a substance emits radiation the perceived color of the object will be that of the emitted radiation and it may be an additive color resulting from the emission of more than one wavelength of radiation. When a substance absorbs radiation its color is determined by the subtraction of those wavelengths from white light. For example, absorption of red light results in the object being perceived as green. Color may also be formed by scattering, including the diffraction that occurs when light falls on a material with a grid of variation in texture of refractive index having dimensions comparable to the wavelength of light, for example, a bird's plumage.

E17.3(b) 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, $\approx 10^{-9}$ s, is typical of a process in which the rate determining step is a spontaneous radiative transition between states of the same multiplicity; slower than a stimulated transition, but faster than phosphorescence; (3) it occurs at longer wavelength (higher frequency) than the inducing radiation; (4) its vibrational structure is characteristic of that of a transition from the ground vibrational level of the excited electronic state to the vibrational levels of the ground electronic state; and (5), the observed shifting and in some instances quenching of the fluorescence spectrum by interactions with the solvent.

E17.4(b) See Table 17.4 for a summary of the characteristics of laser radiation that result in its many advantages for chemical and biochemical investigations. Two important applications of lasers in chemistry have been to Raman spectroscopy and to the development of time resolved spectroscopy. Prior to the invention of lasers the source of intense monochromatic radiation required for Raman spectroscopy was a large spiral discharge tube with liquid mercury electrodes. The intense heat generated by the large current required to produce the radiation had to be dissipated by clumsy water cooled jackets and exposures of several weeks were sometimes necessary to observe the weaker Raman lines. These problems have been eliminated with the introduction of lasers as the source of the required monochromatic radiation. As a consequence, Raman spectroscopy has been revitalized and is now almost as routine as infrared spectroscopy. See Section 17.7(b). Time resolved laser spectroscopy can be used to study the dynamics of chemical reactions. Laser pulses are used to obtain the absorption, emission, and Raman spectrum of reactants, intermediates, products, and even transition states of reactions. When we want to study the rates at which energy is transferred from one mode to another in a molecule, we need femotosecond and picosecond pulses. These time scales are available from mode-locked lasers and their development has opened up the possibility of examining the details of chemical reactions at a level which would have been unimaginable before.

Numerical exercises

E17.5(b) To obtain the parities of Fig. 14.38 of the text we recognize that what is shown in the figure are the signs (light = positive, dark = negative) of the upper (positive z-direction) lobe of the p_z orbitals. The lower lobes (not shown) have opposite signs. Inversion through the centre changes + to − for the p_z lobes of a_2 and e_2, but the e_1 and b_2 lobes do not change sign. Therefore a_2 and e_2 are u, e_1 and b_2 are g.

E17.6(b) According to Hund's rule, we expect one $1\pi_u$ electron and one $2\pi_g$ electron to be unpaired. Hence $S = 1$ and the multiplicity of the spectroscopic term is $\boxed{3}$. The overall parity is $\mathrm{u} \times \mathrm{g} = \boxed{\mathrm{u}}$ since (apart from the complete core), one electron occupies a u orbital another occupies a g orbital.

E17.7(b) Use the Beer–Lambert law

$$\log \frac{\mathcal{I}}{\mathcal{I}_0} = -\varepsilon[\mathrm{J}]l = (-327\,\mathrm{L\,mol^{-1}\,cm^{-1}}) \times (2.22 \times 10^{-3}\,\mathrm{mol\,L^{-1}}) \times (0.15\,\mathrm{cm})$$

$$= -0.108\overline{89}$$

$$\frac{\mathcal{I}}{\mathcal{I}_l} = 10^{-0.108\overline{89}} = 0.778$$

The reduction in intensity is $\boxed{22.2 \text{ per cent}}$

E17.8(b)

$$\varepsilon = -\frac{1}{[\mathrm{J}]l} \log \frac{\mathcal{I}}{\mathcal{I}_0} [16.9, 16.10]$$

$$= \frac{-1}{(6.67 \times 10^{-4}\,\mathrm{mol\,L^{-1}}) \times (0.35\,\mathrm{cm})} \log 0.655 = 78\overline{7}\,\mathrm{L\,mol^{-1}\,cm^{-1}}$$

$$= 78\overline{7}\,\mathrm{dm^3\,mol^{-1}cm^{-1}} = 78\overline{7} \times 10^3\,\mathrm{cm^3\,mol^{-1}\,cm^{-1}} \quad [1\,\mathrm{dm} = 10\,\mathrm{cm}]$$

$$= \boxed{7.9 \times 10^5\,\mathrm{cm^2\,mol^{-1}}}$$

E17.9(b) The Beer–Lambert law is

$$\log \frac{\mathcal{I}}{\mathcal{I}_0} = -\varepsilon[\mathrm{J}]l \quad \text{so} \quad [\mathrm{J}] = \frac{-1}{\varepsilon l} \log \frac{\mathcal{I}}{\mathcal{I}_0}$$

$$[\mathrm{J}] = \frac{-1}{(323\,\mathrm{L\,mol^{-1}\,cm^{-1}} \times (0.750\,\mathrm{cm})} \log(1 - 0.523) = \boxed{1.33 \times 10^{-3}\,\mathrm{mol\,L^{-1}}}$$

E17.10(b) Note. A parabolic lineshape is symmetrical, extending an equal distance on either side of its peak. The given data are not consistent with a parabolic lineshape when plotted as a function of either wavelength or wavenumber, for the peak does not fall at the centre of either the wavelength or the wavenumber range. The exercise will be solved with the given data assuming a triangular lineshape as a function of wavenumber.

The integrated absorption coefficient is the area under an absorption peak

$$A = \int \varepsilon \, \mathrm{d}\tilde{\nu}$$

If the peak is triangular, this area is

$$\begin{aligned} A &= \tfrac{1}{2}(\text{base}) \times (\text{height}) \\ &= \tfrac{1}{2}[(199 \times 10^{-9}\,\mathrm{m})^{-1} - (275 \times 10^{-9}\,\mathrm{m})^{-1}] \times (2.25 \times 10^{4}\,\mathrm{L\,mol^{-1}\,cm^{-1}}) \\ &= 1.5\bar{6} \times 10^{10}\,\mathrm{L\,m^{-1}\,mol^{-1}\,cm^{-1}} = \frac{(1.5\bar{6} \times 10^{9}\,\mathrm{L\,m^{-1}\,mol^{-1}\,cm^{-1}}) \times (100\,\mathrm{cm\,m^{-1}})}{10^{3}\,\mathrm{L\,m^{-3}}} \\ &= 1.5\bar{6} \times 10^{9}\,\mathrm{m\,mol^{-1}} = \boxed{1.5\bar{6} \times 10^{8}\,\mathrm{L\,mol^{-1}\,cm^{-2}}} \end{aligned}$$

E17.11(b) Modelling the π electrons of 1,3,5-hexatriene as free electrons in a linear box yields non-degenerate energy levels of

$$E_n = \frac{n^2h^2}{8m_eL^2}$$

The molecule has six π electrons, so the lowest-energy transition is from $n = 3$ to $n = 4$. The length of the box is 5 times the C—C bond distance R. So

$$\Delta E_{\text{linear}} = \frac{(4^2 - 3^3)h^2}{8m_e(5R)^2}$$

Modelling the π electrons of benzene as free electrons on a ring of radius R yields energy levels of

$$E_{m_l} = \frac{m_l^2\hbar^2}{2I}$$

where I is the moment of inertia: $I = m_eR^2$. These energy levels are doubly degenerate, except for the non-degenerate $m_l = 0$. The six π electrons fill the $m_l = 0$ and 1 levels, so the lowest-energy transition is from $m_l = 1$ to $m_l = 2$

$$\Delta E_{\text{ring}} = \frac{(2^2 - 1^2)\hbar^2}{2m_eR^2} = \frac{(2^2 - 1^2)h^2}{8\pi^2m_eR^2}$$

Comparing the two shows

$$\Delta E_{\text{linear}} = \frac{7}{25}\left(\frac{h^2}{8m_eR^2}\right) < \Delta E_{\text{ring}} = \frac{3}{\pi^2}\left(\frac{h^2}{8m_eR^2}\right)$$

Therefore, the lowest-energy absorption will $\boxed{\text{rise}}$ in energy.

E17.12(b) The Beer–Lambert law is

$$\log\frac{\mathcal{I}}{\mathcal{I}_0} = -\varepsilon[\mathrm{J}]l = \log T$$

so a plot (Fig. 17.1) of $\log T$ versus [J] should give a straight line through the origin with a slope m of $-\varepsilon l$. So $\varepsilon = -m/l$.

The data follow

$[\text{dye}]/(\text{mol L}^{-1})$	T	$\log T$
0.0010	0.73	-0.1367
0.0050	0.21	-0.6778
0.0100	0.042	-1.3768
0.0500	1.33×10^{-7}	-6.8761

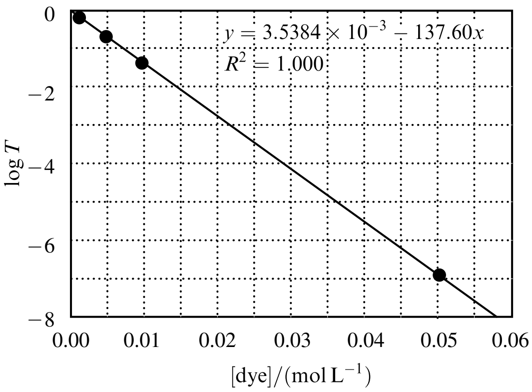


Figure 17.1

The molar absorptivity is

$$\varepsilon = -\frac{-138\,\text{L mol}^{-1}}{0.250\,\text{cm}} = \boxed{552\,\text{L mol}^{-1}\,\text{cm}^{-1}}$$

E17.13(b) The Beer–Lambert law is

$$\log T = -\varepsilon[\text{J}]l \quad \text{so} \quad \varepsilon = \frac{-1}{[\text{J}]l}\log T$$

$$\varepsilon = \frac{-1}{(0.0155\,\text{mol L}^{-1}) \times (0.250\,\text{cm})}\log 0.32 = \boxed{12\bar{8}\,\text{L mol}^{-1}\,\text{cm}^{-1}}$$

Now that we have ε, we can compute T of this solution with any size of cell

$$T = 10^{-\varepsilon[\text{J}]l} = 10^{-\{(12\underline{8}\,\text{L mol}^{-1}\,\text{cm}^{-1}) \times (0.0155\,\text{mol L}^{-1}) \times (0.450\,\text{cm})\}} = \boxed{0.13}$$

E17.14(b) The Beer–Lambert law is

$$\log\frac{\mathcal{I}}{\mathcal{I}_0} = -\varepsilon[\text{J}]l \quad \text{so} \quad l = -\frac{1}{\varepsilon[\text{J}]}\log\frac{\mathcal{I}}{\mathcal{I}_0}$$

(a) $l = -\dfrac{1}{(30\,\text{L mol}^{-1}\,\text{cm}^{-1}) \times (1.0\,\text{mol L}^{-1})} \times \log\dfrac{1}{2} = \boxed{0.020\,\text{cm}}$

(b) $l = -\dfrac{1}{(30\,\text{L mol}^{-1}\,\text{cm}^{-1}) \times (1.0\,\text{mol L}^{-1})} \times \log 0.10 = \boxed{0.033\,\text{cm}}$

E17.15(b) The integrated absorption coefficient is the area under an absorption peak

$$A = \int \varepsilon \, \mathrm{d}\tilde{\nu}$$

We are told that ε is a Gaussian function, i.e. a function of the form

$$\varepsilon = \varepsilon_{\max} \exp\left(\frac{-x^2}{a^2}\right)$$

where $x = \tilde{\nu} - \tilde{\nu}_{\max}$ and a is a parameter related to the width of the peak. The integrated absorption coefficient, then, is

$$A = \int_{-\infty}^{\infty} \varepsilon_{\max} \exp\left(\frac{-x^2}{a^2}\right) \mathrm{d}x = \varepsilon_{\max} a \sqrt{\pi}$$

We must relate a to the half-width at half-height, $x_{1/2}$

$$\tfrac{1}{2}\varepsilon_{\max} = \varepsilon_{\max} \exp\left(\frac{-x_{1/2}^2}{a^2}\right) \quad \text{so} \quad \ln\tfrac{1}{2} = \frac{-x_{1/2}^2}{a^2} \quad \text{and} \quad a = \frac{x_{1/2}}{\sqrt{\ln 2}}$$

$$\begin{aligned} \text{So } A &= \varepsilon_{\max} x_{1/2} \left(\frac{\pi}{\ln 2}\right)^{1/2} = (1.54 \times 10^4\,\mathrm{L\,mol^{-1}\,cm^{-1}}) \times (4233\,\mathrm{cm^{-1}}) \times \left(\frac{\pi}{\ln 2}\right)^{1/2} \\ &= \boxed{1.39 \times 10^8\,\mathrm{L\,mol^{-1}\,cm^{-2}}} \end{aligned}$$

In SI base units

$$\begin{aligned} A &= \frac{(1.39 \times 10^8\,\mathrm{L\,mol^{-1}\,cm^{-2}}) \times (1000\,\mathrm{cm^3\,L^{-1}})}{100\,\mathrm{cm\,m^{-1}}} \\ &= \boxed{1.39 \times 10^9\,\mathrm{m\,mol^{-1}}} \end{aligned}$$

E17.16(b) F_2^+ is formed when F_2 loses an antibonding electron, so we would expect F_2^+ to have a shorter bond than F_2. The difference in equilibrium bond length between the ground state (F_2) and excited state ($F_2^+ + e^-$) of the photoionization experiment leads us to expect some vibrational excitation in the upper state. The vertical transition of the photoionization will leave the molecular ion with a stretched bond relative to its equilibrium bond length. A stretched bond means a vibrationally excited molecular ion, hence a $\boxed{\text{stronger}}$ transition to a vibrationally excited state than to the vibrational ground state of the cation.

Solutions to problems

Solutions to numerical problems

P17.3 Initially we cannot decide whether the dissociation products are produced in their ground atomic states or excited states. But we note that the two convergence limits are separated by an amount of energy exactly equal to the excitation energy of the bromine atom: $18\,345\,\mathrm{cm^{-1}} - 14\,660\,\mathrm{cm^{-1}} = 3685\,\mathrm{cm^{-1}}$. Consequently, dissociation at $14\,660\,\mathrm{cm^{-1}}$ must yield bromine atoms in their ground state. Therefore, the possibilities for the dissociation energy are $14\,660\,\mathrm{cm^{-1}}$ or

$14\,660\,\mathrm{cm^{-1}} - 7598\,\mathrm{cm^{-1}} = 7062\,\mathrm{cm^{-1}}$ depending upon whether the iodine atoms produced are in their ground or excited electronic state.

In order to decide which of these two possibilities is correct we can set up the following Born–Haber cycle

(1)	$\mathrm{IBr(g)}$	$\rightarrow$	$\frac{1}{2}\mathrm{I_2(g)} + \frac{1}{2}\mathrm{Br_2(l)}$	$\Delta H_1^{\ominus} = -\Delta_\mathrm{f} H^{\ominus}(\mathrm{IBr, g})$
(2)	$\frac{1}{2}\mathrm{I_2(s)}$	$\rightarrow$	$\frac{1}{2}\mathrm{I_2(g)}$	$\Delta H_2^{\ominus} = \frac{1}{2}\Delta_\mathrm{sub} H^{\ominus}(\mathrm{I_2, s})$
(3)	$\frac{1}{2}\mathrm{Br_2(l)}$	$\rightarrow$	$\frac{1}{2}\mathrm{Br_2(g)}$	$\Delta H_3^{\ominus} = \frac{1}{2}\Delta_\mathrm{vap} H^{\ominus}(\mathrm{Br_{2,}\ l})$
(4)	$\frac{1}{2}\mathrm{I_2(g)}$	$\rightarrow$	$\mathrm{I(g)}$	$\Delta H_4^{\ominus} = \frac{1}{2}\Delta H(\mathrm{I{-}I})$
(5)	$\frac{1}{2}\mathrm{Br_2(g)}$	$\rightarrow$	$\mathrm{Br(g)}$	$\Delta H_5^{\ominus} = \frac{1}{2}\Delta H(\mathrm{Br{-}Br})$
	$\mathrm{IBr(g)}$	$\rightarrow$	$\mathrm{I(g)} + \mathrm{Br(g)}$	$\Delta H^{\ominus}$

$$\begin{aligned}\Delta H^{\ominus} &= -\Delta_\mathrm{f} H^{\ominus}(\mathrm{IBr, g}) + \tfrac{1}{2}\Delta_\mathrm{sub} H^{\ominus}(\mathrm{I_2, s}) + \tfrac{1}{2}\Delta_\mathrm{vap} H^{\ominus}(\mathrm{Br_2, l}) \\ &\quad + \tfrac{1}{2}\Delta H(\mathrm{I{-}I}) + \tfrac{1}{2}\Delta H(\mathrm{Br{-}Br}) \\ &= \left\{-40.79 + \tfrac{1}{2} \times 62.44 + \tfrac{1}{2} \times 30.907 + \tfrac{1}{2} \times 151.24 + \tfrac{1}{2} \times 192.85\right\}\mathrm{kJ\,mol^{-1}} \\ &\qquad [\text{Table 2.6 and data provided}] \\ &= 177.93\,\mathrm{kJ\,mol^{-1}} = \boxed{14\,874\,\mathrm{cm^{-1}}}\end{aligned}$$

Comparison to the possibilities $\boxed{14\,660\,\mathrm{cm^{-1}}}$ and $7062\,\mathrm{cm^{-1}}$ shows that it is the former that is the correct dissociation energy.

P17.5 We write $\varepsilon = \varepsilon_\mathrm{max}\mathrm{e}^{-x^2} = \varepsilon_\mathrm{max}\mathrm{e}^{-\tilde{\nu}^2/2\Gamma}$ the variable being $\tilde{\nu}$ and Γ being a constant. $\tilde{\nu}$ is measured from the band centre, at which $\tilde{\nu} = 0$. $\varepsilon = \frac{1}{2}\varepsilon_\mathrm{max}$ when $\tilde{\nu}^2 = 2\Gamma\ln 2$. Therefore, the width at half-height is

$$\Delta\tilde{\nu}_{1/2} = 2 \times (2\Gamma\ln 2)^{1/2}, \quad \text{implying that} \quad \Gamma = \frac{\Delta\tilde{\nu}_{1/2}^2}{8\ln 2}$$

Now we carry out the intregration

$$\begin{aligned}\mathcal{A} &= \int \varepsilon\,\mathrm{d}\tilde{\nu} = \varepsilon_\mathrm{max}\int_{-\infty}^{\infty} \mathrm{e}^{-\tilde{\nu}^2/2\Gamma}\,\mathrm{d}\tilde{\nu} = \varepsilon_\mathrm{max}(2\Gamma\pi)^{1/2}\left[\int_{-\infty}^{\infty}\mathrm{e}^{-x^2}\,\mathrm{d}x = \pi^{1/2}\right] \\ &= \varepsilon_\mathrm{max}\left(\frac{2\pi\,\Delta\tilde{\nu}_{1/2}^2}{8\ln 2}\right)^{1/2} = \left(\frac{\pi}{4\ln 2}\right)^{1/2}\varepsilon_\mathrm{max}\Delta\tilde{\nu}_{1/2} = 1.0645\varepsilon_\mathrm{max}\Delta\tilde{\nu}_{1/2}\end{aligned}$$

$\mathcal{A} = 1.0645\varepsilon_\mathrm{max}\Delta\tilde{\nu}_{1/2}$, with $\tilde{\nu}$ centred on $\tilde{\nu}_0$

Since $\tilde{\nu} = \dfrac{1}{\lambda}$, $\Delta\tilde{\nu}_{1/2} \approx \dfrac{\Delta\lambda_{1/2}}{\lambda_0^2}$ $[\lambda \approx \lambda_0]$

$$\mathcal{A} = 1.0645\varepsilon_\mathrm{max}\left(\frac{\Delta\lambda_{1/2}}{\lambda_0^2}\right)$$

From Fig. 17.52 of the text, we find $\Delta\lambda_{1/2} = 38\,\mathrm{nm}$ with $\lambda_0 = 290\,\mathrm{nm}$ and $\varepsilon_\mathrm{max} \approx 235\,\mathrm{L\,mol^{-1}\,cm^{-1}}$; hence

$$\mathcal{A} = \frac{1.0645 \times (235\,\mathrm{L\,mol^{-1}\,cm^{-1}}) \times (38 \times 10^{-7}\,\mathrm{cm})}{(290 \times 10^{-7}\,\mathrm{cm})^2} = \boxed{1.1 \times 10^6\,\mathrm{L\,mol^{-1}\,cm^{-2}}}$$

Since the dipole moment components transform as $A_1(z)$, $B_1(x)$, and $B_2(y)$, excitations from A_1 to A_1, B_1, and B_2 terms are allowed.

P17.8 Draw up a table like the following:

Hydrocarbon	$h\nu_{\max}/\mathrm{eV}$	$E_{\mathrm{HOMO}}/\mathrm{eV}^*$
Benzene	4.184	−9.7506
Biphenyl	3.654	−8.9169
Naphthalene	3.452	−8.8352
Phenanthrene	3.288	−8.7397
Pyrene	2.989	−8.2489
Anthracene	2.890	−8.2477

*Semi-empirical, PM3 level, PC Spartan Pro™

Figure 17.2 shows a good correlation: $r^2 = 0.972$.

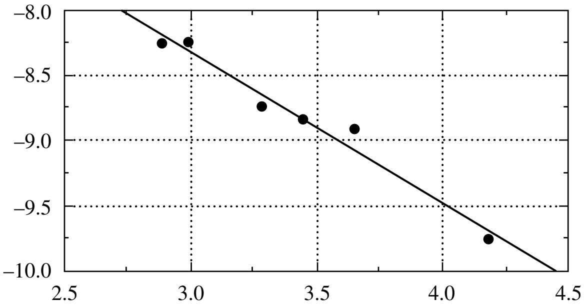


Figure 17.2

P17.11 Refer to Fig. 14.30 of the text. The lowest binding energy corresponds to the highest occupied orbital, the next lowest to next highest orbital, and so on.

We draw up the following table

	Line E_K/eV	Binding energy/eV	Assignment
N_2	5.6	15.6	3σ
	4.5	16.7	1π
	2.4	18.8	$2\sigma^*$
CO	7.2	14.0	3σ
	4.9	16.3	1π
	1.7	19.5	$2\sigma^*$

The spacing of the 4.5 eV lines in N_2 is 0.24 eV, or about 1940 $\mathrm{cm^{-1}}$. The spacing of the 4.9 eV lines in CO is 0.23 eV, or about 1860 $\mathrm{cm^{-1}}$. These are estimates from the illustrations of the separation of the vibrational levels of the N_2^+ and CO^+ ions in their excited states.

P17.13 0.125 eV corresponds to 1010 $\mathrm{cm^{-1}}$, markedly less than the 1596 $\mathrm{cm^{-1}}$ of the bending mode. This suggests that the ejected electron tended to bond between the two hydrogens of the water molecule.

Solutions to theoretical problems

P17.14 We need to establish whether the transition dipole moments

$$\boldsymbol{\mu}_{\mathrm{fi}} = \int \Psi_{\mathrm{f}}^{*}\boldsymbol{\mu}\Psi_{\mathrm{i}}\,\mathrm{d}\tau \ [16.20]$$

connecting the states 1 and 2 and the states 1 and 3 are zero or nonzero. The particle in a box wavefunctions are $\Psi_n = \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)$ [12.8]

Thus $\mu_{2,1} \propto \int \sin\left(\frac{2\pi x}{L}\right) x \sin\left(\frac{\pi x}{L}\right)\mathrm{d}x \propto \int x\left[\cos\left(\frac{\pi x}{L}\right) - \cos\left(\frac{3\pi x}{L}\right)\right]\mathrm{d}x$

and $\mu_{3,1} \propto \int \sin\left(\frac{3\pi x}{L}\right) x \sin\left(\frac{\pi x}{L}\right)\mathrm{d}x \propto \int x\left[\cos\left(\frac{2\pi x}{L}\right) - \cos\left(\frac{4\pi x}{L}\right)\right]\mathrm{d}x$

having used $\sin\alpha\sin\beta = \frac{1}{2}\cos(\alpha-\beta) - \frac{1}{2}\cos(\alpha+\beta)$. Both of these integrals can be evaluated using the standard form

$$\int x(\cos ax)\,\mathrm{d}x = \frac{1}{a^2}\cos ax + \frac{x}{a}\sin ax$$

$$\int_0^L x\cos\left(\frac{\pi x}{L}\right)\mathrm{d}x = \frac{1}{\left(\frac{\pi}{L}\right)^2}\cos\left(\frac{\pi x}{L}\right)\Big|_0^L + \frac{x}{\left(\frac{\pi}{L}\right)}\sin\left(\frac{\pi x}{L}\right)\Big|_0^L = -2\left(\frac{L}{\pi}\right)^2 \neq 0$$

$$\int_L^0 x\cos\left(\frac{3\pi x}{L}\right)\mathrm{d}x = \frac{1}{\left(\frac{3\pi}{L}\right)^2}\cos\left(\frac{3\pi x}{L}\right)\Big|_0^L + \frac{x}{\left(\frac{3\pi}{L}\right)}\sin\left(\frac{3\pi x}{L}\right)\Big|_0^L = -2\left(\frac{L}{3\pi}\right)^2 \neq 0$$

Thus $\mu_{2,1} \neq 0$.

In a similar manner $\mu_{3,1} = 0$.

Comment. A general formula for $\boldsymbol{\mu}_{\mathrm{fi}}$ applicable to all possible particle in a box transitions may be derived. The result is ($n = \mathrm{f}, m = \mathrm{i}$)

$$\mu_{nm} = -\frac{eL}{\pi^2}\left[\frac{\cos(n-m)\pi - 1}{(n-m)^2} - \frac{\cos(n+m)\pi - 1}{(n+m)^2}\right]$$

For m and n both even or both odd numbers, $\mu_{nm} = 0$; if one is even and the other odd, $\mu_{nm} \neq 0$. See also Problem 17.18.

Question. Can you establish the general relation for μ_{nm} above?

P17.16 We need to determine how the oscillator strength (Problem 17.17) depends on the length of the chain. We assume that wavefunctions of the conjugated electrons in the linear polyene can be approximated by the wavefunctions of a particle in a one-dimensional box. Then

$$f = \frac{8\pi^2 m_{\mathrm{e}}\nu}{3he^2}|\boldsymbol{\mu}_{\mathrm{fi}}^2| \ [\text{Problem 17.17}]$$

$$\mu_x = -e\int_0^L \Psi_{n'}(x)x\Psi_n(x)\,\mathrm{d}x, \quad \Psi_n = \left(\frac{2}{L}\right)^{1/2}\sin\left(\frac{n\pi x}{L}\right)$$

$$= -\frac{2e}{L}\int_0^L x\sin\left(\frac{n'\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)\mathrm{d}x$$

$$= \begin{cases} 0 & \text{if } n' = n+2 \\ +\left(\dfrac{8eL}{\pi^2}\right)\dfrac{n(n+1)}{(2n+1)^2} & \text{if } n' = n+1 \end{cases}$$

The integral is standard, but may also be evaluated using $2\sin A \sin B = \cos(A-B) - \cos(A+B)$ as in Problem 17.14

$$h\nu = E_{n+1} - E_n = (2n+1)\frac{h^2}{8m_eL^2}$$

Therefore, for the transition $n+1 \leftarrow n$,

$$f = \left(\frac{8\pi^2}{3}\right)\left(\frac{m_e}{he^2}\right)\left(\frac{h}{8m_eL^2}\right)(2n+1)\left(\frac{8eL}{\pi^2}\right)^2\frac{n^2(n+1)^2}{(2n+1)^4} = \left(\frac{64}{3\pi^2}\right)\left[\frac{n^2(n+1)^2}{(2n+1)^3}\right]$$

Therefore, $f \propto \dfrac{n^2(n+1)^2}{(2n+1)^3}$

The value of n depends on the number of bonds: each π bond supplies two π electrons and so n increases by 1. For large n,

$$f \propto \frac{n^4}{8n^3} \to \frac{n}{8} \quad \text{and} \quad f \propto n$$

Therefore, for the longest wavelength transitions f increases as the chain length is increased. The energy of the transition is proportional to $\dfrac{(2n+1)}{L^2}$; but as $n \propto L$, this energy is proportional to $\dfrac{1}{L}$.

Since $E_n = \dfrac{n^2h^2}{8m_eL^2}$, $\Delta E = \dfrac{(2n+1)h^2}{8m_eL^2}[\Delta n = +1]$

but $L = 2nd$ is the length of the chain (Exercise 17.11(a)), with d the carbon–carbon interatomic distance. Hence

$$\Delta E = \frac{\left(\frac{L}{2d}+1\right)h^2}{8m_eL^2} \approx \frac{h^2}{16m_edL} \propto \frac{1}{L}$$

Therefore, the transition moves toward the red as $\boxed{L \text{ is increased}}$ and the apparent color of the dye $\boxed{\text{shifts towards blue}}$.

P17.17 $\mu = -e\displaystyle\int \Psi_{v'}x\Psi_v\,\mathrm{d}x$

From Problem 12.15, $\mu_{10} = -e\displaystyle\int \Psi_1 x \Psi_0\,\mathrm{d}x = -e\left[\frac{\hbar}{2(m_ek)^{1/2}}\right]^{1/2}$

Hence, $f = \dfrac{8\pi^2 m_e\nu}{3he^2} \times \dfrac{e^2\hbar}{2(m_ek)^{1/2}} = \boxed{\dfrac{1}{3}}\ \left[2\pi\nu = \left(\dfrac{k}{m_e}\right)^{1/2}\right]$

P17.19 **(a)** Vibrational energy spacings of the $\boxed{\text{lower}}$ state are determined by the spacing of the peaks of A. From the spectrum, $\tilde{\nu} \approx 1800\,\text{cm}^{-1}$.

(b) Nothing can be said about the spacing of the upper state levels (without a detailed analysis of the intensities of the lines). For the second part of the question, we note that after some vibrational decay the benzophenone (which does absorb near 360 nm) can transfer its energy to naphthalene. The latter then emits the energy radiatively.

P17.21 (a) The Beer–Lambert Law is:

$$A = \log \frac{I_0}{I} = \varepsilon[\mathrm{J}]l.$$

The absorbed intensity is:

$$I_{\mathrm{abs}} = I_0 - I \quad \text{so} \quad I = I_0 - I_{\mathrm{abs}}.$$

Substitute this expression into the Beer–Lambert law and solve for I_{abs}:

$$\log \frac{I_0}{I_0 - I_{\mathrm{abs}}} = \varepsilon[\mathrm{J}]l \quad \text{so} \quad I_0 - I_{\mathrm{abs}} = I_0 \times 10^{-\varepsilon[\mathrm{J}]l},$$

$$\text{and} \qquad I_{\mathrm{abs}} = \boxed{I_0 \times (1 - 10^{-\varepsilon[\mathrm{J}]l})}.$$

(b) The problem states that $I_{\mathrm{f}}(\tilde{\nu}_{\mathrm{f}})$ is proportional to ϕ_{f} and to $I_{\mathrm{abs}}(\tilde{\nu})$, so:

$$I_{\mathrm{f}}(\tilde{\nu}_{\mathrm{f}}) \propto \phi_{\mathrm{f}} I_0(\tilde{\nu}) \times (1 - 10^{\varepsilon[\mathrm{J}]l}).$$

If the exponent is small, we can expand $1 - 10^{-\varepsilon[\mathrm{J}]l}$ in a power series:

$$10^{-\varepsilon[\mathrm{J}]l} = (\mathrm{e}^{\ln 10})^{-\varepsilon[\mathrm{J}]l} \approx 1 - \varepsilon[\mathrm{J}]l \ln 10 + \cdots,$$

$$\text{and} \qquad I_{\mathrm{f}}(\tilde{\nu}_{\mathrm{f}}) \propto \boxed{\phi_{\mathrm{f}} I_0(\tilde{\nu}) \varepsilon[\mathrm{J}]l \ln 10}.$$

P17.22 Use the Clebsch–Gordan series [Chapter 13] to compound the two resultant angular momenta, and impose the conservation of angular momentum on the composite system.

(a) O_2 has $S = 1$ [it is a spin triplet]. The configuration of an O atom is [He]$2s^2 2p^4$, which is equivalent to a Ne atom with two electron-like "holes". The atom may therefore exist as a spin singlet or as a spin triplet. Since $S_1 = 1$ and $S_2 = 0$ or $S_1 = 1$ and $S_2 = 1$ may each combine to give a resultant with $S = 1$, both may be the products of the reaction. Hence multiplicities $\boxed{3+1}$ and $\boxed{3+3}$ may be expected.

(b) N_2, $S = 0$. The configuration of an N atom is [He] $2s^2 2p^3$. The atoms may have $S = \frac{3}{2}$ or $\frac{1}{2}$. Then we note that $S_1 = \frac{3}{2}$ and $S_1 = \frac{3}{2}$ can combine to give $S = 0$; $S_1 = \frac{1}{2}$ and $S_2 = \frac{1}{2}$ can also combine to give $S = 0$ (but $S_1 = \frac{3}{2}$ and $S_2 = \frac{1}{2}$ cannot). Hence, the multiplicities $\boxed{4+4}$ and $\boxed{2+2}$ may be expected.

Solutions to applications

P17.24 The integrated absorption coefficient is

$$\mathcal{A} = \int \varepsilon(\tilde{\nu})\,\mathrm{d}\tilde{\nu} \ [16.12]$$

If we can express ε as an analytical function of $\tilde{\nu}$, we can carry out the integration analytically. Following the hint in the problem, we seek to fit ε to an exponential function, which means that a plot of $\ln \varepsilon$ versus $\tilde{\nu}$ ought to be a straight line (Fig. 17.3). So if

$$\ln \varepsilon = m\tilde{\nu} + b \quad \text{then} \quad \varepsilon = \exp(m\tilde{\nu})\exp(b)$$

and $\mathcal{A} = \dfrac{e^b}{m}\exp(m\tilde{\nu})$ (evaluated at the limits integration). We draw up the following table and find the best-fit line

λ/nm	$\varepsilon/(\mathrm{L\,mol^{-1}\,cm^{-1}})$	$\tilde{\nu}/\mathrm{cm^{-1}}$	$\ln \varepsilon/(\mathrm{L\,mol^{-1}\,cm^{-1}})$
292.0	1512	34248	4.69
296.3	865	33748	4.13
300.8	477	33248	3.54
305.4	257	32748	2.92
310.1	135.9	32248	2.28
315.0	69.5	31746	1.61
320.0	34.5	31250	0.912

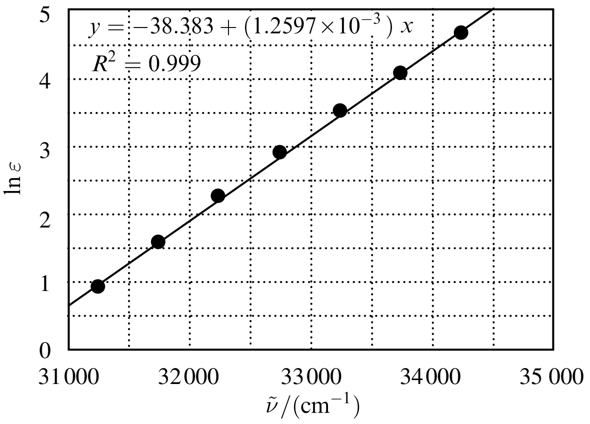


Figure 17.3

$$\text{So } \mathcal{A} = \frac{e^{-38.383}}{1.26\times10^{-3}\,\mathrm{cm}}\left[\exp\left(\frac{1.26\times10^{-3}\,\mathrm{cm}}{290\times10^{-7}\,\mathrm{cm}}\right) - \exp\left(\frac{1.26\times10^{-3}\,\mathrm{cm}}{320\times10^{-7}\,\mathrm{cm}}\right)\right]\mathrm{L\,mol^{-1}\,cm^{-1}}$$

$$= \boxed{1.24\times10^{5}\,\mathrm{L\,mol^{-1}\,cm^{-2}}}$$

P17.25 The concentration of the hypothetical pure layer is

$$[\mathrm{O_3}] = \frac{n}{V} = \frac{p}{RT} = \frac{1\,\mathrm{atm}}{(0.08206\,\mathrm{L\,atm\,mol^{-1}\,K^{-1}})\times(273\,\mathrm{K})} = 4.46\times10^{-2}\,\mathrm{mol\,L^{-1}}$$

So for 300 DU

$$A = \varepsilon cl = (476\,\mathrm{L\,mol^{-1}\,cm^{-1}})\times(0.300\,\mathrm{cm})\times(4.46\times10^{-2}\,\mathrm{mol\,L^{-1}}) = \boxed{6.37}$$

and for 100 DU

$$A = \varepsilon cl = (476\,\mathrm{L\,mol^{-1}\,cm^{-1}})\times(0.100\,\mathrm{cm})\times(4.46\times10^{-2}\,\mathrm{mol\,L^{-1}}) = \boxed{2.12}$$

P17.27 The reaction enthalpy for process (2) is

$$\Delta_r H^{\ominus} = \Delta_f H^{\ominus}(\mathrm{Cl}) + \Delta_f H^{\ominus}(\mathrm{OClO}^+) + \Delta_f H^{\ominus}(\mathrm{e}^-) - \Delta_f H^{\ominus}(\mathrm{Cl_2O_2})$$

so $\Delta_f H^{\ominus}(\mathrm{Cl_2O_2}) = \Delta_f H^{\ominus}(\mathrm{Cl}) + \Delta_f H^{\ominus}(\mathrm{OClO}^+) + \Delta_f H^{\ominus}(\mathrm{e}^-) - \Delta_r H^{\ominus}$

$$\begin{aligned}\Delta_f H^{\ominus}(\mathrm{Cl_2O_2}) &= (121.68 + 1096 + 0)\,\mathrm{kJ\,mol^{-1}} - (10.95\,\mathrm{eV}) \times (96.485\,\mathrm{kJ\,eV^{-1}}) \\ &= 161\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

We see that the Cl_2O_2 in process (2) is different from that in process (1), for its heat of formation is $\boxed{28\,\mathrm{kJ\,mol^{-1}}}$ greater. This is consistent with the computations, which say that ClOOCl is likely to be the lowest-energy isomer. Experimentally we see that the Cl_2O_2 of process (2), which is not ClOOCl, is not very much greater in energy than the lowest-energy isomer.

18 Spectroscopy 3: magnetic resonance

Solutions to exercises

Discussion questions

E18.1(b) Before the application of a pulse the magnetization vector, $\boldsymbol{M}$, points along the direction of the static external magnetic field $\mathcal{B}_0$. There are more α spins than β spins. When we apply a rotating magnetic field $\mathcal{B}_1$ at right angles to the static field, the magnetization vector as seen in the rotating frame begins to precess about the $\mathcal{B}_1$ field with angular frequency $\omega_1 = \gamma \mathcal{B}_1$. The angle through which M rotates is $\theta = \gamma \mathcal{B}_1 t$, where t is the time for which the $\mathcal{B}_1$ pulse is applied. When $t = \pi/2\gamma\mathcal{B}_1$, $\theta = \pi/2 = 90^\circ$, and $\boldsymbol{M}$ has rotated into the xy plane. Now there are equal numbers of α and β spins. A 180° pulse applied for a time $\pi/\gamma\mathcal{B}_1$, rotates $\boldsymbol{M}$ antiparallel to the static field. Now there are more β spins than α spins. A population inversion has occurred.

E18.2(b) The basic COSY experiment uses the simplest of all two-dimensional pulse sequences: a single 90° pulse to excite the spins at the end of the preparation period, and a mixing period containing just a second 90° pulse (see Fig. 18.44 of the text).

The key to the COSY technique is the effect of the second 90° pulse, which can be illustrated by consideration of the four energy levels of an AX system (as shown in Fig. 18.12). At thermal equilibrium, the population of the αAαX level is the greatest, and that of βAβX level is the smallest; the other two levels have the same energy and an intermediate population. After the first 90° pulse, the spins are no longer at thermal equilibrium. If a second 90° pulse is applied at a time t_1 that is short compared to the spin-lattice relaxation time T_1 the extra input of energy causes further changes in the populations of the four states. The changes in populations will depend on how far the individual magnetizations have precessed during the evolution period.

For simplicity, let us consider a COSY experiment in which the second 90° pulse is split into two selective pulses, one applied to X and one to A. Depending on the evolution time t_1, the 90° pulse that excites X may leave the population differences across each of the two X transitions unchanged, inverted, or somewhere in between. Consider the extreme case in which one population difference is inverted and the other unchanged (Fig. 18.45). The 90° pulse that excites A will now generate an FID in which one of the two A transitions has increased in intensity, and the other has decreased. The overall effect is that precession of the X spins during the evolution period determines the amplitudes of the signals from the A spins obtained during the detection period. As the evolution time t_1 is increased, the intensities of the signals from A spins oscillate at rates determined by the frequencies of the two X transitions.

This transfer of information between spins is at the heart of two-dimensional NMR spectroscopy and leads to the correlation of different signals in a spectrum. In this case, information transfer tells us that there is a scalar coupling between A and X. If we conduct a series of experiments in which t_1 is incremented, Fourier transformation of the FIDs on t_2 yields a set of spectra $I(\nu_1, \nu_2)$ in which the A signal amplitudes oscillate as a function of t_1. A second Fourier transformation, this time on t_1, converts these oscillations into a two-dimensional spectrum $I(\nu_1, \nu_2)$. The signals are spread out in ν_1 according to their precession frequencies during the detection period. Thus, if we apply the COSY pulse sequence to our AX spin system (Fig. 18.44), the result is a two-dimensional spectrum that contains four groups of signals centred on the two chemical shifts in ν_1 and ν_2. Each group will show fine structure, consisting of a block of four signals separated by J_{AX}. The diagonal peaks are signals centerd on $(\delta_{\mathrm{A}}\delta_{\mathrm{A}})$ and $(\delta_{\mathrm{X}}\delta_{\mathrm{X}})$ and lie along the diagonal $\nu_1 = \nu_2$. They arise from signals that did not change chemical shift between t_1 and t_2. The cross peaks (or *off-diagonal peaks*) are signals centred on $(\delta_{\mathrm{A}}\delta_{\mathrm{X}})$ and $(\delta_{\mathrm{X}}\delta_{\mathrm{A}})$ and owe their existence to the coupling between A and X.

Consequently, cross peaks in COSY spectra allow us to map the couplings between spins and to trace out the bonding network in complex molecules. Figure 18.46 shows a simple example of a proton COSY spectrum of 1-nitropropane.

E18.3(b) The molecular orbital occupied by the unpaired electron in an organic radical can be identified through the observation of hyperfine splitting in the EPR spectrum of the radical. The magnitude of this splitting is proportional to the spin density of the unpaired electron at those positions in the radical having atoms with nuclear moments. In addition, the spin density on carbon atoms adjacent to the magnetic nuclei can be determined indirectly through the McConnell relation. Thus, for example, in the benzene negative ion, unpaired spin densities on both the carbon atoms and hydrogen atoms can be determined from the EPR hyperfine splittings. The next step then is to construct a molecular orbital which will theoretically reproduce these experimentally determined spin densities. A good match indicates that we have found a good molecular orbital for the radical.

Numerical exercises

E18.4(b) For $^{19}\mathrm{F}\ \dfrac{\mu}{\mu_\mathrm{N}} = 2.62835,\ g = 5.2567$

$$\nu = \nu_\mathrm{L} = \frac{\gamma\mathcal{B}}{2\pi} \quad \text{with } \gamma = \frac{g_I\mu_\mathrm{N}}{\hbar}$$

Hence, $\nu = \dfrac{g_I\mu_\mathrm{N}\mathcal{B}}{h} = \dfrac{(5.2567)\times(5.0508\times10^{-27}\,\mathrm{J\,T^{-1}})\times(16.2\,\mathrm{T})}{(6.626\times10^{-34}\,\mathrm{J\,s})}$

$$= 6.49\times10^{8}\,\mathrm{s^{-1}} = \boxed{649\,\mathrm{MHz}}$$

E18.5(b) $E_{m_I} = -\gamma\hbar\mathcal{B}m_I = -g_I\mu_\mathrm{N}\mathcal{B}m_I$

$m_I = 1, 0, -1$

$E_{m_I} = -(0.404)\times(5.0508\times10^{-27}\,\mathrm{J\,T^{-1}})\times(11.50\,\mathrm{T})m_I$

$= -(2.34\overline{66}\times10^{-26}\,\mathrm{J})m_I$

$\boxed{-2.35\times10^{-26}\,\mathrm{J},\ 0,\ +2.35\times10^{-26}\,\mathrm{J}}$

E18.6(b) The energy separation between the two levels is

$$\Delta E = h\nu \quad \text{where } \nu = \frac{\gamma\mathcal{B}}{2\pi} = \frac{(1.93\times10^{7}\,\mathrm{T^{-1}\,s^{-1}})\times(15.4\,\mathrm{T})}{2\pi}$$

$$= 4.73\times10^{7}\,\mathrm{s^{-1}} = \boxed{47.3\,\mathrm{MHz}}$$

E18.7(b) A 600 MHz NMR spectrometer means 600 MHz is the resonance field for protons for which the magnetic field is 14.1 T as shown in Exercise 18.4(a). In high-field NMR it is the field not the frequency that is fixed.

(a) A ^{14}N nucleus has three energy states in a magnetic field corresponding to $m_I = +1, 0, -1$. But $\Delta E(+1 \to 0) = \Delta E(0 \to -1)$

$$\Delta E = E_{m_I'} - E_{m_I} = -\gamma\hbar\mathcal{B}m_I' - (-\gamma\hbar\mathcal{B}m_I)$$

$$= -\gamma\hbar\mathcal{B}(m_I' - m_I) = -\gamma\hbar\mathcal{B}\Delta m_I$$

The allowed transitions correspond to $\Delta m_I = \pm1$; hence

$$\Delta E = h\nu = \gamma\hbar\mathcal{B} = g_I\mu_N\mathcal{B} = (0.4036)\times(5.051\times10^{-27}\,\mathrm{J\,T^{-1}})\times(14.1\,\mathrm{T})$$

$$= \boxed{2.88\times10^{-26}\,\mathrm{J}}$$

(b) We assume that the electron g-value in the radical is equal to the free electron g-value, $g_e = 2.0023$. Then

$$\Delta E = h\nu = g_e\mu_B\mathcal{B}[37] = (2.0023) \times (9.274 \times 10^{-24}\,\mathrm{J\,T^{-1}}) \times (0.300\,\mathrm{T})$$
$$= \boxed{5.57 \times 10^{-24}\,\mathrm{J}}$$

Comment. The energy level separation for the electron in a free radical in an ESR spectrometer is far greater than that of nuclei in an NMR spectrometer, despite the fact that NMR spectrometers normally operate at much higher magnetic fields.

E18.8(b) $\Delta E = h\nu = \gamma\hbar\mathcal{B} = g_I\mu_N\mathcal{B}$ [Exercise 18.4(a)]

Hence, $\mathcal{B} = \dfrac{h\nu}{g_I\mu_N} = \dfrac{(6.626 \times 10^{-34}\,\mathrm{J\,Hz^{-1}}) \times (150.0 \times 10^6\,\mathrm{Hz})}{(5.586) \times (5.051 \times 10^{-27}\,\mathrm{J\,T^{-1}})} = \boxed{3.523\,\mathrm{T}}$

E18.9(b) In all cases the selection rule $\Delta m_I = \pm 1$ is applied; hence (Exercise 18.7(b)(**a**))

$$\mathcal{B} = \frac{h\nu}{g_I\mu_N} = \frac{6.626 \times 10^{-34}\,\mathrm{J\,Hz^{-1}}}{5.0508 \times 10^{-27}\,\mathrm{J\,T^{-1}}} \times \frac{\nu}{g_I}$$
$$= (1.3119 \times 10^{-7}) \times \frac{\left(\frac{\nu}{\mathrm{Hz}}\right)}{g_I}\mathrm{T} = (0.13119) \times \frac{\left(\frac{\nu}{\mathrm{MHz}}\right)}{g_I}\mathrm{T}$$

We can draw up the following table

	$\mathcal{B}/\mathrm{T}$	$^{14}\mathrm{N}$	$^{19}\mathrm{F}$	$^{31}\mathrm{P}$
	g_I	0.40356	5.2567	2.2634
(a)	300 MHz	97.5	7.49	17.4
(b)	750 MHz	244	18.7	43.5

Comment. Magnetic fields above 20 T have not yet been obtained for use in NMR spectrometers. As discussed in the solution to Exercise 18.7(b), it is the field, not the frequency, that is fixed in high-field NMR spectrometers. Thus an NMR spectrometer that is called a 300 MHz spectrometer refers to the resonance frequency for protons and has a magnetic field fixed at 7.05 T.

E18.10(b) The relative population difference for spin $-\frac{1}{2}$ nuclei is given by

$$\frac{\delta N}{N} = \frac{N_\alpha - N_\beta}{N_\alpha + N_\beta} \approx \frac{\gamma\hbar\mathcal{B}}{2kT} = \frac{g_I\mu_N\mathcal{B}}{2kT} \quad [\textit{Justification } 18.1]$$
$$= \frac{1.405(5.05 \times 10^{-27}\,\mathrm{J\,T^{-1}})\mathcal{B}}{2(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K})} = 8.62 \times 10^{-7}(\mathcal{B}/\mathrm{T})$$

(a) For 0.50 T $\dfrac{\delta N}{N} = (8.62 \times 10^{-7}) \times (0.50) = \boxed{4.3 \times 10^{-7}}$

(b) For 2.5 T $\dfrac{\delta N}{N} = (8.62 \times 10^{-7}) \times (2.5) = \boxed{2.2 \times 10^{-6}}$

(c) For 15.5 T $\dfrac{\delta N}{N} = (8.62 \times 10^{-7}) \times (15.5) = \boxed{1.34 \times 10^{-5}}$

E18.11(b) The ground state has

$$m_I = +\tfrac{1}{2} = \alpha \text{ spin}, \qquad m_I = -\tfrac{1}{2} = \beta \text{ spin}$$

Hence, with

$$\delta N = N_\alpha - N_\beta$$

$$\frac{\delta N}{N} = \frac{N_\alpha - N_\beta}{N_\alpha + N_\beta} = \frac{N_\alpha - N_\alpha e^{-\Delta E/kT}}{N_\alpha + N_\alpha e^{-\Delta E/kT}} \quad [\textit{Justification } 18.1]$$

$$= \frac{1 - e^{-\Delta E/kT}}{1 + e^{-\Delta E/kT}} \approx \frac{1 - (1 - \Delta E/kT)}{1+1} \approx \frac{\Delta E}{2kT} = \frac{g_I \mu_N \mathcal{B}}{2kT} \quad [\text{for } \Delta E \ll kT]$$

$$\delta N = \frac{N g_I \mu_N \mathcal{B}}{2kT} = \frac{Nh\nu}{2kT}$$

Thus, $\delta N \propto \nu$

$$\frac{\delta N(800\,\text{MHz})}{\delta N(60\,\text{MHz})} = \frac{800\,\text{MHz}}{60\,\text{MHz}} = \boxed{13}$$

This ratio is not dependent on the nuclide as long as the approximation $\Delta E \ll kT$ holds.

(a) $\delta = \dfrac{\nu - \nu^\circ}{\nu^\circ} \times 10^6$ [18.25]

Since both ν and ν° depend upon the magnetic field in the same manner, namely

$$\nu = \frac{g_I \mu_N \mathcal{B}}{h} \quad \text{and} \quad \nu^\circ = \frac{g_I \mu_N \mathcal{B}_0}{h} \quad [\text{Exercise 18.4(a)}]$$

δ is $\boxed{\text{independent}}$ of both $\mathcal{B}$ and ν.

(b) Rearranging [10] $\nu - \nu^\circ = \nu^\circ \delta \times 10^{-6}$

and we see that the relative chemical shift is

$$\frac{\nu - \nu^\circ(800\,\text{MHz})}{\nu - \nu^\circ(60\,\text{MHz})} = \frac{800\,\text{MHz}}{60\,\text{MHz}} = \boxed{13}$$

Comment. This direct proportionality between $\nu - \nu^\circ$ and ν° is one of the major reasons for operating an NMR spectrometer at the highest frequencies possible.

E18.12(b)

$$\mathcal{B}_{\text{loc}} = (1 - \sigma)\mathcal{B}$$

$$|\Delta \mathcal{B}_{\text{loc}}| = |(\Delta\sigma)|\mathcal{B} \approx |[\delta(\text{CH}_3) - \delta(\text{CH}_2)]|\mathcal{B}$$

$$= |1.16 - 3.36| \times 10^{-6}\mathcal{B} = 2.20 \times 10^{-6}\mathcal{B}$$

(a) $\mathcal{B} = 1.9\,\text{T}$, $|\Delta \mathcal{B}_{\text{loc}}| = (2.20 \times 10^{-6}) \times (1.9\,\text{T}) = \boxed{4.2 \times 10^{-6}\,\text{T}}$

(b) $\mathcal{B} = 16.5\,\text{T}$, $|\Delta \mathcal{B}_{\text{loc}}| = (2.20 \times 10^{-6}) \times (16.5\,\text{T}) = \boxed{3.63 \times 10^{-5}\,\text{T}}$

E18.13(b)

$$\nu - \nu^\circ = \nu^\circ \delta \times 10^{-6}$$

$$|\Delta\nu| \equiv (\nu - \nu^\circ)(\text{CH}_2) - (\nu - \nu^\circ)(\text{CH}_3) = \nu(\text{CH}_2) - \nu(\text{CH}_3)$$

$$= \nu^\circ[\delta(\text{CH}_2) - \delta(\text{CH}_3)] \times 10^{-6}$$

$$= (3.36 - 1.16) \times 10^{-6}\nu^\circ = 2.20 \times 10^{-6}\nu^\circ$$

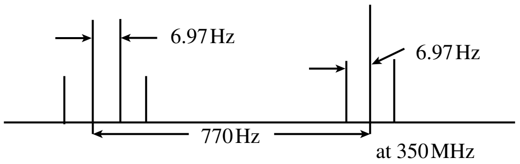


Figure 18.1

(a) $\nu^\circ = 350\,\text{MHz} \qquad |\Delta\nu| = (2.20\times10^{-6})\times(350\,\text{MHz}) = 770\,\text{Hz}$ [Fig. 18.1]

(b) $\nu^\circ = 650\,\text{MHz} \qquad |\Delta\nu| = (2.20\times10^{-6})\times(650\,\text{MHz}) = 1.43\,\text{kHz}$

At 650 MHz, the spin–spin splitting remains the same at 6.97 Hz, but as $\Delta\nu$ has increased to 1.43 kHz, the splitting appears narrower on the δ scale.

E18.14(b) The difference in resonance frequencies is

$$\Delta\nu = (\nu^\circ\times10^{-6})\Delta\delta = (350\,\text{s}^{-1})\times(6.8-5.5) = 4.6\times10^{2}\,\text{s}^{-1}$$

The signals will be resolvable as long as the conformations have lifetimes greater than

$$\tau = (2\pi\,\Delta\delta)^{-1}$$

The interconversion rate is the reciprocal of the lifetime, so a resolvable signal requires an interconversion rate less than

$$\text{rate} = (2\pi\,\Delta\delta) = 2\pi(4.6\times10^{2}\,\text{s}^{-1}) = \boxed{2.9\times10^{3}\,\text{s}^{-1}}$$

E18.15(b) $\nu = \dfrac{g_I\mu_N\mathcal{B}}{h}$ [Exercise 18.4(a)]

Hence, $\dfrac{\nu(^{31}\text{P})}{\nu(^{1}\text{H})} = \dfrac{g(^{31}\text{P})}{g(^{1}\text{H})}$

or $\nu(^{31}\text{P}) = \dfrac{2.2634}{5.5857}\times 500\,\text{MHz} = \boxed{203\,\text{MHz}}$

The proton resonance consists of 2 lines $\left(2\times\frac{1}{2}+1\right)$ and the ^{31}P resonance of 5 lines $\left[2\times\left(4\times\frac{1}{2}\right)+1\right]$. The intensities are in the ratio 1 : 4 : 6 : 4 : 1 (Pascal's triangle for four equivalent spin $\frac{1}{2}$ nuclei, Section 18.6). The lines are spaced $\dfrac{5.5857}{2.2634} = 2.47$ times greater in the phosphorus region than the proton region. The spectrum is sketched in Fig. 18.2.

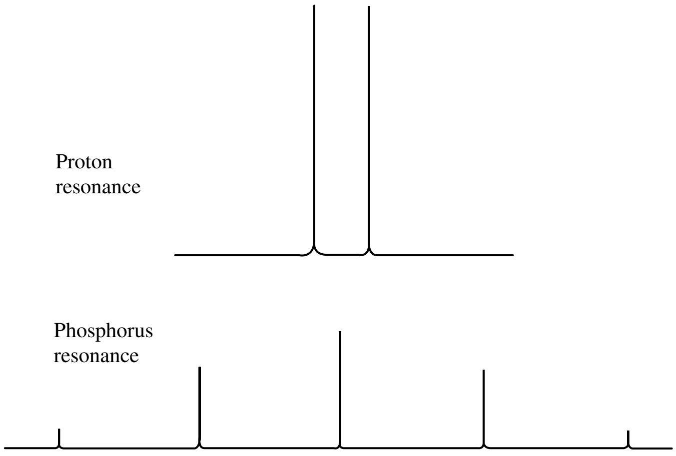


Figure 18.2

E18.16(b) Look first at A and M, since they have the largest splitting. The A resonance will be split into a widely spaced triplet (by the two M protons); each peak of that triplet will be split into a less widely spaced sextet (by the five X protons). The M resonance will be split into a widely spaced triplet (by the two A protons); each peak of that triplet will be split into a narrowly spaced sextet (by the five X protons). The X resonance will be split into a less widely spaced triplet (by the two A protons); each peak of that triplet will be split into a narrowly spaced triplet (by the two M protons). (See Fig. 18.3.)

Only the splitting of the central peak of Fig. 18.3(a) is shown in Fig. 18.3(b).

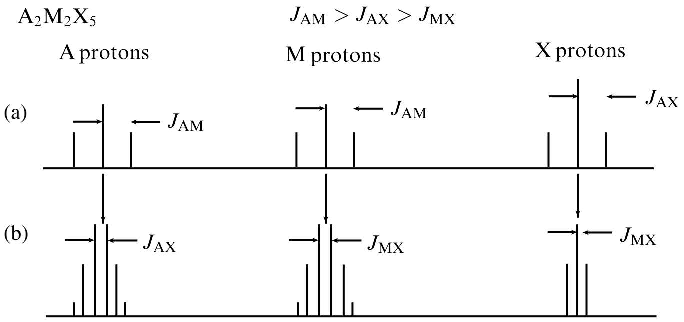


Figure 18.3

E18.17(b) **(a)** Since all J_{HF} are equal in this molecule (the CH_2 group is perpendicular to the CF_2 group), the H and F nuclei are both chemically and magnetically equivalent.

(b) Rapid rotation of the PH_3 groups about the Mo–P axes makes the P and H nuclei chemically and magnetically equivalent in both the *cis*- and *trans*-forms.

E18.18(b) Precession in the rotating frame follows

$$\nu_L = \frac{\gamma\mathcal{B}_1}{2\pi} \quad \text{or} \quad \omega_1 = \gamma\mathcal{B}_1$$

Since ω is an angular frequency, the angle through which the magnetization vector rotates is

$$\theta = \gamma\mathcal{B}_1 t = \frac{g_I\mu_N}{\hbar}\mathcal{B}_1 t$$

$$\text{So } \mathcal{B}_1 = \frac{\theta\hbar}{g_I\mu_N t} = \frac{(\pi)\times(1.0546\times10^{-34}\,\mathrm{J\,s})}{(5.586)\times(5.0508\times10^{-27}\,\mathrm{J\,T^{-1}})\times(12.5\times10^{-6}\,\mathrm{s})} = \boxed{9.40\times10^{-4}\,\mathrm{T}}$$

a 90° pulse requires $\frac{1}{2}\times 12.5\,\mu\mathrm{s} = \boxed{6.25\,\mu\mathrm{s}}$

E18.19(b)
$$\mathcal{B} = \frac{h\nu}{g_e\mu_B} = \frac{hc}{g_e\mu_B\lambda}$$
$$= \frac{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{8}\,\mathrm{m\,s^{-1}})}{(2)\times(9.274\times10^{-24}\,\mathrm{J\,T^{-1}})\times(8\times10^{-3}\,\mathrm{m})} = \boxed{1.\bar{3}\,\mathrm{T}}$$

E18.20(b) The g factor is given by

$$g = \frac{h\nu}{\mu_B\mathcal{B}}; \quad \frac{h}{\mu_B} = \frac{6.62608\times10^{-34}\,\mathrm{J\,s}}{9.2740\times10^{-24}\,\mathrm{J\,T^{-1}}} = 7.1448\times10^{-11}\,\mathrm{T\,Hz^{-1}} = 71.448\,\mathrm{mT\,GHz^{-1}}$$

$$g = \frac{71.448\,\mathrm{mT\,GHz^{-1}}\times 9.2482\,\mathrm{GHz}}{330.02\,\mathrm{mT}} = \boxed{2.0022}$$

E18.21(b) The hyperfine coupling constant for each proton is $\boxed{2.2\,\text{mT}}$, the difference between adjacent lines in the spectrum. The g value is given by

$$g = \frac{h\nu}{\mu_B \mathcal{B}} = \frac{(71.448\,\text{mT GHz}^{-1}) \times (9.332\,\text{GHz})}{334.7\,\text{mT}} = \boxed{1.992}$$

E18.22(b) If the spectrometer has sufficient resolution, it will see a signal split into eight equal parts at $\pm 1.445 \pm 1.435 \pm 1.055\,\text{mT}$ from the centre, namely

$$\boxed{328.865, 330.975, 331.735, 331.755, 333.845, 333.865, 334.625,\ \text{and}\ 336.735\,\text{mT}}$$

If the spectrometer can only resolve to the nearest 0.1 mT, then the spectrum will appear as a sextet with intensity ratios of 1 : 1 : 2 : 2 : 1 : 1. The four central peaks of the more highly resolved spectrum would be the two central peaks of the less resolved spectrum.

E18.23(b) **(a)** If the CH_2 protons have the larger splitting there will be a triplet (1 : 2 : 1) of quartets (1 : 3 : 3 : 1). Altogether there will be 12 lines with relative intensities 1(4 lines), 2(2 lines), 3(4 lines), and 6(2 lines). Their positions in the spectrum will be determined by the magnitudes of the two proton splittings which are not given.

(b) If the CD_2 deuterons have the larger splitting there will be a quintet (1 : 2 : 3 : 2 : 1) of septets (1 : 3 : 6 : 7 : 6 : 3 : 1). Altogether there will be 35 lines with relative intensities 1(4 lines), 2(4 lines), 3(6 lines), 6(8 lines), 7(2 lines), 9(2 lines), 12(4 lines), 14(2 lines), 18(2 lines), and 21(1 line). Their positions in the spectrum will be determined by the magnitude of the two deuteron splittings which are not given.

E18.24(b) The hyperfine coupling constant for each proton is $\boxed{2.2\,\text{mT}}$, the difference between adjacent lines in the spectrum. The g value is given by

$$g = \frac{h\nu}{\mu_B \mathcal{B}} \quad \text{so} \quad \mathcal{B} = \frac{h\nu}{\mu_B g}, \quad \frac{h}{\mu_B} = 71.448\,\text{mT GHz}^{-1}$$

(a) $$\mathcal{B} = \frac{(71.448\,\text{mT GHz}^{-1}) \times (9.312\,\text{GHz})}{2.0024} = \boxed{332.3\,\text{mT}}$$

(b) $$\mathcal{B} = \frac{(71.448\,\text{mT GHz}^{-1}) \times (33.88\,\text{GHz})}{2.0024} = \boxed{1209\,\text{mT}}$$

E18.25(b) Two nuclei of spin $\boxed{I = 1}$ give five lines in the intensity ratio 1 : 2 : 3 : 2 : 1 (Fig. 18.4).

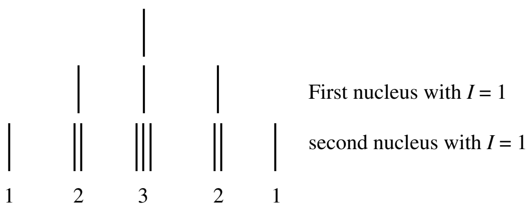


Figure 18.4

E18.26(b) The X nucleus produces four lines of equal intensity. The three H nuclei split each into a 1 : 3 : 3 : 1 quartet. The three D nuclei split each line into a septet with relative intensities 1 : 3 : 6 : 7 : 6 : 3 : 1 (see Exercise 18.23(a)). (See Fig. 18.5.)

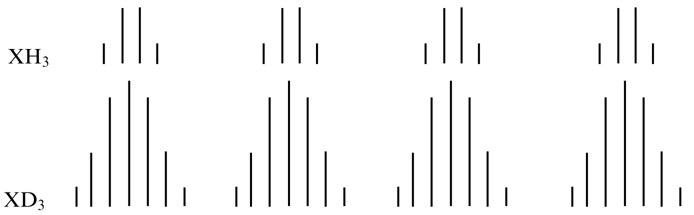


Figure 18.5

Solutions to problems

Solutions to numerical problems

P18.2

$$\tau_J \approx \frac{1}{2\pi\delta\nu} = \frac{1}{(2\pi) \times ((5.2 - 4.0) \times 10^{-6}) \times (60 \times 10^{6}\,\text{Hz})}$$

$$\approx 2.2\,\text{ms},\ \text{corresponding to a rate of jumping of } 450\,\text{s}^{-1}.$$

When $\nu = 300\,\text{MHz}$

$$\tau_J \approx \frac{1}{(2\pi) \times \{(5.2 - 4.0) \times 10^{-6}\} \times (300 \times 10^{6}\,\text{Hz})} = 0.44\,\text{ms}$$

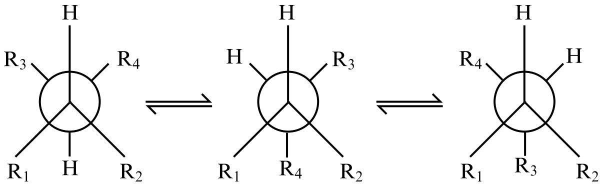
corresponding to a jump rate of $2.3 \times 10^{3}\,\text{s}^{-1}$. Assume an Arrhenius-like jumping process (Chapter 25)

$$\text{rate} \propto \mathrm{e}^{-E_\mathrm{a}/RT}$$

Then, $\ln\left[\dfrac{\text{rate}(T')}{\text{rate}(T)}\right] = \dfrac{-E_\mathrm{a}}{R}\left(\dfrac{1}{T'} - \dfrac{1}{T}\right)$

and therefore $E_\mathrm{a} = \dfrac{R\ln(r'/r)}{\frac{1}{T} - \frac{1}{T'}} = \dfrac{8.314\,\text{J K}^{-1}\,\text{mol}^{-1} \times \ln\frac{2.3\times10^{3}}{450}}{\frac{1}{280\,\text{K}} - \frac{1}{300\,\text{K}}} = \boxed{57\,\text{kJ mol}^{-1}}$

P18.5 It seems reasonable to assume that only staggered conformations can occur. Therefore the equilibria are



When $R_3 = R_4 = H$, all three of the above conformations occur with equal probability; hence

$$^{3}J_{\mathrm{HH}}(\text{methyl}) = \tfrac{1}{3}\left(^{3}J_\mathrm{t} + 2\,^{3}J_\mathrm{g}\right) \quad [\mathrm{t} = \text{trans},\ \mathrm{g} = \text{gauche};\ \mathrm{CHR_3R_4} = \text{methyl}]$$

Additional methyl groups will avoid being staggered between both R_1 and R_2. Therefore

$$^{3}J_{\mathrm{HH}}(\text{ethyl}) = \tfrac{1}{2}(J_\mathrm{t} + J_\mathrm{g}) \quad [R_3 = H, R_4 = CH_3]$$

$$^{3}J_{\mathrm{HH}}(\text{isopropyl}) = J_\mathrm{t} \quad [R_3 = R_4 = CH_3]$$

We then have three simultaneous equations in two unknowns J_t and J_g.

$$\tfrac{1}{3}({}^3J_t + 2\,{}^3J_g) = 7.3\,\text{Hz} \tag{1}$$

$$\tfrac{1}{2}({}^3J_t + {}^3J_g) = 8.0\,\text{Hz} \tag{2}$$

$$^3J_t = 11.2\,\text{Hz}$$

The two unknowns are overdetermined. The first two equations yield $^3J_t = 10.1$, $^3J_g = 5.9$. However, if we assume that $^3J_t = 11.2$ as measured directly in the ethyl case then $^3J_g = 5.4$ (eqn 1) or 4.8 (eqn 2), with an average value of 5.1.

Using the original form of the Karplus equation

$$^3J_t = A\cos^2(180^\circ) + B = 11.2$$

$$^3J_g = A\cos^2(60^\circ) + B = 5.1$$

or

$$11.2 = A + B$$

$$5.1 = 0.25A + B$$

These simultaneous equations yield $A = 6.8\,\text{Hz}$ and $B = 4.8\,\text{Hz}$. With these values of A and B, the original form of the Karplus equation fits the data exactly (at least to within the error in the values of ^3J_t and ^3J_g and in the measured values reported).

From the form of the Karplus equation in the text [21] we see that those values of A, B, and C cannot be determined from the data given, as there are three constants to be determined from only two values of J. However, if we use the values of A, B, and C given in the text, then

$$J_t = 7\,\text{Hz} - 1\,\text{Hz}(\cos 180^\circ) + 5\,\text{Hz}(\cos 360^\circ) = 11\,\text{Hz}$$

$$J_g = 7\,\text{Hz} - 1\,\text{Hz}(\cos 60^\circ) + 5\,\text{Hz}(\cos 120^\circ) = 5\,\text{Hz}$$

The agreement with the modern form of the Karplus equation is excellent, but not better than the original version. $\boxed{\text{Both fit the data equally well.}}$ But the modern version is preferred as it is more generally applicable.

P18.8 Refer to the figure in the solution to Exercise 18.23(a). The width of the CH_3 spectrum is $3a_H = \boxed{6.9\,\text{mT}}$. The width of the CD_3 spectrum is $6a_D$. It seems reasonable to assume, since the hyperfine interaction is an interaction of the magnetic moments of the nuclei with the magnetic moment of the electron, that the strength of the interactions is proportional to the nuclear moments.

$$\mu = g_I\mu_N I \quad \text{or} \quad \mu_z = g_I\mu_N m_I \ [18.14, 18.15]$$

and thus nuclear magnetic moments are proportional to the nuclear g-values; hence

$$a_D \approx \frac{0.85745}{5.5857} \times a_H = 0.1535a_H = 0.35\,\text{mT}$$

Therefore, the overall width is $6a_D = \boxed{2.1\,\text{mT}}$

P18.10 We write $P(\text{N}2s) = \dfrac{5.7\,\text{mT}}{55.2\,\text{mT}} = \boxed{0.10}$ (10 percent of its time)

$$P(\text{N}2p_z) = \frac{1.3\,\text{mT}}{3.4\,\text{mT}} = \boxed{0.38} \text{ (38 percent of its time)}$$

The total probability is

(a) $P(\mathrm{N}) = 0.10 + 0.38 = \boxed{0.48}$ (48 percent of its time).

(b) $P(\mathrm{O}) = 1 - P(\mathrm{N}) = \boxed{0.52}$ (52 percent of its time).

The hybridization ratio is

$$\frac{P(\mathrm{N}2p)}{P(\mathrm{B}2s)} = \frac{0.38}{0.10} = \boxed{3.8}$$

The unpaired electron therefore occupies an orbital that resembles as sp^3 hybrid on N, in accord with the radical's nonlinear shape.

From the discussion in Section 14.3 we can write

$$a^2 = \frac{1 + \cos\Phi}{1 - \cos\Phi}$$

$$b^2 = 1 - a^2 = \frac{-2\cos\Phi}{1 - \cos\Phi}$$

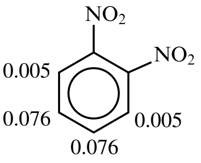
$$\lambda = \frac{b'^2}{a'^2} = \frac{-1\cos\Phi}{1 + \cos\Phi}, \text{ implying that} \cos\Phi = \frac{\lambda}{2 + \ell}$$

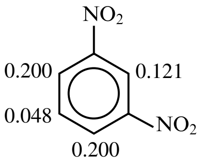
Then, since $\lambda = 3.8$, $\cos\Phi = -0.66$, so $\Phi = \boxed{131^\circ}$

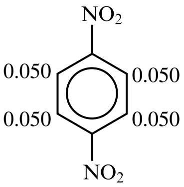
P18.11 For $C_6H_6^-$, $a = Q\rho$ with $Q = 2.25\,\mathrm{mT}$ [18.52]. If we assume that the value of Q does not change from this value (a good assumption in view of the similarity of the anions), we may write

$$\rho = \frac{a}{Q} = \frac{a}{2.25\,\mathrm{mT}}$$

Hence, we can construct the following maps







Solutions to theoretical problems

P18.14 $$\mathcal{B}_{\mathrm{nuc}} = -\frac{\gamma\hbar\mu_0 m_I}{4\pi R^3}(1 - 3\cos^2\theta)\ [18.36] = \frac{g_I\mu_{\mathrm{N}}\mu_0}{4\pi R^3} \quad [m_I = +\tfrac{1}{2}, \theta = 0, \gamma\hbar = g_I\mu_{\mathrm{N}}]$$

which rearranges to

$$R = \left(\frac{g_I\mu_{\mathrm{N}}\mu_0}{4\pi\mathcal{B}_{\mathrm{nuc}}}\right)^{1/3} = \left(\frac{(5.5857) \times (5.0508 \times 10^{-27}\mathrm{JT^{-1}}) \times (4\pi \times 10^{-7}\mathrm{T^2J^{-1}m^3})}{(4\pi) \times (0.715 \times 10^{-3}\mathrm{T})}\right)^{1/3}$$

$$= (3.946 \times 10^{-30}\,\mathrm{m^3})^{1/3} = \boxed{158\,\mathrm{pm}}$$

P18.17 We have seen (Problem 18.16) that, if $G \propto \cos \omega_0 t$, then $I(\omega) \propto \dfrac{1}{[1+(\omega_0-\omega)^2\tau^2]}$ which peaks at $\omega \approx \omega_0$. Therefore, if

$$G(t) \propto a \cos \omega_1 t + b \cos \omega_2 t$$

we can anticipate that

$$I(\omega) \propto \frac{a}{1+\omega_1-\omega)^2\tau^2} + \frac{b}{1+(\omega_2-\omega)^2\tau^2}$$

and explicit calculation shows this to be so. Therefore, $I(\omega)$ consists of two absorption lines, one peaking at $\omega \approx \omega_1$ and the other at $\omega \approx \omega_2$.

P18.21 The desired result is the linear equation:

$$[\mathrm{I}]_0 = \frac{[\mathrm{E}]_0 \Delta\nu}{\delta\nu} - K,$$

so the first task is to express quantities in terms of $[\mathrm{I}]_0$, $[\mathrm{E}]_0$, $\Delta\nu$, $\delta\nu$, and K, eliminating terms such as [I], [EI], [E], ν_I, ν_EI, and ν. (Note: symbolic mathematical software is helpful here.) Begin with ν:

$$\nu = \frac{[\mathrm{I}]}{[\mathrm{I}]+[\mathrm{EI}]}\nu_\mathrm{I} + \frac{[\mathrm{EI}]}{[\mathrm{I}]+[\mathrm{EI}]}\nu_\mathrm{EI} = \frac{[\mathrm{I}]_0-[\mathrm{EI}]}{[\mathrm{I}]_0}\nu_\mathrm{I} + \frac{[\mathrm{EI}]}{[\mathrm{I}]_0}\nu_\mathrm{EI},$$

where we have used the fact that total I (*i.e.*, free I plus bound I) is the same as intitial I. Solve this expression for [EI]:

$$[\mathrm{EI}] = \frac{[\mathrm{I}]_0(\nu-\nu_\mathrm{I})}{\nu_\mathrm{EI}-\nu_\mathrm{I}} = \frac{[\mathrm{I}]_0\delta\nu}{\Delta\nu},$$

where in the second equality we notice that the frequency differences that appear are the ones defined in the problem. Now take the equilibrium constant:

$$K = \frac{[\mathrm{E}][\mathrm{I}]}{[\mathrm{EI}]} = \frac{([\mathrm{E}]_0-[\mathrm{EI}])([\mathrm{I}]_0-[\mathrm{EI}])}{[\mathrm{EI}]} \approx \frac{([\mathrm{E}]_0-[\mathrm{EI}])[\mathrm{I}]_0}{[\mathrm{EI}]}.$$

We have used the fact that total I is much greater than total E (from the condition that $[\mathrm{I}]_0 \gg [\mathrm{E}]_0$), so it must also be much greater than [EI], even if all E binds I. Now solve this for $[\mathrm{E}]_0$:

$$[\mathrm{E}]_0 = \frac{K+[\mathrm{I}]_0}{[\mathrm{I}]_0}[\mathrm{EI}] = \left(\frac{K+[\mathrm{I}]_0}{[\mathrm{I}]_0}\right)\left(\frac{[\mathrm{I}]_0\delta\nu}{\Delta\nu}\right) = \frac{(K+[\mathrm{I}]_0)\delta\nu}{\Delta\nu}.$$

The expression contains the desired terms and only those terms. Solving for $[\mathrm{I}]_0$ yields:

$$\boxed{[\mathrm{I}]_0 = \frac{[\mathrm{E}]_0\Delta\nu}{\delta\nu} - K},$$

which would result in a straight line with slope $[\mathrm{E}]_0\Delta\nu$ and y-intercept K if one plots $[\mathrm{I}]_0$ against $1/\delta\nu$.

19 Statistical thermodynamics: the concepts

Solutions to exercises

Discussion questions

E19.1(b) Consider the value of the partition function at the extremes of temperature. The limit of q as T approaches zero, is simply g_0, the degeneracy of the ground state. As T approaches infinity, each term in the sum is simply the degeneracy of the energy level. If the number of levels is infinite, the partition function is infinite as well. In some special cases where we can effectively limit the number of states, the upper limit of the partition function is just the number of states. In general, we see that the molecular partition function gives an indication of the average number of states thermally accessible to a molecule at the temperature of the system.

E19.2(b) The statistical entropy may be defined in terms of the Boltzmann formula, $S = k \ln W$, where W is the statistical weight of the most probable configuration of the system. The relation between the entropy and the partition function is developed in two stages. In the first stage, we justify Boltzmann's formula, in the second, we express W in terms of the partition function. The justification for Boltzmann's formula is presented in *Justification* 19.6. Without repeating the details of this justification, we can see that the entropy defined through the formula has the properties we expect of the entropy. W can be thought of as a measure of disorder, hence the greater W, the greater the entropy; and the logarithmic form is consistent with the additive properties of the entropy. We expect the total disorder of a combined system to be the product of the individual disorders and $S = k \ln W = k \ln W_1W_2 = k \ln W_1 + k \ln W_2 = S_1 + S_2$.

In the second stage the formula relating entropy and the partition function is derived. This derivation is presented in *Justification* 19.7. The expression for W, eqn 19.1, is recast in terms of probabilities, which in turn are expressed in terms of the partition function through eqn 10. The final expression which is eqn 19.34 then follows immediately.

E19.3(b) Since β and temperature are inversely related, strictly speaking one can never replace the other. The concept of temperature is useful in indicating the direction of the spontaneous transfer of energy in the form of heat. It seems natural to us to think of the spontaneous direction for this transfer to be from a body at high T to one at low T. In terms of β, the spontaneous direction would be from low to high and this has an unnatural feel.

On the other hand, β has a direct connection to the energy level pattern of systems of atoms and molecules. It arises in a natural, purely mathematical, manner from our knowledge of how energy is distributed amongst the particles of our atomic/molecular system. We would not have to invoke the abstract laws of thermodynamics, namely the zeroth and second laws in order to define our concept of temperature if we used β as the property to indicate the natural direction of heat flow. We can easily demonstrate that β is directly related to the statistical weight W through the relation $\beta = (\partial \ln W/\partial U)_N$. W, U, and N are all concrete properties of an atomic/molecular system.

E19.4(b) Identical particles can be regarded as distinguishable when they are localized as in a crystal lattice where we can assign a set of coordinates to each particle. Strictly speaking it is the lattice site that carries the set of coordinates, but as long as the particle is fixed to the site, it too can be considered distinguishable.

Numerical exercises

E19.5(b) $$n_i = \frac{N\mathrm{e}^{-\beta\varepsilon_i}}{q} \quad \text{where } q = \sum_j \mathrm{e}^{-\beta\varepsilon_j}$$

Thus

$$\frac{n_2}{n_1} = \frac{\mathrm{e}^{-\beta\varepsilon_2}}{\mathrm{e}^{-\beta\varepsilon_1}} = \mathrm{e}^{-\beta(\varepsilon_2-\varepsilon_1)} = \mathrm{e}^{-\beta\Delta\varepsilon} = \mathrm{e}^{-\Delta\varepsilon/kT}$$

Given $\frac{n_2}{n_1} = \frac{1}{2}$, $\Delta\varepsilon = 300\,\mathrm{cm}^{-1}$

$$k = (1.38066 \times 10^{-23}\,\mathrm{J\,K}^{-1}) \times \left(\frac{1\,\mathrm{cm}^{-1}}{1.9864 \times 10^{-23}\,\mathrm{J}}\right) = 0.69506\,\mathrm{cm}^{-1}\,\mathrm{K}^{-1}$$

$$\frac{n_2}{n_1} = \mathrm{e}^{-\Delta\varepsilon/kT}$$

$$\ln\left(\frac{n_2}{n_1}\right) = -\Delta\varepsilon/kT$$

$$T = \frac{-\Delta\varepsilon}{k\ln(n_2/n_1)} = \frac{\Delta\varepsilon}{k\ln(n_1/n_2)}$$

$$= \frac{300\,\mathrm{cm}^{-1}}{(0.69506\,\mathrm{cm}^{-1}\,\mathrm{K}^{-1})\ln(2)} = 622.\overline{7}\,\mathrm{K} \approx \boxed{623\,\mathrm{K}}$$

E19.6(b) **(a)** $$\Lambda = h\left(\frac{\beta}{2\pi m}\right)^{1/2} [19.22] = h\left(\frac{1}{2\pi mkT}\right)^{1/2}$$

$$= (6.626 \times 10^{-34}\,\mathrm{J\,s}) \times \left(\frac{1}{(2\pi) \times (39.95) \times (1.6605 \times 10^{-27}\,\mathrm{kg}) \times (1.381 \times 10^{-23}\,\mathrm{J\,K}^{-1}) \times T}\right)^{1/2}$$

$$= \frac{276\,\mathrm{pm}}{(T/\mathrm{K})^{1/2}}$$

(b) $$q = \frac{V}{\Lambda^3}[22] = \frac{(1.00 \times 10^{-6}\,\mathrm{m}^3) \times (T/\mathrm{K})^{3/2}}{(2.76 \times 10^{-10}\,\mathrm{m})^3} = 4.76 \times 10^{22}(T/\mathrm{K})^{3/2}$$

(i) $T = 300\,\mathrm{K}$, $\Lambda = 1.59 \times 10^{-11}\,\mathrm{m} = \boxed{15.9\,\mathrm{pm}}$, $q = \boxed{2.47 \times 10^{26}}$

(ii) $T = 3000\,\mathrm{K}$, $\Lambda = \boxed{5.04\,\mathrm{pm}}$, $q = \boxed{7.82 \times 10^{27}}$

Question. At what temperature does the thermal wavelength of an argon atom become comparable to its diameter?

E19.7(b) The translational partition function is

$$q_{\mathrm{tr}} = \frac{V}{h^3}(2kT\pi m)^{3/2}$$

$$\text{so } \frac{q_{\mathrm{Xe}}}{q_{\mathrm{He}}} = \left(\frac{m_{\mathrm{Xe}}}{m_{\mathrm{He}}}\right)^{3/2} = \left(\frac{131.3\,\mathrm{u}}{4.003\,\mathrm{u}}\right)^{3/2} = \boxed{187.9}$$

E19.8(b)

$$q = \sum_{\text{levels}} g_j \mathrm{e}^{-\beta\varepsilon_j} = 2 + 3\mathrm{e}^{-\beta\varepsilon_1} + 2\mathrm{e}^{-\beta\varepsilon_2}$$

$$\beta\varepsilon = \frac{hc\tilde{\nu}}{kT} = \frac{1.4388(\tilde{\nu}/\mathrm{cm}^{-1})}{T/\mathrm{K}}$$

Thus $q = 2 + 3\mathrm{e}^{-(1.4388\times 1250/2000)} + 2\mathrm{e}^{-(1.4388\times 1300/2000)}$

$$= 2 + 1.2207 + 0.7850 = \boxed{4.006}$$

E19.9(b)

$$E = U - U(0) = -\frac{N}{q}\frac{\mathrm{d}q}{\mathrm{d}\beta} = -\frac{N}{q}\frac{\mathrm{d}}{\mathrm{d}\beta}(2 + 3\mathrm{e}^{-\beta\varepsilon_1} + 2\mathrm{e}^{-\beta\varepsilon_2})$$

$$= -\frac{N}{q}\left(-3\varepsilon_1\mathrm{e}^{-\beta\varepsilon_1} - 2\varepsilon_2\mathrm{e}^{-\beta\varepsilon_2}\right) = \frac{Nhc}{q}\left(3\tilde{\nu}_1\mathrm{e}^{-\beta hc\tilde{\nu}_1} + 2\tilde{\nu}_2\mathrm{e}^{-\beta hc\nu_2}\right)$$

$$= \left(\frac{N_{\mathrm{A}}hc}{4.006}\right) \times \left\{3(1250\,\mathrm{cm}^{-1}) \times \left(\mathrm{e}^{-(1.4388\times 1250/2000)}\right)\right.$$

$$\left. + 2(1300\,\mathrm{cm}^{-1}) \times \left(\mathrm{e}^{-(1.4388\times 1300/2000)}\right)\right\}$$

$$= \left(\frac{N_{\mathrm{A}}hc}{4.006}\right) \times (2546\,\mathrm{cm}^{-1})$$

$$= (6.022\times 10^{23}\,\mathrm{mol}^{-1}) \times (6.626\times 10^{-34}\,\mathrm{J\,s}) \times (2.9979\times 10^{10}\,\mathrm{cm\,s}^{-1}) \times (2546\,\mathrm{cm}^{-1})$$

$$= \boxed{7.605\,\mathrm{kJ\,mol}^{-1}}$$

E19.10(b) In fact there are two upper states, but one upper level. And of course the answer is different if the question asks when 15 per cent of the molecules are in the upper level, or if it asks when 15 per cent of the molecules are in *each* upper state. The solution below assumes the former.

The relative population of *states* is given by the Boltzmann distribution

$$\frac{n_2}{n_1} = \exp\left(\frac{-\Delta E}{kT}\right) = \exp\left(\frac{-hc\tilde{\nu}}{kT}\right) \quad \text{so} \quad \ln\frac{n_2}{n_1} = \frac{-hc\tilde{\nu}}{kT}$$

Thus $T = \dfrac{-hc\tilde{\nu}}{k\ln(n_2/n_1)}$

Having 15 per cent of the molecules in the upper level means

$$\frac{2n_2}{n_1} = \frac{0.15}{1-0.15} \quad \text{so} \quad \frac{n_2}{n_1} = 0.088$$

and $T = \dfrac{-(6.626\times 10^{-34}\,\mathrm{J\,s}) \times (2.998\times 10^{10}\,\mathrm{cm\,s}^{-1}) \times (360\,\mathrm{cm}^{-1})}{(1.381\times 10^{-23}\,\mathrm{J\,K}^{-1}) \times (\ln 0.088)}$

$$= \boxed{21\bar{3}\,\mathrm{K}}$$

E19.11(b) The energies of the states relative to the energy of the state with $m_I = 0$ are $-\gamma_{\mathrm{N}}\hbar\mathcal{B}, 0, +\gamma_{\mathrm{N}}\hbar\mathcal{B}$, where $\gamma_{\mathrm{N}}\hbar = 2.04\times 10^{-27}\,\mathrm{J\,T}^{-1}$. With respect to the lowest level they are $0, \gamma_{\mathrm{N}}\hbar, 2\gamma_{\mathrm{N}}\hbar$.

The partition function is

$$q = \sum_{\text{states}} \mathrm{e}^{-E_{\text{state}}/kT}$$

where the energies are measured with respect to the lowest energy. So in this case

$$q = 1 + \exp\left(\frac{-\gamma_{\mathrm{N}}\hbar\mathcal{B}}{kT}\right) + \exp\left(\frac{-2\gamma_{\mathrm{N}}\hbar\mathcal{B}}{kT}\right)$$

As $\mathcal{B}$ is increased at any given T, q decays from $q = 3$ toward $q = 1$ as shown in Fig. 19.1(a).

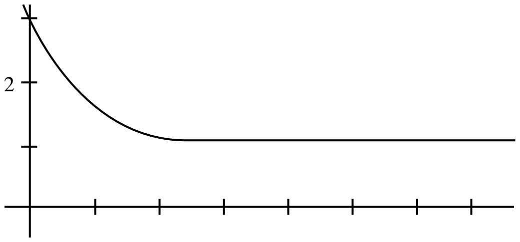


Figure 19.1(a)

The average energy (measured with respect to the lowest state) is

$$\langle E\rangle = \frac{\sum_{\text{states}} E_{\text{state}} e^{-E_{\text{state}}/kT}}{q} = \frac{1+\gamma_N\hbar\mathcal{B}\exp\left(\frac{-\gamma_N\hbar\mathcal{B}}{kT}\right)+2\gamma_N\hbar\mathcal{B}\exp\left(\frac{-2\gamma_N\hbar\mathcal{B}}{kT}\right)}{1+\exp\left(\frac{-\gamma_N\hbar\mathcal{B}}{kT}\right)+\exp\left(\frac{-2\gamma_N\hbar\mathcal{B}}{kT}\right)}$$

The expression for the mean energy measured based on zero spin having zero energy becomes

$$\langle E\rangle = \frac{\gamma_N\hbar\mathcal{B}-\gamma_N\hbar\mathcal{B}\exp\left(\frac{-2\gamma_N\hbar\mathcal{B}}{kT}\right)}{1+\exp\left(\frac{-\gamma_N\hbar\mathcal{B}}{kT}\right)+\exp\left(\frac{-2\gamma_N\hbar\mathcal{B}}{kT}\right)} = \frac{\gamma_N\hbar\mathcal{B}\left(1-\exp\left(\frac{-2\gamma_N\hbar\mathcal{B}}{kT}\right)\right)}{1+\exp\left(\frac{-\gamma_N\hbar\mathcal{B}}{kT}\right)+\exp\left(\frac{-2\gamma_N\hbar\mathcal{B}}{kT}\right)}$$

As $\mathcal{B}$ is increased at constant T, the mean energy varies as shown in Fig. 19.1(b).

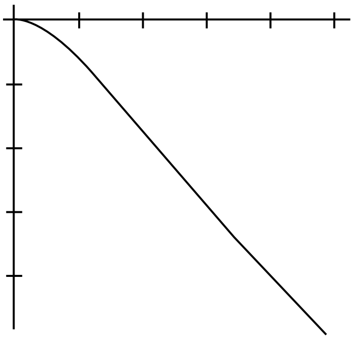


Figure 19.1(b)

The relative populations (with respect to that of the lowest state) are given by the Boltzmann factor

$$\exp\left(\frac{-\Delta E}{kT}\right) = \exp\left(\frac{-\gamma_N\hbar\mathcal{B}}{kT}\right) \quad \text{or} \quad \exp\left(\frac{-2\gamma_N\hbar\mathcal{B}}{kT}\right)$$

Note that $\frac{\gamma_N\hbar\mathcal{B}}{k} = \frac{(2.04\times10^{-27}\,\text{J}\,\text{T}^{-1})\times(20.0\,\text{T})}{1.381\times10^{-23}\,\text{J}\,\text{K}^{-1}} = 2.95\times10^{-3}\,\text{K}$

so the populations are

(a) $\exp\left(\frac{-2.95\times10^{-3}\,\text{K}}{1.0\,\text{K}}\right) = \boxed{0.99\bar{7}}$ and $\exp\left(\frac{2(-2.95\times10^{-3}\,\text{K})}{1.0\,\text{K}}\right) = \boxed{0.99\bar{4}}$

(b) $\exp\left(\frac{-2.95\times10^{-3}\text{K}}{298}\right) = \boxed{1-1\times10^{-5}}$

and $\exp\left(\frac{2(-2.95\times10^{-3}\,\text{K})}{298}\right) = \boxed{1-2\times10^{-5}}$

E19.12(b) **(a)** The ratio of populations is given by the Boltzmann factor

$$\frac{n_2}{n_1} = \exp\left(\frac{-\Delta E}{kT}\right) = \mathrm{e}^{-25.0\,\mathrm{K}/T} \quad \text{and} \quad \frac{n_3}{n_1} = \mathrm{e}^{-50.0\,\mathrm{K}/T}$$

(1) At 1.00 K

$$\frac{n_2}{n_1} = \exp\left(\frac{-25.0\,\mathrm{K}}{1.00\,\mathrm{K}}\right) = \boxed{1.39 \times 10^{-11}}$$

$$\text{and } \frac{n_3}{n_1} = \exp\left(\frac{-50.0\,\mathrm{K}}{1.00\,\mathrm{K}}\right) = \boxed{1.93 \times 10^{-22}}$$

(2) At 25.0 K

$$\frac{n_2}{n_1} = \exp\left(\frac{-25.0\,\mathrm{K}}{25.0\,\mathrm{K}}\right) = \boxed{0.368} \quad \text{and} \quad \frac{n_3}{n_1} = \exp\left(\frac{-50.0\,\mathrm{K}}{25.0\,\mathrm{K}}\right) = \boxed{0.135}$$

(3) At 100 K

$$\frac{n_2}{n_1} = \exp\left(\frac{-25.0\,\mathrm{K}}{100\,\mathrm{K}}\right) = \boxed{0.779} \quad \text{and} \quad \frac{n_3}{n_1} = \exp\left(\frac{-50.0\,\mathrm{K}}{100\,\mathrm{K}}\right) = \boxed{0.607}$$

(b) The molecular partition function is

$$q = \sum_{\text{states}} \mathrm{e}^{-E_{\text{state}}/kT} = 1 + \mathrm{e}^{-25.0\,\mathrm{K}/T} + \mathrm{e}^{-50.0\,\mathrm{K}/T}$$

At 25.0 K, we note that $\mathrm{e}^{-25.0\,\mathrm{K}/T} = \mathrm{e}^{-1}$ and $\mathrm{e}^{-50.0\,\mathrm{K}/T} = \mathrm{e}^{-2}$

$$q = 1 + \mathrm{e}^{-1} + \mathrm{e}^{-2} = \boxed{1.503}$$

(c) The molar internal energy is

$$U_\mathrm{m} = U_\mathrm{m}(0) - \frac{N_\mathrm{A}}{q}\left(\frac{\partial q}{\partial \beta}\right) \quad \text{where } \beta = (kT)^{-1}$$

$$\text{So } U_\mathrm{m} = U_\mathrm{m}(0) - \frac{N_\mathrm{A}}{q}(-25.0\,\mathrm{K})k\left(\mathrm{e}^{-25.0\,\mathrm{K}/T} + 2\mathrm{e}^{-50.0\,\mathrm{K}/T}\right)$$

At 25.0 K

$$\begin{aligned} U_\mathrm{m} - U_\mathrm{m}(0) &= -\frac{(6.022 \times 10^{23}\,\mathrm{mol}^{-1}) \times (-25.0\,\mathrm{K}) \times (1.381 \times 10^{-23}\,\mathrm{J\,K}^{-1})}{1.503} \\ &\quad \times (\mathrm{e}^{-1} + 2\mathrm{e}^{-2}) \\ &= \boxed{88.3\,\mathrm{J\,mol}^{-1}} \end{aligned}$$

(d) The molar heat capacity is

$$\begin{aligned} C_{V,\mathrm{m}} &= \left(\frac{\partial U_\mathrm{m}}{\partial T}\right)_V = N_\mathrm{A}(25.0\,\mathrm{K})k\frac{\partial}{\partial T}\frac{1}{q}\left(\mathrm{e}^{-25.0\,\mathrm{K}/T} + 2\mathrm{e}^{-50.0\,\mathrm{K}/T}\right) \\ &= N_\mathrm{A}(25.0\,\mathrm{K})k \times \left(\frac{25.0\,\mathrm{K}}{qT^2}\left(\mathrm{e}^{-25.0\,\mathrm{K}/T} + 4\mathrm{e}^{-50.0\,\mathrm{K}/T}\right)\right. \\ &\quad \left. -\frac{1}{q^2}\left(\mathrm{e}^{-25.0\,\mathrm{K}/T} + 2\mathrm{e}^{-50.0\,\mathrm{K}/T}\right)\frac{\partial q}{\partial T}\right) \end{aligned}$$

$$\text{where } \frac{\partial q}{\partial T} = \frac{25.0\,\mathrm{K}}{T^2}\left(\mathrm{e}^{-25.0\,\mathrm{K}/T} + 2\mathrm{e}^{-50.0\,\mathrm{K}/T}\right)$$

$$\text{so } C_{V,\mathrm{m}} = \frac{N_{\mathrm{A}}(25.0\,\mathrm{K})^2 k}{T^2 q}\left(\mathrm{e}^{-25.0\,\mathrm{K}/T} + 4\mathrm{e}^{-50.0\,\mathrm{K}/T} - \frac{(\mathrm{e}^{-25.0\,\mathrm{K}/T} + 2\mathrm{e}^{-50.0\,\mathrm{K}/T})^2}{q}\right)$$

At 25.0 K

$$\begin{aligned} C_{V,\mathrm{m}} &= \frac{(6.022\times10^{23}\,\mathrm{mol^{-1}})\times(25.0\,\mathrm{K})^2\times(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})}{(25.0\,\mathrm{K})^2\times(1.503)} \\ &\quad\times\left(\mathrm{e}^{-1} + 4\mathrm{e}^{-2} - \frac{(\mathrm{e}^{-1}+2\mathrm{e}^{-2})^2}{1.503}\right) \\ &= \boxed{3.53\,\mathrm{J\,K^{-1}\,mol^{-1}}} \end{aligned}$$

(e) The molar entropy is

$$S_{\mathrm{m}} = \frac{U_{\mathrm{m}} - U_{\mathrm{m}}(0)}{T} + N_{\mathrm{A}}k\ln q$$

At 25.0 K

$$\begin{aligned} S_{\mathrm{m}} &= \frac{88.3\,\mathrm{J\,mol^{-1}}}{25.0\,\mathrm{K}} + (6.022\times10^{23}\,\mathrm{mol^{-1}})\times(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\ \ln 1.503 \\ &= \boxed{6.92\,\mathrm{J\,K^{-1}\,mol^{-1}}} \end{aligned}$$

E19.13(b) $\dfrac{n_1}{n_0} = \dfrac{g_1\mathrm{e}^{-\varepsilon_1/kT}}{g_0\mathrm{e}^{-\varepsilon_0/kT}} = g_1\mathrm{e}^{-\Delta\varepsilon/kT} = 3\mathrm{e}^{-hcB/kT}$

Set $\dfrac{n_1}{n_0} = \dfrac{1}{\mathrm{e}}$ and solve for T.

$$\ln\left(\frac{1}{\mathrm{e}}\right) = \ln 3 + \left(\frac{-hcB}{kT}\right)$$

$$\begin{aligned} T &= \frac{hcB}{k(1+\ln 3)} \\ &= \frac{6.626\times10^{-34}\,\mathrm{J\,s}\times2.998\times10^{10}\,\mathrm{cm\,s^{-1}}\times10.593\,\mathrm{cm^{-1}}}{+1.381\times10^{-23}\,\mathrm{J\,K^{-1}}\times(1+1.0986)} \\ &= \boxed{7.26\,\mathrm{K}} \end{aligned}$$

E19.14(b) The Sackur–Tetrode equation gives the entropy of a monoatomic gas as

$$S = nR\ln\left(\frac{\mathrm{e}^{5/2}kT}{p\Lambda^3}\right)\quad \text{where } \Lambda = \frac{h}{\sqrt{2kT\pi m}}$$

(a) At 100 K

$$\begin{aligned} \Lambda &= \frac{6.626\times10^{-34}\,\mathrm{J\,s}}{\left\{2(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(100\,\mathrm{K})\times\pi(131.3\,\mathrm{u})\times(1.66054\times10^{-27}\,\mathrm{kg\,u^{-1}})\right\}^{1/2}} \\ &= 1.52\times10^{-11}\,\mathrm{m} \end{aligned}$$

$$\text{and } S_\mathrm{m} = (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \ln\left(\frac{\mathrm{e}^{5/2}(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(100\,\mathrm{K})}{(1.013\times10^{5}\,\mathrm{Pa})\times(1.52\times10^{-11}\,\mathrm{m})^3}\right)$$

$$= \boxed{147\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

(b) At 298.15 K

$$\Lambda = \frac{6.626\times10^{-34}\,\mathrm{J\,s}}{\left\{2(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298.15\,\mathrm{K})\times\pi(131.3\,\mathrm{u})\times(1.66054\times10^{-27}\,\mathrm{kg\,u^{-1}})\right\}^{1/2}}$$

$$= 8.822\times10^{-12}\,\mathrm{m}$$

$$\text{and } S_\mathrm{m} = (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \ln\left(\frac{\mathrm{e}^{5/2}(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298.15\,\mathrm{K})}{(1.013\times10^{5}\,\mathrm{Pa})\times(8.822\times10^{-12}\,\mathrm{m})^3}\right)$$

$$= \boxed{169.6\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

E19.15(b)

$$q = \frac{1}{1-\mathrm{e}^{-\beta\varepsilon}} = \frac{1}{1-\mathrm{e}^{-hc\beta\tilde{\nu}}}$$

$$hc\beta\tilde{\nu} = \frac{(1.4388\,\mathrm{cm\,K})\times(321\,\mathrm{cm^{-1}})}{600\,\mathrm{K}} = 0.769\overline{76}$$

$$\text{Thus } q = \frac{1}{1-\mathrm{e}^{-0.769\overline{76}}} = 1.86\overline{3}$$

The internal energy due to vibrational excitation is

$$U - U(0) = \frac{N\varepsilon\mathrm{e}^{-\beta\varepsilon}}{1-\mathrm{e}^{-\beta\varepsilon}}$$

$$= \frac{Nhc\tilde{\nu}\mathrm{e}^{-hc\tilde{\nu}\beta}}{1-\mathrm{e}^{-hc\tilde{\nu}\beta}} = \frac{Nhc\tilde{\nu}}{\mathrm{e}^{hc\tilde{\nu}\beta}-1} = (0.86\overline{3})\times(Nhc)\times(321\,\mathrm{cm^{-1}})$$

$$\text{and hence } \frac{S_\mathrm{m}}{N_\mathrm{A}k} = \frac{U-U(0)}{N_\mathrm{A}kT} + \ln q = (0.863)\times\left(\frac{hc}{kT}\right)\times(321\,\mathrm{cm^{-1}}) + \ln(1.86\overline{3})$$

$$= \frac{(0.86\overline{3})\times(1.4388\,\mathrm{K\,cm})\times(321\,\mathrm{cm^{-1}})}{600\,\mathrm{K}} + \ln(1.86\overline{3})$$

$$= 0.66\overline{4} + 0.6219\overline{9} = 1.28\overline{6}$$

$$\text{and } S_\mathrm{m} = 1.28\overline{6}R = \boxed{10.7\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

E19.16(b) Inclusion of a factor of $(N!)^{-1}$ is necessary when considering indistinguishable particles. Because of their translational freedom, gases are collections of indistinguishable particles. The factor, then, must be included in calculations on $\boxed{\text{(a) } \mathrm{CO_2} \text{ gas}}$.

Solutions to problems

Solutions to numerical problems

P19.4 $S = k\ln W \quad \text{or} \quad W = \mathrm{e}^{S/k}$ [19.30]

$$\left(\frac{\partial W}{\partial V}\right)_{T,N} = \frac{W}{k}\left(\frac{\partial S}{\partial V}\right)_{T,N}$$

$$S = nR\ln\frac{\mathrm{e}^{5/2}V}{N\Lambda^3} = nR\left[\ln V + \ln\frac{\mathrm{e}^{5/2}}{N\Lambda^3}\right]$$

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = nR\left(\frac{\partial \ln V}{\partial V}\right)_{T,N} = \frac{nR}{V} = \frac{NR}{N_\mathrm{A}V}$$

$$\left(\frac{\partial W}{\partial V}\right)_{T,N} = \frac{NRW}{N_\mathrm{A}kV} = \frac{NW}{V}$$

$$\frac{\Delta W}{W} \approx N\frac{\Delta V}{V} = \frac{pV}{kT}\frac{\Delta V}{V}$$

$$\approx \frac{(1\times 10^5\,\mathrm{Pa})\times(20\,\mathrm{m}^3)\times(1\times 10^{-5})}{(1.381\times 10^{-23}\,\mathrm{J\,K^{-1}})\times(300\,\mathrm{K})}$$

$$\approx \boxed{4.8\times 10^{21}}$$

Notice that the value of W is much larger than that of $\Delta W/W$. For example, at the conventional temperature the molar entropy of helium is $126\,\mathrm{J\,K^{-1}\,mol^{-1}}$. Therefore,

$$S = nS_\mathrm{m} = \left(\frac{pV}{RT}\right)S_\mathrm{m} = \frac{(1\times 10^5\,\mathrm{Pa})\times(20\,\mathrm{m}^3)\times(126\,\mathrm{J\,K^{-1}\,mol^{-1}})}{(8.315\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})}$$

$$= 1.02\times 10^5\,\mathrm{J\,K^{-1}}$$

$$\frac{S}{k} = \frac{1.02\times 10^5\,\mathrm{J\,K^{-1}}}{1.381\times 10^{-23}\,\mathrm{J\,K^{-1}}} = 7.36\times 10^{27}$$

$$W = \mathrm{e}^{S/k} = \mathrm{e}^{7.36\times 10^{27}} = 10^{3.20\times 10^{27}}$$

P19.6 $$\frac{n_1}{n_0} = \frac{g_1\mathrm{e}^{-\varepsilon_1/kT}}{g_0\mathrm{e}^{-\varepsilon_0/kT}} = \frac{4}{2}\times\mathrm{e}^{-\Delta\varepsilon/kT} = \frac{4}{2}\times\mathrm{e}^{-hc\tilde{\nu}/kT} = 2\mathrm{e}^{-\{(1.4388\times 450)/300\}} = 0.23$$

The observed ratio is $\frac{0.30}{0.70} = 0.43$. Hence the populations are $\boxed{\text{not at equilibrium}}$.

P19.8 First we evaluate the partition function

$$q = \sum_j g_j\mathrm{e}^{-\beta\varepsilon_j}[19.12] = \sum_j g_j\mathrm{e}^{-hc\beta\tilde{\nu}_j}$$

At $3287°\mathrm{C} = 3560\,\mathrm{K}$, $hc\beta = \frac{1.43877\,\mathrm{cm\,K}}{3560\,\mathrm{K}} = 4.041\times 10^{-4}\,\mathrm{cm}$

$$\begin{aligned} q &= 5 + 7\mathrm{e}^{-\{(4.041\times 10^{-4}\,\mathrm{cm})\times(170\,\mathrm{cm^{-1}})\}} + 9\mathrm{e}^{-\{(4.041\times 10^{-4}\,\mathrm{cm})\times(387\,\mathrm{cm^{-1}})\}} \\ &\quad + 3\mathrm{e}^{-\{(4.041\times 10^{-4}\,\mathrm{cm})\times(6557\,\mathrm{cm^{-1}})\}} \\ &= (5) + (7)\times(0.934) + (9)\times(0.855) + (3)\times(0.0707) = 19.445 \end{aligned}$$

The fractions of molecules in the various states are

$$p_j = \frac{g_j\mathrm{e}^{-\beta\varepsilon_j}}{q}[19.10] = \frac{g_j\mathrm{e}^{-hc\beta\tilde{\nu}_j}}{q}$$

$$p(^3\mathrm{F}_2) = \frac{5}{19.445} = \boxed{0.257} \qquad p(^3\mathrm{F}_3) = \frac{(7)\times(0.934)}{19.445} = \boxed{0.336}$$

$$p(^3\mathrm{F}_4) = \frac{(9)\times(0.855)}{19.445} = \boxed{0.396} \qquad p(^4\mathrm{F}_1) = \frac{(3)\times(0.0707)}{19.445} = \boxed{0.011}$$

Comment. $\sum_j p_j = 1$. Note that the most highly populated level is not the ground state.

P19.10 The partition function is the sum over states of the Boltzmann factor

$$q = \sum_{\text{states}} \exp\left(-\frac{E}{kT}\right) = \sum_{\text{states}} \exp\left(-\frac{hcG}{kT}\right) = \sum_{\text{levels}} g \exp\left(-\frac{hcG}{kT}\right)$$

where g is the degeneracy. So, at 298 K

$$q = 1 + 3\exp\left(-\frac{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{10}\,\mathrm{cm\,s^{-1}})\times(557.1\,\mathrm{cm^{-1}})}{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}\right)+\cdots$$

$$= \boxed{1.209}$$

At 1000 K

$$q = 1 + 3\exp\left(-\frac{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{10}\,\mathrm{cm\,s^{-1}})\times(557.1\,\mathrm{cm^{-1}})}{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(1000\,\mathrm{K})}\right)+\cdots$$

$$= \boxed{3.004}$$

P19.11 $q = \sum_i \mathrm{e}^{-\beta\varepsilon_i} = \sum_i \mathrm{e}^{-hc\beta\tilde{\nu}_i}$ [19.11]

At 100 K, $hc\beta = \dfrac{1}{69.50\,\mathrm{cm^{-1}}}$ and at 298 K, $hc\beta = \dfrac{1}{207.22\,\mathrm{cm^{-1}}}$. Therefore, at 100 K

(a) $q = 1 + \mathrm{e}^{-213.30/69.50} + \mathrm{e}^{-435.39/69.50} + \mathrm{e}^{-636.27/69.50} + \mathrm{e}^{-845.93/69.50} = \boxed{1.049}$

and at 298 K

(b) $q = 1 + \mathrm{e}^{-213.30/207.22} + \mathrm{e}^{-425.39/207.22} + \mathrm{e}^{-636.27/207.22} + \mathrm{e}^{-845.93/207.22} = \boxed{1.55}$

In each case, $p_i = \dfrac{\mathrm{e}^{-hc\beta\tilde{\nu}_i}}{q}$ [19.10]

$$p_0 = \frac{1}{q} = \textbf{(a)}\ \boxed{0.953},\quad \textbf{(b)}\ \boxed{0.645}$$

$$p_1 = \frac{\mathrm{e}^{-hc\beta\tilde{\nu}_1}}{q} = \textbf{(a)}\ \boxed{0.044},\quad \textbf{(b)}\ \boxed{0.230}$$

$$p_2 = \frac{\mathrm{e}^{-hc\beta\tilde{\nu}_2}}{q} = \textbf{(a)}\ \boxed{0.002},\quad \textbf{(b)}\ \boxed{0.083}$$

For the molar entropy we need to form $U_\mathrm{m} - U_\mathrm{m}(0)$ by explicit summation

$$U_\mathrm{m} - U_\mathrm{m}(0) = \frac{N_\mathrm{A}}{q}\sum_i \varepsilon_i \mathrm{e}^{-\beta\varepsilon_i} = \frac{N_\mathrm{A}}{q}\sum_i hc\tilde{\nu}_i \mathrm{e}^{-hc\beta\tilde{\nu}_i}\ [19.25, 19.26]$$

$$= \boxed{123\,\mathrm{J\,mol^{-1}}\ (\text{at }100\,\mathrm{K})}, \boxed{1348\,\mathrm{J\,mol^{-1}}\ (\text{at }298\,\mathrm{K})}$$

$$S_\mathrm{m} = \frac{U_\mathrm{m} - U_\mathrm{m}(0)}{T} + R\ln q\ [19.34]$$

(a) $S_\mathrm{m} = \dfrac{123\,\mathrm{J\,mol^{-1}}}{100\,\mathrm{K}} + R\ln 1.049 = \boxed{1.63\,\mathrm{J\,K^{-1}\,mol^{-1}}}$

(b) $S_\mathrm{m} = \dfrac{1348\,\mathrm{J\,mol^{-1}}}{298\,\mathrm{K}} + R\ln 1.55 = \boxed{8.17\,\mathrm{J\,K^{-1}\,mol^{-1}}}$

Solutions to theoretical problems

P19.13

$$\begin{aligned}
p &= kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} \quad [20.4] \\
&= kT\left(\frac{\partial \ln(q^N/N!)}{\partial V}\right)_{T,N} \quad [19.46] \\
&= kT\left(\frac{\partial[N\ln q - \ln N!]}{\partial V}\right)_{T,N} = NkT\left(\frac{\partial \ln q}{\partial V}\right)_{T,N} \\
&= NkT\left(\frac{\partial \ln(V/\Lambda^3)}{\partial V}\right)_{T,N} \\
&= NkT\left(\frac{\partial[\ln V - \ln \Lambda^3]}{\partial V}\right)_{T,N} = NkT\left(\frac{\partial \ln V}{\partial V}\right)_{T,N} \\
&= \frac{NkT}{V} \quad \text{or} \quad \boxed{pV = NkT = nRT}
\end{aligned}$$

P19.15 We draw up the following table

0	ε	2ε	3ε	4ε	5ε	6ε	7ε	8ε	9ε	W
8	0	0	0	0	0	0	0	0	1	9
7	1	0	0	0	0	0	0	1	0	72
7	0	1	0	0	0	0	1	0	0	72
7	0	0	1	0	0	1	0	0	0	72
7	0	0	0	1	1	0	0	0	0	72
6	2	0	0	0	0	0	1	0	0	252
6	0	2	0	0	1	0	0	0	0	252
6	0	0	3	0	0	0	0	0	0	84
6	1	0	0	2	0	0	0	0	0	252
6	1	1	0	0	0	1	0	0	0	504
6	1	0	1	0	1	0	0	0	0	504
6	0	1	1	1	0	0	0	0	0	504
5	3	0	0	0	0	1	0	0	0	504
5	0	3	1	0	0	0	0	0	0	504
5	2	1	0	0	1	0	0	0	0	1512
5	2	0	1	1	0	0	0	0	0	1512
5	1	2	0	1	0	0	0	0	0	1512
5	1	1	2	0	0	0	0	0	0	1512
4	4	0	0	0	1	0	0	0	0	630
4	3	1	0	1	0	0	0	0	0	2520
4	3	0	2	0	0	0	0	0	0	1260
4	2	2	1	0	0	0	0	0	0	3780
3	5	0	0	1	0	0	0	0	0	504
3	4	1	1	0	0	0	0	0	0	2520
2	6	0	1	0	0	0	0	0	0	252
2	5	2	0	0	0	0	0	0	0	756
1	7	1	0	0	0	0	0	0	0	72
0	9	0	0	0	0	0	0	0	0	1

The most probable configuration is the "almost exponential" $\boxed{\{4, 2, 2, 1, 0, 0, 0, 0, 0, 0\}}$

P19.16 $\dfrac{n_j}{n_0} = \mathrm{e}^{-\beta(\varepsilon_j-\varepsilon_0)} = \mathrm{e}^{-\beta j\varepsilon}$, which implies that $-j\beta\varepsilon = \ln n_j - \ln n_0$

and therefore that $\boxed{\ln n_j = \ln n_0 - \dfrac{j\varepsilon}{kT}}$

Therefore, a plot of $\ln n_j$ against j should be a straight line with slope $-\dfrac{\varepsilon}{kT}$. Alternatively, plot $\ln p_j$ against j, since

$$\boxed{\ln p_j = \text{const} - \frac{j\varepsilon}{kT}}$$

We draw up the following table using the information in Problem 19.8

j	0	1	2	3	
n_j	4	2	2	1	[most probable configuration]
$\ln n_j$	1.39	0.69	0.69	0	

These are points plotted in Fig. 19.2 (full line). The slope is −0.46, and since $\dfrac{\varepsilon}{hc} = 50\,\mathrm{cm^{-1}}$, the slope corresponds to a temperature

$$T = \frac{(50\,\mathrm{cm^{-1}}) \times (2.998 \times 10^{10}\,\mathrm{cm\,s^{-1}}) \times (6.626 \times 10^{-34}\,\mathrm{J\,s})}{(0.46) \times (1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}})} = \boxed{160\,\mathrm{K}}$$

(A better estimate, 104 K represented by the dashed line in Fig. 19.2, is found in Problem 19.18.)

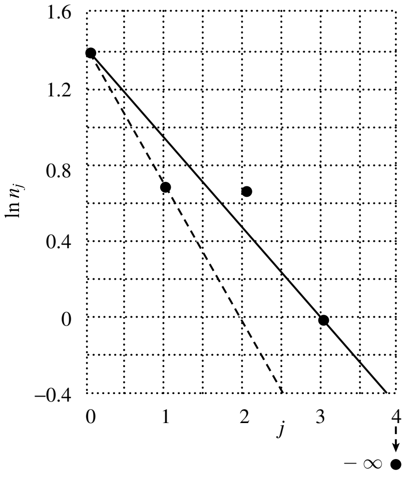


Figure 19.2

(b) Choose one of the weight 2520 configurations and one of the weight 504 configurations, and draw up the following table

	j	0	1	2	3	4
$W = 2520$	n_j	4	3	1	0	1
	$\ln n_j$	1.39	1.10	0	$-\infty$	0
$W = 504$	n_j	6	0	1	1	1
	$\ln n_j$	1.79	$-\infty$	0	0	0

Inspection confirms that these data give very crooked lines.

P19.19 **(a)** The form of Stirling's approximation used in the text in the derivation of the Boltzmann distribution is

$$\ln x! = x\ln x - x\ [19.2] \quad \text{or} \quad \ln N! = N\ln N - N$$

and $\ln n_i! = n_i \ln n_i - n_i$ which then leads to $\left[N \text{ is cancelled by } -\sum_i n_i\right]$

$$\ln W = N\ln N - \sum_i n_i \ln n_i\ [19.3]$$

If $N! = N^N,\ \ln N! = N\ln N$, likewise $\ln n_i! = n_i \ln n_i$ and eqn 3 is again obtained.

(b) For $\ln x! = \left(x + \frac{1}{2}\right)\ln x - x + \frac{1}{2}\ln 2\pi$ [Marginal note, p. 631],
Since the method of undetermined multipliers requires only (*Justification* 19.3) $\mathrm{d}\ln W$, only the terms $\mathrm{d}\ln n_i!$ survive. The constant term, $\frac{1}{2}\ln 2\pi$, drops out, as do all terms in N. The difference, then, is in terms arising from $\ln n_i!$ We need to compare $n_i \ln n_i$ to $\frac{1}{2}\ln n_i$, as both these terms survive the differentiation. The derivatives are

$$\frac{\partial}{\partial n_i}(n_i \ln n_i) = 1 + \ln n_i \approx \ln n_i\ [\text{large } n_i]$$

$$\frac{\partial}{\partial n_i}\left(\frac{1}{2}\ln n_i\right) = \frac{1}{2n_i}$$

Whereas $\ln n_i$ increases as n_i increases, $\dfrac{1}{2n_i}$ decreases and in the limit becomes negligible. For $n_i = 1\times 10^6,\ \ln n_i = 13.8,\ \dfrac{1}{2n_i} = 5\times 10^{-7}$; the ratio is about 2×10^8 which could probably not be seen in experiments. However, for experiments on, say, 1000 molecules, such as molecular dynamics simulations, there could be a measurable difference.

Solutions to applications

P19.21

$$\frac{p(h)}{p(h_0)} = \frac{N(h)/V}{N(h_0)/V} = \mathrm{e}^{-\{(\varepsilon(h)-\varepsilon(h_0))/kT\}}\ [19.6]$$

$$= \mathrm{e}^{-mg(h-h_0)/kT}$$

For $p(0) \equiv p_0$,

$$\boxed{\frac{p(h)}{p_0} = \mathrm{e}^{-mgh/kT}}$$

$$\frac{\mathcal{N}(8.0\,\mathrm{km})}{\mathcal{N}(0)} = \frac{N(8.0\,\mathrm{km})/V}{N(0)/V} = \mathrm{e}^{\frac{-M(\mathrm{O_2})gh}{RT}}$$

$$\frac{\mathcal{N}(8.0\,\mathrm{km})}{\mathcal{N}(0)}[\mathrm{O_2}] = \mathrm{e}^{-\left\{\frac{(0.032\,\mathrm{kg\,mol^{-1}})\times(9.81\,\mathrm{m\,s^{-2}})\times(8.0\times 10^3\,\mathrm{m})}{(8.315\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})}\right\}}$$

$$= \boxed{0.36} \text{ for } \mathrm{O_2}$$

$$\frac{\mathcal{N}(8.0\,\mathrm{km})}{\mathcal{N}(0)}[\mathrm{H_2O}] = \mathrm{e}^{-\left\{\frac{(0.018\,\mathrm{kg\,mol^{-1}})\times(9.81\,\mathrm{m\,s^{-2}})\times(8.0\times 10^3\,\mathrm{m})}{(8.315\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})}\right\}}$$

$$= \boxed{0.57} \quad \text{for } \mathrm{H_2O}$$

P19.23 **(a)** The electronic partition function, q_E, of a perfect, atomic hydrogen gas consists of the electronic energies E_n that can be written in the form:

$$E_n = \left(1 - \frac{1}{n^2}\right) hcR_\mathrm{H}, \quad n = 1, 2, 3, \ldots, \infty,$$

where we have used the state $n = 1$ as the zero of energy (in contrast to the usual zero being at infinite separation of the proton and electron, eqn 13.13). The degeneracy of each level is $g_n = 2n^2$ where the n^2 factor is the orbital degeneracy of each shell and the factor of 2 accounts for spin degeneracy.

$$q_\mathrm{E} = \sum_{n=1}^{\infty} g_n \mathrm{e}^{-E_n/kT} = 2\sum_{n=1}^{\infty} n^2 \mathrm{e}^{-\left(1-\frac{1}{n^2}\right)C},$$

where $C = hcR_\mathrm{H}/kT_\text{photosphere} = 27.301$. q_E, when written as an infinite sum, is infinitely large because $\lim\limits_{n\to\infty}\left\{n^2\mathrm{e}^{-(1-\frac{1}{n^2})C}\right\} = \lim\limits_{n\to\infty}\left\{n^2\mathrm{e}^{-C}\right\} = \mathrm{e}^{-C}\lim\limits_{n\to\infty}(n^2) = \infty$. The inclusion of partition function terms corresponding to large n values is clearly an error.

(b) States corresponding to large n values have very large average radii and most certainly interact with other atoms, thereby, blurring the distinct energy level of the state. Blurring interaction most likely occurs during the collision between an atom in state n and an atom in the ground state $n = 1$. Collisional lifetime broadening (eqn 16.25) is given by:

$$\delta E_n = \frac{h}{2\pi\tau} = \frac{z_n h}{2\pi},$$

where z_n = collisional frequency of nth state of atomic perfect gas

$$= \frac{\sqrt{2}\sigma_n \bar{c}\rho}{kT} = \frac{\sqrt{2}\sigma_n \bar{c}\rho N_\mathrm{A}}{M_\mathrm{H}} \quad \text{(eqn 24.12)}$$

$$\bar{c} = \text{mean speed} = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}} = 1.106 \times 10^4\ \mathrm{m\,s^{-1}} \quad \text{(eqn 24.7)}$$

σ_n = collisional cross-section of nth state (Fig. 24.9)

$$= \pi(\langle r\rangle_n + a_0)^2$$

$$= \pi a_0^2\left(\frac{3_n^2 + 2}{2}\right)^2 \text{ (Example 13.2)}$$

Any quantum state within δE of the continuum of an isolated atom will have its energy blurred by collisions so as to be indistinguishable from the continuum. Only states having energies in the range $0 \le E < E_\infty - \delta E$ will be a distinct atomic quantum state.

The maximum term, n_max, that should be retained in the partition function of a hydrogen atom is given by

$$E_{n_\text{max}} = E_\infty - \delta E_{n_\text{max}}$$

$$\left(1 - \frac{1}{n_\text{max}^2}\right) hcR_\mathrm{H} = hcR_\mathrm{H} - \frac{\sqrt{2}\pi a_0^2\left(\frac{3n_\text{max}^2+2}{2}\right)^2 \bar{c}\rho^{N_A h}}{2\pi M_\mathrm{H}}$$

with $\rho = 1.99 \times 10^{-4}\ \mathrm{kg\,m^{-3}}$ and $M_\mathrm{H} = 0.001\ \mathrm{kg\,mol^{-1}}$.

The root function of a calculator or mathematical software may be used to solve this equation for n_{max}.

$\boxed{n_{\text{max}} = 28}$ for atomic hydrogen of the photosphere

Furthermore, examination of the partition function terms $n = 2, 3, \ldots, n_{\text{max}}$ indicates that they are negligibly small and may be discarded. The point is that very large n values should not be included in q_{E} because they do not reflect reality.

(c) $$\rho_n = \frac{2\,n^2\,\mathrm{e}^{-E_n/kT}}{q_{\text{E}}} \quad \text{where} \quad T = 5780\,\text{K} \qquad \text{(eqn 19.6)}$$

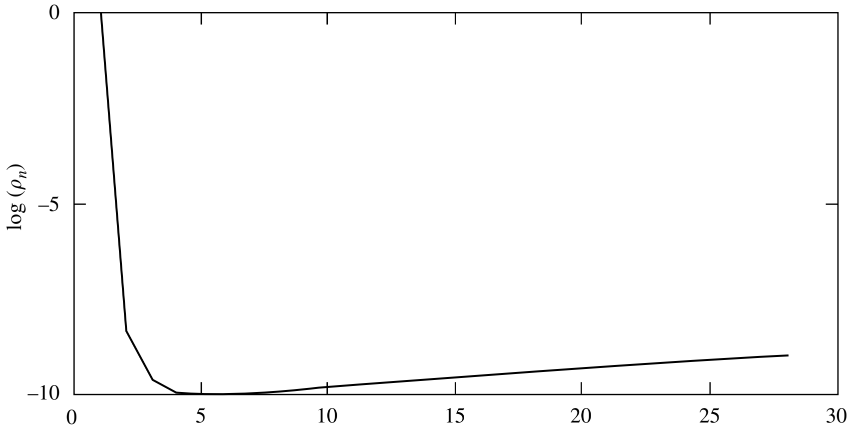


Figure 19.3

Even at the high temperature of the Sun's photosphere only the ground electronic state is significantly populated. This leads us to expect that at more ordinary temperatures only the ground state of atom and molecules are populated at equilibrium. It would be a mistake to thoughtlessly apply equilibrium populations to a study of the Sun's photosphere, however, it is bombarded with extremely high energy radiation from the direction of the Sun's core while radiating at a much low energy. The photosphere may show significant deviations from equilibrium.

See S. J. Strickler, *J. Chem. Ed.*, *43*, 364 (1966).

20 Statistical thermodynamics: the machinery

Solutions to exercises

Discussion questions

E20.1(b) The symmetry number, σ, is a correction factor to prevent the over-counting of rotational states when computing the high temperature form of the rotational partition function. An elementary interpretation of σ is that it recognizes that in a homonuclear diatomic molecule AA the orientations AA$'$ and A$'$A are indistinguishable, and should not be counted twice, so the quantity $q = kT/hcB$ is replaced by $q = kT/\sigma hcB$ with $\sigma = 2$. A more sophisticated interpretation is that the Pauli principle allows only certain rotational states to be occupied, and the symmetry factor adjusts the high temperature form of the partition function (which is derived by taking a sum over all states), to account for this restriction. In either case the symmetry number is equal to the number of indistinguishable orientations of the molecule. More formally, it is equal to the order of the rotational subgroup of the molecule.

E20.2(b) The temperature is always high enough (provided the gas is above its condensation temperature) for the mean translational energy to be $\frac{3}{2}kT$. The equipartition value. Therefore, the molar constant-volume heat capacity for translation is $C^{\mathrm{T}}_{V,\mathrm{m}} = \frac{3}{2}R$.

Translation is the only mode of motion for a monatomic gas, so for such a gas $C_{V,\mathrm{m}} = \frac{3}{2}R = 12.47\,\mathrm{J\,K^{-1}\,mol^{-1}}$: This result is very reliable: helium, for example has this value over a range of 2000 K.

When the temperature is high enough for the rotations of the molecules to be highly excited (when $T \gg \theta_{\mathrm{R}}$) we can use the equipartition value kT for the mean rotational energy (for a linear rotor) to obtain $C_{V,\mathrm{m}} = R$. For nonlinear molecules, the mean rotational energy rises to $\frac{3}{2}kT$, so the molar rotational heat capacity rises to $\frac{3}{2}R$ when $T \gg \theta_{\mathrm{R}}$. Only the lowest rotational state is occupied when the temperature is very low, and then rotation does not contribute to the heat capacity. We can calculate the rotational heat capacity at intermediate temperatures by differentiating the equation for the mean rotational energy (eqn 20.29). The resulting expression, which is plotted in Fig. 20.9 of the text shows that the contribution rises from zero (when $T = 0$) to the equipartition value (when $T \gg \theta_{\mathrm{R}}$). Because the translational contribution is always present, we can expect the molar heat capacity of a gas of diatomic molecules ($C^{\mathrm{T}}_{V,\mathrm{m}} + C^{\mathrm{R}}_{V,\mathrm{m}}$) to rise from $\frac{3}{2}R$ to $\frac{5}{2}R$ as the temperature is increased above θ_{R}.

Molecular vibrations contribute to the heat capacity, but only when the temperature is high enough for them to be significantly excited. The equipartition mean energy is kT for each mode, so the maximum contribution to the molar heat capacity is R. However, it is very unusual for the vibrations to be so highly excited that equipartition is valid and it is more appropriate to use the full expression for the vibrational heat capacity which is obtained by differentiating eqn 20.32. The curve in Fig. 20.10 of the text shows how the vibrational heat capacity depends on temperature. Note that even when the temperature is only slightly above the vibrational temperature, the heat capacity is close to its equipartition value.

The total heat capacity of a molecular substance is the sum of each contribution (Fig. 20.11 of the text). When equipartition is valid (when the temperature is well above the characteristic temperature of the mode $T \gg \theta_{\mathrm{M}}$) we can estimate the heat capacity by counting the numbers of modes that are active. In gases, all three translational modes are always active and contribute $3/2\,R$ to the molar heat capacity. If we denote the number of active rotational modes by ν^*_{R} (so for most molecules at normal temperatures $\nu^*_{\mathrm{R}} = 2$ for linear molecules, and 3 for nonlinear molecules), then the rotational contribution is $1/2\,\nu^*_{\mathrm{R}}R$. If the temperature is high enough for ν^*_{V} vibrational modes to be active the vibrational contribution to the molar heat capacity is $\nu_R^* R$. In most cases $\nu_V \approx 0$. It follows that the total molar heat capacity is

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

E20.3(b) See *Justification* 20.4 for a derivation of the general expression (eqn 20.54) for the equilibrium constant in terms of the partition functions and difference in molar energy, $\Delta_r E_0$, of the products and reactants in a chemical reaction. The partition functions are functions of temperature and the ratio of partition functions in eqn 20.54 will therefore vary with temperature. However, the most direct effect of temperature on the equilibrium constant is through the exponential term $e^{-\Delta_r E_0/RT}$. The manner in which both factors affect the magnitudes of the equilibrium constant and its variation with temperature is described in detail for a simple $R \rightleftharpoons P$ gas phase equilibrium in Section 20.7(c) and *Justification* 20.5.

Numerical exercises

E20.4(b) $C_{V,\mathrm{m}} = \tfrac{1}{2}(3 + \nu_R^* + 2\nu_V^*)R$ [20.40]

with a mode active if $T > \theta_M$. At low temperatures, the vibrational modes are not active, that is, $\nu_V^* = 0$; at high temperatures they are active and approach the equipartition value. Therefore

(a) O_3: $C_{V,\mathrm{m}} = 3R$ or $6R$ $(3 \times 3 - 6)$ vibrational modes

(b) C_2H_6: $C_{V,\mathrm{m}} = 3R$ or $21R$ $(3 \times 8 - 6)$ vibrational modes

(c) CO_2: $C_{V,\mathrm{m}} = \tfrac{5}{2}R$ or $6.5R$ $(3 \times 3 - 5)$ vibrational modes

where the first value applies to low temperatures and the second to high.

E20.5(b) The equipartition theorem would predict a contribution to molar heat capacity of $\tfrac{1}{2}R$ for every translational and rotational degree of freedom and R for each vibrational mode. For an ideal gas, $C_{p,\mathrm{m}} = R + C_{V,\mathrm{m}}$. So for CO_2

With vibrations $\quad C_{V,\mathrm{m}}/R = 3\left(\tfrac{1}{2}\right) + 2\left(\tfrac{1}{2}\right) + (3 \times 4 - 6) = 6.5 \quad$ and $\quad \gamma = \dfrac{7.5}{6.5} = \boxed{1.15}$

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

Experimental $\quad \gamma = \dfrac{37.11\,\mathrm{J\,mol^{-1}\,K^{-1}}}{37.11 - 8.3145\,\mathrm{J\,mol^{-1}\,K^{-1}}} = \boxed{1.29}$

The experimental result is closer to that obtained by neglecting vibrations, but not so close that vibrations can be neglected entirely.

E20.6(b) The rotational partition function of a linear molecule is

$$q^R = \frac{kT}{\sigma hcB} = \frac{(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}})T}{\sigma(6.626 \times 10^{-34}\,\mathrm{J\,s}) \times (2.998 \times 10^{10}\,\mathrm{cm\,s^{-1}})B} = \frac{0.6952(T/\mathrm{K})}{\sigma B/\mathrm{cm^{-1}}}$$

(a) At 25°C $\quad q^R = \dfrac{0.6952(25 + 273)}{1.4457} = \boxed{143}$

(b) At 250°C $\quad q^R = \dfrac{0.6952(250 + 273)}{1.4457} = \boxed{251}$

E20.7(b) The symmetry number is the order of the rotational subgroup of the group to which a molecule belongs (except for linear molecules, for which $\sigma = 2$ if the molecule has inversion symmetry and 1 otherwise).

(a) CO_2: Full group $D_{\infty h}$; subgroup C_2 $\boxed{\sigma = 2}$

(b) O_3: Full group C_{2v}; subgroup C_2 $\boxed{\sigma = 2}$

(c) SO_3: Full group D_{3h}; subgroup $\{E, C_3, C_3^2, 3C_2\}$ $\boxed{\sigma = 6}$

(d) SF_6: O_h $\boxed{\sigma = 24}$

(e) Al_2Cl_6: D_{2d} $\boxed{\sigma = 4}$

E20.8(b) The rotational partition function of nonlinear molecule is given by

$$\begin{aligned} q^{\mathrm{R}} &= \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{ABC}\right)^{1/2} \\ &= \frac{1}{2}\left(\frac{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{10}\,\mathrm{cm\,s^{-1}})}\right)^{3/2} \\ &\quad\times\left(\frac{\pi}{(2.02736)\times(0.34417)\times(0.293535)\,\mathrm{cm^{-3}}}\right)^{1/2} = \boxed{5.84\times10^{3}} \end{aligned}$$

This high-temperature approximation is valid if $T \gg \theta_{\mathrm{R}}$, where θ_{R}, the rotational temperature, is

$$\begin{aligned} \theta_{\mathrm{R}} &= \frac{hc(ABC)^{1/3}}{k} \\ &= \frac{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{10}\,\mathrm{cm\,s^{-1}})}{1.381\times10^{-23}\,\mathrm{J\,K^{-1}}} \\ &\quad\times[(2.02736)\times(0.34417)\times(0.293535)\,\mathrm{cm^{-3}}]^{1/3} \\ &= \boxed{0.8479\,\mathrm{K}} \end{aligned}$$

E20.9(b) $q^{\mathrm{R}} = 583\overline{7}$ [Exercise 20.8(b)]

All rotational modes of SO_2 are active at 25°C; therefore

$$\begin{aligned} U_{\mathrm{m}}^{\mathrm{R}} - U_{\mathrm{m}}^{\mathrm{R}}(0) &= E^{\mathrm{R}} = \tfrac{3}{2}RT \\ S_{\mathrm{m}}^{\mathrm{R}} &= \frac{E^{\mathrm{R}}}{T} + R\ln q^{\mathrm{R}} \\ &= \tfrac{3}{2}R + R\ln(583\overline{6.9}) = \boxed{84.57\,\mathrm{J\,K^{-1}\,mol^{-1}}} \end{aligned}$$

E20.10(b) **(a)** The partition function is

$$q = \sum_{\text{states}} \mathrm{e}^{-E_{\text{state}}/kT} = \sum_{\text{levels}} g\mathrm{e}^{-E_{\text{level}}/kT}$$

where g is the degeneracy of the level. For rotations of a symmetric rotor such as CH_3CN, the energy levels are $E_J = hc[BJ(J+1) + (A-B)K^2]$ and the degeneracies are $g_{J,K} = 2(2J+1)$ if $K \neq 0$ and $2J+1$ if $K = 0$. The partition function, then, is

$$q = 1 + \sum_{J=1}^{\infty}(2J+1)\mathrm{e}^{-\{hcBJ(J+1)/kT\}}\left(1 + 2\sum_{K=1}^{J}\mathrm{e}^{-\{hc(A-B)K^2/kT\}}\right)$$

To evaluate this sum explicitly, we set up the following columns in a spreadsheet (values for $B = 5.2412\,\mathrm{cm^{-1}}$ and $T = 298.15\,\mathrm{K}$)

J	$J(J+1)$	$2J+1$	$e^{-\{hcBJ(J+1)/kT\}}$	J term	$e^{-\{hc(A-B)K^2/kT\}}$	K sum	J sum
0	0	1	1	1	1	1	1
1	2	3	0.997	8.832	0.976	2.953	9.832
2	6	5	0.991	23.64	0.908	4.770	33.47
3	12	7	0.982	43.88	0.808	6.381	77.35
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
82	6806	165	4.18×10^{-5}	0.079	8×10^{-71}	11.442	7498.95
83	6972	167	3.27×10^{-5}	0.062	2×10^{-72}	11.442	7499.01

The column labelled K sum is the term in large parentheses, which includes the inner summation. The J sum converges (to 4 significant figures) only at about $J = 80$; the K sum converges much more quickly. But the sum fails to take into account nuclear statistics, so it must be divided by the symmetry number. At 298 K, $q^{\mathrm{R}} = \boxed{2.50\times10^3}$. A similar computation at $T = 500\,\mathrm{K}$ yields $q^{\mathrm{R}} = \boxed{5.43\times10^3}$.

(b) The rotational partition function of a nonlinear molecule is given by

$$q^{\mathrm{R}} = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{ABC}\right)^{1/2}$$

$$\text{At 298 K}\quad q^{\mathrm{R}} = \frac{1}{3}\left(\frac{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{10}\,\mathrm{cm\,s^{-1}})}\right)^{3/2}\times\left(\frac{\pi}{(5.28)\times(0.307)^2\,\mathrm{cm^{-3}}}\right)^{1/2} = \boxed{2.50\times10^3}$$

$$\text{At 500 K}\quad q^{\mathrm{R}} = \frac{1}{3}\left(\frac{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(500\,\mathrm{K})}{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{10}\,\mathrm{cm\,s^{-1}})}\right)^{3/2}\times\left(\frac{\pi}{(5.28)\times(0.307)^2\,\mathrm{cm^{-3}}}\right)^{1/2} = \boxed{5.43\times10^3}$$

E20.11(b) The rotational partition function of a nonlinear molecule is given by

$$q^{\mathrm{R}} = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{ABC}\right)^{1/2}$$

(a) At 25°C

$$q^{\mathrm{R}} = \frac{1}{1}\left(\frac{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{10}\,\mathrm{cm\,s^{-1}})}\right)^{3/2}\times\left(\frac{\pi}{(3.1252)\times(0.3951)\times(0.3505)\,\mathrm{cm^{-3}}}\right)^{1/2} = \boxed{8.03\times10^3}$$

(b) At 100°C

$$q^{\mathrm{R}} = \frac{1}{1}\left(\frac{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(373\,\mathrm{K})}{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{10}\,\mathrm{cm\,s^{-1}})}\right)^{3/2}$$

$$\times\left(\frac{\pi}{(3.1252)\times(0.3951)\times(0.3505)\,\mathrm{cm^{-3}}}\right)^{1/2}$$

$$= \boxed{1.13\times10^{4}}$$

E20.12(b) The molar entropy of a collection of oscillators is given by

$$S_{\mathrm{m}} = \frac{N_{\mathrm{A}}\langle\varepsilon\rangle}{T} + R\ln q$$

where $\langle\varepsilon\rangle = \dfrac{hc\tilde{\nu}}{\mathrm{e}^{\beta hc\tilde{\nu}}-1} = k\dfrac{\theta}{\mathrm{e}^{\theta/T}-1}$ and $q = \dfrac{1}{1-\mathrm{e}^{-\beta hc\tilde{\nu}}} = \dfrac{1}{1-\mathrm{e}^{-\theta/T}}$

where θ is the vibrational temperature $hc\tilde{\nu}/k$. Thus

$$S_{\mathrm{m}} = \frac{R(\theta/T)}{\mathrm{e}^{\theta/T}} - R\ln(1-\mathrm{e}^{-\theta/T})$$

A plot of S_{m}/R versus T/θ is shown in Fig. 20.1.

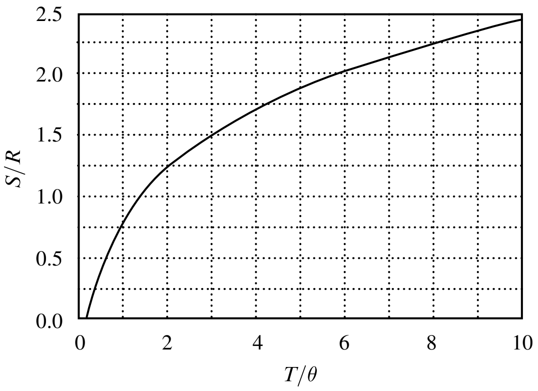


Figure 20.1

The vibrational entropy of ethyne is the sum of contributions of this form from each of its seven normal modes. The table below shows results from a spreadsheet programmed to compute S_{m}/R at a given temperature for the normal-mode wavenumbers of ethyne.

		$T = 298\,\mathrm{K}$		$T = 500\,\mathrm{K}$	
$\tilde{\nu}/\mathrm{cm^{-1}}$	θ/K	T/θ	S_{m}/R	T/θ	S_{m}/R
612	880	0.336	0.208	0.568	0.491
729	1049	0.284	0.134	0.479	0.389
1974	2839	0.105	0.000766	0.176	0.0228
3287	4728	0.0630	0.00000217	0.106	0.000818
3374	4853	0.0614	0.00000146	0.103	0.000652

The total vibrational heat capacity is obtained by summing the last column (twice for the first two entries, since they represent doubly degenerate modes).

(a) At 298 K $S_m = 0.685R = \boxed{5.70\,\mathrm{J\,mol^{-1}\,K^{-1}}}$

(b) At 500 K $S_m = 1.784R = \boxed{14.83\,\mathrm{J\,mol^{-1}\,K^{-1}}}$

E20.13(b) The contributions of rotational and vibrational modes of motion to the molar Gibbs energy depend on the molecular partition functions

$$G_m - G_m(0) = -RT\ln q$$

The rotational partition function of a nonlinear molecule is given by

$$q^R = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{ABC}\right)^{1/2} = \frac{1.0270}{\sigma}\left(\frac{(T/\mathrm{K})^3}{ABC/\mathrm{cm^{-3}}}\right)^{1/2}$$

and the vibrational partition function for each vibrational mode is given by

$$q^V = \frac{1}{1-e^{-\theta/T}} \quad \text{where } \theta = hc\tilde{\nu}/k = 1.4388(\tilde{\nu}/\mathrm{cm^{-1}})/(T/\mathrm{K})$$

$$\text{At 298 K} \quad q^R = \frac{1.0270}{2}\left(\frac{298^3}{(3.553)\times(0.4452)\times(0.3948)}\right)^{1/2} = 3.35\times 10^3$$

$$\text{and } G_m^R - G_m^R(0) = -(8.3145\,\mathrm{J\,mol^{-1}\,K^{-1}})\times(298\,\mathrm{K})\ln 3.35\times 10^3$$

$$= -20.1\times 10^3\,\mathrm{J\,mol^{-1}} = \boxed{-20.1\,\mathrm{kJ\,mol^{-1}}}$$

The vibrational partition functions are so small that we are better off taking

$$\ln q^V = -\ln(1-e^{-\theta/T}) \approx e^{-\theta/T}$$

$$\ln q_1^V \approx e^{-\{1.4388(1110)/298\}} = 4.70\times 10^{-3}$$

$$\ln q_2^V \approx e^{-\{1.4388(705)/298\}} = 3.32\times 10^{-2}$$

$$\ln q_3^V \approx e^{-\{1.4388(1042)/298\}} = 6.53\times 10^{-3}$$

$$\text{so } G_m^V - G_m^V(0) = -(8.3145\,\mathrm{J\,mol^{-1}\,K^{-1}})\times(298\,\mathrm{K})\times(4.70\times 10^{-3}+3.32\times 10^{-2}+6.53\times 10^{-3})$$

$$= -110\,\mathrm{J\,mol^{-1}} = \boxed{-0.110\,\mathrm{kJ\,mol^{-1}}}$$

E20.14(b) $q = \sum_j g_j e^{-\beta\varepsilon_j}, \quad g = (2S+1)\times\begin{cases}1 \text{ for } \Sigma \text{ states}\\ 2 \text{ for } \Pi, \Delta, \ldots \text{ states}\end{cases}$ [Section 17.1]

Hence

$q = 3 + 2e^{-\beta\varepsilon}$ [the ${}^3\Sigma$ term is triply degenerate, and the ${}^1\Delta$ term is doubly (orbitally) degenerate]

At 400 K

$$\beta\varepsilon = \frac{(1.4388\,\mathrm{cm\,K})\times(7918.1\,\mathrm{cm^{-1}})}{400\,\mathrm{K}} = 28.48$$

Therefore, the contribution to G_m is

$$G_m - G_m(0) = -RT\ln q \text{ [Table 20.1, } n = 1]$$

$$-RT\ln q = (-8.314\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(400\,\mathrm{K})\times\ln(3+2\times e^{-28.48})$$

$$= (-8.314\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(400\,\mathrm{K})\times(\ln 3) = \boxed{-3.65\,\mathrm{kJ\,mol^{-1}}}$$

E20.15(b) The degeneracy of a species with $S = \frac{5}{2}$ is 6. The electronic contribution to molar entropy is

$$S_\mathrm{m} = \frac{U_\mathrm{m} - U_\mathrm{m}(0)}{T} + R\ln q = R\ln q$$

(The term involving the internal energy is proportional to a temperature-derivative of the partition function, which in turn depends on excited state contributions to the partition function; those contributions are negligible.)

$$S_\mathrm{m} = (8.3145\,\mathrm{J\,mol^{-1}\,K^{-1}})\ln 6 = \boxed{14.9\,\mathrm{J\,mol^{-1}\,K^{-1}}}$$

E20.16(b) Use $S_\mathrm{m} = R\ln s$ [20.52]
Draw up the following table

n:	0	1	2			3			4			5	6
			o	*m*	*p*	*a*	*b*	*c*	*o*	*m*	*p*		
s	1	6	6	6	3	6	6	2	6	6	3	6	1
S_m/R	0	1.8	1.8	1.8	1.1	1.8	1.8	0.7	1.8	1.8	1.1	1.8	0

where a is the 1, 2, 3 isomer, b the 1, 2, 4 isomer, and c the 1, 3, 5 isomer.

E20.17(b) We need to calculate

$$\begin{aligned} K &= \prod_\mathrm{J}\left(\frac{q^\ominus_\mathrm{J,m}}{N_\mathrm{A}}\right)^{\nu_\mathrm{J}} \times \mathrm{e}^{-\Delta E_0/RT}\ [\textit{Justification } 20.4] \\ &= \frac{q^\ominus_\mathrm{m}(^{79}\mathrm{Br}_2)q^\ominus_\mathrm{m}(^{81}\mathrm{Br}_2)}{q^\ominus_\mathrm{m}(^{79}\mathrm{Br}^{81}\mathrm{Br})^2}\mathrm{e}^{-\Delta E_0/RT} \end{aligned}$$

Each of these partition functions is a product

$$q^\mathrm{T}_\mathrm{m}q^\mathrm{R}q^\mathrm{V}q^\mathrm{E}$$

with all $q^\mathrm{E} = 1$.

The ratio of the translational partition functions is virtually 1 (because the masses nearly cancel; explicit calculation gives 0.999). The same is true of the vibrational partition functions. Although the moments of inertia cancel in the rotational partition functions, the two homonuclear species each have $\sigma = 2$, so

$$\frac{q^\mathrm{R}(^{79}\mathrm{Br}_2)q^\mathrm{R}(^{81}\mathrm{Br}_2)}{q^\mathrm{R}(^{79}\mathrm{Br}^{81}\mathrm{Br})^2} = 0.25$$

The value of ΔE_0 is also very small compared with RT, so

$$K \approx \boxed{0.25}$$

Solutions to problems

Solutions to numerical problems

P20.2

$$\Delta\varepsilon = \varepsilon = g\mu_\mathrm{B}\mathcal{B}\ [18.48,\ \text{Section } 18.14]$$

$$q = 1 + \mathrm{e}^{-\beta\varepsilon}$$

$$C_{V,\mathrm{m}}/R = \frac{x^2\mathrm{e}^{-x}}{(1+\mathrm{e}^{-x})^2}\ [\text{Problem } 20.1], \quad x = 2\mu_\mathrm{B}\mathcal{B}\beta \quad [g = 2]$$

Therefore, if $\mathcal{B} = 5.0\,\mathrm{T}$,

$$x = \frac{(2) \times (9.274 \times 10^{-24}\,\mathrm{J\,T^{-1}}) \times (5.0\,\mathrm{T})}{(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times T} = \frac{6.72}{T/\mathrm{K}}$$

(a) $T = 50\,\mathrm{K}$, $x = 0.134$, $C_V = 4.47 \times 10^{-3} R$, implying that $C_V = 3.7 \times 10^{-2}\,\mathrm{J\,K^{-1}\,mol^{-1}}$. Since the equipartition value is about $3R$ [$\nu_\mathrm{R}^* = 3$, $\nu_\mathrm{V}^* \approx 0$], the field brings about a change of about $\boxed{0.1 \text{ per cent}}$

(b) $T = 298\,\mathrm{K}$, $x = 2.26 \times 10^{-2}$, $C_V = 1.3 \times 10^{-4} R$, implying that $C_V = 1.1\,\mathrm{mJ\,K^{-1}\,mol^{-1}}$, a change of about $\boxed{4 \times 10^{-3} \text{ per cent}}$

Question. What percentage change would a magnetic field of 1 kT cause?

P20.4 $q = 1 + 5\mathrm{e}^{-\beta\varepsilon} \quad [g_j = 2J + 1]$

$$\varepsilon = E(J = 2) - E(J = 0) = 6hcB \quad [E = hcBJ(J + 1)]$$

$$\frac{U - U(0)}{N} = -\frac{1}{q}\frac{\partial q}{\partial \beta} = \frac{5\varepsilon \mathrm{e}^{-\beta\varepsilon}}{1 + 5\mathrm{e}^{-\beta\varepsilon}}$$

$$C_{V,\mathrm{m}} = -k\beta^2 \left(\frac{\partial U_\mathrm{m}}{\partial \beta}\right)_V \quad [20.35]$$

$$C_{V,\mathrm{m}}/R = \frac{5\varepsilon^2\beta^2\mathrm{e}^{-\beta\varepsilon}}{(1 + 5\mathrm{e}^{-\beta\varepsilon})^2} = \frac{180(hcB\beta)^2\mathrm{e}^{-6hcB\beta}}{(1 + 5\mathrm{e}^{-6hcB\beta})^2}$$

$$\frac{hcB}{k} = 1.4388\,\mathrm{cm\,K} \times 60.864\,\mathrm{cm^{-1}} = 87.571\,\mathrm{K}$$

Hence,

$$C_{V,\mathrm{m}}/R = \frac{1.380 \times 10^6 \mathrm{e}^{-525.4\,\mathrm{K}/T}}{(1 + 5\mathrm{e}^{-525.4\,\mathrm{K}/T}) \times (T/\mathrm{K})^2}$$

We draw up the following table

T/K	50	100	150	200	250	300	350	400	450	500
$C_{V,\mathrm{m}}/R$	0.02	0.68	1.40	1.35	1.04	0.76	0.56	0.42	0.32	0.26

These points are plotted in Fig. 20.2.

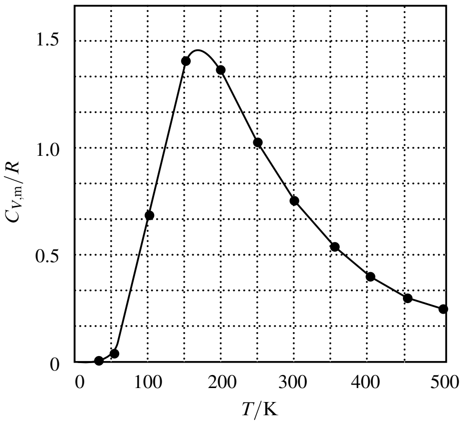


Figure 20.2

P20.6

$$\frac{q_{\mathrm{m}}^{\mathrm{T}}}{N_{\mathrm{A}}} = 2.561 \times 10^{-2} \times (T/\mathrm{K})^{5/2} \times (M/\mathrm{g\,mol^{-1}})^{3/2} \text{ [Table 20.3]}$$

$$= (2.561 \times 10^{-2}) \times (298)^{5/2} \times (28.02)^{3/2} = 5.823 \times 10^{6}$$

$$q^{\mathrm{R}} = \frac{1}{2} \times 0.6950 \times \frac{298}{1.9987} \text{[Table 20.3]} = 51.81$$

$$q^{\mathrm{V}} = \frac{1}{1 - \mathrm{e}^{-2358/207.2}} \text{[Table 20.3]} = 1.00$$

Therefore

$$\frac{q_{\mathrm{m}}^{\ominus}}{N_{\mathrm{A}}} = (5.82\overline{3} \times 10^{6}) \times (51.8\overline{1}) \times (1.00) = 3.02 \times 10^{8}$$

$$U_{\mathrm{m}} - U_{\mathrm{m}}(0) = \tfrac{3}{2}RT + RT = \tfrac{5}{2}RT \quad [T \gg \theta_{\mathrm{T}}, \theta_{\mathrm{R}}]$$

Hence

$$S_{\mathrm{m}}^{\ominus} = \frac{U_{\mathrm{m}} - U_{\mathrm{m}}(0)}{T} + R\left(\ln \frac{q_{\mathrm{m}}^{\ominus}}{N_{\mathrm{A}}} + 1\right)$$

$$= \tfrac{5}{2}R + R\{\ln 3.02 \times 10^{8} + 1\} = 23.03R = \boxed{191.4\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

The difference between the experimental and calculated values is negligible, indicating that the residual entropy is negligible.

P20.9 **(a)** Rotational state probability distribution,

$$P_J^{\mathrm{R}}(T) = \frac{(2J+1)\mathrm{e}^{-hcBJ(J+1)/kT}}{\sum\limits_{J=0} (2J+1)\mathrm{e}^{-hcBJ(J+1)/kT}}, \quad [20.14]$$

is conveniently plotted against J at several temperatures using mathematical software. This distribution at 100 K is shown below as both a bar plot and a line plot.

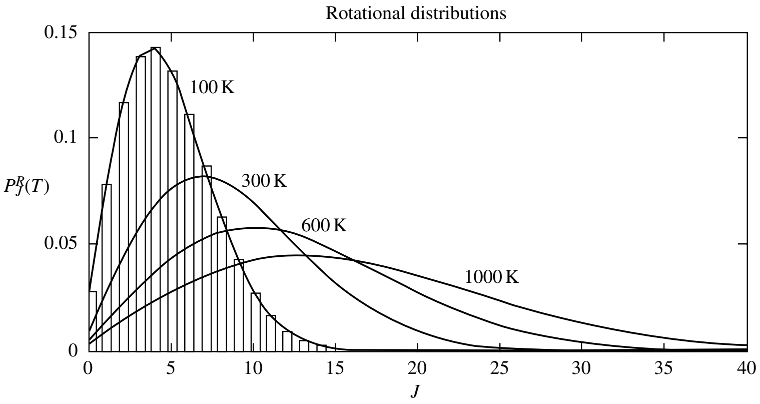


Figure 20.3(a)

The plots show that higher rotational states become more heavily populated at higher temperature. Even at 100 K the most populated state has 4 quanta of rotational energy; it is elevated to 13 quanta at 1000 K.

Values of the vibrational state probability distribution,

$$P_\nu^{\mathrm{V}}(T) = \mathrm{e}^{-\nu hc\tilde{\nu}/kT}(1 - \mathrm{e}^{-hc\tilde{\nu}/kT})^{-1}, \quad [20.21]$$

are conveniently tabulated against ν at several temperatures. Computations may be discontinued when values drop below some small number like 10^{-7}.

	$P_\nu^{\mathrm{V}}(T)$			
ν	100 K	300 K	600 K	1000 K
0	1	1	0.995	0.956
1	2.77×10^{-14}	3.02×10^{-5}	5.47×10^{-3}	0.042
2		9.15×10^{-10}	3.01×10^{-5}	1.86×10^{-3}
3			1.65×10^{-7}	8.19×10^{-5}
4				3.61×10^{-6}
5				1.59×10^{-7}

Only the state $\nu = 0$ is appreciably populated below 1000 K and even at 1000 K only 4% of the molecules have 1 quanta of vibrational energy.

(b)
$$\theta_{\mathrm{R}} = \frac{hcB}{k} = \frac{(6.626 \times 10^{-34}\,\mathrm{J\,s})(3.000 \times 10^{8}\,\mathrm{m\,s^{-1}})(193.1\,\mathrm{m^{-1}})}{1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}} \quad \text{(Section 20.2b)}$$

$$\theta_{\mathrm{R}} = 2.779\,\mathrm{K}$$

Since $\theta_{\mathrm{R}} \ll T$ where T is the lowest temperature of current interest (100 K), we expect that the classical rotational partition function,

$$q^{\mathrm{R}}_{\mathrm{classical}}(T) = \frac{kT}{hcB}, \quad [20.15a]$$

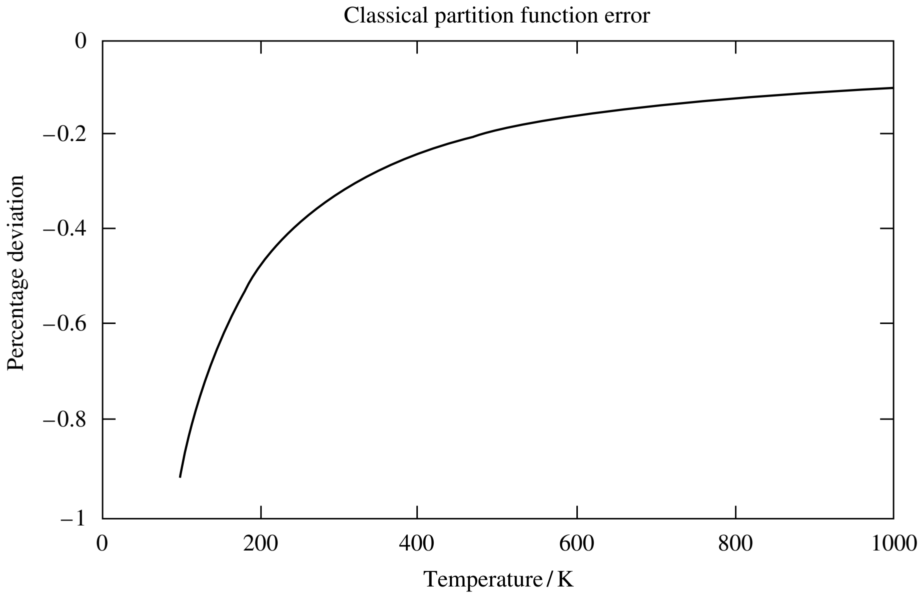


Figure 20.3(a)

should agree well with the rotational partition function calculated with the discrete energy distribution,

$$q^{\mathrm{R}} = \sum_{J=0}(2J+1)\mathrm{e}^{-hcBJ(J+1)/kT}. \quad [20.14]$$

A plot of the percentage deviation $(q^{\mathrm{R}}_{\text{classical}} - q^{\mathrm{R}})100/q^{\mathrm{R}}$ confirms that they agree. The maximum deviation is about -0.9% at 100 K and the magnitude decreases with increasing temperature.

(c) The translational, rotational, and vibrational contributions to the total energy are specified by eqns 20.28, 20.30, and 20.32. As molar quantities, they are:

$$U^{\mathrm{T}} = \tfrac{3}{2}RT, \quad U^{\mathrm{R}} = RT, \quad U^{\mathrm{V}} = \frac{N_{\mathrm{A}}hc\tilde{\nu}}{\mathrm{e}^{hc\tilde{\nu}/kT}-1}$$

The contributions to the energy change from 100 K are $\Delta U^{\mathrm{T}}(T) = U^{\mathrm{T}}(T) - U^{\mathrm{T}}(100\,\mathrm{K})$, etc. The following graph shows the individual contributions to the total molar internal energy change from 100 K. Translational motion contributes 50% more than the rotational motion because it has 3 quadratic degrees of freedom compared to 2 quadratic degrees of freedom for rotation. Very little change occurs in the vibration energy because very high temperatures are required to populate $v = 1, 2, \ldots$. states (see Part a).

$$\begin{aligned} C_{V,\mathrm{m}}(T) &= \left(\frac{\partial U(T)}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\right)_V (U^{\mathrm{T}} + U^{\mathrm{R}} + U^{\mathrm{V}}) \qquad [2.19] \\ &= \frac{3}{2}R + R + \frac{\mathrm{d}U^{\mathrm{V}}}{\mathrm{d}T} = \frac{5}{2}R + \frac{\mathrm{d}U^{\mathrm{V}}}{\mathrm{d}T} \end{aligned}$$

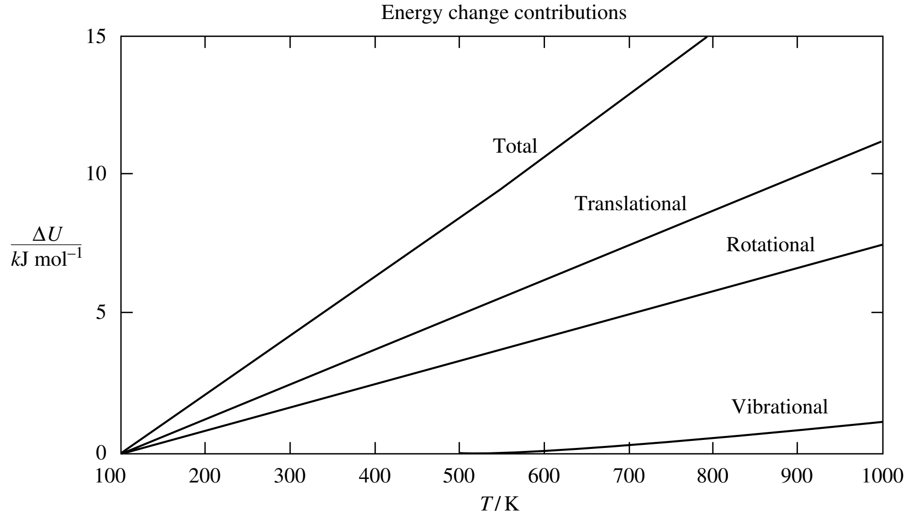


Figure 20.3(c)

The derivative $\mathrm{d}U^{\mathrm{V}}/\mathrm{d}T$ may be evaluated numerically with numerical software (we advise exploration of the technique) or it may be calculated with the analytical function of eqn 20.39:

$$C_{V,\mathrm{m}}^{\mathrm{V}} = \frac{\mathrm{d}U^{\mathrm{V}}}{\mathrm{d}T} = R\left\{\frac{\theta_{\mathrm{V}}}{T}\left(\frac{\mathrm{e}^{-\theta_{\mathrm{V}}/2T}}{1-\mathrm{e}^{-\theta_{\mathrm{V}}/T}}\right)\right\}^2$$

where $\theta_{\mathrm{V}} = hc\tilde{\nu}/k = 3122\,\mathrm{K}$. The following graph shows the ratio of the vibrational contribution to the sum of translational and rotational contributions. Below 300 K, vibrational motions makes a small, perhaps negligible, contribution to the heat capacity. The contribution is about 10% at 600 K and grows with increasing temperature.

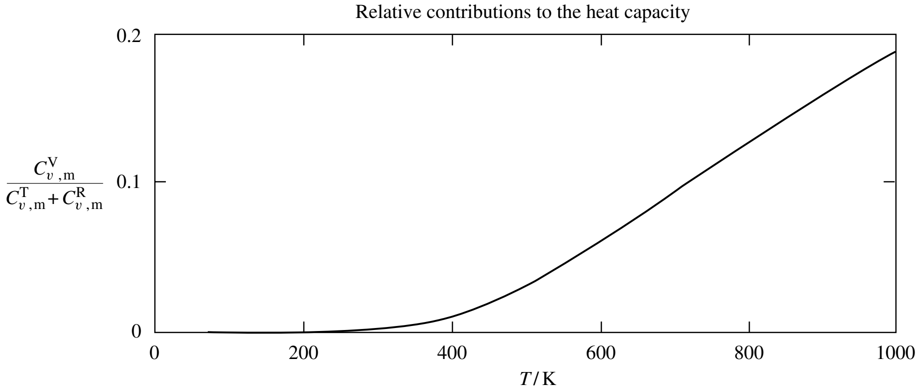


Figure 20.3(d)

The molar entropy change with temperature may be evaluated by numerical integration with mathematical software.

$$\begin{aligned}
\Delta S(T) &= S(T) - S(100\,\mathrm{K}) = \int_{100\,\mathrm{K}}^{T} \frac{C_{p,\mathrm{m}}(T)\,\mathrm{d}T}{T} \qquad [4.19] \\
&= \int_{100\,\mathrm{K}}^{T} \frac{C_{V,\mathrm{m}}(T)+R}{T}\,\mathrm{d}T \qquad [3.20] \\
&= \int_{100\,\mathrm{K}}^{T} \frac{\frac{7}{2}R + C_{V,\mathrm{m}}^{\mathrm{V}}(T)}{T}\,\mathrm{d}T \\
\Delta S(T) &= \underbrace{\frac{7}{2}R\ln\left(\frac{T}{100\,\mathrm{K}}\right)}_{\Delta S^{T+R}(T)} + \underbrace{\int_{100\,\mathrm{K}}^{T} \frac{C_{V,\mathrm{m}}^{V}(T)}{T}\,\mathrm{d}T}_{\Delta S^{\mathrm{V}}(T)}
\end{aligned}$$

Even at the highest temperature the vibrational contribution to the entropy change is less than 2.5% of the contributions from translational and rotational motion.

The vibrational contribution is negligible at low temperature.

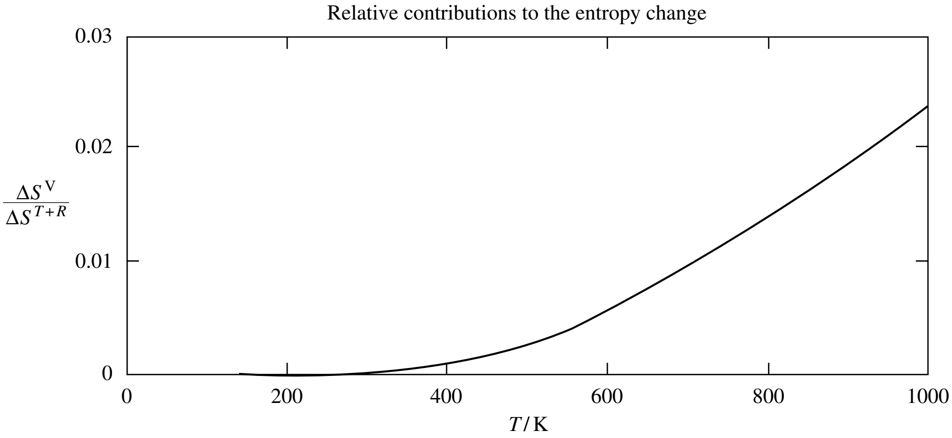


Figure 20.3(e)

P20.10 $K = \dfrac{q_{\rm m}^{\ominus}({\rm CHD_3})q_{\rm m}^{\ominus}({\rm DCl})}{q_{\rm m}^{\ominus}({\rm CD_4})q_{\rm m}^{\ominus}({\rm HCl})}{\rm e}^{-\beta\Delta E_0}$ [20.54, $N_{\rm A}$ factors cancel]

The ratio of translational partition functions is

$$\frac{q_{\rm m}^{\rm T}({\rm CHD_3})q_{\rm m}^{\rm T}({\rm DCl})}{q_{\rm m}^{\rm T}({\rm CD_4})q_{\rm m}^{\rm T}({\rm HCl})} = \left(\frac{M({\rm CHD_3})M({\rm DCl})}{M({\rm CD_4})M({\rm HCl})}\right)^{3/2} = \left(\frac{19.06\times 37.46}{20.07\times 36.46}\right)^{3/2} = 0.964$$

The ratio of rotational partition functions is

$$\frac{q^{\rm R}({\rm CHD_3})q^{\rm R}({\rm DCl})}{q^{\rm R}({\rm CD_4})q^{\rm R}({\rm HCl})} = \frac{\sigma({\rm CD_4})}{\sigma({\rm CHD_3})}\frac{(B({\rm CD_4})/{\rm cm^{-1}})^{3/2}B({\rm HCl})/{\rm cm^{-1}}}{(A({\rm CHD_3})B({\rm CHD_3})^2/{\rm cm^{-3}})^{1/2}B({\rm DCl})/{\rm cm^{-1}}}$$

$$= \frac{12}{3}\times\frac{2.63^{3/2}\times 10.59}{(2.63\times 3.28^2)^{1/2}\times 5.445} = 6.24$$

The ratio of vibrational partition functions is

$$\frac{q^{\rm V}({\rm CHD_3})q^{\rm V}({\rm DCl})}{q^{\rm V}({\rm CD_4})q^{\rm V}({\rm HCl})} = \frac{q(2993)q(2142)q(1003)^3q(1291)^2q(1036)^2q(2145)}{q(2109)q(1092)^2q(2259)^3q(996)^3q(2991)}$$

where $q(x) = \dfrac{1}{1-{\rm e}^{-1.4388x/(T/{\rm K})}}$

We also require ΔE_0, which is equal to the difference in zero point energies

$$\frac{\Delta E_0}{hc} = \frac{1}{2}\{(2993+2142+3\times 1003+2\times 1291+2\times 1036+2145)$$

$$-(2109+2\times 1092+3\times 2259+3\times 996+2991)\}\,{\rm cm^{-1}}$$

$$= -1053\,{\rm cm^{-1}}$$

Hence,

$$K = 0.964\times 6.24\times Q{\rm e}^{+1.4388\times 990/(T/{\rm K})} = 6.02\,Q{\rm e}^{+1424/(T/{\rm K})}$$

where Q is the ratio of vibrational partition functions. We can now evaluate K (on a computer), and obtain the following values

T/K	300	400	500	600	700	800	900	1000
K	698	217	110	72	54	44	38	34

The values of K are plotted in Fig. 20.4.

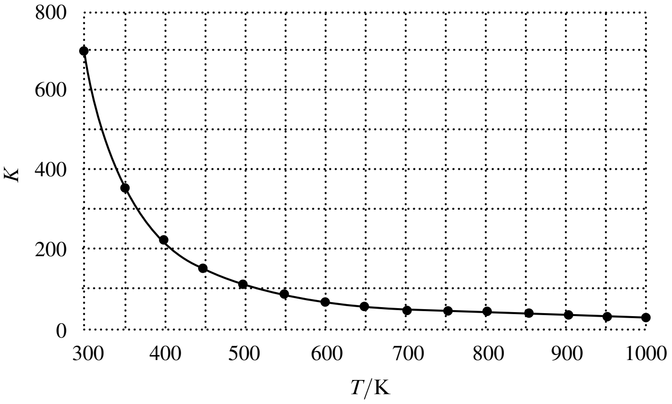


Figure 20.4

Solutions to theoretical problems

P20.13 **(a)** θ_V and θ_R are the constant factors in the numerators of the negative exponents in the sums that are the partition functions for vibration and rotation. They have the dimensions of temperature which occurs in the denominator of the exponents. So high temperature means $T \gg \theta_V$ or θ_R and only then does the exponential become substantial. Thus θ_V is a measure of the temperature at which higher vibrational and rotational states become populated.

$$\theta_R = \frac{hc\beta}{k} = \frac{(2.998 \times 10^8\,\mathrm{m\,s^{-1}}) \times (6.626 \times 10^{-34}\,\mathrm{J\,s}) \times (60.864\,\mathrm{cm^{-1}})}{(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (1\,\mathrm{m}/100\,\mathrm{cm})}$$

$$= \boxed{87.55\,\mathrm{K}}$$

$$\theta_V = \frac{hc\tilde{\nu}}{k} = \frac{(6.626 \times 10^{-34}\,\mathrm{J\,s}) \times (4400.39\,\mathrm{cm^{-1}}) \times (2.998 \times 10^8\,\mathrm{m\,s^{-1}})}{(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (1\,\mathrm{m}/100\,\mathrm{cm})}$$

$$= \boxed{6330\,\mathrm{K}}$$

(b) and **(c)** These parts of the solution were performed with Mathcad 7.0 and are reproduced on the following pages.

Objective: To calculate the equilibrium constant $K(T)$ and $C_p(T)$ for dihydrogen at high temperature for a system made with n mol H_2 at 1 bar.

$$H_2(g) \rightleftharpoons 2H(g)$$

At equilibrium the degree of dissociation, α, and the equilibrium amounts of H_2 and atomic hydrogen are related by the expressions

$$n_{H_2} = (1 - \alpha)n \quad \text{and} \quad n_H = 2\alpha n$$

The equilibrium mole fractions are

$$x_{H_2} = (1-\alpha)n/\{(1-\alpha)n + 2\alpha n\} = (1-\alpha)/(1+\alpha)$$
$$x_H = 2\alpha n/\{(1-\alpha)n + 2\alpha n\} = 2\alpha/(1+\alpha)$$

The partial pressures are

$$p_{H_2} = (1-\alpha)p/(1+\alpha) \quad \text{and} \quad p_H = 2\alpha p/(1+\alpha)$$

The equilibrium constant is

$$\begin{aligned} K(T) = (p_H/p^{\ominus})^2/(p_{H_2}/p^{\ominus}) &= 4\alpha^2(p/p^{\ominus})/(1-\alpha^2) \\ &= 4\alpha^2/(1-\alpha^2) \quad \text{where } p = p^{\ominus} = 1\,\text{bar} \end{aligned}$$

The above equation is easily solved for α

$$\boxed{\alpha = (K/(K+4))^{1/2}}$$

The heat capacity at constant volume for the equilibrium mixture is

$$C_V(\text{mixture}) = n_H C_{V,m}(H) + n_{H_2} C_{V,m}(H_2)$$

The heat capacity at constant volume per mole of dihydrogen used to prepare the equilibrium mixture is

$$\begin{aligned} C_V &= C_V(\text{mixture})/n = \{n_H C_{V,m}(H) + n_{H_2} C_{V,m}(H_2)\}/n \\ &= \boxed{2\alpha C_{V,m}(H) + (1-\alpha) C_{V,m}(H_2)} \end{aligned}$$

The formula for the heat capacity at constant pressure per mole of dihydrogen used to prepare the equilibrium mixture (C_p) can be deduced from the molar relationship

$$\begin{aligned} C_{p,m} &= C_{V,m} + R \\ C_p &= \left\{n_H C_{p,m}(H) + n_{H_2} C_{p,m}(H_2)\right\}/n \\ &= \frac{n_H}{n}\left\{C_{V,m}(H) + R\right\} + \frac{n_{H_2}}{n}\left\{C_{V,m}(H_2) + R\right\} \\ &= \frac{n_H C_{V,m}(H) + n_{H_2} C_{V,m}(H_2)}{n} + R\left(\frac{n_H + n_{H_2}}{n}\right) \\ &= C_V + R(1+\alpha) \end{aligned}$$

Calculations

J = joule
mol = mole
$h = 6.62608 \times 10^{-34}\,\text{J s}$
$R = 8.31451\,\text{J K}^{-1}\,\text{mol}^{-1}$
s = second
g = gram
$c = 2.9979 \times 10^{8}\,\text{m s}^{-1}$
$N_A = 6.02214 \times 10^{23}\,\text{mol}^{-1}$
kJ = 1000 J
bar = 1×10^5 Pa
$k = 1.38066 \times 10^{-23}\,\text{J K}^{-1}$
$p^{\ominus} = 1\,\text{bar}$

Molecular properties of H_2

$\nu = 4400.39\,\text{cm}^{-1}$ $\quad B = 60.864\,\text{cm}^{-1}$ $\quad D = 432.1\,\text{kJ mol}^{-1}$

$$m_H = \frac{1\,\text{g mol}^{-1}}{N_A} \qquad m_{H_2} = 2m_H$$

$$\theta_V = \frac{hc\nu}{k} \qquad \theta_R = \frac{hcB}{k}$$

Computation of $K(T)$ and $\alpha(T)$

$$N = 200 \qquad i = 0, \ldots, N \qquad T_i = 500\,\mathrm{K} + \frac{i \times 5500\,\mathrm{K}}{N}$$

$$\Lambda_{\mathrm{H}_i} = \frac{h}{(2\pi m_{\mathrm{H}} k T_i)^{1/2}} \qquad \Lambda_{\mathrm{H}_{2_i}} = \frac{h}{(2\pi m_{\mathrm{H}_2} k T_i)^{1/2}}$$

$$q_{V_i} = \frac{1}{1 - \mathrm{e}^{-(\theta_{\mathrm{V}}/T_i)}} \qquad q_{\mathrm{R}_i} = \frac{T_i}{2\theta_{\mathrm{R}}}$$

$$\boxed{K_{\mathrm{eq}_i} = \frac{k T_i \left(\Lambda_{\mathrm{H}_{2_i}}\right)^3 \mathrm{e}^{-(D/RT_i)}}{p^{\ominus} q_{V_i} q_{\mathrm{R}_i} \left(\Lambda_{\mathrm{H}_i}\right)^6}} \qquad \alpha_i = \left(\frac{K_{\mathrm{eq}_i}}{K_{\mathrm{eq}_i} + 4}\right)^{1/2}$$

See Fig. 20.5(a) and (b).

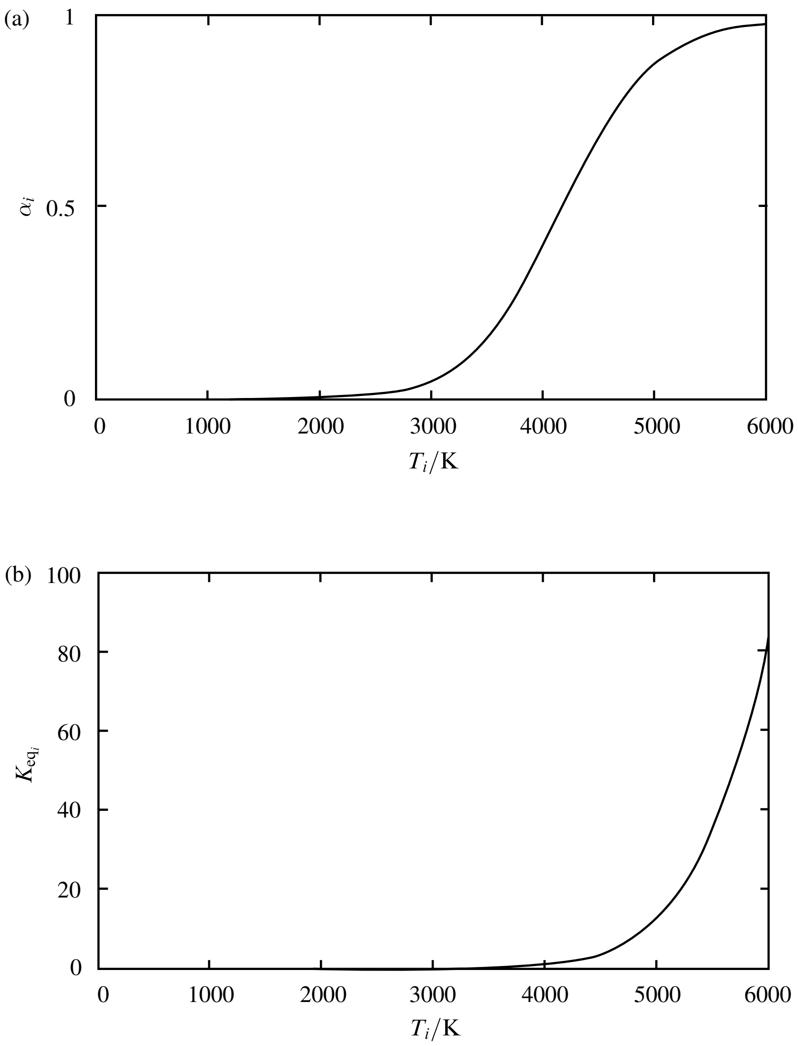


Figure 20.5

Heat capacity at constant volume per mole of dihydrogen used to prepare equilibrium mixture (see Fig. 20.6(a))

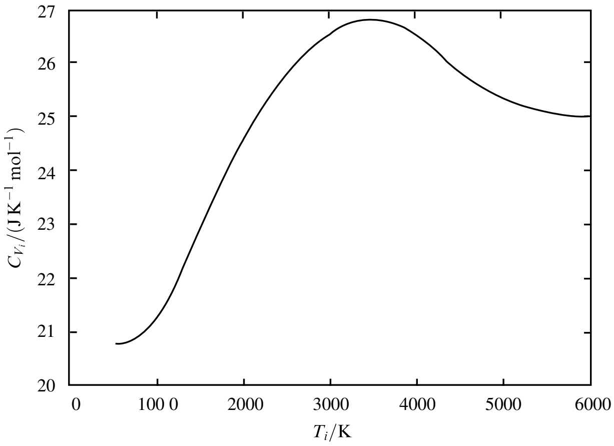


Figure 20.6(a)

$$C_V(\mathrm{H}) = \boxed{1.5R}$$

$$C_V(\mathrm{H}_{2_i}) = \boxed{2.5R + \left[\frac{\theta_\mathrm{V}}{T_i} \times \frac{\mathrm{e}^{-(\theta_\mathrm{V}/2T_i)}}{1-\mathrm{e}^{-(\theta_\mathrm{V}/T_i)}}\right]^2 R} \qquad C_{V_i} = 2\alpha_i C_V(\mathrm{H}) + (1-\alpha_i)C_V(\mathrm{H}_{2_i})$$

The heat capacity at constant pressure per mole of dihydrogen used to prepare the equilibrium mixture is (see Fig. 20.6(b))

$$C_{p_i} = C_{V_i} + R(1+\alpha_i)$$

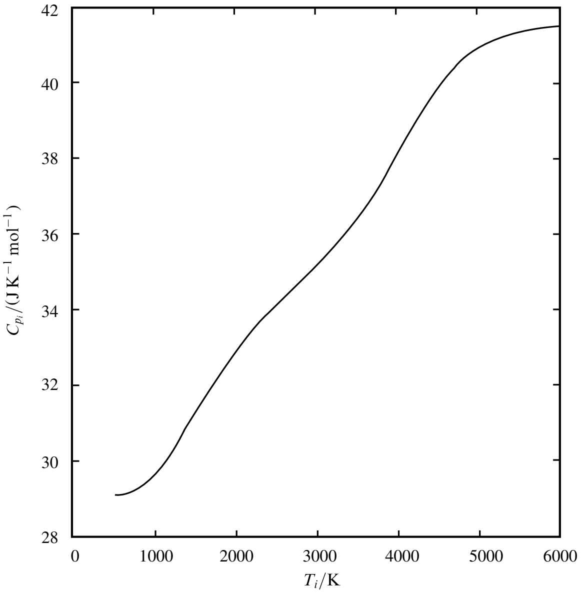


Figure 20.6(b)

P20.14

$$q = \frac{1}{1 - \mathrm{e}^{-x}}, \quad x = \hbar\omega\beta = hc\tilde{\nu}\beta = \frac{\theta_{\mathrm{V}}}{T} \text{ [Table 20.3]}$$

$$U - U(0) = -\frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V = -N(1 - \mathrm{e}^{-x})\frac{\mathrm{d}}{\mathrm{d}\beta}(1 - \mathrm{e}^{-x})^{-1}$$

$$= \frac{N\hbar\omega\mathrm{e}^{-x}}{1 - \mathrm{e}^{-x}} = \boxed{\frac{N\hbar\omega}{\mathrm{e}^{x} - 1}}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = -k\beta^2\frac{\partial U}{\partial \beta} = -k\beta^2\hbar\omega\frac{\partial U}{\partial x}$$

$$= k(\beta\hbar\omega)^2 N\left\{\frac{\mathrm{e}^{x}}{(\mathrm{e}^{x} - 1)^2}\right\} = \boxed{kN\left\{\frac{x^2\mathrm{e}^{x}}{(\mathrm{e}^{x} - 1)^2}\right\}}$$

$$H - H(0) = U - U(0)[q \text{ is independent of } V] = \frac{N\hbar\omega\mathrm{e}^{-x}}{1 - \mathrm{e}^{-x}} = \boxed{\frac{N\hbar\omega}{\mathrm{e}^{x} - 1}}$$

$$S = \frac{U - U(0)}{T} + nR\ln q = \frac{Nkx\mathrm{e}^{-x}}{1 - \mathrm{e}^{-x}} - Nk\ln(1 - \mathrm{e}^{-x})$$

$$= \boxed{Nk\left(\frac{x}{\mathrm{e}^{x} - 1} - \ln(1 - \mathrm{e}^{-x})\right)}$$

$$A - A(0) = G - G(0) = -nRT\ln q$$

$$= \boxed{NkT\ln(1 - \mathrm{e}^{-x})}$$

The functions are plotted in Fig. 20.7.

P20.15 **(a)**

$$\frac{N_J}{N} = \frac{g_J\mathrm{e}^{-\varepsilon_J/kT}}{\sum_J g_J\mathrm{e}^{-\varepsilon_J/kT}} = \frac{g_J\mathrm{e}^{-\varepsilon_J/kT}}{q}$$

For a linear molecule $g_J = 2J + 1$ and $\varepsilon_J = hcBJ(J + 1)$. Therefore,

$$N_J \propto (2J + 1)\mathrm{e}^{-hcBJ(J+1)/kT}$$

(b) $J_{\max}$ occurs when $\mathrm{d}n_J/\mathrm{d}J = 0$.

$$\frac{\mathrm{d}N_J}{\mathrm{d}J} = \frac{N}{q}\frac{\mathrm{d}}{\mathrm{d}J}\left\{(2J + 1)\mathrm{e}^{-\left(\frac{hcBJ(J+1)}{kT}\right)}\right\} = 0$$

$$2 - (2J_{\max} + 1)\left(\frac{hcB}{kT}\right)(2J_{\max} + 1) = 0$$

$$2J_{\max} + 1 = \left(\frac{2kT}{hcB}\right)^{1/2}$$

$$\boxed{J_{\max} = \left(\frac{kT}{2hcB}\right)^{1/2} - \frac{1}{2}}$$

(c) $J_{\max} \approx 3$ because the R branch $J = 3 \rightarrow 4$ transition has the least transmittance. Solving the previous equation for T provides the desired temperature estimate.

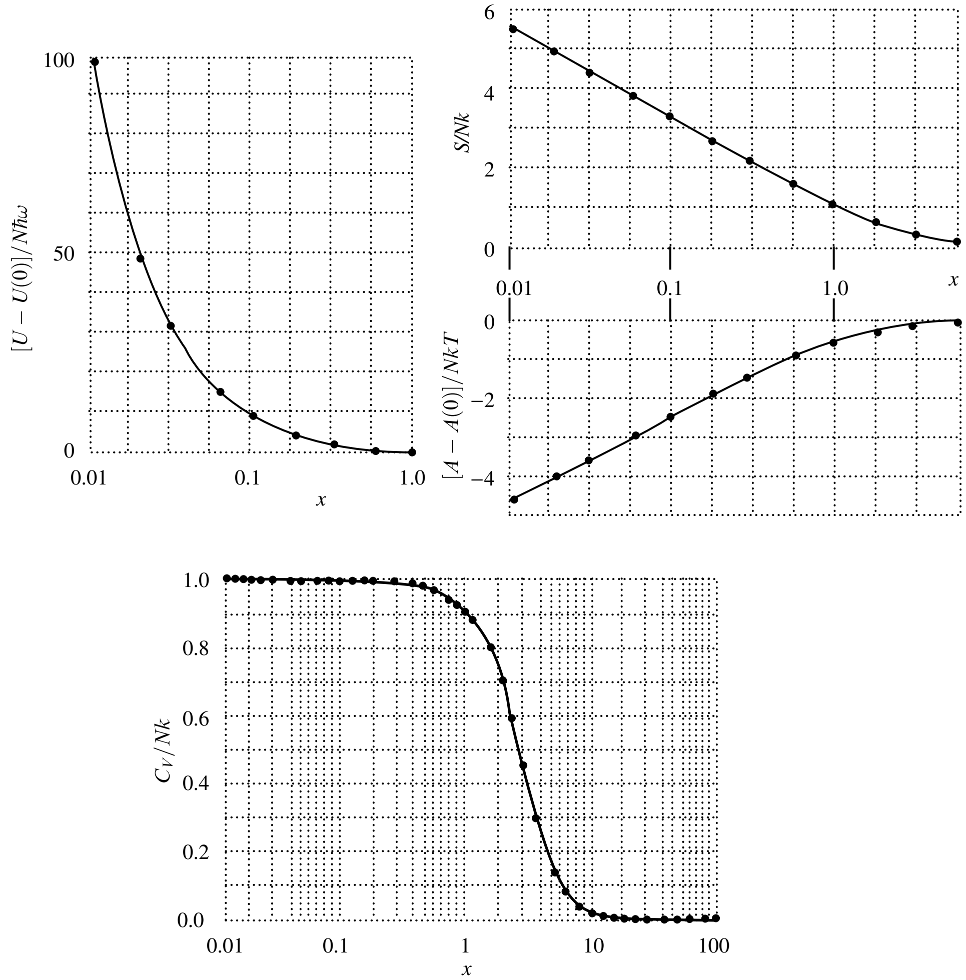


Figure 20.7

$$T \approx \frac{hcB}{2k}(2J_{\max}+1)^2$$

$$\approx \frac{(6.626\times10^{-34}\,\mathrm{J\,s})\times(3.000\times10^{8}\,\mathrm{m\,s^{-1}})\times(10.593\,\mathrm{cm^{-1}})\times\left(\frac{10^2\,\mathrm{cm}}{\mathrm{m}}\right)\times(7)^2}{2(1.38066\times10^{-23}\,\mathrm{J\,K^{-1}})}$$

$$\boxed{T \approx 374\,\mathrm{K}}$$

P20.17 All partition functions other than the electronic partition function are unaffected by a magnetic field; hence the relative change in K is the relative change in q^{E}.

$$q^{\mathrm{E}} = \sum_{M_J} \mathrm{e}^{-g\mu_{\mathrm{B}}\beta\mathcal{B}M_J}, \quad M_J = -\tfrac{3}{2}, -\tfrac{1}{2}, +\tfrac{1}{2}, +\tfrac{3}{2}; \;\; g = \tfrac{4}{3}$$

Since $g\mu_{\mathrm{B}}\beta\mathcal{B} \ll 1$ for normally attainable fields,

$$q^{\mathrm{E}} = \sum_{M_J}\left\{1 - g\mu_{\mathrm{B}}\beta\mathcal{B}M_J + \frac{1}{2}(g\mu_{\mathrm{B}}\beta\mathcal{B}M_J)^2 + \cdots\right\}$$

$$= 4 + \frac{1}{2}(g\mu_B\beta\mathcal{B})^2\sum_{M_J} M_J^2 \left[\sum_{M_J} M_J = 0\right] = 4\left(1 + \frac{10}{9}(\mu_B\beta\mathcal{B})^2\right) \quad \left[g = \frac{4}{3}\right]$$

Therefore, if K is the actual equilibrium constant and K^0 is its value when $\mathcal{B} = 0$, we write

$$\frac{K}{K^0} = \left(1 + \frac{10}{9}(\mu_B\beta\mathcal{B})^2\right)^2 \approx 1 + \frac{20}{9}\mu_B^2\beta^2\mathcal{B}^2$$

For a shift of 1 per cent, we require

$$\tfrac{20}{9}\mu_B^2\beta^2\mathcal{B}^2 \approx 0.01, \quad \text{or} \quad \mu_B\beta\mathcal{B} \approx 0.067$$

Hence

$$\mathcal{B} \approx \frac{0.067kT}{\mu_B} = \frac{(0.067) \times (1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (1000\,\mathrm{K})}{9.274 \times 10^{-24}\,\mathrm{J\,T^{-1}}} \approx \boxed{100\,\mathrm{T}}$$

Solutions to applications

P20.20 The standard molar Gibbs energy is given by

$$G_m^\ominus - G_m^\ominus(0) = RT\ln\frac{q_m^\ominus}{N_A} \quad \text{where } \frac{q_m^\ominus}{N_A} = \frac{q_{m,tr}^\ominus}{N_A}q^R q^V q^E$$

$$\text{Translation:} \quad \frac{q_{m,tr}^\ominus}{N_A} = \frac{kT}{p^\ominus\Lambda^3} = 2.561 \times 10^{-2}(T/\mathrm{K})^{5/2}(M/\mathrm{g\,mol^{-1}})^{3/2}$$

$$= (2.561 \times 10^{-2}) \times (2000)^{5/2} \times (38.90)^{3/2}$$

$$= 1.111 \times 10^9$$

Rotation of a linear molecule:

$$q^R = \frac{kT}{\sigma hcB} = \frac{0.6950}{\sigma} \times \frac{T/\mathrm{K}}{B/\mathrm{cm^{-1}}}$$

The rotational constant is

$$B = \frac{\hbar}{4\pi cI} = \frac{\hbar}{4\pi c m_{\mathrm{eff}}R^2} \quad \text{where } m_{\mathrm{eff}} = \frac{m_B m_{Si}}{m_B + m_{Si}}$$

$$= \frac{(10.81) \times (28.09)}{10.81 + 28.09} \times \frac{10^{-3}\,\mathrm{kg\,mol^{-1}}}{6.022 \times 10^{23}\,\mathrm{mol^{-1}}}$$

$$m_{\mathrm{eff}} = 1.296 \times 10^{-26}\,\mathrm{kg}$$

$$B = \frac{1.0546 \times 10^{-34}\,\mathrm{J\,s}}{4\pi(2.998 \times 10^{10}\,\mathrm{cm\,s^{-1}}) \times (1.296 \times 10^{-26}\,\mathrm{kg}) \times (190.5 \times 10^{-12}\,\mathrm{m})^2} = 0.5952\,\mathrm{cm^{-1}}$$

$$\text{so } q^R = \frac{0.6950}{1} \times \frac{2000}{0.5952} = 2335$$

$$\text{Vibration:}\quad q^{\mathrm{V}} = \frac{1}{1-\mathrm{e}^{-hc\tilde{\nu}/kT}} = \frac{1}{1-\exp\left(\frac{-1.4388(\tilde{\nu}/\mathrm{cm}^{-1})}{T/\mathrm{K}}\right)} = \frac{1}{1-\exp\left(\frac{-1.4388(772)}{2000}\right)}$$

$$= 2.467$$

The Boltzmann factor for the lowest-lying electronic excited state is

$$\exp\left(\frac{-(1.4388)\times(8000)}{2000}\right) = 3.2\times 10^{-3}$$

The degeneracy of the ground level is 4 (spin degeneracy = 4, orbital degeneracy = 1), and that of the excited level is also 4 (spin degeneracy = 2, orbital degeneracy = 2), so

$$q^{\mathrm{E}} = 4(1+3.2\times 10^{-3}) = 4.013$$

Putting it all together yields

$$\begin{aligned} G_{\mathrm{m}}^{\ominus} - G_{\mathrm{m}}^{\ominus}(0) &= (8.3145\,\mathrm{J\,mol^{-1}\,K^{-1}})\times(2000\,\mathrm{K})\ln(1.111\times 10^{9})\times(2335) \\ &\quad \times(2.467)\times(4.013) \\ &= 5.135\times 10^{5}\,\mathrm{J\,mol^{-1}} = \boxed{513.5\,\mathrm{kJ\,mol^{-1}}} \end{aligned}$$

P20.22 The standard molar Gibbs energy is given by

$$G_{\mathrm{m}}^{\ominus} - G_{\mathrm{m}}^{\ominus}(0) = RT\ln\frac{q_{\mathrm{m}}^{\ominus}}{N_{\mathrm{A}}}\quad \text{where}\ \frac{q_{\mathrm{m}}^{\ominus}}{N_{\mathrm{A}}} = \frac{q_{\mathrm{m,tr}}^{\ominus}}{N_{\mathrm{A}}}q^{\mathrm{R}}q^{\mathrm{V}}q^{\mathrm{E}}$$

First, at 10.00 K

$$\text{Translation:}\quad \frac{q_{\mathrm{m,tr}}^{\ominus}}{N_{\mathrm{A}}} = 2.561\times 10^{-2}(T/\mathrm{K})^{5/2}(M/\mathrm{g\,mol^{-1}})^{3/2}$$

$$= (2.561\times 10^{-2})\times(10.00)^{5/2}\times(36.033)^{3/2}$$

$$= 1752$$

Rotation of a nonlinear molecule:

$$q^{\mathrm{R}} = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{ABC}\right)^{1/2} = \frac{1.0270}{\sigma}\times\frac{(T/\mathrm{K})^{3/2}}{(ABC/\mathrm{cm^{-3}})^{1/2}}$$

The rotational constants are

$$B = \frac{\hbar}{4\pi cI}\quad \text{so}\quad ABC = \left(\frac{\hbar}{4\pi c}\right)^{3}\frac{1}{I_{\mathrm{A}}I_{\mathrm{B}}I_{\mathrm{C}}},$$

$$\begin{aligned} ABC &= \left(\frac{1.0546\times 10^{-34}\,\mathrm{J\,s}}{4\pi(2.998\times 10^{10}\,\mathrm{cm\,s^{-1}})}\right)^{3} \\ &\quad \times\frac{(10^{10}\,\text{Å}\,\mathrm{m^{-1}})^{6}}{(39.340)\times(39.032)\times(0.3082)\times(\mathrm{u}\,\text{Å}^{2})^{3}\times(1.66054\times 10^{-27}\,\mathrm{kg\,u^{-1}})^{3}} \\ &= 101.2\,\mathrm{cm^{-3}} \end{aligned}$$

$$\text{so}\ q^{\mathrm{R}} = \frac{1.0270}{2}\times\frac{(10.00)^{3/2}}{(101.2)^{1/2}} = 1.614$$

$$\text{Vibration:}\quad q^{\mathrm{V}} = \frac{1}{1-\mathrm{e}^{-hc\tilde{\nu}/kT}} = \frac{1}{1-\exp\left(\frac{-1.4388(\tilde{\nu}/\mathrm{cm}^{-1})}{T/\mathrm{K}}\right)} = \frac{1}{1-\exp\left(\frac{-1.4388(63.4)}{10.00}\right)}$$

$$= 1.0001$$

Even the lowest-frequency mode has a vibrational partition function of 1; so the stiffer vibrations have q^{V} even closer to 1. The degeneracy of the electronic ground state is 1, so $q^{\mathrm{E}} = 1$. Putting it all together yields

$$\begin{aligned} G_{\mathrm{m}}^{\ominus} - G_{\mathrm{m}}^{\ominus}(0) &= (8.3145\,\mathrm{J\,mol^{-1}\,K^{-1}}) \times (10.00\,\mathrm{K}) \ln(1752) \times (1.614) \times (1) \times (1) \\ &= \boxed{660.8\,\mathrm{J\,mol^{-1}}} \end{aligned}$$

Now at 1000 K

$$\text{Translation:}\quad \frac{q_{\mathrm{m,tr}}^{\ominus}}{N_{\mathrm{A}}} = (2.561 \times 10^{-2}) \times (1000)^{5/2} \times (36.033)^{3/2} = 1.752 \times 10^{8}$$

$$\text{Rotation:}\quad q^{\mathrm{R}} = \frac{1.0270}{2} \times \frac{(1000)^{3/2}}{(101.2)^{1/2}} = 1614$$

$$\begin{aligned} \text{Vibration:}\quad q^{\mathrm{V(1)}} &= \frac{1}{1-\exp\left(-\frac{(1.4388)\times(63.4)}{1000}\right)} = 11.47 \\ q^{\mathrm{V(2)}} &= \frac{1}{1-\exp\left(-\frac{(1.4388)\times(1224.5)}{1000}\right)} = 1.207 \\ q^{\mathrm{V(3)}} &= \frac{1}{1-\exp\left(-\frac{(1.4388)\times(2040)}{1000}\right)} = 1.056 \\ q^{\mathrm{V}} &= (11.47) \times (1.207) \times (1.056) = 14.62 \end{aligned}$$

Putting it all together yields

$$\begin{aligned} G_{\mathrm{m}}^{\ominus} - G_{\mathrm{m}}^{\ominus}(0) &= (8.3145\,\mathrm{J\,mol^{-1}\,K^{-1}}) \times (1000\,\mathrm{K}) \times \ln(1.752 \times 10^{8}) \times (1614) \\ &\quad \times (14.62) \times (1) \\ &= 2.415 \times 10^{5}\,\mathrm{J\,mol^{-1}} = \boxed{241.5\,\mathrm{kJ\,mol^{-1}}} \end{aligned}$$

21 Molecular interactions

Solutions to exercises

Discussion questions

E21.1(b) When the applied field changes direction slowly, the permanent dipole moment has time to reorientate—the whole molecule rotates into a new direction—and follow the field. However, when the frequency of the field is high, a molecule cannot change direction fast enough to follow the change in direction of the applied field and the dipole moment then makes no contribution to the polarization of the sample. Because a molecule takes about 1 ps to turn through about 1 radian in a fluid, the loss of this contribution to the polarization occurs when measurements are made at frequencies greater than about 10^{11} Hz (in the microwave region). We say that the orientation polarization, the polarization arising from the permanent dipole moments, is lost at such high frequencies.

The next contribution to the polarization to be lost as the frequency is raised is the distortion polarization, the polarization that arises from the distortion of the positions of the nuclei by the applied field. The molecule is bent and stretched by the applied field, and the molecular dipole moment changes accordingly. The time taken for a molecule to bend is approximately the inverse of the molecular vibrational frequency, so the distortion polarization disappears when the frequency of the radiation is increased through the infrared. The disappearance of polarization occurs in stages: as shown in *Justification* 21.3, each successive stage occurs as the incident frequency rises above the frequency of a particular mode of vibration.

At even higher frequencies, in the visible region, only the electrons are mobile enough to respond to the rapidly changing direction of the applied field. The polarization that remains is now due entirely to the distortion of the electron distribution, and the surviving contribution to the molecular polarizability is called the electronic polarizability.

E21.2(b) There are three van der Waals type interactions that depend upon distance as $1/r^6$; they are the Keesom interaction between rotating permanent dipoles, the permanent-dipole–induced dipole-interaction, and the induced-dipole–induced-dipole, or London dispersion, interaction. In each case, we can visualize the distance dependence of the potential energy as arising from the $1/r^3$ dependence of the field (and hence the magnitude of the induced dipole) and the $1/r^3$ dependence of the potential energy of interaction of the dipoles (either permanent or induced).

E21.3(b) The goal is to construct the radial distribution function, $g(r)$, which gives the relative locations of the particles in the liquid (eqn 21.35). Once $g(r)$ is known it can be used to calculate the thermodynamic properties of the liquid. This expression is nothing more than the Boltzmann distribution of statistical thermodynamics for two molecules in a field generated by all the other molecules in the system.

There are several ways of building the intermolecular potential into the calculation of $g(r)$. Numerical methods take a box of about 10^3 particles (the number increases as computers grow more powerful), and the rest of the liquid is simulated by surrounding the box with replications of the original box (Fig. 21.29 of the text). Then, whenever a particle leaves the box through one of its faces, its image arrives through the opposite face. When calculating the interactions of a molecule in a box, it interacts with all the molecules in the box and all the periodic replications of those molecules and itself in the other boxes. Once $g(r)$ is known it can be used to calculate the thermodynamic properties of liquids.

(a) Monte Carlo methods

In the Monte Carlo method, the particles in the box are moved through small but otherwise random distances, and the change in total potential energy of the N particles in the box, ΔV_N, is calculated using one of the intermolecular potentials discussed in Sections 21.5 and 21.6. Whether or not this new configuration is accepted is then judged from the following rules:

1 If the potential energy is not greater than before the change, then the configuration is accepted.

2 If the potential energy is greater than before change, the Boltzmann factor $e^{-\Delta V_N/kT}$ is compared with a random number between 0 and 1; if the factor is larger than the random number, the configuration is accepted; if the factor is not larger, the configuration is rejected. This procedure ensures that at equilibrium the probability of occurrence of any configuration is proportional to the Boltzmann factor. The configurations generated in this way can then be used to construct $g(r)$ simply by counting the number of pairs of particles with a separation r and averaging the result over the whole collection of configurations.

(b) Molecular dynamics

In the molecular dynamics approach, the history of an initial arrangement is followed by calculating the trajectories of all the particles under the influence of the intermolecular potentials. Newton's laws are used to predict where each particle will be after a short time interval (about 1 fs. which is shorter than the average time between collisions), and then the calculation is repeated for tens of thousands of such steps. The time-consuming part of the calculation is the evaluation of the net force on the molecule arising from all the other molecules present in the system.

A molecular dynamics calculation gives a series of snapshots of the liquid, and $g(r)$ can be calculated as before. The temperature of the system is inferred by computing the mean kinetic energy of the particles and using the equipartition result that $\langle 1/2\, mv_{\mathrm{q}}^2\rangle = 1/2\, kT$ for each coordinate q.

E21.4(b) Describe how molecular beams are used to investigate intermolecular potentials.

A molecular beam is a narrow stream of molecules with a narrow spread of velocities and, in some cases, in specific internal states or orientations. Molecular beam studies of non-reactive collisions are used to explore the details of intermolecular interactions with a view to determining the shape of the intermolecular potential.

The primary experimental information from a molecular beam experiment is the fraction of the molecules in the incident beam that are scattered into a particular direction. The fraction is normally expressed in terms of dI, the rate at which molecules are scattered into a cone that represents the area covered by the "eye" of the detector (Fig. 21.21 of the text). This rate is reported as the differential scattering cross-section, σ, the constant of proportionality between the value of dI and the intensity, I, of the incident beam, the number density of target molecules, N, and the infinitesimal path length dx through the sample:

$$\mathrm{d}I = \sigma I N \mathrm{d}x.$$

The value of σ (which has the dimensions of area) depends on the impact parameter, b, the initial perpendicular separation of the paths of the colliding molecules (Fig. 21.22), and the details of the intermolecular potential.

The scattering pattern of real molecules, which are not hard spheres, depends on the details of the intermolecular potential, including the anisotropy that is present when the molecules are non-spherical. The scattering also depends on the relative speed of approach of the two particles: a very fast particle might pass through the interaction region without much deflection, whereas a slower one on the same path might be temporarily captured and undergo considerable deflection (Fig. 21.24). The variation of the scattering cross-section with the relative speed of approach therefore gives information about the strength and range of the intermolecular potential.

Another phenomenon that can occur in certain beams is the capturing of one species by another. The vibrational temperature in supersonic beams is so low that van der Waals molecules may be formed, which are complexes of the form AB in which A and B are held together by van der Waals forces or hydrogen bonds. Large numbers of such molecules have been studied spectroscopically, including ArHCl, $(HCl)_2ArCO_2$, and $(H_2O)_2$. More recently, van der Waals clusters of water molecules have been pursued as far as $(H_2O)_6$. The study of their spectroscopic properties gives detailed information about the intermolecular potentials involved.

Numerical exercises

E21.5(b) A molecule that has a centre of symmetry cannot be polar. $SO_3\,(D_{3h})$ and $XeF_4\,(D_{4h})$ cannot be polar. $\boxed{SF_4}$ (see-saw, C_{2v}) may be polar.

E21.6(b) The molar polarization depends on the polarizability through

$$P_m = \frac{N_A}{3\varepsilon_0}\left(\alpha + \frac{\mu^2}{3kT}\right)$$

This is a linear equation in T^{-1} with slope

$$m = \frac{N_A\mu^2}{9\varepsilon_0 k} \quad \text{so} \quad \mu = \left(\frac{9\varepsilon_0 km}{N_A}\right)^{1/2} = (4.275\times10^{-29}\,\text{C m})\times(m/(\text{m}^3\,\text{mol}^{-1}\text{K}))^{1/2}$$

and with y-intercept

$$b = \frac{N_A\alpha}{3\varepsilon_0} \quad \text{so} \quad \alpha = \frac{3\varepsilon_0 b}{N_A} = (4.411\times10^{-35}\,\text{C}^2\,\text{m}^2\,\text{J}^{-1})b/(\text{m}^3\,\text{mol}^{-1})$$

Since the molar polarization is linearly dependent on T^{-1}, we can obtain the slope m and the intercept b

$$m = \frac{P_{m,2}-P_{m,1}}{T_1^{-1}-T_2^{-1}} = \frac{(75.74-71.43)\,\text{cm}^3\,\text{mol}^{-1}}{(320.0\,\text{K})^{-1}-(421.7\,\text{K})^{-1}} = 5.72\times10^3\,\text{cm}^3\,\text{mol}^{-1}\,\text{K}$$

and $b = P_m - mT^{-1} = 75.74\,\text{cm}^3\,\text{mol}^{-1} - (5.72\times10^3\,\text{cm}^3\,\text{mol}^{-1}\,\text{K})\times(320.0\,\text{K})^{-1}$
$= 57.9\,\text{cm}^3\,\text{mol}^{-1}$

It follows that

$$\mu = (4.275\times10^{-29}\,\text{C m})\times(5.72\times10^{-3})^{1/2} = \boxed{3.23\times10^{-30}\,\text{C m}}$$

and $\alpha = (4.411\times10^{-35}\,\text{C}^2\,\text{m}^2\,\text{J}^{-1})\times(57.9\times10^{-6}) = \boxed{2.55\times10^{-39}\,\text{C}^2\,\text{m}^2\,\text{J}^{-1}}$

E21.7(b) The relative permittivity is related to the molar polarization through

$$\frac{\varepsilon_r-1}{\varepsilon_r+2} = \frac{\rho P_m}{M} \equiv C \quad \text{so} \quad \varepsilon_r = \frac{2C+1}{1-C},$$

$$C = \frac{(1.92\,\text{g cm}^{-3})\times(32.16\,\text{cm}^3\,\text{mol}^{-1})}{85.0\,\text{g mol}^{-1}} = 0.726$$

$$\varepsilon_r = \frac{2\times(0.726)+1}{1-0.726} = \boxed{8.97}$$

E21.8(b) If the permanent dipole moment is negligible, the polarizability can be computed from the molar polarization

$$P_\mathrm{m} = \frac{N_\mathrm{A}\alpha}{3\varepsilon_0} \quad \text{so} \quad \alpha = \frac{3\varepsilon_0 P_\mathrm{m}}{N_\mathrm{A}}$$

and the molar polarization from the refractive index

$$\frac{\rho P_\mathrm{m}}{M} = \frac{\varepsilon_\mathrm{r} - 1}{\varepsilon_\mathrm{r} + 2} = \frac{n_\mathrm{r}^2 - 1}{n_\mathrm{r}^2 + 2} \quad \text{so} \quad \alpha = \frac{3\varepsilon_0 M}{N_\mathrm{A}\rho}\left(\frac{n_\mathrm{r}^2 - 1}{n_\mathrm{r}^2 + 2}\right)$$

$$\alpha = \frac{3 \times (8.854 \times 10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}}) \times (65.5\,\mathrm{g\,mol^{-1}})}{(6.022 \times 10^{23}\,\mathrm{mol^{-1}}) \times (2.99 \times 10^{6}\,\mathrm{g\,m^{-3}})} \times \left(\frac{1.622^2 - 1}{1.622^2 + 2}\right)$$

$$= \boxed{3.40 \times 10^{-40}\,\mathrm{C^2\,m^2\,J^{-1}}}$$

E21.9(b) $\mu = qR \quad [q = be, b = \text{bond order}]$

For example, $\mu_\text{ionic}(\text{C—F}) = (1.602 \times 10^{-19}\,\mathrm{C}) \times (1.41 \times 10^{-10}\,\mathrm{m}) = 22.6 \times 10^{-30}\,\mathrm{C\,m} = 6.77\,\mathrm{D}$

Then, per cent ionic character $= \dfrac{\mu_\text{obs}}{\mu_\text{ionic}} \times 100$

$\Delta\chi$ values are based on Pauling electronegativities as found in any general chemistry text.

We draw up the following table

Bond	$\mu_\text{obs}/\mathrm{D}$	$\mu_\text{ionic}/\mathrm{D}$	Per cent	$\Delta\chi$
C—F	1.4	6.77	$\boxed{21}$	1.5
C—O	1.2	6.87	$\boxed{17}$	1.0

The $\boxed{\text{correlation is at best qualitative}}$.

Comment. There are other contributions to the observed dipole moment besides the term qR. These are a result of the delocalization of the charge distribution in the bond orbitals.

Question. Is the correlation mentioned in the text [21.2] any better?

E21.10(b) $\mu = (\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta)^{1/2} \quad [21.3\text{a}]$

$$= [(1.5)^2 + (0.80)^2 + (2) \times (1.5) \times (0.80) \times (\cos 109.5^\circ)]^{1/2}\mathrm{D} = \boxed{1.4\,\mathrm{D}}$$

E21.11(b) The components of the dipole moment vector are

$$\mu_x = \sum_i q_i x_i = (4e) \times (0) + (-2e) \times (162\,\mathrm{pm}) + (-2e) \times (143\,\mathrm{pm}) \times (\cos 30^\circ) = (-572\,\mathrm{pm})e$$

and $\mu_y = \sum_i q_i y_i = (4e) \times (0) + (-2e) \times (0) + (-2e) \times (143\,\mathrm{pm}) \times (\sin 30^\circ) = (-143\,\mathrm{pm})e$

The magnitude is

$$\mu = (\mu_x^2 + \mu_y^2)^{1/2} = ((-570)^2 + (-143)^2)^{1/2}\,\mathrm{pm}\,e = (590\,\mathrm{pm})e$$

$$= (590 \times 10^{-12}\,\mathrm{m}) \times (1.602 \times 10^{-19}\,\mathrm{C}) = \boxed{9.45 \times 10^{-29}\,\mathrm{C\,m}}$$

and the direction is $\theta = \tan^{-1}\dfrac{\mu_y}{\mu_x} = \tan^{-1}\dfrac{-143\,\text{pm}\,e}{-572\,\text{pm}\,e} = \boxed{194.0^\circ}$ from the x-axis (i.e., 14.0° below the negative x-axis).

E21.12(b) The induced dipole moment is

$$\begin{aligned}\mu^* &= \alpha\mathcal{E} = 4\pi\varepsilon_0\alpha'\mathcal{E}\\ &= 4\pi(8.854\times10^{-12}\,\text{J}^{-1}\,\text{C}^2\,\text{m}^{-1})\times(2.22\times10^{-30}\,\text{m}^3)\times(15.0\times10^3\,\text{V}\,\text{m}^{-1})\\ &= \boxed{3.71\times10^{-36}\,\text{C}\,\text{m}}\end{aligned}$$

E21.13(b) The solution to Exercise 21.8(a) showed that

$$\alpha = \left(\frac{3\varepsilon_0 M}{\rho N_\text{A}}\right)\times\left(\frac{n_\text{r}^2-1}{n_\text{r}^2+2}\right) \quad\text{or}\quad \alpha' = \left(\frac{3M}{4\pi\rho N_\text{A}}\right)\times\left(\frac{n_\text{r}^2-1}{n_\text{r}^2+2}\right)$$

which may be solved for n_r to yield

$$n_\text{r} = \left(\frac{\beta'+2\alpha'}{\beta'-\alpha'}\right)^{1/2} \quad\text{with } \beta' = \frac{3M}{4\pi\rho N_\text{A}}$$

$$\beta' = \frac{(3)\times(72.3\,\text{g}\,\text{mol}^{-1})}{(4\pi)\times(0.865\times10^6\,\text{g}\,\text{m}^{-3})\times(6.022\times10^{23}\,\text{mol}^{-1})} = 3.31\bar{4}\times10^{-29}\,\text{m}^3$$

$$n_\text{r} = \left(\frac{33.1\bar{4}+2\times2.2}{33.1\bar{4}-2.2}\right)^{1/2} = \boxed{1.10}$$

E21.14(b) The relative permittivity is related to the molar polarization through

$$\frac{\varepsilon_\text{r}-1}{\varepsilon_\text{r}+2} = \frac{\rho P_\text{m}}{M} \equiv C \quad\text{so}\quad \varepsilon_\text{r} = \frac{2C+1}{1-C}$$

The molar polarization depends on the polarizability through

$$P_\text{m} = \frac{N_\text{A}}{3\varepsilon_0}\left(\alpha+\frac{\mu^2}{3kT}\right) \quad\text{so}\quad C = \frac{\rho N_\text{A}}{3\varepsilon_0 M}\left(4\pi\varepsilon_0\alpha'+\frac{\mu^2}{3kT}\right)$$

$$\begin{aligned}C = {}&\frac{(1491\,\text{kg}\,\text{m}^{-3})\times(6.022\times10^{23}\,\text{mol}^{-1})}{3(8.854\times10^{-12}\,\text{J}^{-1}\,\text{C}^2\,\text{m}^{-1})\times(157.01\times10^{-3}\,\text{kg}\,\text{mol}^{-1})}\\ &\times\Bigg(4\pi(8.854\times10^{-12}\,\text{J}^{-1}\,\text{C}^2\,\text{m}^{-1})\times(1.5\times10^{-29}\,\text{m}^3)\\ &+\frac{(5.17\times10^{-30}\,\text{C}\,\text{m})^2}{3(1.381\times10^{-23}\,\text{J}\,\text{K}^{-1})\times(298\,\text{K})}\Bigg)\end{aligned}$$

$$C = 0.83 \quad\text{and}\quad \varepsilon_\text{r} = \frac{2(0.83)+1}{1-0.83} = \boxed{16}$$

E21.15(b) The rotation of plane-polarized light is described by

$$\Delta\theta = (n_R - n_L)\frac{2\pi l}{\lambda} \quad \text{so} \quad n_R - n_L = \frac{\lambda\Delta\theta}{2\pi l}$$

$$= \left[\frac{(450 \times 10^{-9}\,\mathrm{m}) \times (2 \times 192^\circ)}{2\pi(15 \times 10^{-2}\,\mathrm{m})}\right] \times \left(\frac{2\pi}{360^\circ}\right)$$

$$n_R - n_L = \boxed{3.2 \times 10^{-6}}$$

Solutions to problems

Solutions to numerical problems

P21.2 The energy of the dipole $-\mu_1\mathcal{E}$. To flip it over requires a change in energy of $2\mu_1\mathcal{E}$. This will occur when the energy of interaction of the dipole with the induced dipole of the Ar atom equals $2\mu_1\mathcal{E}$. The magnitude of the dipole–induced dipole interaction is

$$V = \frac{\mu_1^2\alpha_2'}{\pi\varepsilon_0 r^6}[21.26] = 2\mu_1\mathcal{E} \text{ [after flipping over]}$$

$$r^6 = \frac{\mu_1\alpha_2'}{2\pi\varepsilon_0\mathcal{E}} = \frac{(6.17 \times 10^{-30}\,\mathrm{C\,m}) \times (1.66 \times 10^{-30}\,\mathrm{m^3})}{(2\pi) \times (8.854 \times 10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}}) \times (1.0 \times 10^3\,\mathrm{V\,m^{-1}})}$$

$$= 1.8\overline{4} \times 10^{-52}\,\mathrm{m^6}$$

$$r = 2.4 \times 10^{-9}\,\mathrm{m} = \boxed{2.4\,\mathrm{nm}}$$

Comment. This distance is about 24 times the radius of the Ar atom.

P21.4 $$P_m = \left(\frac{M}{\rho}\right) \times \left(\frac{\varepsilon_r - 1}{\varepsilon_r + 2}\right) \quad \text{and} \quad P_m = \frac{4\pi}{3}N_A\alpha' + \frac{N_A\mu^2}{9\varepsilon_0 kT} \text{ [21.15 and 21.16 with } \alpha = 4\pi\varepsilon_0\alpha'\text{]}$$

The data have been corrected for the variation in methanol density, so use $\rho = 0.791\,\mathrm{g\,cm^{-3}}$ for all entries. Obtain μ and α' from the liquid range ($\theta > -95^\circ\mathrm{C}$) results, but note that some molecular rotation occurs even below the freezing point (thus the $-110^\circ\mathrm{C}$ value is close to the $-80^\circ\mathrm{C}$ value). Draw up the following table using $M = 32.0\,\mathrm{g\,mol^{-1}}$.

$\theta/^\circ\mathrm{C}$	−80	−50	−20	0	20
T/K	193	223	253	273	293
$\frac{1000}{T/\mathrm{K}}$	5.18	4.48	3.95	3.66	3.41
ε_r	57	49	42	38	34
$\frac{\varepsilon_r - 1}{\varepsilon_r + 2}$	0.949	0.941	0.932	0.925	0.917
$P_m/(\mathrm{cm^3\,mol^{-1}})$	38.4	38.1	37.7	37.4	37.1

P_m is plotted against $\frac{1}{T}$ in Fig. 21.1.

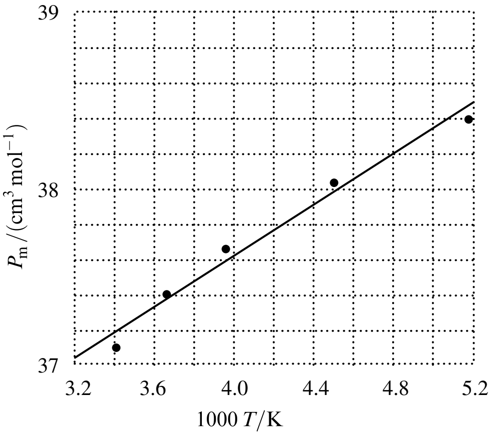


Figure 21.1

The extrapolated intercept at $\frac{1}{T} = 0$ is 34.8 (not shown in the figure) and the slope is 721 (from a least-squares analysis). It follows that

$$\alpha' = \frac{3P_m(\text{at intercept})}{4\pi N_A} = \frac{(3) \times (35.0\,\mathrm{cm^3\,mol^{-1}})}{(4\pi) \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}})} = \boxed{1.38 \times 10^{-23}\,\mathrm{cm^3}}$$

$$\mu = (1.282 \times 10^{-2}\,\mathrm{D}) \times (721)^{1/2}\ [\text{from Problem 21.3}] = \boxed{0.34\,\mathrm{D}}$$

The jump in ε_r which occurs below the melting temperature suggests that the molecules can rotate while the sample is still solid.

P21.6 $$P_m = \frac{4\pi}{3}N_A\alpha' + \frac{N_A\mu^2}{9\varepsilon_0 kT}\ [21.16, \text{with}\ \alpha = 4\pi\varepsilon_0\alpha']$$

Draw up the following table

T/K	384.3	420.1	444.7	484.1	522.0
$\frac{1000}{T/\mathrm{K}}$	2.602	2.380	2.249	2.066	1.916
$P_m/(\mathrm{cm^3\,mol^{-1}})$	57.4	53.5	50.1	46.8	43.1

The points are plotted in Fig. 21.2.

The extrapolated (least-squares) intercept is $3.44\,\mathrm{cm^3\,mol^{-1}}$; the slope is $2.08\bar{4} \times 10^4$.

$$\mu = (1.282 \times 10^{-2}\,\mathrm{D}) \times (\text{slope})^{1/2}\ [\text{Problem 21.3}] = \boxed{1.85\,\mathrm{D}}$$

$$\alpha' = \frac{3P_m(\text{at intercept})}{4\pi N_A} = \frac{(3) \times (3.44\,\mathrm{cm^3\,mol^{-1}})}{(4\pi) \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}})} = \boxed{1.36 \times 10^{-24}\,\mathrm{cm^3}}$$

Comment. The agreement of the value of μ with Table 22.1 is exact, but the polarizability volumes differ by about 8 per cent.

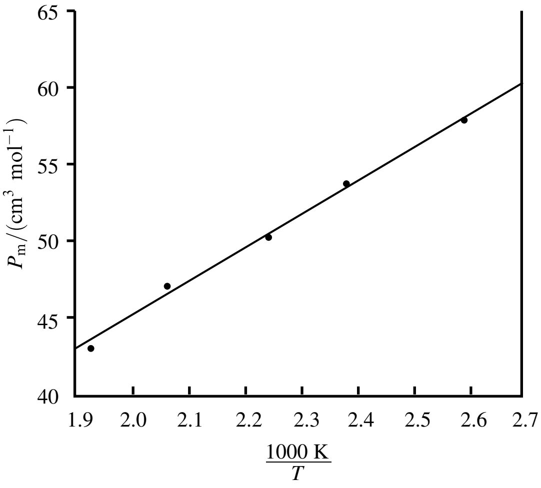


Figure 21.2

P21.7 If there is a simple group-additivity relationship, then α^{elec} ought to be a linear function of the number of $\mathrm{Si_2H_4}$ groups. That is, a plot of α^{elec} versus N ought to be a straight line. The plot is shown in Fig. 21.3 and a table shows values of α^{elec} computed from the best fit of the data and their deviations from the reported values. The equation of the best-fit line is

$$\alpha^{\mathrm{elec}}/(10^{-40}\,\mathrm{J^{-1}C\,m^2}) = 4.8008N - 1.7816$$

so the average contribution per $\mathrm{Si_2H_4}$ unit is $\boxed{4.80 \times 10^{-40}\,\mathrm{J^{-1}\,C\,m^2}}$

N	1	2	3	4	5	6	7	8	9
Reported α^{elec}	3.495	7.766	12.40	17.18	22.04	26.92	31.82	36.74	41.63
Best fit α^{elec}	3.019	7.820	12.62	17.42	22.22	27.02	31.82	36.62	41.43
Deviation	0.476	−0.054	−0.22	−0.24	−0.18	−0.098	−0.002	0.110	0.21

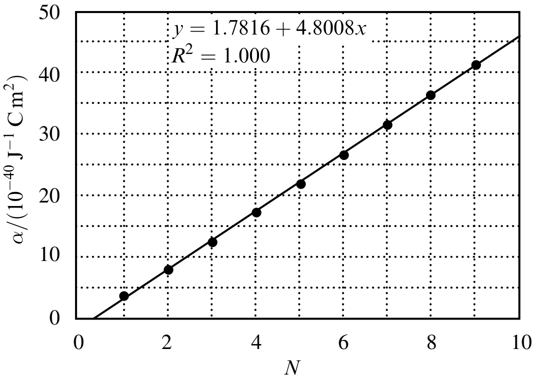


Figure 21.3

The root-mean-square deviation is $\boxed{0.26 \times 10^{-40}\,\mathrm{J^{-1}\,C\,m^2}}$

P21.9 D_0 can be obtained by adding together all the vibrational transitions; then

$$D_e = D_0 + \tfrac{1}{2}\left(1 - \tfrac{1}{2}x_e\right)\tilde{\nu} = D_0 + G(0)$$

The potential obviously has some anharmonicity, for no two transitions have the same or nearly the same energy. But we cannot compute x_e without knowing D_e for

$$x_e = \frac{\tilde{\nu}}{4D_e}$$

For that matter, we do not know $\tilde{\nu}$ exactly either. Our best estimate at the moment is $G(1) - G(0)$, which would equal $\tilde{\nu}$ if the vibration were harmonic, but in general it is

$$G(1) - G(0) = \left(1 + \tfrac{1}{2}\right)\tilde{\nu} - \left(1 + \tfrac{1}{2}\right)^2 x_e\tilde{\nu} - \left(\tfrac{1}{2}\tilde{\nu} - \tfrac{1}{2}^2 x_e\tilde{\nu}\right) = \tilde{\nu}(1 - 2x_e)$$

Our solution is first to compute D_e as if the potential were harmonic, then to compute x_e based on the harmonic D_e and to recompute $\tilde{\nu}$ from $G(1) - G(0)$ and x_e. D_e can then be recomputed based on the improved $\tilde{\nu}$ and x_e and the process repeated until the values stop changing in successive approximations. In the harmonic approximation

$$D_e = 1909.3 + 1060.3 + 386.3 + \tfrac{1}{2}(1909.3)\,\text{m}^{-1} = 4310.6\,\text{m}^{-1}$$

and the parameter a is given by

$$\begin{aligned} a &= \left(\frac{m_{\text{eff}}}{2hcD_e}\right)^{1/2}\omega = \left(\frac{2m_{\text{eff}}c}{hD_e}\right)^{1/2}\pi\tilde{\nu} \\ &= \left(\frac{2(2.2128\times10^{-26}\,\text{kg})\times(2.998\times10^{8}\,\text{m s}^{-1})}{(6.626\times10^{-34}\,\text{J s})\times(4310.6\,\text{m}^{-1})}\right)^{1/2}\times\pi(1909.3\,\text{m}^{-1}) \\ &= 1.293\times10^{10}\,\text{m}^{-1} \end{aligned}$$

The anharmonicity constant is substantial

$$x_e = \frac{1909.3\,\text{m}^{-1}}{4(4310.6\,\text{m}^{-1})} = 0.1107$$

A spreadsheet may be used to recompute the parameters, which converge to

$$x_e = 0.1466,\quad \tilde{\nu} = 2701\,\text{m}^{-1},\quad D_e = 4607\,\text{m}^{-1},\quad \text{and}\quad a = 1.769\times10^{10}\,\text{m}^{-1}$$

or $D_e = \boxed{46.07\,\text{cm}^{-1}}$ and $a = \boxed{1.769\times10^{8}\,\text{cm}^{-1}}$

P21.11 An electric dipole moment may be considered as charge $+q$ and $-q$ separated by a distance l such that

$$\mu = ql \quad \text{so} \quad q = \mu/l = \frac{(1.77\,\text{D})\times(3.336\times10^{-30}\,\text{C m/D})}{299\times10^{-12}\,\text{m}} = 1.97\times0^{-20}\,\text{C}$$

In units of the electron charge

$$q/e = (1.97\times10^{-20}\,\text{C})/(1.602\times10^{-19}\,\text{C}) = \boxed{0.123}$$

P21.12 Neglecting the permanent dipole moment contribution

$$\begin{aligned}
P_{\mathrm{m}} &= \frac{N_{\mathrm{A}}\alpha}{3\varepsilon_0}[21.16] \\
&= \frac{(6.022\times10^{23}\,\mathrm{mol^{-1}})\times(3.59\times10^{-40}\,\mathrm{J^{-1}\,C^2\,m^2})}{3(8.854\times10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}})} \\
&= 8.14\times10^{-6}\,\mathrm{m^3\,mol^{-1}} = \boxed{8.14\,\mathrm{cm^3\,mol^{-1}}} \\
\frac{\varepsilon_{\mathrm{r}}-1}{\varepsilon_{\mathrm{r}}+2} &= \frac{\rho P_{\mathrm{m}}}{M}[21.17] \\
&= \frac{(0.7914\,\mathrm{g\,cm^{-3}})\times(8.14\,\mathrm{cm^3\,mol^{-1}})}{32.04\,\mathrm{g\,mol^{-1}}} = 0.201
\end{aligned}$$

$$\varepsilon_{\mathrm{r}} - 1 = 0.201\varepsilon_{\mathrm{r}} + 0.402; \qquad \boxed{\varepsilon_{\mathrm{r}} = 1.76}$$

$$n_{\mathrm{r}} = \varepsilon_{\mathrm{r}}^{1/2} = (1.76)^{1/2} = \boxed{1.33}\ [21.19]$$

The neglect of the permanent dipole moment contribution means that the results are applicable only to the case for which the applied field has a much larger frequency than the rotational frequency. Since red light has a frequency of 4.3×10^{14} Hz and a typical rotational frequency is about 1×10^{12} Hz, the results apply in the visible.

Answers to theoretical problems

P21.15 The timescale of the oscillations is about $\dfrac{1}{0.55\,\mathrm{GHz}} = 2\times10^{-9}$ s for benzene and toluene, and 2.5×10^{-9} s for the additional oscillations in toluene. Toluene has a permanent dipole moment; benzene does not. Both have dipole moments induced by fluctuations in the solvent. Both have anisotropic polarizabilities (so that the refractive index is modulated by molecular reorientation). Both benzene and toluene have rotational constants of $\approx 0.2\,\mathrm{cm^{-1}}$, which correspond to the energies of microwaves in this frequency range. Pure rotational absorption can occur for toluene, but not for benzene.

P21.18 An 'exponential-6' Lennard–Jones potential has the form

$$V = 4\varepsilon\left[A\mathrm{e}^{-r/\sigma} - \left(\frac{\sigma}{r}\right)^6\right]$$

and is sketched in Fig. 21.4.

The minimum occurs where

$$\frac{\mathrm{d}V}{\mathrm{d}r} = 4\varepsilon\left(\frac{-A}{\sigma}\mathrm{e}^{-r/\sigma} + \frac{6\sigma^6}{r^7}\right) = 0$$

which occurs at the solution of

$$\frac{\sigma^7}{r^7} = \frac{A}{6}\mathrm{e}^{-r/\sigma}$$

Solve this equation numerically. As an example, when $A = \sigma = 1$, a minimum occurs at $r = \boxed{1.63}$.

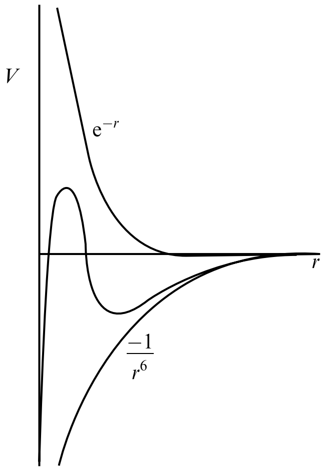


Figure 21.4

P21.19 The number of molecules in a volume element $d\tau$ is $\dfrac{\mathcal{N}\,d\tau}{V} = \mathcal{N}d\tau$. The energy of interaction of these molecules with one at a distance r is $\overline{V}\mathcal{N}\,d\tau$. The total interaction energy, taking into account the entire sample volume, is therefore

$$u = \int \overline{V}\mathcal{N}\,d\tau = \mathcal{N}\int \overline{V}\,d\tau \quad [\overline{V} \text{ is the interaction, not the volume}]$$

The total interaction energy of a sample of N molecules is $\frac{1}{2}Nu$ (the $\frac{1}{2}$ is included to avoid double counting), and so the cohesive energy density is

$$\mathcal{U} = -\frac{U}{V} = \frac{-\frac{1}{2}Nu}{V} = -\tfrac{1}{2}\mathcal{N}u = -\tfrac{1}{2}\mathcal{N}^2\int \overline{V}\,d\tau$$

For $\overline{V} = -\dfrac{C_6}{r^6}$ and $d\tau = 4\pi r^2\,dr$

$$-\frac{U}{V} = 2\pi\mathcal{N}^2 C_6\int_a^\infty \frac{dr}{r^4} = \frac{2\pi}{3} \times \frac{\mathcal{N}^2 C_6}{d^3}$$

However, $\mathcal{N} = \dfrac{N_A\rho}{M}$, where M is the molar mass; therefore

$$\mathcal{U} = \boxed{\left(\frac{2\pi}{3}\right) \times \left(\frac{N_A\rho}{M}\right)^2 \times \left(\frac{C_6}{d^3}\right)}$$

P21.21 Once again (as in Problem 21.20) we can write

$$\theta(v) = \begin{cases} \pi - 2\arcsin\left(\dfrac{b}{R_1 + R_2(v)}\right) & b \le R_1 + R_2(v) \\ 0 & b > R_1 + R_2(v) \end{cases}$$

but R_2 depends on v

$$R_2(v) = R_2 e^{-v/v^*}$$

Therefore, with $R_1 = \frac{1}{2}R_2$ and $b = \frac{1}{2}R_2$

(a) $$\theta(v) = \pi - 2\arcsin\left(\frac{1}{1+2\mathrm{e}^{-v/v^*}}\right)$$

(The restriction $b \le R_1 + R_2(v)$ transforms into $\frac{1}{2}R_2 \le \frac{1}{2}R_2 + R_2\mathrm{e}^{-v/v^*}$, which is valid for all v.) This function is plotted as curve a in Fig. 21.5.

The kinetic energy of approach is $E = \frac{1}{2}mv^2$, and so

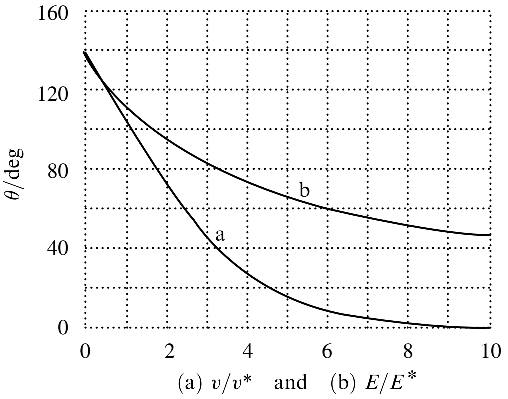


Figure 21.5

(b) $$\theta(E) = \pi - 2\arcsin\left(\frac{1}{1+2\,\mathrm{e}^{-(E/E^*)^{1/2}}}\right)$$

with $E^* = \frac{1}{2}mv^{*2}$. This function is plotted as curve b in Fig. 21.5.

22 Macromolecules and aggregates

Solutions to exercises

Discussion questions

E22.1(b) **(a)** ΔS is the change in conformational entropy of a random coil of a polymer chain. It is the statistical entropy arising from the arrangement of bonds, when a coil containing N bonds of length l is stretched or compressed by nl, where n is a numerical factor giving the amount of stretching in units of l. The amount of stretching relative to the number of monomer units in the chain is $\nu = n/N$.

(b) R_{rms} is one of several measures of the size of a random coil. For a polymer of N monomer units each of length l, the root mean square separation, R_{rms}, is a measure of the average separation of the ends of a random coil. It is the square root of the average value of R^2, calculated by weighting each possible value of R^2 with the probability that R occurs.

(c) R_{g}, the radius of gyration, is another measure of the size of a random coil. It is the radius of a thin hollow spherical shell of the same mass and moment of inertia as the polymer molecule.

All of these expressions are derived for the freely jointed random coil model of polymer chains which is the simplest possibility for the conformation of identical units not capable of forming hydrogen bonds or any other type of specific bond. In this model, any bond is free to make any angle with respect to the preceding one (Fig. 22.3 of the text). We assume that the residues occupy zero volume, so different parts of the chain can occupy the same region of space. We also assume in the derivation of the expression for the probability of the ends of the chain being a distance nl apart, that the chain is compact in the sense that $n \ll N$. This model is obviously an oversimplification because a bond is actually constrained to a cone of angles around a direction defined by its neighbour (Fig. 22.4). In a hypothetical one-dimensional freely jointed chain all the residues lie in a straight line, and the angle between neighbours is either 0° or 180°. The residues in a three-dimensional freely jointed chain are not restricted to lie in a line or a plane.

The random coil model ignores the role of the solvent: a poor solvent will tend to cause the coil to tighten; a good solvent does the opposite. Therefore, calculations based on this model are best regarded as lower bounds to the dimensions of a polymer in a good solvent and as an upper bound for a polymer in a poor solvent. The model is most reliable for a polymer in a bulk solid sample, where the coil is likely to have its natural dimensions.

E22.2(b) No solution.

E22.3(b) The formation of micelles is favored by the interaction between hydrocarbon tails and is opposed by charge repulsion of the polar groups which are placed close together at the micelle surface. As salt concentration is increased, the repulsion of head groups is reduced because their charges are partly shielded by the ions of the salt. This favors micelle formation causing the micelles to be larger and the critical micelle concentration to be smaller.

E22.4(b) A surfactant is a species that is active at the interface of two phases or substances, such as the interface between hydrophilic and hydrophobic phases. A surfactant accumulates at the interface and modifies the properties of the surface, in particular, decreasing its surface tension. A typical surfactant consists of a long hydrocarbon tail and other non-polar materials, and a hydrophilic head group, such as the carboxylate group, $-\text{CO}_2^-$, that dissolves in a polar solvent, typically water. In other words, a surfactant is an amphipathic substance, meaning that it has both hydrophobic and hydrophilic regions.

How does the surfactant decrease the surface tension? Surface tension is a result of cohesive forces and the solute molecules must weaken the attractive forces between solvent molecules. Thus molecules with bulky hydrophobic regions such as fatty acids can decrease the surface tension because they attract solvent molecules less strongly than solvent molecules attract each other. See Section 22.15(b) for an analysis of the thermodynamics involved in this process.

Numerical Exercises

E22.5(b) For a random coil, the r.m.s. separation is

$$R_{\mathrm{rms}} = l(N)^{1/2} = (1.125\,\mathrm{nm}) \times (1200)^{1/2} = \boxed{38.97\,\mathrm{nm}}$$

E22.6(b) Polypropylene is —(CH(CH$_3$)CH$_2$)—$_n$, where n is given by

$$n = \frac{M_{\mathrm{polymer}}}{M_{\mathrm{monomer}}} = \frac{174\,\mathrm{kg\,mol^{-1}}}{42.1 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}} = 4.13 \times 10^3$$

The repeat length is the length of two C—C bonds. The contour length is

$$R_{\mathrm{c}} = nl = (4.13 \times 10^3) \times (2 \times 1.53 \times 10^{-10}\,\mathrm{m}) = \boxed{1.26 \times 10^{-6}\,\mathrm{m}}$$

The r.m.s. separation is

$$R_{\mathrm{rms}} = ln^{1/2} = (2 \times 1.53 \times 10^{-10}\,\mathrm{m}) \times (4.13 \times 10^3)^{1/2} = \boxed{1.97 \times 10^{-8}\,\mathrm{m}} = 19.7\,\mathrm{nm}$$

E22.7(b) The number-average molar mass is

$$\overline{M}_{\mathrm{n}} = \frac{1}{N}\sum_i N_i M_i = \frac{[3 \times (62) + 2 \times (78)]\,\mathrm{kg\,mol^{-1}}}{5} = \boxed{68\,\mathrm{kg\,mol^{-1}}}$$

The mass-average molar mass is

$$\overline{M}_{\mathrm{w}} = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} = \frac{3 \times (62)^2 + 2 \times (78)^2}{3 \times (62) + 2 \times (78)}\,\mathrm{kg\,mol^{-1}} = \boxed{69\,\mathrm{kg\,mol^{-1}}}$$

E22.8(b) For a random coil, the radius of gyration is

$$R_{\mathrm{g}} = l(N/6)^{1/2} \quad \text{so} \quad N = 6(R_{\mathrm{g}}/l)^2 = 6 \times (18.9\,\mathrm{nm}/0.450\,\mathrm{nm})^2 = \boxed{1.06 \times 10^4}$$

E22.9(b) **(a)** Osmometry gives the number-average molar mass, so

$$\overline{M}_{\mathrm{n}} = \frac{N_1M_1 + N_2M_2}{N_1 + N_2} = \frac{\left(\frac{m_1}{M_1}\right)M_1 + \left(\frac{m_2}{M_2}\right)M_2}{\left(\frac{m_1}{M_1}\right) + \left(\frac{m_2}{M_2}\right)} = \frac{m_1 + m_2}{\left(\frac{m_1}{M_1}\right) + \left(\frac{m_2}{M_2}\right)}$$

$$= \frac{100\,\mathrm{g}}{\left(\frac{25\,\mathrm{g}}{22\,\mathrm{kg\,mol^{-1}}}\right) + \left(\frac{75\,\mathrm{g}}{7.3\overline{3}\,\mathrm{kg\,mol^{-1}}}\right)}[\text{assume 100 g of solution}] = \boxed{8.8\,\mathrm{kg\,mol^{-1}}}$$

(b) Light-scattering gives the mass-average molar mass, so

$$\overline{M}_{\mathrm{w}} = \frac{m_1M_1 + m_2M_2}{m_1 + m_2} = [(0.25) \times (22) + (0.75) \times (7.3\overline{3})]\,\mathrm{kg\,mol^{-1}} = \boxed{11\,\mathrm{kg\,mol^{-1}}}$$

E22.10(b) $\tau = \dfrac{4\pi a^3 \eta}{3kT}$ [see E22.10(a)]

$\eta(\mathrm{H_2O}, 20°\mathrm{C}) = 1.00 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}$ [Handbook of Chemistry and Physics, 81st Edition]

$$\tau = \frac{4\pi \times (4.5 \times 10^{-9}\,\mathrm{m})^3 \times 1.00 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}}{3 \times 1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}} \times 293\,\mathrm{K}} = \boxed{9.4 \times 10^{-8}\,\mathrm{s}}$$

E22.11(b) The rate of sedimentation is proportional to the sedimentation constant S

$$S = \frac{b\overline{M}_\mathrm{n}}{fN_\mathrm{A}}$$

The frictional coefficient f is proportional to the radius a of the sedimenting substance. The buoyancy b is the same for both of our substances because the density of the polymers, and therefore their specific volumes, are the same. The mass of a particle varies with its volume, and therefore with the cube of its radius. Thus

$$S \propto a^3/a = a^2 \quad \text{so} \quad \frac{\mathrm{rate}_1}{\mathrm{rate}_2} = \left(\frac{a_1}{a_2}\right)^2 = (8.4)^2 = \boxed{71}$$

with the larger particle sedimenting faster.

E22.12(b) The molar mass is related to the sedimentation constant

$$\overline{M}_\mathrm{n} = \frac{SRT}{bD} = \frac{SRT}{(1 - \rho_\mathrm{water} v_\mathrm{solute})D}$$

where we have assumed the data refer to aqueous solution at 298 K.

$$\overline{M}_\mathrm{n} = \frac{(7.46 \times 10^{-13}\,\mathrm{s}) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})}{[1 - (1000\,\mathrm{kg\,m^{-3}}) \times (8.01 \times 10^{-4}\,\mathrm{m^3\,kg^{-1}})] \times (7.72 \times 10^{-11}\,\mathrm{m^2\,s^{-1}})} = \boxed{120\,\mathrm{kg\,mol^{-1}}}$$

E22.13(b) The drift speed is the speed s at which the frictional force fs precisely balances the gravitational force $m_\mathrm{eff}g$

$$s = \frac{m_\mathrm{eff}g}{f} = \frac{(1 - \rho_\mathrm{solution}/\rho_\mathrm{solute})mg}{6\pi a \eta_\mathrm{solv}}$$

The mass of the particle is

$$\begin{aligned} m &= \rho_\mathrm{solute}V = 4\pi\rho_\mathrm{solute}a^3/3 = 4\pi \times (1250\,\mathrm{kg\,m^{-3}}) \times (15.5 \times (10^{-6}\,\mathrm{m})^3/3 \\ &= 1.95 \times 10^{-11}\,\mathrm{kg} \end{aligned}$$

$$\text{So } s = \frac{[1 - (1000\,\mathrm{kg\,m^{-3}})/(1250\,\mathrm{kg\,m^{-3}})] \times (1.95 \times 10^{-11}\,\mathrm{kg}) \times (9.81\,\mathrm{m\,s^{-2}})}{6\pi \times (15.5 \times 10^{-6}\,\mathrm{m}) \times (8.9 \times 10^{-4}\,\mathrm{kg\,m^{-1}\,s^{-1}})} = \boxed{1.47 \times 10^{-4}\,\mathrm{m\,s^{-1}}}$$

E22.14(b) The molar mass is related to the sedimentation constant

$$\overline{M}_{\mathrm{n}} = \frac{SRT}{bD} = \frac{SRT}{(1-\rho_{\text{solution}}v_{\text{solute}})D}$$

where we have assumed the data refer to aqueous solution at 298 K.

$$\overline{M}_{\mathrm{n}} = \frac{(5.1\times 10^{-13}\,\mathrm{s})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(293\,\mathrm{K})}{[1\,-\,(0.997\,\mathrm{g\,cm^{-3}})\times(0.721\,\mathrm{cm^3\,g^{-1}})]\times(7.9\times 10^{-11}\,\mathrm{m^2\,s^{-1}})} = \boxed{56\,\mathrm{kg\,mol^{-1}}}$$

E22.15(b) In a sedimentation experiment, the mass-average molar mass is given by

$$\overline{M}_{\mathrm{w}} = \frac{2RT}{(r_2^2-r_1^2)b\omega^2}\ln\frac{c_2}{c_1} \quad \text{so} \quad \ln\frac{c_2}{c_1} = \frac{\overline{M}_{\mathrm{w}}(r_2^2-r_1^2)b\omega^2}{2RT}$$

This implies that

$$\ln c = \frac{\overline{M}_{\mathrm{w}}r^2b\omega^2}{2RT} + \text{constant}$$

so the plot of $\ln c$ versus r^2 has a slope m equal to

$$m = \frac{\overline{M}_{\mathrm{w}}b\omega^2}{2RT} \quad \text{and} \quad \overline{M}_{\mathrm{w}} = \frac{2RTm}{b\omega^2}$$

$$\overline{M}_{\mathrm{w}} = \frac{2\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(293\,\mathrm{K})\times(821\,\mathrm{cm^{-2}})\times(100\,\mathrm{cm\,m^{-1}})^2}{[1-(1000\,\mathrm{kg\,m^{-3}})\times(7.2\times 10^{-4}\,\mathrm{m^3\,kg^{-1}})]\times[(1080\,\mathrm{s^{-1}})\times(2\pi)]^2}$$

$$= \boxed{3.1\times 10^3\,\mathrm{kg\,mol^{-1}}}$$

E22.16(b) The centrifugal acceleration is

$$a = r\omega^2 \quad \text{so} \quad a/g = r\omega^2/g$$

$$a/g = \frac{(5.5\,\mathrm{cm})\times[2\pi\times(1.32\times 10^3\,\mathrm{s^{-1}})]^2}{(100\,\mathrm{cm\,m^{-1}})\times(9.8\,\mathrm{m\,s^{-2}})} = \boxed{3.9\times 10^5}$$

Solutions to problems

Solutions to numerical problems

P22.1 For a rigid rod, $R_{\mathrm{g}} \propto l$ [Problem 22.15] $\propto M$, but for a random coil $R_{\mathrm{g}} \propto N^{1/2}$ [22.7] $\propto M^{1/2}$. Therefore, poly (γ-benzyl-L-glutamate) is rod-like whereas polystyrene is a random coil (in butanol).

P22.3

$$\ln\frac{c_1}{c_2} = \frac{mb\omega^2(r_1^2-r_2^2)}{2kT}\ [22.42] = \frac{2\pi^2\overline{M}_{\mathrm{w}}b\nu^2(r_1^2-r_2^2)}{RT} \quad [\omega = 2\pi\nu]$$

and hence

$$\nu = \left(\frac{RT\ln\left(\frac{c_1}{c_2}\right)}{2\pi^2\overline{M}_{\mathrm{w}}b(r_1^2-r_2^2)}\right)^{1/2}$$

$$= \left(\frac{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})\times(\ln 5)}{2\pi^2\times(1\times 10^2\,\mathrm{kg\,mol^{-1}})\times(1-0.75)\times(7.0^2-5.0^2)\times 10^{-4}\,\mathrm{m^2}}\right)^{1/2}$$

$$= 58\,\mathrm{Hz}, \quad \text{or} \quad \boxed{3500\,\text{r.p.m.}}$$

Question. What would the concentration gradient be in this system with a speed of operation of 70 000 r.p.m. in an ultracentrifuge?

P22.4 $b = 1 - \rho v_s = 1 - (0.765\,\text{g cm}^{-3}) \times (0.93\,\text{cm}^3\text{g}^{-1}) = 0.289;$

$T = 308.15\,\text{K}$

$D/(\text{cm}^2\,\text{s}^{-1}) = (1.3 \times 10^{-4}) \times (M_\text{w}/\text{g mol}^{-1})^{-0.497}$

$$\frac{bD}{SRT} = \frac{1}{M_\text{w}}(1 + 2B'c + 3gB'^2c^2 + \cdots)$$

or

$$\frac{b}{SRT} = \frac{1}{M_\text{w}D} + \frac{2B'}{M_\text{w}D}c + \frac{3gB'^2}{M_\text{w}D}c^2 + \cdots$$

$c/(\text{mg cm}^{-3})$	2.0	3.0	4.0	5.0	6.0	7.0
$S/(10^{-13}\,\text{s})$	14.8	13.9	13.1	12.4	11.8	11.2
$(b/SRT)/(\text{g}^{-1}\,\text{cm}^{-2}\,\text{s mol})$	7.62	8.11	8.61	9.10	9.56	10.07

The regression fit of the form

$$\frac{(b/SRT)}{(\text{g}^{-1}\text{cm}^{-2}\text{s mol})} = A + Bc + Cc^2 \quad \text{yields}$$

$A = 6.639$, standard deviation $= 0.040$

$B = 0.494\,\text{mg}^{-1}\,\text{cm}^3$, standard deviation $= 0.019\,\text{mg}^{-1}\,\text{cm}^3$

$C = -0.000\,697\,\text{mg}^{-2}\,\text{cm}^6$, standard deviation $= 0.002\,112\,\text{mg}^{-2}\text{cm}^6$

$R = 0.999\,940$ (Note that the standard deviation of C is greater than its value.)

$$\frac{1}{\overline{M}_\text{w}D} = A(\text{g}^{-1}\,\text{cm}^{-2}\,\text{s mol})$$

$$\frac{1}{\left(\frac{\overline{M}_\text{w}}{\text{g/mol}}\right) \times (1.3 \times 10^{-4}\,\text{cm}^2\,\text{s}^{-1}) \times \left(\frac{\overline{M}_\text{w}}{\text{g/mol}}\right)^{-0.497}} = 6.639\,\text{cm}^{-2}\,\text{s}$$

$$\frac{1}{\left(\frac{\overline{M}_\text{w}}{\text{g/mol}}\right)^{0.503}} = 8.631 \times 10^{-4}$$

$$\boxed{\overline{M}_\text{w} = 1.23 \times 10^6\,\text{g mol}^{-1}}$$

$$\frac{2B'}{\overline{M}_\text{w}D} = B(\text{g}^{-1}\,\text{cm}^{-2}\,\text{s mol})$$

$$B' = \frac{B(\text{g}^{-1}\,\text{cm}^{-2}\text{s mol})}{2(1/\overline{M}_\text{w}D)} = \frac{(0.494\,\text{mg}^{-1}\,\text{cm}^3) \times (\text{g}^{-1}\,\text{cm}^{-2}\,\text{s mol})}{2 \times (6.639\,\text{g}^{-1}\,\text{cm}^{-2}\,\text{s mol})}$$

$$\boxed{B' = 3.72 \times 10^{-2}\,\text{mg}^{-1}\,\text{cm}^3}$$

We might test the significance of the form of the third term in the expression, namely

$$C = \frac{3gB'^2}{\overline{M}_\text{w}D}$$

by using the value of C obtained by the fitting process to calculate the value of g. But we must note again that the standard deviation of C is greater than C itself; hence the value of g obtained by this calculation could not be considered significant. g is about 1/4 for a good solvent, but cyclohexane is a theta solvent for polystyrene. There is no reason for them to agree; they are different samples; there is no fixed value of M for polystyrene.

P22.11 $\dfrac{\Pi}{c} = \left(\dfrac{RT}{\overline{M}_\text{n}}\right) \times \left[1 + \left(\dfrac{B}{\overline{M}_\text{n}}\right)c\right]$ [Example 7.5]

$\Pi = \rho g h$; so

$$\frac{h}{c} = \frac{RT}{\rho g \overline{M}_\text{n}} + \frac{BRT}{\rho g \overline{M}_\text{n}^2} \cdot c$$

and we should plot $\dfrac{h}{c}$ against c. Draw up the following table

$c/(\text{g}/100\,\text{cm}^3)$	0.200	0.400	0.600	0.800	1.00
h/cm	0.48	1.12	1.86	2.76	3.88
$\dfrac{h}{c}\Big/(100\,\text{cm}^4\,\text{g}^{-1})$	2.4	2.80	3.10	3.45	3.88

The points are plotted in Fig. 22.1, and give a least-squares intercept at $2.04\overline{3}$ and a slope $1.80\overline{5}$

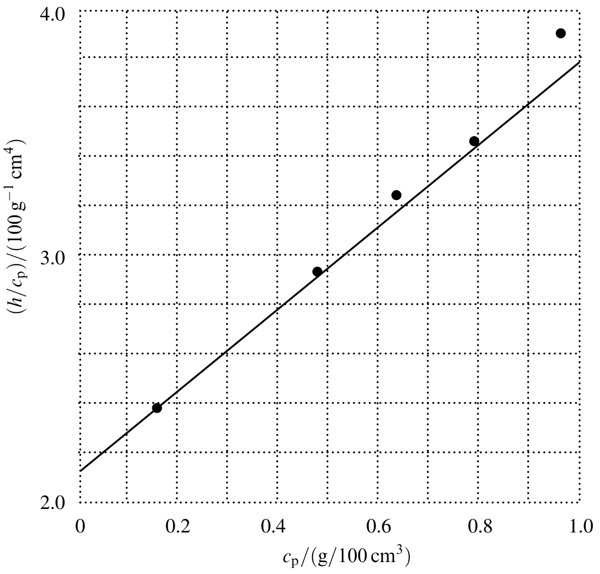


Figure 22.1

Therefore, $\dfrac{RT}{\rho g \overline{M}_\text{n}} = (2.04\overline{3}) \times (100\,\text{cm}^4\,\text{g}^{-1}) = 2.04\overline{3} \times 10^{-3}\,\text{m}^4\,\text{kg}^{-1}$

and hence

$$\overline{M}_\text{n} = \frac{(8.314\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})}{(0.798 \times 10^3\,\text{kg}\,\text{m}^{-3}) \times (9.81\,\text{m}\,\text{s}^{-2}) \times (2.04\overline{3} \times 10^{-3}\,\text{m}^4\,\text{kg}^{-1})} = \boxed{155\,\text{kg}\,\text{mol}^{-1}}$$

From the slope

$$\frac{BRT}{\rho g \overline{M}_\text{n}^2} = (1.80\overline{5}) \times \left(\frac{100\,\text{cm}^4\,\text{g}^{-1}}{\text{g}/(100\,\text{cm}^3)}\right) = 1.80\overline{5} \times 10^4\,\text{cm}^7\,\text{g}^{-2} = 1.80\overline{5} \times 10^{-4}\,\text{m}^7\,\text{kg}^{-2}$$

and hence

$$
\begin{aligned}
B &= \left(\frac{\rho g\overline{M}_{\mathrm{n}}}{RT}\right) \times \overline{M}_{\mathrm{n}} \times (1.80\bar{5} \times 10^{-4}\,\mathrm{m^7\,kg^{-2}}) \\
&= \frac{(155\,\mathrm{kg\,mol^{-1}}) \times (1.80\bar{5} \times 10^{-4}\,\mathrm{m^7\,kg^{-2}})}{2.04\bar{3} \times 10^{-3}\,\mathrm{m^4\,kg^{-1}}} \\
&= \boxed{13.7\,\mathrm{m^3\,mol^{-1}}}
\end{aligned}
$$

Solutions to theoretical problems

P22.12 $\mathrm{d}N \propto \mathrm{e}^{-(M-\overline{M})^2/2\gamma}\mathrm{d}M$

We write the constant of proportionality as K, and evaluate it by requiring that $\int \mathrm{d}N = N$. Put

$$
M - \overline{M} = (2\gamma)^{1/2}x, \quad \text{so} \quad \mathrm{d}M = (2\gamma)^{1/2}\mathrm{d}x
$$

$$
\begin{aligned}
\text{and } N &= K(2\gamma)^{1/2}\int_a^\infty \mathrm{e}^{-x^2}\,\mathrm{d}x \quad \left[a = \frac{-\overline{M}}{(2\gamma)^{1/2}}\right] \\
&\approx K(2\gamma)^{1/2}\int_0^\infty \mathrm{e}^{-x^2}\,\mathrm{d}x[a \approx 0] = K(2\gamma)^{1/2}\tfrac{1}{2}\pi^{1/2}
\end{aligned}
$$

Hence, $K = \left(\dfrac{2}{\pi\gamma}\right)^{1/2} N$. It then follows that

$$
\begin{aligned}
\overline{M}_{\mathrm{n}} &= \left(\frac{2}{\pi\gamma}\right)^{1/2}\int_0^\infty M\mathrm{e}^{-(M-\overline{M}^2)/2\gamma}\mathrm{d}M \\
&= \left(\frac{2}{\pi\gamma}\right)^{1/2}(2\gamma)\int_0^\infty \left(x\mathrm{e}^{-x^2} + \frac{\overline{M}}{(2\gamma)^{1/2}}\mathrm{e}^{-x^2}\right)\mathrm{d}x \\
&= \left(\frac{8\gamma}{\pi}\right)^{1/2} \times \left[\frac{1}{2} + \left(\frac{\pi}{8\gamma}\right)^{1/2}\overline{M}\right] = \boxed{\overline{M} + \left(\frac{2\gamma}{\pi}\right)^{1/2}}
\end{aligned}
$$

P22.14 A simple procedure is to generate numbers in the range 1 to 8, and to step north 1 or 2, east 3 or 4, south for 5 or 6, and west for 7 or 8 on a uniform grid. One such walk is shown in Fig. 22.2.

Roughly, they would appear to vary as $N^{1/2}$.

P22.15 We use the definition of the radius of gyration given in Footnote 4 and Problem 22.17, namely

$$
R_{\mathrm{g}}^2 = \frac{1}{N}\sum_j R_j^2
$$

(a) For a sphere of uniform density, the centre of mass is at the centre of the sphere. We may visualize the sphere as a collection of a very large number, N. of small particles distributed with equal

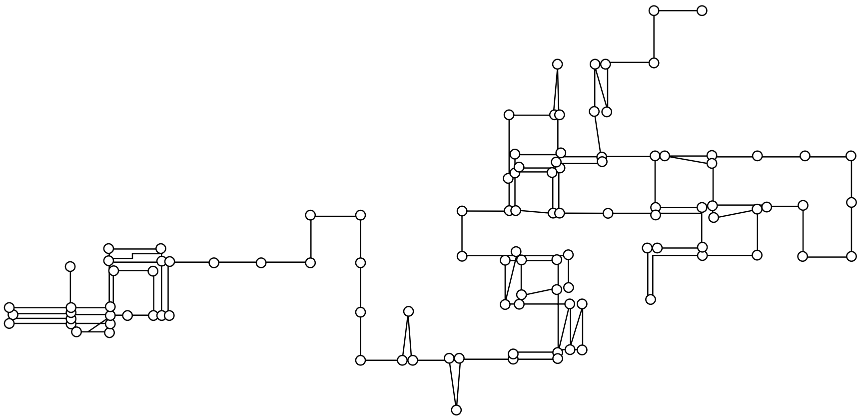


Figure 22.2

number density throughout the sphere. Then the summation above may be replaced with an integration.

$$R_g^2 = \frac{\frac{1}{N}\int_0^a Nr^2 P(r)\,dr}{\int_0^a P(r)\,dr}$$

$P(r)$ is the probability per unit distance that a small particle will be found at distance r from the centre, that is, within a spherical shell of volume $4\pi r^2\,dr$. Hence, $P(r) = 4\pi r^2\,dr$. The denominator ensures normalization. Hence

$$R_g^2 = \frac{\int_0^a r^2 P(r)\,dr}{\int_0^a P(r)\,dr} = \frac{\int_0^a 4\pi r^4 dr}{\int_0^a 4\pi r^2\,dr} = \frac{\frac{1}{5}a^5}{\frac{1}{3}a^3} = \frac{3}{5}a^2, \quad \boxed{R_g = \left(\frac{3}{5}\right)^{1/2} a}$$

(b) For a long straight rod of uniform density the centre of mass is at the centre of the rod and $P(r)$ is constant for a rod of uniform radius; hence,

$$R_g^2 = \frac{2\int_0^{(1/2)l} r^2 dr}{2\int_0^{(1/2)l} dr} = \frac{\frac{1}{3}\left(\frac{1}{2}l\right)^3}{\frac{1}{2}l} = \frac{1}{12}l^2, \quad \boxed{R_g = \frac{l}{2\sqrt{3}}}$$

For a spherical macromolecule

$$a = \left(\frac{3V_m}{4\pi N_A}\right)^{1/3} = \left(\frac{3v_s M}{4\pi N_A}\right)^{1/3}$$

and so

$$\begin{aligned} R_g &= \left(\frac{3}{5}\right)^{1/2} \times \left(\frac{3v_s M}{4\pi N_A}\right)^{1/3} \\ &= \left(\frac{3}{5}\right)^{1/2} \times \left(\frac{(3v_s/\text{cm}^3\,\text{g}^{-1}) \times \text{cm}^3\,\text{g}^{-1} \times (M/\text{g mol}^{-1}) \times \text{g mol}^{-1}}{(4\pi) \times (6.022 \times 10^{23}\,\text{mol}^{-1})}\right)^{1/3} \\ &= (5.690 \times 10^{-9}) \times (v_s/\text{cm}^3\,\text{g}^{-1})^{1/3} \times (M/\text{g mol}^{-1})^{1/3}\,\text{cm} \\ &= (5.690 \times 10^{-11}\text{m}) \times \{(v_s/\text{cm}^3\,\text{g}^{-1}) \times (M/\text{g mol}^{-1})\}^{1/3}\,\text{cm} \end{aligned}$$

That is, $R_g/\text{nm} = \boxed{0.05690 \times \{(v_s/\text{cm}^3\,\text{g}^{-1} \times (M/\text{g mol}^{-1})\}^{1/3}}$

When $M = 100\,\mathrm{kg\,mol^{-1}}$ and $v_\mathrm{s} = 0.750\,\mathrm{cm^3\,g^{-1}}$,

$$R_\mathrm{g}/\mathrm{nm} = (0.05690) \times \{0.750 \times 1.00 \times 10^5\}^{1/3} = \boxed{2.40}$$

For a rod, $v_\mathrm{mol} = \pi a^2 l$, so

$$\begin{aligned} R_\mathrm{g} &= \frac{v_\mathrm{mol}}{2\pi a^2\sqrt{3}} = \frac{v_\mathrm{s}M}{N_\mathrm{A}} \times \frac{1}{2\pi a^2\sqrt{3}} \\ &= \frac{(0.750\,\mathrm{cm^3\,g^{-1}}) \times (1.00 \times 10^5\,\mathrm{g\,mol^{-1}})}{(6.022 \times 10^{23}\,\mathrm{mol^{-1}}) \times (2\pi) \times (0.5 \times 10^{-7}\,\mathrm{cm})^2 \times \sqrt{3}} \\ &= 4.6 \times 10^{-6}\,\mathrm{cm} = \boxed{46\,\mathrm{nm}} \end{aligned}$$

Comment. R_g may also be defined through the relation

$$R_g^2 = \frac{\sum_i m_i r_i^2}{\sum_i m_i}$$

Question. Does this definition lead to the same formulas for the radii of gyration of the sphere and the rod as those derived above?

P22.17 Refer to Fig. 22.3.

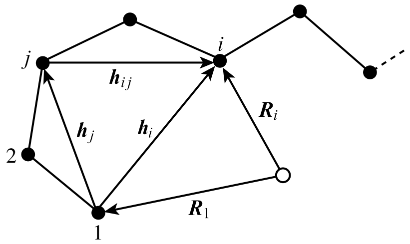


Figure 22.3

Since $\boldsymbol{R}_i = \boldsymbol{R}_1 + \boldsymbol{h}_i$ and $\sum_i \boldsymbol{R}_i = 0$,

$$N\boldsymbol{R}_1 + \sum_i \boldsymbol{h}_i = 0$$

and hence $\boldsymbol{R}_1 = -\dfrac{1}{N}\displaystyle\sum_i \boldsymbol{h}_i$

$$R_1^2 = \frac{1}{N^2}\sum_{ij} \boldsymbol{h}_i \cdot \boldsymbol{h}_j, \quad \boldsymbol{R}_1 \cdot \sum_i \boldsymbol{h}_i = -\frac{1}{N}\sum_{ij} \boldsymbol{h}_i \cdot \boldsymbol{h}_j$$

$$\begin{aligned} R_\mathrm{g}^2 &= \frac{1}{N}\sum_i R_i^2 \text{ [new defintion]} = \frac{1}{N}\sum_i \{(\boldsymbol{R}_1 + \boldsymbol{h}_i) \cdot (\boldsymbol{R}_1 + \boldsymbol{h}_i)\} \\ &= \frac{1}{N}\left(NR_1^2 + \sum_i h_i^2 + 2\boldsymbol{R}_1 \cdot \sum_i \boldsymbol{h}_i\right) = \frac{1}{N}\left(\sum_i h_i^2 - \frac{1}{N}\sum_{ij} \boldsymbol{h}_i \cdot \boldsymbol{h}_j\right) \end{aligned}$$

Since $\boldsymbol{h}_i \cdot \boldsymbol{h}_j = \frac{1}{2}(h_i^2 + h_j^2 - h_{ij}^2)$ [cosine rule]

$$R_g^2 = \frac{1}{N}\left(\sum_i h_i^2 + \frac{1}{2N}\sum_{ij} h_{ij}^2 - \frac{1}{2}\sum_i h_i^2 - \frac{1}{2}\sum_j h_j^2\right)$$

$$= \boxed{\frac{1}{2N^2}\sum_{ij} h_{ij}^2 \text{ [the original definition]}}$$

(In the last two terms, the summation over the second index contributes a factor N.)

P22.21 **(a)** We seek an expression for a ratio of scattering intensities of a macromolecule in two different conformations, a rigid rod or a closed circle. The dependence on scattering angle θ is contained in the Rayleigh ratio R_θ. The definition of this quantity, in eqn 22.25, may be inverted to give an expression for the scattering intensity at scattering angle θ:

$$I_\theta = R_\theta I_0 \frac{\sin^2\phi}{r^2},$$

where ϕ is an angle related to the polarization of the incident light and r the distance between sample and detector. Thus, for any given scattering angle, the ratio of scattered intensity of two conformations is the same as the ratio of their Rayleigh ratios:

$$\frac{I_\text{rod}}{I_\text{cc}} = \frac{P_\text{rod}}{R_\text{cc}} = \frac{P_\text{rod}}{P_\text{cc}}.$$

The last equality, stems from eqn 22.28, which related the Rayleigh ratios to a number of angle- independent factors that would be the same for both conformations and the structure factor (P_θ) that depends on both conformation and scattering angle. Finally, eqn 22.30 gives an approximate value of the structure factor as a function of the macromolecule's radius of gyration R_g, the wavelength of light, and the scattering angle:

$$P_\theta \approx 1 - \frac{16\pi^2 R_\text{g}^2 \sin^2(\frac{1}{2}\theta)}{3\lambda^2} = \frac{3\lambda^2 - 16\pi^2 R_\text{g}^2 \sin^2(\frac{1}{2}\theta)}{3\lambda^2}.$$

The radius of gyration of a rod of length l is

$$R_\text{rod} = l/[2(3)^{1/2}].$$

For a closed circle, the radius of gyration, which is the rms distance from the center of mass, is simply the radius of a circle whose circumference is l:

$$l = 2\pi R_\text{cc} \quad \text{so} \quad R_\text{cc} = \frac{1}{2\pi}.$$

The intensity ratio is:

$$\frac{I_\text{rod}}{I_\text{cc}} = \frac{3\lambda^2 - \frac{4}{3}\pi^2 l^2 \sin^2(\frac{1}{2}\theta)}{3\lambda^2 - 4l^2 \sin^2(\frac{1}{2}\theta)}.$$

Putting the numbers in yields:

$\theta/°$	20	45	90
I_rod/I_cc	0.976	0.876	0.514

(b) I would work at a detection angle at which the ratio is smallest, *i.e.*, most different from unity, provided I had sufficient intensity to make accurate measurements. Of the angles considered in part a, $\boxed{90^\circ}$ is the best choice. With the help of a spreadsheet or symbolic mathematical program, the ratio can be computed for a large range of scattering angles and plotted:

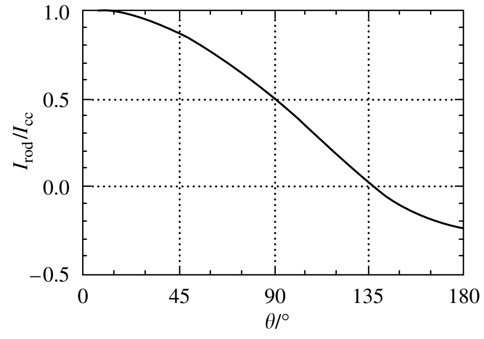


Figure 22.4

A look at the results of such a calculation shows that both the intensity ratio and the intensities themselves decrease with increasing scattering angle from 0° through 180°, that of the closed circle conformation changing much more slowly than that of the rod. Note: the approximation used above yields negative numbers for $P_{\rm rod}$ at large scattering angles; this is because the approximation, which depends on the molecule being much smaller than the wavelength, is shaky at best, particularly at large angles.

P22.22 $\ln c = \text{const.} + \dfrac{\overline{M}_{\rm w} b\omega^2 r^2}{2RT}$ [22.42, rearranged] and a plot of $\ln c$ against r^2 should be a straight line of slope $\dfrac{\overline{M}_{\rm w} b}{RT}$. We draw up the following table

r/cm	5.0	5.1	5.2	5.3	5.4
$c/(\text{mg cm}^{-3})$	0.536	0.284	0.148	0.077	0.039
$r^2/(\text{cm}^2)$	25.0	26.0	27.0	28.1	29.2
$\ln(c/\text{mg cm}^{-3})$	−0.624	−1.259	−1.911	−2.564	−3.244

The points are plotted in Fig. 22.5. The least-squares slope is −0.623. Therefore

$$\frac{\overline{M}_{\rm w}(1-\rho v_{\rm s})\omega^2}{2RT} = -0.623\,\text{cm}^{-2} = -0.623\times10^4\,\text{m}^{-2}$$

It follows that

$$\overline{M}_{\rm w} = \frac{(-0.623\times10^4\,\text{m}^{-2})\times(2)\times(8.314\,\text{J K}^{-1}\,\text{mol}^{-1})\times(293\,\text{K})}{\{(1)-(1.001\,\text{g cm}^{-3})\times(1.112\,\text{cm}^3\,\text{g}^{-1})\}\times[(2\pi)\times(322\,\text{s}^{-1})]^2} = \boxed{65.6\,\text{kg mol}^{-1}}$$

P22.24 The sedimentation constant S must first be calculated from the experimental data.

$$S = \frac{s}{r\omega^2}[11] = \frac{1}{\omega^2}\frac{\mathrm{d}\ln r}{\mathrm{d}t}\ \text{[Problem 22.2]}$$

Therefore, a plot of $\ln r$ against t will give S. We draw up the following table

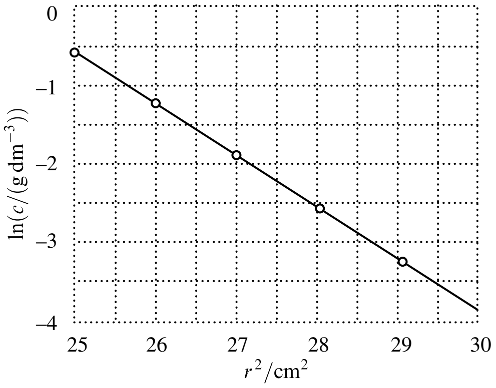


Figure 22.5

t/s	0	300	600	900	1200	1500	1800
r/cm	6.127	6.153	6.179	6.206	6.232	6.258	6.284
ln(r/cm)	1.813	1.817	1.821	1.826	1.830	1.834	1.838

The least-squares slope is $1.408 \times 10^{-5}\,\mathrm{s}^{-1}$, so

$$S = \frac{1.408 \times 10^{-5}\,\mathrm{s}^{-1}}{[(2\pi) \times (50 \times 10^3/60\,\mathrm{s})]^2} = 5.14 \times 10^{-13}\ \mathrm{s} = \boxed{5.14\,\mathrm{Sv}}$$

$$\text{Then } \overline{M}_\mathrm{n} = \frac{SRT}{bD}\,[22.41] = \frac{(5.14 \times 10^{-13}\,\mathrm{s}) \times (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (293\,\mathrm{K})}{(1 - 0.9981 \times 0.728) \times (7.62 \times 10^{-11}\mathrm{m^2\,s})^2} =$$

$$\boxed{60.1\,\mathrm{kg\,mol^{-1}}}$$

We need to determine the ratio of the actual frictional coefficient, f, of the macromolecule to that of the frictional coefficient, f_0, of a sphere of the same volume, so that by interpolating in Table 23.1 we can obtain the dimensions of the molecular ellipsoid.

$$f = \frac{kT}{D} = \frac{(1.381 \times 10^{-23}\mathrm{J\,K^{-1}}) \times (293\,\mathrm{K})}{7.62 \times 10^{-11}\,\mathrm{m^2\,s^{-1}}} = 5.31 \times 10^{-11}\,\mathrm{kg\,s^{-1}}$$

$$V_\mathrm{m} = (0.728\,\mathrm{cm^3\,g^{-1}}) \times (60.1 \times 10^3\mathrm{g\,mol^{-1}}) = 43.8 \times 10^3\,\mathrm{cm^3\,mol^{-1}}$$
$$= 4.38 \times 10^{-2}\,\mathrm{m^3\,mol^{-1}}$$

$$\text{Then, } a = \left(\frac{3\,V_\mathrm{m}}{4\pi N_\mathrm{A}}\right)^{1/3} = \left(\frac{(3) \times (4.38 \times 10^{-2}\,\mathrm{m^3\,mol^{-1}})}{(4\pi) \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}})}\right)^{1/3} = 2.59\,\mathrm{nm}$$

$$f_0 = 6\pi a\eta = (6\pi) \times (2.59 \times 10^{-9}\,\mathrm{m}) \times (1.00 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}) = 4.89 \times 10^{-11}\,\mathrm{kg\,s^{-1}}$$

which gives $\dfrac{f}{f_0} = \dfrac{5.31}{4.89} = 1.09$

Therefore, the molecule is either prolate or oblate, with an axial ratio of about 2.8 (Table 22.3).

P22.25 The peaks are separated by $104\,\mathrm{g\,mol^{-1}}$, so this is the molar mass of the repeating unit of the polymer. This peak separation is consistent with the identification of the polymer as polystyrene, for the repeating group of $CH_2CH(C_6H_5)$ (8 C atoms and 8 H atoms) has a molar mass of $8 \times (12 + 1)\,\mathrm{g\,mol^{-1}} = 104\,\mathrm{g\,mol^{-1}}$. A consistent difference between peaks suggests a pure system and against different numbers of subunits (of different molecular weight) being incorporated into the polymer molecules. The most intense peak has a molar mass equal to that of n repeating groups plus that of a silver cation plus that of terminal groups:

$$M(\text{peak}) = nM(\text{repeat}) + M(\text{Ag}^+) + M(\text{terminal}).$$

If the both ends of the polymer have terminal t-butyl groups, then

$$M(\text{terminal}) = 2M(t\text{-butyl}) = 2(4 \times 12 + 9)\,\text{g mol}^{-1} = 114\,\text{g mol}^{-1},$$

and $n = \dfrac{M(\text{peak}) - M(\text{Ag}^+) - M(\text{terminal})}{M(\text{repeat})} = \dfrac{25578 - 108 - 114}{104} = 243.8.$

Obviously this is not an integer. Revisit the assumption of two t-butyl groups on the ends:

$$M(\text{terminal}) = M(\text{peak}) - nM(\text{repeat}) - M(\text{Ag}^+).$$

If $n = 243$, then

$$M(\text{terminal}) = (25578 - 243 \times 104 - 108)\,\text{g mol}^{-1} = 198\,\text{g mol}^{-1},$$

which does not correspond to a whole number of t-butyl groups! Try again, supposing this time that there is a single t-butyl group at one end and a hydrogen atom at the other. Then:

$$n = \frac{M(\text{peak}) - M(\text{Ag}^+) - M(\text{terminal})}{M(\text{repeat})} = \frac{25578 - 108 - 58}{104} = 244.3.$$

This is not an integer either. If $n = 244$, then

$$M(\text{terminal}) = (25578 - 244 \times 104 - 108)\,\text{g mol}^{-1} = 94\,\text{g mol}^{-1},$$

not a whole number of butyl or butane groups.

P22.26 **(a)** $\dfrac{\eta}{\eta^*} = 1 + [\eta]c + k'[\eta]^2c^2 = \dfrac{t}{t^*}$

or $F = \dfrac{t/t^* - 1}{c} = [\eta] + k'[\eta]^2 c$

A linear regression of F against c yields an intercept equal to $[\eta]$ and a slope equal to $k'[\eta]^2$.

(1) *In toluene*: Linear regression ($R = 0.999\,54$) yields

$$[\eta] = 0.085\overline{66}\,\text{L g}^{-1} = \boxed{0.086\,\text{L g}^{-1}}; \quad \text{standard deviation} = 0.000\,20\,\text{L g}^{-1}$$

$$k'[\eta]^2 = 0.002\,6\overline{88}\,\text{L}^2\text{g}^{-2}; \quad \text{standard deviation} = 0.000\,057\,\text{L}^2\text{g}^{-2}$$

Then

$$k' = \frac{0.002\,6\overline{88}\,\text{L}^2\text{g}^{-2}}{(0.085\,\overline{66}\,\text{L g}^{-1})^2} = \boxed{0.37}$$

(2) *In cyclohexane*: Linear regression ($R = 0.981\,98$) yields

$$[\eta] = 0.041\overline{50}\,\text{L g}^{-1} = \boxed{0.042\,\text{L g}^{-1}}; \quad \text{standard deviation} = 0.000\,18\,\text{L g}^{-1}$$

$$k'[\eta]^2 = 0.000\,6\overline{00\,1}\,\text{L}^2\text{g}^{-2}; \quad \text{standard deviation} = 0.000\,116\,\text{L}^2\text{g}^{-2}$$

Then

$$k' = \frac{0.000\;60\overline{01}\,\mathrm{L}^2\,\mathrm{g}^{-2}}{(0.041\;\overline{50}\,\mathrm{L\,g^{-1}})^2} = \boxed{0.35}$$

(b) $[\eta] = K\overline{M}_\mathrm{v}^a \quad \text{or} \quad \overline{M}_\mathrm{v} = \left(\dfrac{[\eta]}{K}\right)^{1/a}$

(1) *In toluene*

$$\overline{M}_\mathrm{v} = \left(\frac{0.085\;\overline{66}\,\mathrm{L\,g^{-1}}}{1.15\times10^{-5}\,\mathrm{L\,g^{-1}}}\right)^{(1/0.72)}\,\mathrm{g\,mol^{-1}} = \boxed{2.4\times10^{5}\,\mathrm{g\,mol^{-1}}}$$

(2) *In cyclohexane*

$$\overline{M}_\mathrm{v} = \left(\frac{0.041\;\overline{50}\,\mathrm{L\,g^{-1}}}{8.2\times10^{-5}\,\mathrm{L\,g^{-1}}}\right)^{\left(\frac{1}{1/2}\right)}\,\mathrm{g\,mol^{-1}} = \boxed{2.6\times10^{5}\,\mathrm{g\,mol^{-1}}}$$

(c) $[\eta]/(\mathrm{L\,g^{-1}}) = \Phi(r_\mathrm{rms}/\mathrm{m})^3/M, \quad \Phi = 2.84\times10^{26}$

$$r_\mathrm{rms} = \left(\frac{[\eta]M}{\Phi}\right)^{1/3}\,\mathrm{m}, \quad \text{where } r_\mathrm{rms} = \langle r^2\rangle^{1/2}$$

(1) *In toluene*: $r_\mathrm{rms} = \left(\dfrac{0.085\overline{66}\times2.3\overline{9}\times10^5}{2.84\times10^{26}}\right)^{1/3}\,\mathrm{m} = \boxed{42\,\mathrm{nm}}$

(2) *In cyclohexane*: $r_\mathrm{rms} = \left(\dfrac{0.041\overline{50}\times2.5\overline{6}\times10^5}{2.84\times10^{26}}\right)^{1/3}\,\mathrm{m} = \boxed{33\,\mathrm{nm}}$

(d) $M(\text{styrene}) = 104\,\mathrm{g\,mol^{-1}}$
average number of monomeric units, $\langle n\rangle$ is

$$\langle n\rangle = \frac{\overline{M}_\mathrm{v}}{M(\text{styrene})}$$

(1) *In toluene*

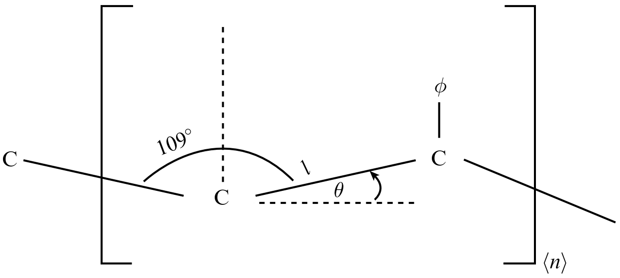
$$\langle n\rangle = \frac{2.3\overline{9}\times10^5\,\mathrm{g\,mol^{-1}}}{104\,\mathrm{g\,mol^{-1}}} = \boxed{2.3\times10^3}$$

(2) *In cyclohexane*

$$\langle n\rangle = \frac{2.5\overline{6}\times10^5\,\mathrm{g\,mol^{-1}}}{104\,\mathrm{g\,mol^{-1}}} = \boxed{2.5\times10^3}$$

(e) Consider the geometry in Fig. 22.6.
For a polymer molecule consisting of $\langle n\rangle$ monomers, the maximum molecular length, L_max, is

$$\begin{aligned} L_\mathrm{max} &= 2l\langle n\rangle\cos\theta \\ &= 2(0.154\,\mathrm{nm})\langle n\rangle\cos35^\circ \\ &= (0.2507\,\mathrm{nm})\langle n\rangle \end{aligned}$$



$$\theta = 90^\circ - \frac{109^\circ}{2} \approx 35^\circ$$

Figure 22.6

(1) *In toluene*: $L_{\text{max}} = (0.2507\,\text{nm}) \times (2.3\bar{0} \times 10^3) = \boxed{5.8 \times 10^2\,\text{nm}}$

(2) *In cyclohexane*: $L_{\text{max}} = (0.2507\,\text{nm}) \times (2.4\bar{6} \times 10^3) = \boxed{6.2 \times 10^2\,\text{nm}}$

(f) $$R_{\text{g}} = \left(\frac{\langle n\rangle}{3}\right)^{1/2} l = (0.0889\,\text{nm})\langle n\rangle^{1/2}$$

$$\text{Kirkwood–Riseman} : r_{\text{rms}}^{\text{KR}} = \left(\frac{[\eta]M}{\Phi}\right)^{1/3} = \left(\frac{[\eta]M}{2.84 \times 10^{26}}\right)^{1/3}$$

$$r_{\text{rms}} = (2\langle n\rangle)^{1/2} l[39] \quad \text{or} \quad \langle n\rangle^{1/2} l$$

Solvent	$\langle n\rangle$	R_{g}/ nm	$r_{\text{rms}}^{\text{KR}}$/nm	r_{rms}/nm
Toluene	$2.3\bar{0} \times 10^3$	$\boxed{4.3}$	42	$\boxed{10.\bar{4} \text{ or } 7.4}$
Cyclohexane	$2.4\bar{6} \times 10^3$	$\boxed{4.4}$	33	$\boxed{10.\bar{8} \text{ or } 7.6}$

(g) There is no reason for them to agree; they are different samples; there is no fixed value of M for polystyrene. The manufacturer's claim appears to be valid.

23 The solid state

Solutions to exercises

Discussion questions

E23.1(b) We can use the Debye–Scherrer powder diffraction method, follow the procedure of Example 23.3, and in particular look for systematic absences in the diffraction patterns. We can proceed through the following sequence

1. Measure distances of the lines in the diffraction pattern from the centre.
2. From the known radius of the camera, convert the distances to angles.
3. Calculate $\sin^2\theta$.
4. Find the common factor $A = \lambda^2/4\mathrm{a}^2$ in $\sin^2\theta = (\lambda^2/4a^2)(h^2+k^2+l^2)$.
5. Index the lines using $\sin^2\theta/A = h^2+k^2+l^2$.
6. Look for the systematic absences in (hkl). See Fig. 23.22 of the text. For body-centred cubic, diffraction lines corresponding to $h+k+l$ that are odd will be absent. For face-centred cubic, only lines for which h, k, and l are either all even or all odd will be present, other will be absent.
7. Solve $A = \lambda^2/4a^2$ for a.

E23.2(b) The phase problem arises with the analysis of data in X-ray diffraction when seeking to perform a Fourier synthesis of the electron density. In order to carry out the sum it is necessary to know the signs of the structure factors; however, because diffraction intensities are proportional to the square of the structure factors, the intensities do not provide information on the sign. For non-centrosymmetric crystals, the structure factors may be complex, and the phase α in the expression $F_{hkl} = |F_{hkl}|\mathrm{e}^{\mathrm{i}\alpha}$ is indeterminate. The phase problem may be evaded by the use of a Patterson synthesis or tackled directly by using the so-called direct methods of phase allocation.

The Patterson synthesis is a technique of data analysis in X-ray diffraction which helps to circumvent the phase problem. In it, a function P is formed by calculating the Fourier transform of the squares of the structure factors (which are proportional to the intensities):

$$P(r) = \frac{1}{V}\sum_{hkl}|F_{hkl}|^2\,\mathrm{e}^{-2\pi\mathrm{i}(hx+ky+lz)}$$

The outcome is a map of the *separations* of the atoms in the unit cell of the crystal. If some atoms are heavy (perhaps because they have been introduced by isomorphous replacement), they dominate the Patterson function, and their locations can be deduced quite simply. Their locations can then be used in the determination of the locations of lighter atoms.

E23.3(b) In a face-centred cubic close-packed lattice, there is an octahedral hole in the centre. The rock-salt structure can be thought of as being derived from an fcc structure of $\mathrm{Cl^-}$ ions in which $\mathrm{Na^+}$ ions have filled the octahedral holes.

The caesium-chloride structure can be considered to be derived from the ccp structure by having $\mathrm{Cl^-}$ ions occupy all the primitive lattice points and octahedral sites, with all tetrahedral sites occupied by $\mathrm{Cs^+}$ ions. This is exceedingly difficult to visualize and describe without carefully constructed figures or models. Refer to S.-M. Ho and B. E. Douglas, *J. Chem. Educ.* **46**, 208, 1969, for the appropriate diagrams.

E23.4(b) A metallic conductor is a substance with a conductivity that decreases as the temperature is raised. A semiconductor is a substance with a conductivity that increases as the temperature is raised. A semiconductor generally has a lower conductivity than that typical of metals, but the magnitude of the conductivity is not the criterion of the distinction. It is conventional to classify semiconductors with very low electrical conductivities, such as most synthetic polymers, as insulators. We shall use this term. But it should be appreciated that it is one of convenience rather than one of fundamental significance.

The conductivity of these three kinds of materials is explained by band theory. When each of N atoms of a metallic element contributes one atomic orbital to the formation of molecular orbitals, the resulting N molecular orbitals form an almost continuous band of levels. The orbital at the bottom of the band is fully bonding between all neighbours, and the orbital at the top of the band is fully antibonding between all immediate neighbours. If the atomic orbitals are s-orbitals, then the resulting band is called an s-band; if the original orbitals are p-orbitals, then they form a p-band. In a typical case, there is so large an energy difference between the s and p atomic orbitals that the resulting s- and p-bands are separated by a region of energy in which there are no orbitals. This region is called the band gap, and its whidth is denoted E_g.

When electrons occupy the orbitals in the bands, they do so in accord with the Pauli principle. If insufficient electrons are present to fill the band, the electrons close to the top of the band are mobile and the solid is a metallic conductor. An unfilled band is called a conduction band and the energy of the highest occupied orbital at $T = 0$ K is called the Fermi level. Only the electrons close to the Fermi level can contribute to conduction and to the heat capacity of a metal. If the band is full, then the electrons cannot transport a current readily, and the solid is an insulator; more formally, it is a species of semiconductor with a large band gap. A full band is called a valence band. The detailed population of the levels in a band taking into account the role of temperature is expressed by the Fermi–Dirac distribution.

The distinction between metallic conductors and semiconductors can be traced to their band structure: a metallic conductor has an incomplete band, its conductance band, and a semiconductor has full bands, and hence lacks a conductance band. The decreasing conductance of a metallic conductor with temperature stems from the scattering of electrons by the vibrating atoms of the metal lattice. The increasing conductance of a semiconductor arises from the increasing population of an upper empty band as the temperature is increased. Many substances, however, have such large band gaps that their ability to conduct an electric current remains very low at all temperatures: it is conventional to refer to such solids as insulators. The ability of a semiconductor to transport charge is enhanced by doping it, or adding substances in controlled quantities. If the dopant provides additional electrons, then the semiconductor is classified as n-type. If it removes electrons from the valence band and thereby increases the number of positive holes, it is classified as p-type.

E23.5(b) The Fermi–Dirac distribution is a version of the Boltzmann distribution that takes into account the effect of the Pauli exclusion principle. It can therefore be used to calculate the population, P, of a state of given energy in a many-electron system at a temperature T:

$$P = \frac{1}{e^{(E-\mu)/kT} + 1}$$

In this expression, μ is the Fermi energy, or chemical potential, the energy of the level for which $P = 1/2$. The Fermi energy should be distinguished from the Fermi level, which is the energy of the highest occupied state at $T = 0$. See Fig. 23.53 of the text.

From thermodynamics (Chapter 5) we know that $\mathrm{d}U = -p\,\mathrm{d}V + T\,\mathrm{d}S + \mu\,\mathrm{d}n$ for a one-component system. This may also be written $\mathrm{d}U = -p\,\mathrm{d}V + T\,\mathrm{d}S + \mu\,\mathrm{d}N$, and this μ is the chemical potential per particle that appears in the F–D distribution law. The term in $\mathrm{d}U$ containing μ is the chemical work and gives the change in internal energy with change in the number of particles. Thus, μ has a wider significance than its interpretation as a partial molar Gibbs energy and it is not surprising that it occurs in the F–D expression in comparision to the energy of the particle. The Helmholtz energy, A, and μ are related through $\mathrm{d}A = -p\,\mathrm{d}V - S\,\mathrm{d}T + \mu\,\mathrm{d}N$, and so μ also gives the change in the Helmholtz energy with change in number of particles. To fully understand how the chemical potential μ enters into the F–D expression for P, we must examine its derivation (see *Further reading*) which makes use of the relation between μ and A and of that between A and the partition function for F–D particles.

Numerical exercises

E23.6(b) $\left(\frac{1}{2},\ 0,\ \frac{1}{2}\right)$ is the midpoint of a face. All face midpoints are alike, including $\boxed{\left(\frac{1}{2},\ \frac{1}{2},\ 0\right) \text{ and } \left(0,\ \frac{1}{2},\ \frac{1}{2}\right)}$. There are six faces to each cube, but each face is shared by two cubes. So other face midpoints can be described by one of these three sets of coordinates on an adjacent unit cell.

E23.7(b) Taking reciprocals of the coordinates yields $\left(1, \frac{1}{3}, -1\right)$ and $\left(\frac{1}{2},\ \frac{1}{3},\ \frac{1}{4}\right)$ respectively. Clearing the fractions yields the Miller indices $\boxed{(31\bar{3}) \text{ and } (643)}$

E23.8(b) The distance between planes in a cubic lattice is

$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$$

This is the distance between the origin and the plane which intersects coordinate axes at $(h/a, k/a, l/a)$.

$$d_{121} = \frac{523\,\text{pm}}{(1 + 2^2 + 1)^{1/2}} = \boxed{214\,\text{pm}}$$

$$d_{221} = \frac{523\,\text{pm}}{(2^2 + 2^2 + 1)^{1/2}} = \boxed{174\,\text{pm}}$$

$$d_{244} = \frac{523\,\text{pm}}{(2^2 + 4^2 + 4^2)^{1/2}} = \boxed{87.2\,\text{pm}}$$

E23.9(b) The Bragg law is

$$n\lambda = 2d \sin\theta$$

Assuming the angle given is for a first-order reflection, the wavelength must be

$$\lambda = 2(128.2\,\text{pm}) \sin 19.76^\circ = \boxed{86.7\,\text{pm}}$$

E23.10(b) Combining the Bragg law with Miller indices yields, for a cubic cell

$$\sin\theta_{hkl} = \frac{\lambda}{2a}(h^2 + k^2 + l^2)^{1/2}$$

In a face-centred cubic lattice, h, k, and l must be all odd or all even. So the first three reflections would be from the (1 1 1), (2 0 0), and (2 2 0) planes. In an fcc cell, the face diagonal of the cube is

$4R$, where R is the atomic radius. The relationship of the side of the unit cell to R is therefore

$$(4R)^2 = a^2 + a^2 = 2a^2 \quad \text{so} \quad a = \frac{4R}{\sqrt{2}}$$

Now we evaluate

$$\frac{\lambda}{2a} = \frac{\lambda}{4\sqrt{2}R} = \frac{154\,\text{pm}}{4\sqrt{2}(144\,\text{pm})} = 0.189$$

We set up the following table

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

E23.11(b) In a circular camera, the distance between adjacent lines is $D = R\Delta(2\theta)$, where R is the radius of the camera (distance from sample to film) and θ is the diffraction angle. Combining these quantities with the Bragg law ($\lambda = 2d\sin\theta$, relating the glancing angle to the wavelength and separation of planes), we get

$$\begin{aligned} D &= 2R\Delta\theta = 2R\Delta\left(\sin^{-1}\frac{\lambda}{2d}\right) \\ &= 2(5.74\,\text{cm}) \times \left(\sin^{-1}\frac{96.035}{2(82.3\,\text{pm})} - \sin^{-1}\frac{95.401\,\text{pm}}{2(82.3\,\text{pm})}\right) = \boxed{0.054\,\text{cm}} \end{aligned}$$

E23.12(b) The volume of a hexagonal unit cell is the area of the base times the height c. The base is equivalent to two equilateral triangles of side a. The altitude of such a triangle is $a\sin 60^\circ$. So the volume is

$$\begin{aligned} V &= 2\left(\tfrac{1}{2}a \times a\sin 60^\circ\right)c = a^2c\sin 60^\circ = (1692.9\,\text{pm})^2 \times (506.96\,\text{pm}) \times \sin 60^\circ \\ &= 1.2582 \times 10^9\,\text{pm}^3 = \boxed{1.2582\,\text{nm}^3} \end{aligned}$$

E23.13(b) The volume of an orthorhombic unit cell is

$$V = abc = (589\,\text{pm}) \times (822\,\text{pm}) \times (798\,\text{pm}) = \frac{3.86 \times 10^8\,\text{pm}^3}{(10^{10}\,\text{pm}\,\text{cm}^{-1})^3} = 3.86 \times 10^{-22}\,\text{cm}^3$$

The mass per formula unit is

$$m = \frac{135.01\,\text{g}\,\text{mol}^{-1}}{6.022 \times 10^{23}\,\text{mol}^{-1}} = 2.24 \times 10^{-22}\,\text{g}$$

The density is related to the mass m per formula unit, the volume V of the unit cell, and the number N of formula units per unit cell as follows

$$d = \frac{Nm}{V} \quad \text{so} \quad N = \frac{dV}{m} = \frac{(2.9\,\text{g}\,\text{cm}^{-3}) \times (3.86 \times 10^{-22}\,\text{cm}^3)}{2.24 \times 10^{-22}\,\text{g}} = \boxed{5}$$

A more accurate density, then, is

$$d = \frac{5(2.24 \times 10^{-22}\,\text{g})}{3.86 \times 10^{-22}\,\text{cm}^3} = \boxed{2.90\,\text{g}\,\text{cm}^{-3}}$$

E23.14(b) The distance between the origin and the plane which intersects coordinate axes at $(h/a, k/b, l/c)$ is given by

$$
\begin{aligned}
d_{hkl} &= \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)^{-1/2} = \left(\frac{3^2}{(679\,\text{pm})^2} + \frac{2^2}{(879\,\text{pm})^2} + \frac{2^2}{(860\,\text{pm})^2}\right)^{-1/2} \\
d_{322} &= \boxed{182\,\text{pm}}
\end{aligned}
$$

E23.15(b) The fact that the 111 reflection is the third one implies that the cubic lattice is simple, where all indices give reflections. The 111 reflection would be the first reflection in a face-centred cubic cell and would be absent from a body-centred cubic

The Bragg law

$$\sin\theta_{hkl} = \frac{\lambda}{2a}(h^2 + k^2 + l^2)^{1/2}$$

can be used to compute the cell length

$$a = \frac{\lambda}{2\sin\theta_{hkl}}(h^2 + k^2 + l^2)^{1/2} = \frac{137\,\text{pm}}{2\sin 17.7^\circ}(1^2 + 1^2 + 1^2)^{1/2} = 390\,\text{pm}$$

With the cell length, we can predict the glancing angles for the other reflections expected from a simple cubic

$$
\begin{aligned}
\theta_{hkl} &= \sin^{-1}\left(\frac{\lambda}{2a}(h^2 + k^2 + l^2)^{1/2}\right) = \sin^{-1}(0.176(h^2 + k^2 + l^2)^{1/2}) \\
\theta_{100} &= \sin^{-1}(0.176(1^2 + 0 + 0)^{1/2}) = 10.1^\circ \text{ (checks)} \\
\theta_{110} &= \sin^{-1}(0.176(1^2 + 1^2 + 0)^{1/2}) = 14.4^\circ \text{ (checks)} \\
\theta_{200} &= \sin^{-1}(0.176(2^2 + 0 + 0)^{1/2}) = 20.6^\circ \text{ (checks)}
\end{aligned}
$$

These angles predicted for a simple cubic fit those observed, confirming the hypothesis of a simple lattice; the reflections are due to the $\boxed{(1\,0\,0),\ (1\,1\,0),\ (1\,1\,1), \text{ and } (2\,0\,0)}$ planes.

E23.16(b) The Bragg law relates the glancing angle to the separation of planes and the wavelength of radiation

$$\lambda = 2d\sin\theta \quad \text{so} \quad \theta = \sin^{-1}\frac{\lambda}{2d}$$

The distance between the orgin and plane which intersects coordinate axes at $(h/a, k/b, l/c)$ is given by

$$d_{hkl} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)^{-1/2}$$

So we can draw up the following table

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

E23.17(b) All of the reflections present have $h + k + l$ even, and all of the even $h + k + l$ are present. The unit cell, then, is $\boxed{\text{body-centred cubic}}$.

E23.18(b) The structure factor is given by

$$F_{hkl} = \sum_i f_i \mathrm{e}^{\mathrm{i}\phi_i} \quad \text{where} \quad \phi_i = 2\pi(hx_i + ky_i + lz_i)$$

All eight of the vertices of the cube are shared by eight cubes, so each vertex has a scattering factor of $f/8$.

The coordinates of all vertices are integers, so the phase ϕ is a multiple of 2π and $\mathrm{e}^{\mathrm{i}\phi} = 1$. The body-centre point belongs exclusively to one unit cell, so its scattering factor is f. The phase is

$$\phi = 2\pi\left(\tfrac{1}{2}h + \tfrac{1}{2}k + \tfrac{1}{2}l\right) = \pi(h + k + l)$$

When $h+k+l$ is even, ϕ is a multiple of 2π and $\mathrm{e}^{\mathrm{i}\phi} = 1$; when $h+k+l$ is odd, ϕ is $\pi + a$ multiple of 2π and $\mathrm{e}^{\mathrm{i}\phi} = -1$. So $\mathrm{e}^{\mathrm{i}\phi} = (-1)^{h+k+l}$ and

$$\begin{aligned} F_{hkl} &= 8(f/8)(1) + f(-1)^{h+k+l} \\ &= \boxed{2f \text{ for } h+k+l \text{ even} \quad \text{and} \quad 0 \text{ for } h+k+l \text{ odd}} \end{aligned}$$

E23.19(b) There are two smaller (white) triangles to each larger (grey) triangle. Let the area of the larger triangle be A and the area of the smaller triangle be a. Since $b = \frac{1}{2}B$(base) and $h = \frac{1}{2}H$(height), $a = \frac{1}{4}A$. The white space is then $2NA/4$, for N of the larger triangles. The total space is then $\left(NA + \frac{NA}{2}\right) = 3NA/2$. Therefore the fraction filled is $NA/(3NA/2) = \boxed{\frac{2}{3}}$

E23.20(b) See Fig. 23.1.

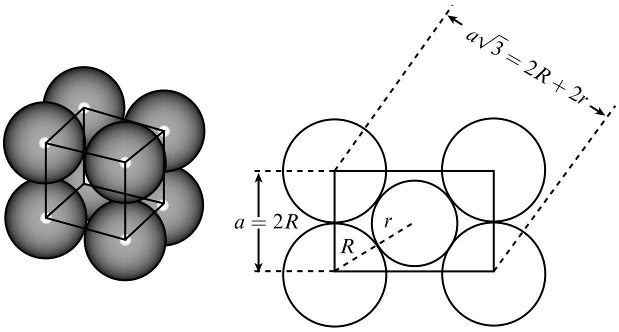


Figure 23.1

The body diagonal of a cube is $a\sqrt{3}$. Hence

$$\begin{aligned} a\sqrt{3} &= 2R + 2r \quad \text{or} \quad \sqrt{3}R = R + r \quad [a = 2R] \\ \frac{r}{R} &= \boxed{0.732} \end{aligned}$$

E23.21(b) The ionic radius of K^+ is 138 pm when it is 6-fold coordinated, 151 pm when it is 8-fold coordinated.

(a) The smallest ion that can have 6-fold coordination with it has a radius of $\left(\sqrt{2}-1\right) \times (138\,\text{pm}) = \boxed{57\,\text{pm}}$.

(b) The smallest ion that can have 8-fold coordination with it has a radius of $\left(\sqrt{3}-1\right) \times (151\,\text{pm}) = \boxed{111\,\text{pm}}$.

E23.22(b) The diagonal of the face that has a lattice point in its centre is equal to $4r$, where r is the radius of the atom. The relationship between this diagonal and the edge length a is

$$4r = a\sqrt{2} \quad \text{so} \quad a = 2\sqrt{2}r$$

The volume of the unit cell is a^3, and each cell contains 2 atoms. (Each of the 8 vertices is shared among 8 cells; each of the 2 face points is shared by 2 cells.) So the packing fraction is

$$\frac{2V_{\text{atom}}}{V_{\text{cell}}} = \frac{2(4/3)\pi r^3}{(2\sqrt{2}r)^3} = \frac{\pi}{3(2)^{3/2}} = \boxed{0.370}$$

E23.23(b) The volume of an atomic crystal is proportional to the cube of the atomic radius divided by the packing fraction. The packing fractions for hcp, a close-packed structure, is 0.740; for bcc, it is 0.680. So for titanium

$$\frac{V_{\text{bcc}}}{V_{\text{hcp}}} = \frac{0.740}{0.680}\left(\frac{122\,\text{pm}}{126\,\text{pm}}\right)^3 = 0.99$$

The bcc structure has a smaller volume, so the transition involves a $\boxed{\text{contraction}}$. (Actually, the data are not precise enough to be sure of this. 122 could mean 122.49 and 126 could mean 125.51, in which case an expansion would occur.)

E23.24(b) Draw points corresponding to the vectors joining each pair of atoms. Heavier atoms give more intense contributions than light atoms. Remember that there are two vectors joining any pair of atoms ($\overrightarrow{AB}$ and $\overleftarrow{AB}$); don't forget the AA zero vectors for the centre point of the diagram. See Fig. 23.2 for C_6H_6.

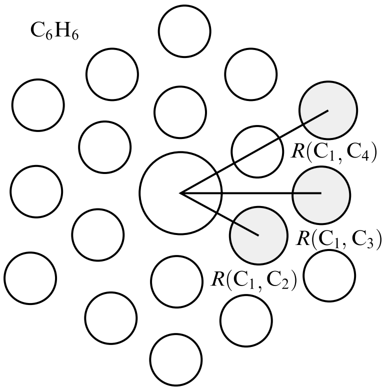


Figure 23.2

E23.25(b) Combine $E = \frac{1}{2}kT$ and $E = \frac{1}{2}mv^2 = \frac{h^2}{2m\lambda^2}$, to obtain

$$\lambda = \frac{h}{(mkT)^{1/2}} = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{[(1.675 \times 10^{-27}\,\mathrm{kg}) \times (1.381 \times 10^{-23}\,\mathrm{JK^{-1}}) \times (300\,\mathrm{K})]^{1/2}} = \boxed{252\,\mathrm{pm}}$$

E23.26(b) $$\lambda = \frac{h}{p} = \frac{h}{m_\mathrm{e}v}$$

$$\tfrac{1}{2}m_\mathrm{e}v^2 = e\Delta\phi \quad \text{so} \quad v = \left(\tfrac{2e\Delta\phi}{m_\mathrm{e}}\right)^{1/2}$$

$$\text{and } \lambda = \left(\frac{h^2}{2m_\mathrm{e}e\Delta\phi}\right)^{1/2} = \frac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{[(2) \times (9.109 \times 10^{-31}\,\mathrm{kg}) \times (1.602 \times 10^{-19}\,\mathrm{C}) \times (\Delta\phi)]^{1/2}}$$

$$= \frac{1.227\,\mathrm{nm}}{(\Delta\phi/V)^{1/2}}$$

(a) $\Delta\phi = 1.0\,\mathrm{kV}, \quad \lambda = \dfrac{1.227\,\mathrm{nm}}{(1.0 \times 10^3)^{1/2}} = \boxed{39\,\mathrm{pm}}$

(b) $\Delta\phi = 10\,\mathrm{KV}, \quad \lambda = \dfrac{1.227\,\mathrm{nm}}{(1.0 \times 10^4)^{1/2}} = \boxed{12\,\mathrm{pm}}$

(c) $\Delta\phi = 40\,\mathrm{KV}, \quad \lambda = \dfrac{1.227\,\mathrm{nm}}{(4.0 \times 10^4)^{1/2}} = \boxed{6.1\,\mathrm{pm}}$

E23.27(b) The lattice enthalpy is the difference in enthalpy between an ionic solid and the corresponding isolated ions. In this exercise, it is the enthalpy corresponding to the process

$$\mathrm{MgBr_2(s) \rightarrow Mg^{2+}(g) + 2Br^-(g)}$$

The standard lattice enthalpy can be computed from the standard enthalpies given in the exercise by considering the formation of $\mathrm{MgBr_2(s)}$ from its elements as occuring through the following steps: sublimation of Mg(s), removing two electrons from Mg(g), vaporization of $\mathrm{Br_2(1)}$, atomization of $\mathrm{Br_2(g)}$, electron attachment to Br(g), and formation of the solid $\mathrm{MgBr_2}$ lattice from gaseous ions

$$\begin{aligned}\Delta_\mathrm{f}H^\ominus(\mathrm{MgBr_2, s}) &= \Delta_\mathrm{sub}H^\ominus(\mathrm{Mg, s}) + \Delta_\mathrm{ion}H^\ominus(\mathrm{Mg, g}) + \Delta_\mathrm{vap}H^\ominus(\mathrm{Br_2, 1}) \\ &\quad + \Delta_\mathrm{at}H^\ominus(\mathrm{Br_2, g}) + 2\Delta_\mathrm{eg}H^\ominus(\mathrm{Br, g}) - \Delta_\mathrm{L}H^\ominus(\mathrm{MgBr_2, s})\end{aligned}$$

So the lattice enthalpy is

$$\begin{aligned}\Delta_\mathrm{L}H^\ominus(\mathrm{MgBr_2, s}) &= \Delta_\mathrm{sub}H^\ominus(\mathrm{Mg, s}) + \Delta_\mathrm{ion}H^\ominus(\mathrm{Mg, g}) + \Delta_\mathrm{vap}H^\ominus(\mathrm{Br_2, 1}) \\ &\quad + \Delta_\mathrm{at}H^\ominus(\mathrm{Br_2, g}) + 2\Delta_\mathrm{eg}H^\ominus(\mathrm{Br, g}) - \Delta_\mathrm{f}H^\ominus(\mathrm{MgBr_2, s}) \\ \Delta_L H^\ominus(\mathrm{MgBr_2, s}) &= [148 + 2187 + 31 + 193 - 2(331) + 524]\,\mathrm{kJ\,mol^{-1}} = \boxed{2421\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

E23.28(b) Tension reduces the disorder in the rubber chains; hence, if the rubber is sufficiently stretched, crystallization may occur at temperatures above the normal crystallization temperature. In unstretched rubber the random thermal motion of the chain segments prevents crystallization. In stretched rubber these random thermal motions are drastically reduced. At higher temperatures the random motions may still have been sufficient to prevent crystallization even in the stretched rubber, but lowering the temperature to 0°C may have resulted in a transition to the crystalline form. Since it is random motion of the chains that resists the stretching force and allows the rubber to respond to forced dimensional changes, this ability ceases when the motion ceases. Hence, the seals failed.

Comment. The solution to the problem of the cause of the Challenger disaster was the final achievement, just before his death, of Richard Feynman, a Nobel prize winner in physics and a person who loved to solve problems. He was an outspoken person who abhorred sham, especially in science and technology. Feynman concluded his personal report on the disaster by saying, 'For a successful technology, reality must take precedence over public relations, for nature cannot be fooled' (James Gleick, Genius: the life and science of Richard Feynman. Pantheon Books, New York (1992).)

E23.29(b) Young's modulus is defined as:

$$E = \frac{\text{normal stress}}{\text{normal strain}}$$

where stress is deforming force per unit area and strain is a fractional deformation. Here the deforming force is gravitational, mg, acting across the cross-sectional area of the wire, πr^2. So the strain induced in the exercise is

$$\text{strain} = \frac{\text{stress}}{E} = \frac{mg}{\pi(d/2)^2E} = \frac{4mg}{\pi d^2 E} = \frac{4(10.0\,\text{kg})(9.8\,\text{m s}^{-2})}{\pi(0.10\times10^{-3}\,\text{m})^2(215\times10^9\,\text{Pa})} = \boxed{5.8\times10^{-2}}$$

The wire would stretch by 5.8%.

E23.30(b) Poisson's ratio is defined as:

$$\nu_{\text{P}} = \frac{\text{transverse strain}}{\text{normal strain}}$$

where normal strain is the fractional deformation along the direction of the deforming force and transverse strain is the fractional deformation in the directions transverse to the deforming force. Here the length of a cube of lead is stretched by 2.0 per cent, resulting in a contraction by 0.41 × 2.0 per cent, or 0.82 per cent, in the width and height of the cube. The relative change in volume is:

$$\frac{V+\Delta V}{V} = (1.020)(0.9918)(0.9918) = 1.003$$

and the absolute change is:

$$\Delta V = (1.003-1)(1.0\,\text{dm}^3) = \boxed{0.003\,\text{dm}^3}$$

E23.31(b) $m = g_{\text{e}}\{S(S+1)\}^{1/2}\mu_{\text{B}}$ [23.34, with S in place of s]

Therefore, since $m = 4.00\mu_{\text{B}}$

$$S(S+1) = \left(\tfrac{1}{4}\right)\times(4.00)^2 = 4.00, \quad \text{implying that} \quad S = 1.56$$

Since $S \approx \frac{3}{2}$, implying three unpaired spins.

In actuality most Mn^{2+} compounds have $\boxed{5}$ unpaired spins.

E23.32(b) $$\chi_m = \chi V_m = \frac{\chi M}{\rho} = \frac{(-7.9 \times 10^{-6}) \times (84.15\,\mathrm{g\,mol^{-1}})}{0.811\,\mathrm{g\,cm^{-3}}}$$
$$= \boxed{-8.2 \times 10^{-4}\,\mathrm{cm^3\,mol^{-1}}}$$

E23.33(b) The molar susceptibility is given by

$$\chi_m = \frac{N_A g_e^2 \mu_0 \mu_B^2 S(S+1)}{3kT}$$

NO_2 is an odd-electron species, so it must contain at least one unpaired spin; in its ground state it has one unpaired spin, so $S = \frac{1}{2}$. Therefore,

$$\chi_m = (6.022 \times 10^{23}\,\mathrm{mol^{-1}}) \times (2.0023)^2 \times (4\pi \times 10^{-7}\,\mathrm{T^2\,J^{-1}m^3})$$
$$\times \frac{(9.274 \times 10^{-24}\,\mathrm{J\,T^{-1}})^2 \times \left(\frac{1}{2}\right) \times \left(\frac{1}{2} + 1\right)}{3(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K})}$$
$$= \boxed{1.58 \times 10^{-8}\,\mathrm{m^3 mol^{-1}}}$$

The expression above does not indicate any pressure-dependence in the molar susceptibility. However, the observed decrease in susceptibility with increased pressure is consistent with the fact that NO_2 has a tendency to dimerize, and that dimerization is favoured by higher pressure. The dimer has no unpaired electrons, so the dimerization reaction effectively reduced the number of paramagnetic species.

E23.34(b) The molar susceptibility is given by

$$\chi_m = \frac{N_A g_e^2 \mu_0 \mu_B^2 S(S+1)}{3kT} \quad \text{so} \quad S(S+1) = \frac{3kT\chi_m}{N_A g_e^2 \mu_0 \mu_B^2}$$

$$S(S+1) = \frac{3(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K})}{(6.022 \times 10^{23}\,\mathrm{mol^{-1}}) \times (2.0023)^2}$$
$$\times \frac{(6.00 \times 10^{-8}\,\mathrm{m^3\,mol^{-1}})}{(4\pi \times 10^{-7}\,\mathrm{T^2\,J^{-1}\,m^3}) \times (9.274 \times 10^{-24}\,\mathrm{J\,T^{-1}})^2}$$
$$= 2.84 \quad \text{so} \quad S = \frac{-1 + \sqrt{1 + 4(2.84)}}{2} = 1.26$$

corresponding to $\boxed{2.52}$ effective unpaired spins. The theoretical number is $\boxed{2}$. The magnetic moments in a crystal are close together, and the interact rather strongly. The discrepancy is most likely due to an interaction among the magnetic moments.

E23.35(b) The molar susceptibility is given by

$$\chi_m = \frac{N_A g_e^2 \mu_0 \mu_B^2 S(S+1)}{3kT}$$

Mn^{2+} has five unpaired spins, so $S = 2.5$ and

$$\chi_m = \frac{(6.022\times 10^{23}\,\text{mol}^{-1})\times(2.0023)^2\times(4\pi\times 10^{-7}\,\text{T}^2\,\text{J}^{-1}\,\text{m}^3)}{3(1.381\times 10^{-23}\,\text{J}\,\text{K}^{-1})} \times\frac{(9.274\times 10^{-24}\,\text{J}\,\text{T}^{-1})^2\times(2.5)\times(2.5+1)}{(298\,\text{K})} = \boxed{1.85\times 10^{-7}\,\text{m}^3\,\text{mol}^{-1}}$$

E23.36(b) The orientational energy of an electron spin system in a magnetic field is

$$E = g_e\mu_B M_S B$$

The Boltzmann distribution says that the population ratio r of the various states is proportional to

$$r = \exp\left(\frac{-\Delta E}{kT}\right)$$

where ΔE is the difference between them. For a system with $S = 1$, the M_S states are 0 and ± 1. So between adjacent states

$$r = \exp\left(\frac{-g_e\mu_B M_S B}{kT}\right) = \exp\left(\frac{-(2.0023)\times(9.274\times 10^{-24}\,\text{J}\,\text{T}^{-1})\times(1)\times(15.0\,\text{T})}{(1.381\times 10^{-23}\,\text{J}\,\text{K}^{-1})\times(298\,\text{K})}\right) = \boxed{0.935}$$

The population of the highest-energy state is r^2 times that of the lowest; $r^2 = \boxed{0.873}$

Solutions to problems

Solutions to numerical problems

P23.1 $\lambda = 2d_{hkl}\sin\theta_{hkl} = \dfrac{2a\sin\theta_{hkl}}{(h^2+k^2+l^2)^{1/2}}$ [eqn 23.5, inserting eqn 23.2] $= 2a\sin 6.0^\circ = 0.209a$

In an NaCl unit cell (Fig. 23.3) the number of formula units is 4 (each corner ion is shared by 8 cells, each edge ion by 4, and each face ion by 2).

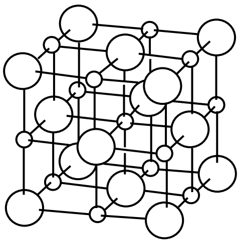


Figure 23.3

Therefore,

$$\rho = \frac{NM}{VN_A} = \frac{4M}{a^3N_A}, \quad \text{implying that} \quad a = \left(\frac{4M}{\rho N_A}\right)^{1/3} \quad \text{[Exercise 23.13(a)]}$$

$$a = \left(\frac{(4) \times (58.44\,\text{g mol}^{-1})}{(2.17 \times 10^{16}\,\text{g m}^{-3}) \times (6.022 \times 10^{23}\,\text{mol}^{-1})}\right)^{1/3} = 563.\bar{5}\,\text{pm}$$

and hence $\lambda = (0.209) \times (563.\bar{5}\,\text{pm}) = \boxed{118\,\text{pm}}$

P23.4 Note that since $R = 28.7\,\text{mm}$, $\theta/\text{deg} = \left(\frac{D}{2R}\right) \times \left(\frac{180}{\pi}\right) = D/\text{mm}$. Then proceed through the following sequence:

1. Measure the distances from the figure.
2. Convert from distances to angle using $\theta/\text{deg} = D/\text{mm}$.
3. Calculate $\sin^2\theta$.
4. Find the common factor $A = \frac{\lambda^2}{4a^2}$ in $\sin^2\theta = \left(\frac{\lambda^2}{4a^2}\right)(h^2 + k^2 + l^2)$.
5. Index the lines using $\frac{\sin^2\theta}{A} = h^2 + k^2 + l^2$.
6. Solve $A = \frac{\lambda^2}{4a^2}$ for a.

(a)

D/mm	22	30	36	44	50	58	67	77
θ/deg	22	30	36	44	50	58	67	77
$10^3 \sin^2\theta$	140	250	345	482	587	719	847	949

Analysis of face-centred cubic possibility

$(h\,k\,l)$	(1 1 1)	(2 0 0)	(2 1 1)	(3 1 1)	(2 2 2)	(4 0 0)	(3 3 1)	(4 2 0)
$10^4 A$	467	625	431	438	489	449	446	475

Analysis of body-centred cubic possibility

$(h\,k\,l)$	(1 1 0)	(2 0 0)	(2 1 1)	(2 2 0)	(3 1 0)	(2 2 2)	(3 2 1)	(4 0 0)
$10^4 A$	700	625	575	603	587	599	605	593

Begin by performing steps 1–3 in order to determine D, θ, and $\sin^2\theta$ and place them in tabular form as above. It is now possible to reject the primitive (simple) cubic cell possibility immediately because the separation between the sixth and seventh lines is not significantly larger than the separation between the fifth and sixth lines (see Problem 23.2 and Fig. 23.22).

The relatively large uncertainties of the separation measurements force the modification of steps 4 and 5 for the identification of the unit cell as being either face-centred cubic or body-centred cubic. We analyse both possibilities by calculating the common factor $A = \sin^2\theta/h^2 + k^2 + l^2)$ for each datum in each case. Comparison of the standard deviations of the average of A determines the unit cell type.

The analysis of both the face-centred cubic and body-centred cubic possibilities is found in the above table. Successive reflective planes are determined with the rules found in Fig. 23.22.

fcc possibility: $A_{\text{av.}} = 0.0478, \quad \sigma_{\text{A}} = 0.0063$ (13 per cent)

bcc possibility: $A_{\text{av.}} = 0.0611, \quad \sigma_{\text{A}} = 0.0016$ (6 per cent)

These standard deviations (σ_{A}) indicate that the cell type is $\boxed{\text{body-centred cubic}}$

The Q test of the (1 1 0) reflection datum for A yields $Q = 0.6$. Consequently this datum may be rejected with better than 95 per cent confidence. This yields a better average value for A.

$A_{\text{av.}} = 0.0598, \qquad \sigma_{\text{A}} = 0.0016$ (3 per cent)

$$\text{Then } a = \frac{\lambda}{2A^{1/2}} = \frac{154\,\text{pm}}{(2) \times (0.0598)^{1/2}} = \boxed{315\,\text{pm}}$$

$$4R = \sqrt{3}a, \quad \text{so} \quad \boxed{R = 136\,\text{pm}} \text{ [Fig. 23.1 above with } r = R\text{]}$$

(b)

D/mm	21	25	37	45	47	59	67	72
θ/deg	21	25	37	45	47	59	67	72
$10^3 \sin^2\theta$	128	179	362	500	535	735	847	905

Analysis of face-centred cubic possibility

$(h\,k\,l)$	(1 1 1)	(2 0 0)	(2 2 0)	(3 1 1)	(2 2 2)	(4 0 0)	(3 3 1)	(4 2 0)
$10^4 A$	427	448	453	455	446	459	446	453

Analysis of body-centred cubic possibility

$(h\,k\,l)$	(1 1 0)	(2 0 0)	(2 1 1)	(2 2 0)	(3 1 0)	(2 2 2)	(3 2 1)	(4 0 0)
$10^4 A$	640	448	603	625	535	613	605	566

Following the procedure established in part (a), the above table is constructed.

fcc possibility: $A_{\text{av.}} = 0.0448, \quad \sigma_{\text{A}} = 0.0010$ (2 per cent)

bcc possibility: $A_{\text{av.}} = 0.0579, \quad \sigma_{\text{A}} = 0.0063$ (11 per cent)

The standard deviations indicate that the cell type is $\boxed{\text{face-centred cubic}}$

$$\text{Then} \quad a = \frac{\lambda}{2A^{1/2}} = \frac{154\,\text{pm}}{(2) \times (0.0448)^{1/2}} = \boxed{364\,\text{pm}}$$

$$4R = \sqrt{2}a, \quad \text{so} \quad R = \boxed{129\,\text{pm}}$$

P23.6 When a very narrow X-ray beam (with a spread of wavelenths) is directed on the centre of a genuine pearl, all the crystallites are irradiated parallel to a trigonal axis and the result is a Laue photograph with sixfold symmetry. In a cultured pearl the narrow beam will have an arbitrary orientation with respect to the crystallite axes (of the central core) and an unsymmetrical Laue photograph will result. (See J. Bijvoet *et al., X-ray analysis of crystals.* Butterworth (1951).)

P23.8 $V = abc \sin\beta$

and the information given tells us that $a = 1.377b$, $c = 1.436b$, and $\beta = 122^\circ 49'$; hence

$$V = (1.377) \times (1.436b^3) \sin 122^\circ 49' = 1.662b^3$$

Since $\rho = \dfrac{NM}{VN_A} = \dfrac{2M}{1.662b^3 N_A}$ we find that

$$b = \left(\frac{2M}{1.662\rho N_A}\right)^{1/3}$$

$$= \left(\frac{(2) \times (128.18\,\text{g mol}^{-1})}{(1.662) \times (1.152 \times 10^6\,\text{g m}^{-3}) \times (6.022 \times 10^{23}\,\text{mol}^{-1})}\right)^{1/3} = 605.8\,\text{pm}$$

Therefore, $a = \boxed{834\,\text{pm}}$, $b = \boxed{606\,\text{pm}}$, $c = \boxed{870\,\text{pm}}$

P23.10 In a monoclinic cell, the area of parallelogram faces whose sides are a and c is

$$A = ca \cos(\beta - 90^\circ)$$

so the volume of the unit cell is

$$\begin{aligned} V &= abc \cos(\beta - 90^\circ) = (1.0427\,\text{nm}) \times (0.8876\,\text{nm}) \times (1.3777\,\text{nm}) \times \cos(93.254^\circ - 90^\circ) \\ &= 1.2730\,\text{nm}^3 \end{aligned}$$

The mass per unit cell is

$$m = \rho V = (2.024\,\text{g cm}^{-3}) \times (1.2730\,\text{nm}^3) \times (10^{-7}\text{cm nm}^{-1})^3 = 2.577 \times 10^{-21}\,\text{g}$$

The monomer is $CuC_7H_{13}N_5O_8S$, so its molar mass is

$$\begin{aligned} M &= 63.546 + 7(12.011) + 13(1.008) + 5(14.007) + 8(15.999) + 32.066\,\text{g mol}^{-1} \\ &= 390.82\,\text{g mol}^{-1} \end{aligned}$$

The number of monomer units, then, is the mass of the unit cell divided by the mass of the monomer

$$N = \frac{mN_A}{M} = \frac{(2.577 \times 10^{-21}\,\text{g}) \times (6.022 \times 10^{23}\,\text{mol}^{-1})}{390.82\,\text{g mol}^{-1}} = 3.97 \quad \text{or} \quad \boxed{4}$$

P23.12 The problem asks for an estimate of $\Delta_f H^\ominus(\text{CaCl})$. A Born–Haber cycle would envision formation of CaCl(s) from its elements as sublimation of Ca(s), ionization of Ca(g), atomization of Cl_2(g) electrom gain of Cl(g), and formation of CaCl(s) from gaseous ions. Therefore

$$\begin{aligned} \Delta_f H^\ominus(\text{CaCl, s}) &= \Delta_{\text{sub}} H^\ominus(\text{Ca, s}) + \Delta_{\text{ion}} H^\ominus(\text{Ca, g}) + 2\Delta_f H^\ominus(\text{Cl, g}) \\ &\qquad + 2\Delta_{eg} H^\ominus(\text{Cl, g}) - \Delta_L H^\ominus(\text{CaCl, s}) \end{aligned}$$

Before we can estimate the lattice enthalpy of CaCl, we select a lattice with the aid of the radius-ratio rule. The ionic radius for Cl^- is 181 pm; use the ionic radius of K^+ (138 pm) for Ca^+

$$\gamma = \frac{138\,\text{pm}}{181\,\text{pm}} = 0.762$$

suggesting the CsCl structure. We can interpret the Born–Mayer equation (eqn 23.15) as giving the negative of the lattice enthalpy

$$\Delta_L H^\ominus \approx \frac{A|z_1 z_2|N_A e^2}{4\pi\varepsilon_0 d}\left(1 - \frac{d*}{d}\right)$$

The distance d is

$$\begin{aligned} d &= 138 + 181\,\text{pm} = 319\,\text{pm} \\ \text{so } \Delta_{\text{L}}H^{\ominus} &\approx \frac{(1.763)|(1)(-1)|(6.022\times10^{23}\,\text{mol}^{-1})(1.602\times10^{-19}\,\text{C})^2}{4\pi(8.854\times10^{-12}\,\text{J}^{-1}\text{C}^2\,\text{m}^{-1})(319\times10^{-12}\,\text{m})}\left(1-\frac{34.5\,\text{pm}}{319\,\text{pm}}\right) \\ \Delta_{\text{L}}H^{\ominus} &\approx 6.85\times10^{5}\,\text{J mol}^{-1} = 685\,\text{kJ mol}^{-1} \end{aligned}$$

The enthalpy of formation, then, is

$$\Delta_{\text{f}}H^{\ominus}(\text{CaCl, s}) \approx [176 + 589.7 + 2(121.7 - 348.7) - 685]\,\text{kJ mol}^{-1} = \boxed{-373\,\text{kJ mol}^{-1}}.$$

Although formation of CaCl(s) from its elements is exothermic, formation of CaCl_2(s) is still more favoured energetically. Consider the reaction

$$\begin{aligned} &2\ \text{CaCl(s)} \rightarrow \text{Ca(s)} + \text{CaCl}_2\text{(s)} \\ \text{for which } \Delta H^{\ominus} &= \Delta_{\text{f}}H^{\ominus}(\text{Ca}) + \Delta_{\text{f}}H^{\ominus}(\text{CaCl}_2) - 2\Delta_{\text{f}}H^{\ominus}(\text{CaCl}) \\ &\approx [0 - 795.8 - 2(-373)]\,\text{kJ mol}^{-1} \\ \Delta H^{\ominus} &\approx -50\,\text{kJ mol}^{-1} \end{aligned}$$

Note: Using the tabulated ionic radius of Ca (i.e., that of Ca^{2+}) would be less valid than using the atomic radius of a neighbouring monovalent ion, for the problem asks about a hypothetical compound of monovalent calcium. Predictions with the smaller Ca^{2+} radius (100 pm) differ substantially from those listed above: the expected structure changes to rock-salt, the lattice enthalpy to 758 kJ mol^{-1}, $\Delta_{\text{f}}H^{\ominus}$(CaCl) to -446 kJ mol^{-1} and the final reaction enthalpy to $+96$ kJ mol^{-1}.

Solutions to theoretical problems

P23.15 If the sides of the unit cell define the vectors $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$, then its volume is $V = \boldsymbol{a}\cdot\boldsymbol{b}\times\boldsymbol{c}$ [given]. Introduce the orthogonal set of unit vectors $\hat{\boldsymbol{i}}, \hat{\boldsymbol{j}}, \hat{\boldsymbol{k}}$ so that

$$\begin{aligned} \boldsymbol{a} &= a_x\hat{\boldsymbol{i}} + a_y\hat{\boldsymbol{j}} + a_z\hat{\boldsymbol{k}} \\ \boldsymbol{b} &= b_x\hat{\boldsymbol{i}} + b_y\hat{\boldsymbol{j}} + b_z\hat{\boldsymbol{k}} \\ \boldsymbol{c} &= c_x\hat{\boldsymbol{i}} + c_y\hat{\boldsymbol{j}} + c_z\hat{\boldsymbol{k}} \end{aligned}$$

Then $V = \boldsymbol{a}\cdot\boldsymbol{b}\times\boldsymbol{c} = \begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix}$

Therefore

$$\begin{aligned} V^2 &= \begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix}\begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix} \\ &= \begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix}\begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix} \end{aligned}$$

[interchange rows and columns, no change in value]

$$= \begin{vmatrix} a_xa_x + a_ya_y + a_za_z & a_xb_x + a_yb_y + a_zb_z & a_xc_x + a_yc_y + a_zc_z \\ b_xa_x + b_ya_y + b_za_z & b_yb_x + b_yb_y + b_zb_z & b_xc_x + b_yc_y + b_zc_z \\ c_xa_x + c_ya_y + c_za_z & c_xb_x + c_yb_y + c_zb_z & c_xc_x + c_yc_y + c_zc_z \end{vmatrix}$$

$$= \begin{vmatrix} a^2 & \boldsymbol{a}\cdot\boldsymbol{b} & \boldsymbol{a}\cdot\boldsymbol{c} \\ \boldsymbol{b}\cdot\boldsymbol{a} & b^2 & \boldsymbol{b}\cdot\boldsymbol{c} \\ \boldsymbol{c}\cdot\boldsymbol{a} & \boldsymbol{c}\cdot\boldsymbol{b} & c^2 \end{vmatrix} = \begin{vmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ac\cos\beta & bc\cos\alpha & c^2 \end{vmatrix}$$

$$= a^2b^2c^2(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)^{1/2}$$

Hence $\boxed{V = abc(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)^{1/2}}$

For a monoclinic cell, $\alpha = \gamma = 90°$

$$V = abc(1 - \cos^2\beta)^{1/2} = \boxed{abc\sin\beta}$$

For an orthorhombic cell, $\alpha = \beta = \gamma = 90°$, and

$$V = \boxed{abc}$$

P23.18 $F_{hkl} = \sum_i f_i e^{2\pi i(hx_i + ky_i lz_i)}$ [23.7]

For each A atom use $\frac{1}{8}f_A$ (each A atom shared by eight cells) but use f_B for the central atom (since it contributes solely to the cell).

$$\begin{aligned} F_{hkl} &= \tfrac{1}{8}f_A\left\{1 + e^{2\pi ih} + e^{2\pi ik} + e^{2\pi il} + e^{2\pi i(h+k)} + e^{2\pi i(h+l)} + e^{2\pi i(k+l)} + e^{2\pi i(h+k+l)}\right\} \\ &\quad + f_B e^{2\pi i(h+k+l)} \\ &= f_A + (-1)^{(h+k+l)} f_B \quad [h, k, l \text{ are all integers, } e^{i\pi} = -1] \end{aligned}$$

(a) $f_A = f, \quad f_B = 0; \quad F_{hkl} = f$ $\boxed{\text{no systematic absences}}$

(b) $f_B = \frac{1}{2}f_A; \quad F_{hkl} = f_A\left[1 + \frac{1}{2}(-1)^{(h+k+l)}\right]$

Therefore, when $h + k + l$ is odd, $F_{hkl} = f_A\left(1 - \frac{1}{2}\right) = \frac{1}{2}f_A$, and when $h + k + l$ is even, $F_{hkl} = \frac{3}{2}f_A$.

That is, there is an $\boxed{\text{alternation of intensity}}$ $(I \propto F^2)$ according to $\boxed{\text{whether } h+k+l \text{ is odd or even}}$.

(c) $f_A = f_B = f; \quad F_{h+k+l} = f\left\{1 + (-1)^{h+k+l}\right\} = 0$ if $h + k + l$ is odd.

Thus, $\boxed{\text{all } h+k+l \text{ odd lines are missing}}$.

P23.20 Write $t = aT$, then

$$\left(\frac{\partial t}{\partial T}\right)_l = a, \quad \left(\frac{\partial U}{\partial l}\right)_T = t - aT \text{ [Problem 23.19]} = 0$$

and the internal energy is independent of the extension. Therefore

$$\boxed{t = -T\left(\frac{\partial S}{\partial l}\right)_T} \text{ [Problem 23.19]}$$

and the tension is proportional to the variation of entropy with extension. The extension reduces the disorder of the chains, and they tend to revert to their disorderly (nonextended) state.

P23.22 **(a)** The density of energy levels is:

$$\rho(E) = \frac{\mathrm{d}k}{\mathrm{d}E} = \left(\frac{\mathrm{d}E}{\mathrm{d}k}\right)^{-1}$$

where $\dfrac{\mathrm{d}E}{\mathrm{d}k} = \dfrac{\mathrm{d}}{\mathrm{d}k}\left(\alpha + 2\beta\cos\dfrac{k\pi}{N+1}\right) = -\dfrac{2\pi\beta}{N+1}\sin\dfrac{k\pi}{N+1}$

so $\rho(E) = -\dfrac{N+1}{2\pi\beta}\left(\sin\dfrac{k\pi}{N+1}\right)^{-1}$

Unlike the expression just derived, the relationship the problem asks us to derive has no trigonometric functions and it contains E and α within a square root. This comparison suggests that the trigonometric identity $\sin^2\theta + \cos^2\theta = 1$ will be of use here. Let $\theta = k\pi/(N+1)$; then

$$\sin\theta = 1(1-\cos^2\theta)^{1/2}$$

however, $\cos\theta$ is related to the energy

$$E = \alpha + 2\beta\cos\theta \quad \text{so} \quad \cos\theta = \frac{E-\alpha}{2\beta}$$

and $\sin\theta = \left[1 - \left(\dfrac{E-\alpha}{2\beta}\right)^2\right]^{1/2}$

Finally, $\boxed{\rho(E) = \dfrac{-\frac{N+1}{2\pi\beta}}{\left[1-\left(\frac{E-\alpha}{2\beta}\right)^2\right]^{1/2}}}$

(b) The denominator of this expression vanishes as the energy approaches $\alpha \pm 2\beta$. Near those limits, $E-\alpha$ becomes $\pm 2\beta$, making the quantity under the square root zero, and $\rho(E)$ approach infinity.

P23.23 $\xi = \dfrac{-e^2}{6m_\mathrm{e}}\langle r^2\rangle$

$$\begin{aligned}\langle r^2\rangle &= \int_0^\infty r^2\psi^2\,\mathrm{d}\tau \quad \text{with } \psi = \left(\frac{1}{\pi a_0^3}\right)^{1/2}\mathrm{e}^{-r/a_0}\\ &= 4\pi\int_0^\infty r^4\psi^2\,\mathrm{d}r \quad [\mathrm{d}\tau = 4\pi r^2\,\mathrm{d}r]\\ &= \frac{4}{a_0^3}\int_0^\infty r^4\mathrm{e}^{-2r/a_0}\,\mathrm{d}r = 3a_0^2 \quad \left[\int_0^\infty x^n\mathrm{e}^{-ax}\,\mathrm{d}x = \frac{n!}{a^{n+1}}\right]\end{aligned}$$

Therefore, $\boxed{\xi = \dfrac{-e^2a_0^2}{2m_\mathrm{e}}}$

Then, since $\chi_\mathrm{m} = N_\mathrm{A}\mu_0\xi$ [23.32, $m=0$]

$$\chi_\mathrm{m} = \boxed{\frac{-N_\mathrm{A}\mu_0e^2a_0^2}{2m_\mathrm{e}}}$$

P23.25 If the proportion of molecules in the upper level is P, where they have a magnetic moment of $2\mu_B$ (which replaces $\{S(S+1)\}^{1/2}\mu_B$ in eqn 23.35), the molar susceptibility

$$\chi_m = \frac{(6.3001) \times [S(S+1)]}{T/K} \text{ cm}^3 \text{ mol}^{-1} \text{[Illustration 23.1]}$$

is changed to

$$\chi_m = \frac{(6.3001) \times (4) \times P}{T/K} \text{ cm}^3 \text{ mol}^{-1} [2^2 \text{replaces } S(S+1)] = \frac{25.2P}{T/K} \text{cm}^3 \text{mol}^{-1}$$

The proportion of molecules in the upper state is

$$P = \frac{e^{-hc\tilde{\nu}/kT}}{1 + e^{-hc\tilde{\nu}/kT}} \text{[Boltzmann distribution]} = \frac{1}{1 + e^{hc\tilde{\nu}/kT}}$$

and $\dfrac{hc\tilde{\nu}}{kT} = \dfrac{(1.4388 \text{ cm K}) \times (121 \text{ cm}^{-1})}{T} = \dfrac{174}{T/K}$

Therefore, $\chi_m = \dfrac{25.2 \text{ cm}^3 \text{ mol}^{-1}}{(T/K) \times (1 + e^{174/(T/K)})}$

This function is plotted in Fig. 23.4

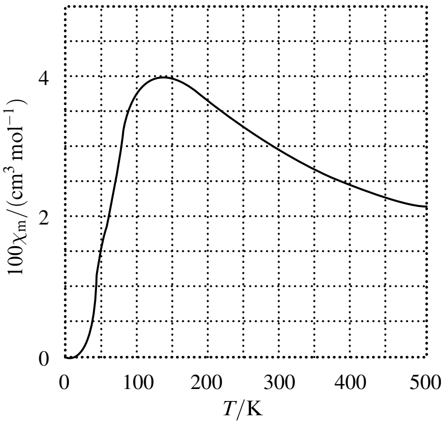


Figure 23.4

Comment. The explanation of the magnetic properties of NO is more complicated and subtle than indicated by the solution here. In fact the full solution for this case was one of the important triumphs of the quantum theory of magnetism which was developed about 1930. See J. H. van Vleck, *The theory of electric and magnetic susceptibilities*. Oxford University Press (1932).

Solutions to applications

P23.29 $\theta(100 \text{ K}) = 22°2'25''$, $\theta(300 \text{ K}) = 21°57'59''$

$$\sin\theta(100 \text{ K}) = 0.37526, \quad \sin\theta(300 \text{ K}) = 0.37406$$

$$\frac{\sin\theta(300 \text{ K})}{\sin\theta\,(100 \text{ K})} = 0.99681 = \frac{a(100 \text{ K})}{a(300 \text{ K})} \text{[see Problem 21.7]}$$

$$a(300\,\mathrm{K}) = \frac{\lambda\sqrt{3}}{2\sin\theta} = \frac{(154.062\,\mathrm{pm}) \times \sqrt{3}}{(2) \times (0.37406)} = 356.67\,\mathrm{pm}$$

$$a(100\,\mathrm{K}) = (0.99681) \times (356.67\,\mathrm{pm}) = 355.53\,\mathrm{pm}$$

$$\frac{\delta a}{a} = \frac{356.67 - 355.53}{355.53} = 3.206 \times 10^{-3}$$

$$\frac{\delta V}{V} = \frac{356.67^3 - 355.53^3}{355.53^3} = 9.650 \times 10^{-3}$$

$$\alpha_{\mathrm{volume}} = \frac{1}{V}\frac{\delta V}{\delta T} = \frac{9.560 \times 10^{-3}}{200\,\mathrm{K}} = \boxed{4.8 \times 10^{-5}\,\mathrm{K}^{-1}}$$

$$\alpha_{\mathrm{volume}} = \frac{1}{a}\frac{\delta a}{\delta T} = \frac{3.206 \times 10^{-3}}{200\,\mathrm{K}} = \boxed{1.6 \times 10^{-5}\,\mathrm{K}^{-1}}$$

Part 3: Change

24 Molecules in motion

Solutions to exercises

Discussion questions

E24.1(b) Diffusion is the migration of particles (molecules) down a concentration gradient. Diffusion can be interpreted at the molecular level as being the result of the random jostling of the molecules in a fluid. The motion of the molecules is the result of a series of short jumps in random directions, a so-called random walk.

In the random walk model of diffusion, although a molecule may take many steps in a given time, it has only a small probability of being found far from its starting point because some of the steps lead it away from the starting point but others lead it back. As a result, the net distance traveled increases only as the square root of the time. There is no net flow of molecules unless there is a concentration gradient in the fluid, alse there are just as many molecules moving in one direction as another. The rate at which the molecules spread out is proportional to the concentration gradient. The constant of proportionality is called the diffusion coefficient.

On the molecular level in a gas, thermal conduction occurs because of random molecular motions in the presence of a temperature gradient. Across any plane in the gas, there is a net flux of energy from the high temperature side, because molecules coming from that side carry a higher average energy per molecule across the plane than those coming from the low temperature side. In solids, the situation is more complex as energy transport occurs through quantized elastic waves (phonons) and, in metals, also by electrons. Conduction in liquids can occur by all the mechanisms mentioned.

At the molecular (ionic) level, electrical conduction in an electrolytic solution is the net migration of ions in any given direction. When a gradient in electrical potential exists in a conductivity cell there will be a greater flow of positive ions in the direction of the negative electrode than in the direction of the positive electrode, hence there is a net flow of positive charge toward the region of low electrical potential. Likewise a net flow of negative ions in the direction of the positive electrode will occur. In metals, only negatively charged electrons contribute to the current.

To see the connection between the flux of momentum and the viscosity, consider a fluid in a state of *Newtonian* flow, which can be imagined as occurring by a series of layers moving past one another (Fig. 24.11 of the text). The layer next to the wall of the vessel is stationary, and the velocity of successive layers varies linearly with distance, z, from the wall. Molecules ceaselessly move between the layers and bring with them the x-component of linear momentum they possessed in their original layer. A layer is retarded by molecules arriving from a more slowly moving layer because they have a low momentum in the x-direction. A layer is accelerated by molecules arriving from a more rapidly moving layer. We interpret the net retarding effect as the fluid's viscosity.

E24.2(b) According to the Grotthuss mechanism, there is an effective motion of a proton that involves the rearrangement of bonds in a group of water molecules. However, the actual mechanism is still highly contentious. Attention now focuses on the $H_9O_4{}^+$ unit in which the nearly trigonal planar H_3O^+ ion is linked to three strongly solvating H_2O molecules. This cluster of atoms is itself hydrated, but the hydrogen bonds in the secondary sphere are weaker than in the primary sphere. It is envisaged that the rate-determining step is the cleavage of one of the weaker hydrogen bonds of this secondary sphere (Fig. 24.19a of the text). After this bond cleavage has taken place, and the released molecule has rotated through a few degrees (a process that takes about 1 ps), there is a rapid adjustment of bond lengths and angles in the remaining cluster, to form an $H_5O_2{}^+$ cation of structure $H_2O\cdots H^+\cdots OH_2$ (Fig. 24.19b). Shortly after this reorganization has occurred, a new $H_9O_4{}^+$ cluster forms as other molecules rotate into a position where they can become members of a secondary hydration sphere, but now the positive charge is located one molecule to the right of its initial location (Fig. 24.19c). According to this model, there is no coordinated motion of a proton along a chain of molecules, simply a very rapid hopping between neighbouring sites, with a low activation energy. The model is consistent with the observation that the molar conductivity of protons increases as the pressure is raised, for increasing pressure ruptures the hydrogen bonds in water.

E24.3(b) Because the drift speed governs the rate at which charge is transported, we might expect the conductivity to decrease with increasing solution viscosity and ion size. Experiments confirm these predictions for bulky ions, but not for small ions. For example, the molar conductivities of the alkali metal ions increase from Li^+ to Cs^+ (Table 24.6) even though the ionic radii increase. The paradox is resolved when we realize that the radius a in the Stokes formula is the hydrodynamic radius (or "Stokes radius") of the ion, its effective radius in the solution taking into account all the H_2O molecules it carries in its hydration sphere. Small ions give rise to stronger electric fields than large ones, so small ions are more extensively solvated than big ions. Thus, an ion of small ionic radius may have a large hydrodynamic radius because it drags many solvent molecules through the solution as it migrates. The hydrating H_2O molecules are often very labile, however, and NMR and isotope studies have shown that the exchange between the coordination sphere of the ion and the bulk solvent is very rapid.

The proton, although it is very small, has a very high molar conductivity (Table 24.6)! Proton and ^{17}O-NMR show that the times characteristic of protons hopping from one molecule to the next are about 1.5 ps, which is comparable to the time that inelastic neutron scattering shows it takes a water molecule to reorientate through about 1 rad (1–2 ps).

Numerical exercises

E24.4(b) **(a)** The mean speed of a gas molecule is

$$\bar{c} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

$$\text{so } \frac{\bar{c}(\text{He})}{\bar{c}(\text{Hg})} = \left(\frac{M(\text{Hg})}{M(\text{He})}\right)^{1/2} = \left(\frac{200.59}{4.003}\right)^{1/2} = \boxed{7.079}$$

(b) The mean kinetic energy of a gas molecule is $\frac{1}{2}mc^2$, where c is the root mean square speed

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

So $\frac{1}{2}mc^2$ is independent of mass, and the ratio of mean kinetic energies of He and Hg is $\boxed{1}$

E24.5(b) **(a)** The mean speed can be calculated from the formula derived in Example 24.1.

$$\bar{c} = \left(\frac{8RT}{\pi M}\right)^{1/2} = \left(\frac{8 \times (8.314\,\text{J K}^{-1}\text{mol}^{-1}) \times (298\,\text{K})}{\pi \times (28.02 \times 10^{-3}\,\text{kg mol}^{-1})}\right)^{1/2} = \boxed{4.75 \times 10^2\,\text{m s}^{-1}}$$

(b) The mean free path is calculated from $\lambda = \dfrac{kT}{2^{1/2}\sigma p}$ [24.14]

with $\sigma = \pi d^2 = \pi \times (3.95 \times 10^{-10}\,\text{m})^2 = 4.90 \times 10^{-19}\,\text{m}^2$

$$\text{Then, } \lambda = \frac{(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (298\,\text{K})}{2^{1/2} \times (4.90 \times 10^{-19}\,\text{m}^2) \times (1 \times 10^{-9}\,\text{Torr}) \times \left(\frac{1\,\text{atm}}{760\,\text{Torr}}\right) \times \left(\frac{1.013 \times 10^5\,\text{Pa}}{1\,\text{atm}}\right)}$$

$$= \boxed{4 \times 10^4\,\text{m}}$$

(c) The collision frequency could be calculated from eqn 31, but is most easily obtained from eqn 32, since λ and $\bar{c}$ have already been calculated $z = \dfrac{\bar{c}}{\lambda} = \dfrac{4.75 \times 10^2\,\mathrm{m\,s^{-1}}}{4.4\overline{6} \times 10^4\,\mathrm{m}} = \boxed{1 \times 10^{-2}\,\mathrm{s^{-1}}}$

Thus there are 100 s between collisions, which is a very long time compared to the usual timescale of molecular events. The mean free path is much larger than the dimensions of the pumping apparatus used to generate the very low pressure.

E24.6(b) $p = \dfrac{kT}{2^{1/2}\sigma\lambda}[24.14]$

$$\sigma = \pi d^2, \quad d = \left(\frac{\sigma}{\pi}\right)^{1/2} = \left(\frac{0.36\,\mathrm{nm}^2}{\pi}\right)^{1/2} = 0.34\,\mathrm{nm}$$

$$p = \frac{(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K})}{(2^{1/2}) \times (0.36 \times 10^{-18}\,\mathrm{m}^2) \times (0.34 \times 10^{-9}\,\mathrm{m})} = \boxed{2.4 \times 10^7\,\mathrm{Pa}}$$

This pressure corresponds to about 240 atm, which is comparable to the pressure in a compressed gas cylinder in which argon gas is normally stored.

E24.7(b) The mean free path is

$$\lambda = \frac{kT}{2^{1/2}\sigma p} = \frac{(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (217\,\mathrm{K})}{2^{1/2}[0.43 \times (10^{-9}\,\mathrm{m})^2] \times (12.1 \times 10^3\,\mathrm{Pa\,atm^{-1}})} = \boxed{4.1 \times 10^{-7}\,\mathrm{m}}$$

E24.8(b) Obtain data from Exercise 24.7(b)

The expression for z obtained in Exercise 24.8(a) is $z = \left(\dfrac{16}{\pi m k T}\right)^{1/2}\sigma p$

Substituting $\sigma = 0.43\,\mathrm{nm}^2$, $p = 12.1 \times 10^3\,\mathrm{Pa}$, $m = (28.02\,\mathrm{u})$, and $T = 217\,\mathrm{K}$ we obtain

$$z = \frac{4 \times (0.43 \times 10^{-18}\,\mathrm{m}^2) \times (12.1 \times 10^3\,\mathrm{Pa})}{[\pi \times (28.02) \times (1.6605 \times 10^{-27}\,\mathrm{kg}) \times (1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (217\,\mathrm{K})]^{1/2}}$$
$$= \boxed{9.9 \times 10^8\,\mathrm{s^{-1}}}$$

E24.9(b) The mean free path is

$$\lambda = \frac{kT}{2^{1/2}\sigma p} = \frac{(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (25 + 273)\,\mathrm{K}}{2^{1/2}[0.52 \times (10^{-9}\,\mathrm{m})^2]p} = \frac{5.5\overline{0} \times 10^{-3}\,\mathrm{m\,Pa}}{p}$$

(a) $\lambda = \dfrac{5.5\overline{0} \times 10^{-3}\,\mathrm{m\,Pa}}{(15\,\mathrm{atm}) \times (1.013 \times 10^5\,\mathrm{Pa\,atm^{-1}})} = \boxed{3.7 \times 10^{-9}\,\mathrm{m}}$

(b) $\lambda = \dfrac{5.5\overline{0} \times 10^{-3}\,\mathrm{m\,Pa}}{(1.0\,\mathrm{bar}) \times (10^5\,\mathrm{Pa\,bar^{-1}})} = \boxed{5.5 \times 10^{-8}\,\mathrm{m}}$

(c) $\lambda = \dfrac{5.5\overline{0} \times 10^{-3}\,\mathrm{m\,Pa}}{(1.0\,\mathrm{Torr}) \times \left(\frac{1.013 \times 10^5\,\mathrm{Pa\,atm^{-1}}}{760\,\mathrm{Torr\,atm^{-1}}}\right)} = \boxed{4.1 \times 10^{-5}\,\mathrm{m}}$

E24.10(b) The fraction F of molecules in the speed range from 200 to 250 $\mathrm{m\,s^{-1}}$ is

$$F = \int_{200\,\mathrm{m\,s^{-1}}}^{250\,\mathrm{m\,s^{-1}}} f(v)\mathrm{d}v$$

where $f(v)$ is the Maxwell distribution. This can be approximated by

$$F \approx f(v)\Delta v = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 \exp\left(\frac{-Mv^2}{2RT}\right)\Delta v,$$

with $f(v)$ evaluated in the middle of the range

$$\begin{aligned} F &\approx 4\pi\left(\frac{44.0\times10^{-3}\,\mathrm{kg\,mol^{-1}}}{2\pi(8.3145\,\mathrm{J\,K^{-1}mol^{-1}})\times(300\,\mathrm{K})}\right)^{3/2}\times(225\,\mathrm{m\,s^{-1}})^2 \\ &\quad\times\exp\left(\frac{-(44.0\times10^{-3}\,\mathrm{kg\,mol^{-1}})\times(225\,\mathrm{m\,s^{-1}})^2}{2(8.3145\,\mathrm{J\,K^{-1}mol^{-1}})\times(300\,\mathrm{K})}\right)\times(50\,\mathrm{m\,s^{-1}}), \\ F &\approx \boxed{9.6\times10^{-2}} \end{aligned}$$

Comment. The approximation we have employed, taking $f(v)$ to be nearly constant over a narrow range of speeds, may not be accurate enough, for that range of speeds includes about 10 per cent of the molecules.

Numerical exercises

E24.11(b) The number of collisions is

$$\begin{aligned} N &= Z_\mathrm{W}At = \frac{pAt}{(2\pi mkT)^{1/2}} \\ &= \frac{(111\,\mathrm{Pa})\times(3.5\times10^{-3}\,\mathrm{m})\times(4.0\times10^{-3}\,\mathrm{m})\times(10\,\mathrm{s})}{\{2\pi\times(4.00\,\mathrm{u})\times(1.66\times10^{-27}\,\mathrm{kg\,u^{-1}})\times(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(1500\,\mathrm{K})\}^{1/2}} \\ &= \boxed{1.1\times10^{21}} \end{aligned}$$

E24.12(b) The mass of the sample in the effusion cell decreases by the mass of the gas which effuses out of it. That mass is the molecular mass times the number of molecules that effuse out

$$\begin{aligned} \Delta m &= mN = mZ_\mathrm{W}At = \frac{mpAt}{(2\pi mkT)^{1/2}} = pAt\left(\frac{m}{2\pi kT}\right)^{1/2} = pAt\left(\frac{M}{2\pi RT}\right)^{1/2} \\ &= (0.224\,\mathrm{Pa})\times\pi\times\left(\tfrac{1}{2}\times3.00\times10^{-3}\,\mathrm{m}\right)^2\times(24.00\,\mathrm{h})\times(3600\,\mathrm{s\,h^{-1}}) \\ &\quad\times\left\{\frac{300\times10^{-3}\,\mathrm{kg\,mol^{-1}}}{2\pi\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(450\,\mathrm{K})}\right\}^{1/2} \\ &= \boxed{4.89\times10^{-4}\,\mathrm{kg}} \end{aligned}$$

E24.13(b) The flux is

$$J = -\kappa\frac{\mathrm{d}T}{\mathrm{d}z} = -\frac{1}{3}\lambda C_{V,\mathrm{m}}\langle v\rangle[\mathrm{X}]\frac{\mathrm{d}T}{\mathrm{d}z}$$

where the minus sign indicates flow toward lower temperature and

$$\lambda = \frac{1}{\sqrt{2}N\sigma}, \quad \langle v\rangle = \left(\frac{8kT}{\pi m}\right)^{1/2} = \left(\frac{8RT}{\pi M}\right)^{1/2}, \quad \text{and} \quad [\mathrm{M}] = n/V = N/N_\mathrm{A}$$

$$\text{So } J = -\frac{2C_{V,\mathrm{m}}}{3\sigma N_\mathrm{A}}\left(\frac{RT}{\pi M}\right)^{1/2}\frac{\mathrm{d}T}{\mathrm{d}z}$$

$$= -\left(\frac{2\times(28.832-8.3145)\,\mathrm{J\,K^{-1}\,mol^{-1}}}{3\times[0.27\times(10^{-9}\,\mathrm{m})^2]\times(6.022\times10^{23}\,\mathrm{mol^{-1}})}\right)$$

$$\times\left(\frac{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(260\,\mathrm{K})}{\pi\times(2.016\times10^{-3}\,\mathrm{kg\,mol^{-1}})}\right)^{1/2}\times(3.5\,\mathrm{K\,m^{-1}})$$

$$= \boxed{0.17\,\mathrm{J\,m^{-2}\,s^{-1}}}$$

E24.14(b) The thermal conductivity is

$$\kappa = \frac{1}{3}\lambda C_{V,\mathrm{m}}\langle v\rangle[\mathrm{X}] = \frac{2C_{V,\mathrm{m}}}{3\sigma N_\mathrm{A}}\left(\frac{RT}{\pi M}\right)^{1/2} \quad \text{so} \quad \sigma = \frac{2C_{V,\mathrm{m}}}{3\kappa N_\mathrm{A}}\left(\frac{RT}{\pi M}\right)^{1/2}$$

$$= (0.240\,\mathrm{mJ\,cm^{-2}\,s^{-1}})\times(\mathrm{K\,cm^{-1}})^{-1} = 0.240\times10^{-1}\,\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}$$

$$\text{so } \sigma = \left(\frac{2\times(29.125-8.3145)\,\mathrm{J\,K^{-1}\,mol^{-1}}}{3\times(0.240\times10^{-1}\,\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}})\times(6.022\times10^{23}\,\mathrm{mol^{-1}})}\right)$$

$$\times\left(\frac{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})}{\pi\times(28.013\times10^{-3}\,\mathrm{kg\,mol^{-1}})}\right)^{1/2}$$

$$= \boxed{1.61\times10^{-19}\,\mathrm{m^2}}$$

E24.15(b) Assuming the space between sheets is filled with air, the flux is

$$J = -\kappa\frac{\mathrm{d}T}{\mathrm{d}z} = [(0.241\times10^{-3}\,\mathrm{J\,cm^{-2}\,s^{-1}})\times(\mathrm{K\,cm^{-1}})^{-1}]\times\left(\frac{[50-(-10)]\,\mathrm{K}}{10.0\,\mathrm{cm}}\right)$$

$$= 1.4\bar{5}\times10^{-3}\,\mathrm{J\,cm^{-2}\,s^{-1}}.$$

So the rate of energy transfer and energy loss is

$$JA = (1.4\bar{5}\times10^{-3}\,\mathrm{J\,cm^{-2}\,s^{-1}})\times(1.50\,\mathrm{m^2})\times(100\,\mathrm{cm\,m^{-1}})^2 = \boxed{22\,\mathrm{J\,s^{-1}}}$$

E24.16(b) The time dependence of the pressure of a gas effusing without replenishment is

$$p = p_0 \mathrm{e}^{-t/\tau} \quad \text{where } \tau \propto \sqrt{m}$$

The time t it takes for the pressure to go from any initial pressure p_0 to a prescribed fraction of that pressure fp_0 is

$$t = \tau \ln \frac{fp_0}{p_0} = \tau \ln f$$

so the time is proportional to τ and therefore also to $\sqrt{m}$. Therefore, the ratio of times it takes two different gases to go from the same initial pressure to the same final pressure is related to their molar masses as follows

$$\frac{t_1}{t_2} = \left(\frac{M_1}{M_2}\right)^{1/2} \quad \text{and} \quad M_2 = M_1 \left(\frac{t_2}{t_1}\right)^2$$

So $M_{\text{fluorocarbon}} = (28.01\,\text{g mol}^{-1}) \times \left(\dfrac{82.3\,\text{s}}{18.5\,\text{s}}\right)^2 = \boxed{554\,\text{g mol}^{-1}}$

E24.17(b) The time dependence of the pressure of a gas effusion without replenishment is

$$p = p_0 \mathrm{e}^{-t/\tau} \quad \text{so} \quad t = \tau \ln p_0/p$$

where $\tau = \dfrac{V}{A_0}\left(\dfrac{2\pi m}{kT}\right)^{1/2} = \dfrac{V}{A_0}\left(\dfrac{2\pi M}{RT}\right)^{1/2}$

$$= \left(\frac{22.0\,\text{m}^3}{\pi \times (0.50 \times 10^{-3}\,\text{m})^2}\right) \times \left(\frac{2\pi \times (28.0 \times 10^{-3}\,\text{kg mol}^{-1})}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (293\,\text{K})}\right)^{1/2} = 2.4 \times 10^5\,\text{s}$$

so $t = (8.6 \times 10^5\,\text{s}) \ln \dfrac{122\,\text{kPa}}{105\,\text{kPa}} = \boxed{1.5 \times 10^4\,\text{s}}$

E24.18(b) The coefficient of viscosity is

$$\eta = \tfrac{1}{3}\lambda m N \langle v \rangle = \frac{2}{3\sigma}\left(\frac{mkT}{\pi}\right)^{1/2} \quad \text{so} \quad \sigma = \frac{2}{3\eta}\left(\frac{mkT}{\pi}\right)^{1/2}$$

$$= 1.66\,\mu\text{P} = 166 \times 10^{-7}\,\text{kg m}^{-1}\,\text{s}^{-1}$$

so $\sigma = \left(\dfrac{2}{3 \times (166 \times 10^{-7}\,\text{kg m}^{-1}\,\text{s}^{-1})}\right)$

$$\times \left(\frac{(28.01 \times 10^{-3}\,\text{kg mol}^{-1}) \times (1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (273\,\text{K})}{\pi \times (6.022 \times 10^{23}\,\text{mol}^{-1})}\right)^{1/2}$$

$$= \boxed{3.00 \times 10^{-19}\,\text{m}^2}$$

E24.19(b) The rate of fluid flow through a tube is described by

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{(p_{\text{in}}^2 - p_{\text{out}}^2)\pi r^4}{16 l \eta p_0} \quad \text{so} \quad p_{\text{in}} = \left(\frac{16 l \eta p_0}{\pi r^4}\frac{\mathrm{d}V}{\mathrm{d}t} + p_{\text{out}}^2\right)^{1/2}$$

Several of the parameters need to be converted to MKS units

$$r = \tfrac{1}{2}(15 \times 10^{-3}\,\text{m}) = 7.5 \times 10^{-3}\,\text{m}$$

and $\dfrac{\mathrm{d}V}{\mathrm{d}t} = 8.70\,\text{cm}^3 \times (10^{-2}\,\text{m cm}^{-1})^3\,\text{s}^{-1} = 8.70 \times 10^{-6}\,\text{m}^3\,\text{s}^{-1}.$

Also, we have the viscosity at 293 K from the table. According to the $T^{1/2}$ temperature dependence, the viscosity at 300 K ought to be

$$\begin{aligned}\eta(300\,\mathrm{K}) &= \eta(293\,\mathrm{K}) \times \left(\frac{300\,\mathrm{K}}{293\,\mathrm{K}}\right)^{1/2} = (176 \times 10^{-7}\,\mathrm{kg\,m^{-1}\,s^{-1}}) \times \left(\frac{300}{293}\right)^{1/2} \\ &= 1.78 \times 10^{-7}\,\mathrm{kg\,m^{-1}\,s^{-1}} \\ p_{\mathrm{in}} &= \left\{\left(\frac{16(10.5\,\mathrm{m}) \times (178 \times 10^{-7}\,\mathrm{kg\,m^{-1}\,s^{-1}}) \times (1.00 \times 10^{5}\,\mathrm{Pa})}{\pi \times (7.5 \times 10^{-3}\,\mathrm{m})^4}\right)\right. \\ &\qquad \left. \times (8.70 \times 10^{-6}\,\mathrm{m^3\,s^{-1}}) + (1.00 \times 10^{5}\,\mathrm{Pa})^2\right\}^{1/2} \\ &= \boxed{1.00 \times 10^{5}\,\mathrm{Pa}}\end{aligned}$$

Comment. For the exercise as stated the answer is not sensitive to the viscosity. The flow rate is so low that the inlet pressure would equal the outlet pressure (to the precision of the data) whether the viscosity were that of N_2 at 300 K or 293 K—or even liquid water at 293 K!

E24.20(b) The coefficient of viscosity is

$$\begin{aligned}\eta &= \tfrac{1}{3}\lambda m N\langle v\rangle = \frac{2}{3\sigma}\left(\frac{mkT}{\pi}\right)^{1/2} \\ &= \left(\frac{2}{3[0.88 \times (10^{-9}\,\mathrm{m})^2]}\right) \times \left(\frac{(78.12 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}) \times (1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}})T}{\pi \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}})}\right)^{1/2} \\ &= 5.7\bar{2} \times 10^{-7} \times (T/\mathrm{K})^{1/2}\ \mathrm{kg\,m^{-1}\,s^{-1}}\end{aligned}$$

(a) At 273 K $\quad \eta = (5.7\bar{2} \times 10^{-7}) \times (273)^{1/2}\,\mathrm{kg\,m^{-1}\,s^{-1}} = \boxed{0.95 \times 10^{-5}\,\mathrm{kg\,m^{-1}\,s^{-1}}}$

(b) At 298 K $\quad \eta = (5.7\bar{2} \times 10^{-7}) \times (298)^{1/2}\,\mathrm{kg\,m^{-1}\,s^{-1}} = \boxed{0.99 \times 10^{-5}\,\mathrm{kg\,m^{-1}\,s^{-1}}}$

(c) At 1000 K $\quad \eta = (5.7\bar{2} \times 10^{-7}) \times (1000)^{1/2}\,\mathrm{kg\,m^{-1}\,s^{-1}} = \boxed{1.81 \times 10^{-5}\,\mathrm{kg\,m^{-1}\,s^{-1}}}$

E24.21(b) The thermal conductivity is

$$\kappa = \tfrac{1}{3}\lambda C_{V,\mathrm{m}}\langle v\rangle[\mathrm{X}] = \frac{2C_{V,\mathrm{m}}}{3\sigma N_{\mathrm{A}}}\left(\frac{RT}{\pi M}\right)^{1/2}$$

(a)
$$\begin{aligned}\kappa &= \left(\frac{2 \times [(20.786 - 8.3145)\,\mathrm{J\,K^{-1}\,mol^{-1}}]}{3[0.24 \times (10^{-9}\,\mathrm{m})^2] \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}})}\right) \\ &\quad \times \left(\frac{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (300\,\mathrm{K})}{\pi(20.18 \times 10^{-3}\,\mathrm{kg\,mol^{-1}})}\right)^{1/2} \\ &= \boxed{0.011\bar{4}\,\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}}\end{aligned}$$

The flux is

$$J = -\kappa\frac{\mathrm{d}T}{\mathrm{d}z} = (0.011\bar{4}\,\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}) \times \left(\frac{(305-295)\,\mathrm{K}}{0.15\,\mathrm{m}}\right) = 0.76\,\mathrm{J\,m^{-2}\,s^{-1}}$$

so the rate of energy loss is

$$JA = (0.76\,\mathrm{J\,m^{-2}\,s^{-1}}) \times (0.15\,\mathrm{m})^2 = \boxed{0.017\,\mathrm{J\,s^{-1}}}$$

(b)
$$\kappa = \left(\frac{2 \times [(29.125 - 8.3145)\,\mathrm{J\,K^{-1}\,mol^{-1}}]}{3[0.43 \times (10^{-9}\,\mathrm{m})^2] \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}})}\right)$$
$$\times \left(\frac{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (300\,\mathrm{K})}{\pi(28.013 \times 10^{-3}\,\mathrm{kg\,mol^{-1}})}\right)^{1/2}$$
$$= \boxed{9.0 \times 10^{-3}\,\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}}$$

The flux is

$$J = -\kappa\frac{\mathrm{d}T}{\mathrm{d}z} = (9.0 \times 10^{-3}\,\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}) \times \left(\frac{(305-295)\,\mathrm{K}}{0.15\,\mathrm{m}}\right) = 0.60\,\mathrm{J\,m^{-2}\,s^{-1}}$$

so the rate of energy loss is

$$JA = (0.60\,\mathrm{J\,m^{-2}\,s^{-1}}) \times (0.15\,\mathrm{m})^2 = \boxed{0.014\,\mathrm{J\,s^{-1}}}$$

E24.22(b) The rate of fluid flow through a tube is described by

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{(p_{\mathrm{in}}^2 - p_{\mathrm{out}}^2)\pi r^4}{16l\eta p_0}$$

so the rate is inversely proportional to the viscosity, and the time required for a given volume of gas to flow through the same tube under identical pressure conditions is directly proportional to the viscosity

$$\frac{t_1}{t_2} = \frac{\eta_1}{\eta_2} \quad \text{so} \quad \eta_2 = \frac{\eta_1 t_2}{t_1}$$

$$\eta_{\mathrm{CFC}} = \frac{(208\,\mu\mathrm{P}) \times (18.0\,\mathrm{s})}{72.0\,\mathrm{s}} = \boxed{52.0\,\mu\mathrm{P}} = 52.0 \times 10^{-7}\,\mathrm{kg\,m^{-1}\,s^{-1}}$$

The coefficient of viscosity is

$$\eta = \tfrac{1}{3}\lambda m N\langle v\rangle = \left(\frac{2}{3\sigma}\right) \times \left(\frac{mkT}{\pi}\right)^{1/2} = \left(\frac{2}{3\pi d^2}\right) \times \left(\frac{mkT}{\pi}\right)^{1/2}$$

so the molecular diameter is

$$d = \left(\frac{2}{3\pi\eta}\right)^{1/2} \times \left(\frac{mkT}{\pi}\right)^{1/4}$$
$$= \left(\frac{2}{3\pi(52.0 \times 10^{-7}\,\mathrm{kg\,m^{-1}\,s^{-1}})}\right)^{1/2}$$
$$\times \left(\frac{(200 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}) \times (1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K})}{\pi \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}})}\right)^{1/4}$$
$$= 9.23 \times 10^{-10}\,\mathrm{m} = \boxed{923\,\mathrm{pm}}$$

E24.23(b)

$$\kappa = \tfrac{1}{3}\lambda C_{V,\mathrm{m}}\langle v\rangle[\mathrm{X}] = \frac{2C_{V,\mathrm{m}}}{3\sigma N_\mathrm{A}}\left(\frac{RT}{\pi M}\right)^{1/2}$$

$$= \left(\frac{2\times(29.125-8.3145)\,\mathrm{J\,K^{-1}\,mol^{-1}}}{3[0.43\times(10^{-9}\,\mathrm{m})^2]\times(6.022\times10^{23}\,\mathrm{mol^{-1}})}\right)\times\left(\frac{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(300\,\mathrm{K})}{\pi\times(28.013\times10^{-3}\,\mathrm{kg\,mol^{-1}})}\right)^{1/2}$$

$$= \boxed{9.0\times10^{-3}\,\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}}$$

E24.24(b) The diffusion constant is

$$D = \tfrac{1}{3}\lambda\langle v\rangle = \frac{2(RT)^{3/2}}{3\sigma pN_\mathrm{A}(\pi M)^{1/2}}$$

$$= \frac{2[(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})]^{3/2}}{3[0.43\times(10^{-9}\,\mathrm{m})^2]p(6.022\times10^{23}\,\mathrm{mol^{-1}})\times\left\{\pi(28.013\times10^{-3}\,\mathrm{kg\,mol^{-1}})\right\}^{1/2}}$$

$$= \frac{1.07\,\mathrm{m^2\,s^{-1}}}{p/\mathrm{Pa}}$$

The flux due to diffusion is

$$J = -D\frac{\mathrm{d}[\mathrm{X}]}{\mathrm{d}x} = -D\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{n}{V}\right) = -\left(\frac{D}{RT}\right)\frac{\mathrm{d}p}{\mathrm{d}x}$$

where the minus sign indicates flow from high pressure to low. So for a pressure gradient of $0.10\,\mathrm{atm\,cm^{-1}}$

$$J = \left(\frac{D/(\mathrm{m^2\,s^{-1}})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})}\right)\times(0.20\times10^5\,\mathrm{Pa\,m^{-1}})$$

$$= (8.1\,\mathrm{mol\,m^{-2}\,s^{-1}})\times(D/(\mathrm{m^2\,s^{-1}}))$$

(a) $D = \dfrac{1.07\,\mathrm{m^2\,s^{-1}}}{10.0} = \boxed{0.107\,\mathrm{m^2\,s^{-1}}}$

and $J = (8.1\,\mathrm{mol\,m^{-2}\,s^{-1}})\times(0.107) = \boxed{0.87\,\mathrm{mol\,m^{-2}\,s^{-1}}}$

(b) $D = \dfrac{1.07\,\mathrm{m^2\,s^{-1}}}{100\times10^3} = \boxed{1.07\times10^{-5}\,\mathrm{m^2\,s^{-1}}}$

and $J = (8.1\,\mathrm{mol\,m^{-2}\,s^{-1}})\times(1.07\times10^{-5}) = \boxed{8.7\times10^{-5}\,\mathrm{mol\,m^{-2}\,s^{-1}}}$

(c) $D = \dfrac{1.07\,\mathrm{m^2\,s^{-1}}}{15.0\times10^6} = \boxed{7.13\times10^{-8}\,\mathrm{m^2\,s^{-1}}}$

and $J = (8.1\,\mathrm{mol\,m^{-2}\,s^{-1}})\times(7.13\times10^{-8}) = \boxed{5.8\times10^{-7}\,\mathrm{mol\,m^{-2}\,s^{-1}}}$

E24.25(b) Molar ionic conductivity is related to mobility by

$$\lambda = zuF = (1)\times(4.24\times10^{-8}\,\mathrm{m^2\,s^{-1}V^{-1}})\times(96\,485\,\mathrm{C\,mol^{-1}})$$

$$= \boxed{4.09\times10^{-3}\,\mathrm{S\,m^2\,mol^{-1}}}$$

E24.26(b) The drift speed is given by

$$s = u\mathcal{E} = \frac{u\Delta\phi}{l} = \frac{(4.01\times10^{-8}\,\mathrm{m^2\,s^{-1}\,V^{-1}})\times(12.0\,\mathrm{V})}{1.00\times10^{-2}\,\mathrm{m}} = \boxed{4.81\times10^{-5}\,\mathrm{m\,s^{-1}}}$$

E24.27(b) The limiting transport number for $\mathrm{Cl^-}$ in aqueous NaCl at 25° C is

$$t_-^\circ = \frac{u_-}{u_+ + u_-} = \frac{7.91}{5.19 + 7.91} = \boxed{0.604}$$

(The mobilities are in $10^{-8}\,\mathrm{m^2\,s^{-1}\,V^{-1}}$.)

E24.28(b) The limiting molar conductivity of a dissolved salt is the sum of that of its ions, so

$$\begin{aligned}\Lambda_\mathrm{m}^\circ(\mathrm{MgI_2}) &= \lambda(\mathrm{Mg^{2+}}) + 2\lambda(\mathrm{I^-}) = \Lambda_\mathrm{m}^\circ(\mathrm{Mg(C_2H_3O_2)_2}) + 2\Lambda_\mathrm{m}^\circ(\mathrm{NaI}) - 2\Lambda_\mathrm{m}^\circ(\mathrm{NaC_2H_3O_2})\\ &= (18.78 + 2(12.69) - 2(9.10))\,\mathrm{mS\,m^2\,mol^{-1}} = \boxed{25.96\,\mathrm{mS\,m^2\,mol^{-1}}}\end{aligned}$$

E24.29(b) Molar ionic conductivity is related to mobility by

$$\lambda = zuF \quad \text{so} \quad u = \frac{\lambda}{zF}$$

$$\mathrm{F^-}: \quad u = \frac{5.54 \times 10^{-3}\,\mathrm{S\,m^2\,mol^{-1}}}{(1) \times (96\,485\,\mathrm{C\,mol^{-1}})} = \boxed{5.74 \times 10^{-8}\,\mathrm{m^2\,V^{-1}\,s^{-1}}}$$

$$\mathrm{Cl^-}: \quad u = \frac{7.635 \times 10^{-3}\,\mathrm{S\,m^2\,mol^{-1}}}{(1) \times (96\,485\,\mathrm{C\,mol^{-1}})} = \boxed{7.913 \times 10^{-8}\,\mathrm{m^2\,V^{-1}\,s^{-1}}}$$

$$\mathrm{Br^-}: \quad u = \frac{7.81 \times 10^{-3}\,\mathrm{S\,m^2\,mol^{-1}}}{(1) \times (96\,485\,\mathrm{C\,mol^{-1}})} = \boxed{8.09 \times 10^{-8}\,\mathrm{m^2\,V^{-1}\,s^{-1}}}$$

E24.30(b) The diffusion constant is related to the mobility by

$$\begin{aligned}D &= \frac{uRT}{zF} = \frac{(4.24 \times 10^{-8}\,\mathrm{m^2\,s^{-1}\,V^{-1}}) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})}{(1) \times (96\,485\,\mathrm{C\,mol^{-1}})}\\ &= \boxed{1.09 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}}\end{aligned}$$

E24.31(b) The mean square displacement for diffusion in one dimension is

$$\langle x^2 \rangle = 2Dt$$

In fact, this is also the mean square displacement in any direction in two- or three-dimensional diffusion from a concentrated source. In three dimensions

$$r^2 = x^2 + y^2 + z^2 \quad \text{so} \quad \langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle = 3\langle x^2 \rangle = 6Dt$$

So the time it takes to travel a distance $\sqrt{\langle r^2 \rangle}$ is

$$t = \frac{\langle r^2 \rangle}{6D} = \frac{(1.0 \times 10^{-2}\,\mathrm{m})^2}{6(4.05 \times 10^{-9}\,\mathrm{m^2\,s^{-1}})} = \boxed{4.1 \times 10^3\,\mathrm{s}}$$

E24.32(b) The diffusion constant is related to the viscosity of the medium and the size of the diffusing molecule as follows

$$D = \frac{kT}{6\pi\eta a} \quad \text{so} \quad a = \frac{kT}{6\pi\eta D} = \frac{(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K})}{6\pi(1.00 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}) \times (1.055 \times 10^{-9}\,\mathrm{m^2\,s^{-1}})}$$

$$a = 2.07 \times 10^{-10}\,\mathrm{m} = \boxed{207\,\mathrm{pm}}$$

E24.33(b) The Einstein–Smoluchowski equation related the diffusion constant to the unit jump distance and time

$$D = \frac{\lambda^2}{2\tau} \quad \text{so} \quad \tau = \frac{\lambda^2}{2D}$$

If the jump distance is about one molecular diameter, or two effective molecular radii, then the jump distance can be obtained by use of the Stokes–Einstein equation

$$D = \frac{kT}{6\pi\eta a} = \frac{kT}{3\pi\eta\lambda} \quad \text{so} \quad \lambda = \frac{kT}{3\pi\eta D}$$

$$\text{and } \tau = \frac{(kT)^2}{18(\pi\eta)^2 D^3} = \frac{[(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})]^2}{18[\pi(0.387\times10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}})]^2\times(3.17\times10^{-9}\,\mathrm{m^2\,s^{-1}})^3}$$

$$= \boxed{2.00\times10^{-11}\,\mathrm{s}} = 20\,\mathrm{ps}$$

E24.34(b) The mean square displacement is (from Exercise 24.31(b))

$$\langle r^2\rangle = 6Dt \quad \text{so} \quad t = \frac{\langle r^2\rangle}{6D} = \frac{(1.0\times10^{-6}\,\mathrm{m})^2}{6(1.0\times10^{-11}\,\mathrm{m^2\,s^{-1}})} = \boxed{1.7\times10^{-2}\,\mathrm{s}}$$

Solutions to problems

Solutions to numerical problems

P24.3 $\langle X\rangle = \frac{1}{N}\sum_i N_i X_i$ [See Problem 24.2]

(a) $\langle h\rangle = \frac{1}{53}\{1.80\,\mathrm{m} + 2\times(1.82\,\mathrm{m}) + \cdots + 1.98\,\mathrm{m}\}\ \boxed{1.89\,\mathrm{m}}$

(b) $\langle h^2\rangle = \frac{1}{53}\left\{(1.80\,\mathrm{m})^2 + 2\times(1.82\,\mathrm{m})^2 + \cdots + (1.98\,\mathrm{m})^2\right\} = 3.57\,\mathrm{m}^2$

$$\sqrt{\langle h^2\rangle} = \boxed{1.89\,\mathrm{m}}$$

P24.4 $\kappa = \frac{1}{3}\lambda\bar{c}C_{V,\mathrm{m}}[\mathrm{A}]$ [24.28]

$$\bar{c} = \left(\frac{8kT}{\pi m}\right)^{1/2} [24.7] \propto T^{1/2}$$

Hence, $\kappa \propto T^{1/2}C_{V,\mathrm{m}}$, so $\frac{\kappa'}{\kappa} = \left(\frac{T'}{T}\right)^{1/2}\times\left(\frac{C'_{V,\mathrm{m}}}{C_{V,\mathrm{m}}}\right)$

At 300 K, $C_{V,\mathrm{m}} \approx \frac{3}{2}R + R = \frac{5}{2}R$ At 10 K, $C_{V,\mathrm{m}} \approx \frac{3}{2}R$ [rotation not excited]

Therefore, $\frac{\kappa'}{\kappa} = \left(\frac{300}{10}\right)^{1/2}\times\left(\frac{5}{3}\right) = \boxed{9.1}$

P24.7 The atomic current is the number of atoms emerging from the slit per second, which is $Z_{\mathrm{W}}A$ with $A = 1\times10^{-7}\,\mathrm{m}^2$. We use

$$Z_{\mathrm{W}} = \frac{p}{(2\pi mkT)^{1/2}} \; [24.15]$$

$$= \frac{p/\mathrm{Pa}}{[(2\pi)\times(M/\mathrm{g\,mol^{-1}})\times(1.6605\times10^{-27}\,\mathrm{kg})\times(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(380\,\mathrm{K})]^{1/2}}$$

$$= (1.35\times10^{23}\,\mathrm{m^{-2}\,s^{-1}})\times\left(\frac{p/\mathrm{Pa}}{(M/\mathrm{g\,mol^{-1}})^{1/2}}\right)$$

(a) Cadmium:

$$Z_W A = (1.35 \times 10^{23}\,\mathrm{m^{-2}\,s^{-1}}) \times (1 \times 10^{-7}\,\mathrm{m^2}) \times \left(\frac{0.13}{(112.4)^{1/2}}\right) = \boxed{2 \times 10^{14}\,\mathrm{s^{-1}}}$$

(b) Mercury:

$$Z_W A = (1.35 \times 10^{23}\,\mathrm{m^{-2}\,s^{-1}}) \times (1 \times 10^{-7}\,\mathrm{m^2}) \times \left(\frac{152}{(200.6)^{1/2}}\right) = \boxed{1 \times 10^{17}\,\mathrm{s^{-1}}}$$

P24.10 $c = \dfrac{\kappa}{\Lambda_m}[24.98] \approx \dfrac{\kappa}{\Lambda_m^\circ}$ [c small, conductivity of water allowed for in the data]

$$c \approx \frac{1.887 \times 10^{-6}\,\mathrm{S\,cm^{-1}}}{138.3\,\mathrm{S\,cm^2\,mol^{-1}}} \text{ [Exercise 24.28(a)]}$$

$$\approx 1.36 \times 10^{-8}\,\mathrm{mol\,cm^{-3}} = \text{solubilit y} = \boxed{1.36 \times 10^{-5}\,\mathrm{M}}$$

P24.12 $t(\mathrm{H^+}) = \dfrac{u(\mathrm{H^+})}{u(\mathrm{H^+}) + u(\mathrm{Cl^-})}[24.61] = \dfrac{3.623}{3.623 + 0.791} = \boxed{0.82}$

When a third ion is present we use

$$t(\mathrm{H^+}) = \frac{I(\mathrm{H^+})}{I(\mathrm{H^+}) + I(\mathrm{Na^+}) + I(\mathrm{Cl^-})} \text{ [24.58]}$$

For each I, $I = zu\nu cFAE = \text{constant} \times cu$. Hence, when NaCl is added

$$t(\mathrm{H^+}) = \frac{c(\mathrm{H^+})u(\mathrm{H^+})}{c(\mathrm{H^+})u(\mathrm{H^+}) + c(\mathrm{Na^+})u(\mathrm{Na^+}) + c(\mathrm{Cl^-})u(\mathrm{Cl^-})}$$

$$= \frac{(1.0 \times 10^{-3}) \times (3.623)}{(1.0 \times 10^{-3}) \times (3.623) + (1.0) \times (0.519) + (1.001) \times (0.791)} = \boxed{0.0028}$$

P24.14 $t_+ = \left(\dfrac{zcAF}{I}\right) \times \left(\dfrac{x}{\Delta t}\right)$ [Problem 24.13]

The density of the solution is $0.682\,\mathrm{g\,cm^{-3}}$; the concentration c is related to the molality m by

$$c/(\mathrm{mol\,L^{-1}}) = \rho/(\mathrm{kg\,L^{-1}}) \times m/(\mathrm{mol\,kg^{-1}})$$

which holds for dilute solutions such as these.

$$A = \pi r^2 = \pi \times (2.073 \times 10^{-3}\,\mathrm{m})^2 = 1.350 \times 10^{-5}\,\mathrm{m^2}$$

$$\frac{czAF}{I\Delta t} = \frac{(1.350 \times 10^{-5}\,\mathrm{m^2}) \times (9.6485 \times 10^4\,\mathrm{C\,mol^{-1}})}{(5.000 \times 10^{-3}\,\mathrm{A}) \times (2500\,\mathrm{s})} \times c = (0.1042\,\mathrm{m^2\,mol^{-1}}) \times c$$

$$= (0.1042\,\mathrm{m^2\,mol^{-1}}) \times \rho \times m = (0.1042\,\mathrm{m^2\,mol^{-1}}) \times (682\,\mathrm{kg\,m^{-3}}) \times m$$

$$= (71.0\overline{6}\,\mathrm{kg\,m^{-1}\,mol^{-1}}) \times m = (0.0710\overline{6}\,\mathrm{kg\,mm^{-1}\,mol^{-1}}) \times m$$

and so $t_+ = (0.0710\overline{6}\,\mathrm{kg\,mm^{-1}\,mol^{-1}}) \times x \times m$

In the first solution $t_+ = (0.0710\overline{6}\,\mathrm{kg\,mm^{-1}\,mol^{-1}}) \times (286.9\,\mathrm{mm}) \times (0.01365\,\mathrm{mol\,kg^{-1}}) = \boxed{0.278}$

In the second solution $t_+ = (0.0710\overline{6}\,\mathrm{kg\,mm^{-1}\,mol^{-1}}) \times (92.03\,\mathrm{mm}) \times (0.04255\,\mathrm{mol\,kg^{-1}}) = \boxed{0.278}$

Therefore, $t(\mathrm{H}^+) = 0.28$, a value much less than in pure water where $t(\mathrm{H}^+) = 0.63$. Hence, the mobility is much less relative to its counterion, NH_2^-.

P24.17 If diffusion is analogous to viscosity [Section 24.5, eqn 24.36] in that it is also an activation energy controlled process, then we expect

$$D \propto \mathrm{e}^{-E_\mathrm{a}/RT}$$

Therefore, if the diffusion constant is D at T and D' at T',

$$E_\mathrm{a} = -\frac{R\ln\left(\frac{D'}{D}\right)}{\left(\frac{1}{T'}-\frac{1}{T}\right)} = -\frac{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}})\times\ln\left(\frac{2.89}{2.05}\right)}{\frac{1}{298\,\mathrm{K}}-\frac{1}{273\,\mathrm{K}}} = 9.3\,\mathrm{kJ\,mol^{-1}}$$

That is, the activation energy for diffusion is $\boxed{9.3\,\mathrm{kJ\,mol^{-1}}}$

P24.19 $\langle x^2\rangle = 2Dt$ [24.91], $\quad D = \dfrac{kT}{6\pi a\eta}$ [24.83]

Hence, $\eta = \dfrac{kT}{6\pi Da} = \dfrac{kTt}{3\pi a\langle x^2\rangle} = \dfrac{1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298.15\,\mathrm{K})\times t}{(3\pi)\times(2.12\times10^{-7}\,\mathrm{m})\times\langle x^2\rangle}$

$$= (2.06\times10^{-15}\,\mathrm{J\,m^{-1}})\times\left(\frac{t}{\langle x^2\rangle}\right)$$

and therefore $\eta/(\mathrm{kg\,m^{-1}s^{-1}}) = \dfrac{2.06\times10^{-11}(t/\mathrm{s})}{(\langle x^2\rangle/\mathrm{cm}^2)}$

We draw up the following table

t/s	30	60	90	120
$10^8\langle x^2\rangle/\mathrm{cm}^2$	88.2	113.4	128	144
$10^3\eta/(\mathrm{kg\,m^{-1}\,s^{-1}})$	0.701	1.09	1.45	1.72

Hence, the mean value is $\boxed{1.2\times10^{-3}\mathrm{kg\,m^{-1}\,s^{-1}}}$.

P24.21 The viscosity of a perfect gas is

$$\eta = \tfrac{1}{3}\mathcal{N}m\lambda\bar{c} = \frac{m\bar{c}}{3\sigma\sqrt{2}} = \frac{2}{3\sigma}\left(\frac{mkT}{\pi}\right)^{1/2} \quad \text{so} \quad \sigma = \frac{2}{3\eta}\left(\frac{mkT}{\pi}\right)^{1/2}$$

The mass is

$$m = \frac{17.03\times10^{-3}\,\mathrm{kg\,mol^{-1}}}{6.022\times10^{23}\,\mathrm{mol^{-1}}} = 2.828\times10^{-26}\,\mathrm{kg}$$

(a)
$$\sigma = \frac{2}{3(9.08\times10^{-6}\,\mathrm{kg\,m^{-1}\,s^{-1}})} \times\left(\frac{(2.828\times10^{-26}\,\mathrm{kg})\times(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(270\,\mathrm{K})}{\pi}\right)^{1/2}$$

$$= 4.25\times10^{-19}\,\mathrm{m}^2 = \pi d^2 \quad \text{so} \quad d = \left(\frac{4.25\times10^{-19}\,\mathrm{m}^2}{\pi}\right)^{1/2} = \boxed{3.68\times10^{-10}\,\mathrm{m}}$$

(b)
$$\sigma = \frac{2}{3(17.49\times 10^{-6}\,\mathrm{kg\,m^{-1}\,s^{-1}})} \times \left(\frac{(2.828\times 10^{-26}\,\mathrm{kg})\times(1.381\times 10^{-23}\,\mathrm{J\,K^{-1}})\times(490\,\mathrm{K})}{\pi}\right)^{1/2}$$
$$= 2.97\times 10^{-19}\,\mathrm{m^2} = \pi d^2 \quad \text{so} \quad d = \left(\frac{2.97\times 10^{-19}\,\mathrm{m^2}}{\pi}\right)^{1/2} = \boxed{3.07\times 10^{-10}\,\mathrm{m}}$$

Comment. The change in diameter with temperature can be interpreted in two ways. First, it shows the approximate nature of the concept of molecular diameter, with different values resulting from measurements of different quantities. Second, it is consistent with the idea that, at higher temperatures, more forceful collisions contract a molecule's perimeter.

P24.22 The diffusion constant of an ion in solution is related to the mobility of the ion and to its radius in separate relations

$$D = \frac{uRT}{zF} = \frac{kT}{6\pi\eta a} \quad \text{so} \quad a = \frac{zFk}{6\pi\eta u R} = \frac{ze}{6\pi\eta u}$$
$$a = \frac{(1)\times(1.602\times 10^{-19}\,\mathrm{C})}{6\pi(0.93\times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}})\times(1.1\times 10^{-8}\,\mathrm{m^2\,V^{-1}\,s^{-1}})} = 8.3\times 10^{-10}\,\mathrm{m} = \boxed{830\,\mathrm{pm}}$$

Solutions to theoretical problems

P24.25 Write the mean velocity initially as a; then in the emerging beam $\langle v_x\rangle = K\int_0^a v_x f(v_x)\,\mathrm{d}v_x$ where K is a constant which ensures that the distribution in the emergent beam is also normalized. That is, $1 = K\int_0^a f(v_x)\,\mathrm{d}v_x = K\left(\frac{m}{2\pi kT}\right)^{1/2}\int_0^a \mathrm{e}^{-mv_x^2/2kT}\,\mathrm{d}v_x$

This integral cannot be evaluated analytically but it can be related to the error function by defining

$$x^2 = \frac{mv_x^2}{2kT}$$

which gives $\mathrm{d}v_x = \left(\frac{2kT}{m}\right)^{1/2}\mathrm{d}x$. Then

$$1 = K\left(\frac{m}{2\pi kT}\right)^{1/2}\left(\frac{2kT}{m}\right)^{1/2}\int_0^b \mathrm{e}^{-x^2}\mathrm{d}x \quad [b = (m/2kT)^{1/2}\times a]$$
$$= \frac{K}{\pi^{1/2}}\int_0^b \mathrm{e}^{-x^2}\mathrm{d}x = \tfrac{1}{2}K\,\mathrm{erf}(b)$$

where erf (z) is the error function [Table 12.2]: $\mathrm{erf}(z) = \frac{2}{\pi^{1/2}}\int_0^z \mathrm{e}^{-x^2}\mathrm{d}x$

Therefore, $K = \frac{2}{\mathrm{erf}(b)}$

The mean velocity of the emerging beam is

$$\langle v_x\rangle = K\left(\frac{m}{2\pi kT}\right)^{1/2}\int_0^a v_x\mathrm{e}^{-mv_x^2/2kT}\mathrm{d}v_x = K\left(\frac{m}{2\pi kT}\right)^{1/2}\left(\frac{-kT}{m}\right)\int_0^a \frac{\mathrm{d}}{\mathrm{d}v_x}(\mathrm{e}^{-mv_x^2/2kT}\mathrm{d}v_x$$

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

Now use $a = \langle v_x \rangle_{\text{initial}} = \left(\frac{2kT}{m\pi}\right)^{1/2}$

This expression for the average magnitude of the one-dimensional velocity in the x direction may be obtained from

$$\langle v_x \rangle = 2\int_0^\infty v_x f(v_x)\mathrm{d}v_x = 2\int_0^\infty v_x\left(\frac{m}{2\pi kT}\right)^{1/2}\mathrm{e}^{-mv_x^2/2kT}\mathrm{d}v_x$$

$$= \left(\frac{m}{2\pi kT}\right)^{1/2}\left(\frac{2kT}{m}\right) = \left(\frac{2kT}{m\pi}\right)^{1/2}$$

It may also be obtained very quickly by setting $a = \infty$ in the expression for $\langle v_x \rangle$ in the emergent beam with $\mathrm{erf}(b) = \mathrm{erf}(\infty) = 1$.

Substituting $a = \left(\frac{2kT}{m\pi}\right)^{1/2}$ into $\langle v_x \rangle$ in the emergent beam $\mathrm{e}^{-ma^2/2kT} = \mathrm{e}^{-1/\pi}$ and $\mathrm{erf}(b) = \mathrm{erf}\left(\frac{1}{\pi^{1/2}}\right)$

Therefore, $\langle v_x \rangle = \left(\frac{2kT}{m\pi}\right)^{1/2} \times \frac{1 - \mathrm{e}^{-1/\pi}}{\mathrm{erf}\left(\frac{1}{\pi^{1/2}}\right)}$

From tables of the error function (expanded version of Table 12.2), or from readily available software, or by interpolating Table 12.2.

$$\mathrm{erf}\left(\frac{1}{\pi^{1/2}}\right) = \mathrm{erf}(0.56) = 0.57 \text{ and } \mathrm{e}^{-1/\pi} = 0.73$$

Therefore, $\langle v_x \rangle = \boxed{0.47\langle v_x \rangle_{\text{initial}}}$

P24.27 The most probable speed, c^*, was evaluated in Problem 24.23 and is

$$c^* = v(\text{most probable}) = \left(\frac{2kT}{m}\right)^{1/2}$$

Consider a range of speeds Δv around c^* and nc^*, then with $v = c^*$

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

Therefore, $\frac{f(3c^*)}{f(c^*)} = 9 \times \mathrm{e}^{-8} = \boxed{3.02 \times 10^{-3}}$ $\frac{f(4c^*)}{f(c^*)} = 16 \times \mathrm{e}^{-15} = \boxed{4.9 \times 10^{-6}}$

P24.28 The current I_j carried by an ion j is proportional to its concentration c_j, mobility u_j, and charge number $|z_j|$. [*Justification* 24.9] Therefore

$$I_j = Ac_ju_jz_j$$

where A is a constant. The total current passing through a solution is

$$I = \sum_j I_j = A\sum_j c_ju_jz_j$$

The transport number of the ion j is therefore

$$t_j = \frac{I_j}{I} = \frac{Ac_j u_j z_j}{A\sum_j c_j u_j z_j} = \frac{c_j u_j z_j}{\sum_j c_j u_j z_j}$$

If there are two cations in the mixture

$$\frac{t'}{t''} = \boxed{\frac{c'u'z'}{c''u''z''}} = \frac{c'u'}{c''u''} \quad \text{if } z' = z''$$

P24.29 $$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}[24.84] \quad \text{with } c = \frac{n_0 \mathrm{e}^{-x^2/4Dt}}{A(\pi Dt)^{1/2}}[24.88]$$

or $c = \dfrac{a}{t^{1/2}}\mathrm{e}^{-bx^2/t}$

then $\dfrac{\partial c}{\partial t} = -\left(\dfrac{1}{2}\right) \times \left(\dfrac{a}{t^{3/2}}\right)\mathrm{e}^{-bx^2/t} + \left(\dfrac{a}{t^{1/2}}\right) \times \left(\dfrac{bx^2}{t^2}\right)\mathrm{e}^{-bx^2/t} = -\dfrac{c}{2t} + \dfrac{bx^2}{t^2}c$

$$\frac{\partial c}{\partial x} = \left(\frac{a}{t^{1/2}}\right) \times \left(\frac{-2bx}{t}\right)\mathrm{e}^{-bx^2/t}$$

$$\begin{aligned}\frac{\partial^2 c}{\partial x^2} &= -\left(\frac{2b}{t}\right) \times \left(\frac{a}{t^{1/2}}\right)\mathrm{e}^{-bx^2/t} + \left(\frac{a}{t^{1/2}}\right) \times \left(\frac{2bx}{t}\right)^2 \mathrm{e}^{-bx^2/t} = -\left(\frac{2b}{t}\right)c + \left(\frac{2bx}{t}\right)^2 c \\ &= -\left(\frac{1}{2Dt}\right)c + \left(\frac{bx^2}{Dt^2}\right)c \\ &= \frac{1}{D}\frac{\partial c}{\partial t} \text{ as required}\end{aligned}$$

Initially the material is concentrated at $x = 0$. Note that $c = 0$ for $x > 0$ when $t = 0$ on account of the very strong exponential factor ($\mathrm{e}^{-bx^2/t} \to 0$ more strongly than $\dfrac{1}{t^{1/2}} \to \infty$). When $x = 0$, $\mathrm{e}^{-x^2/4Dt} = 1$. We confirm the correct behaviour by noting that $\langle x \rangle = 0$ and $\langle x^2 \rangle = 0$ at $t = 0$ [24.90], and so all the material must be at $x = 0$ at $t = 0$.

P24.31 Draw up the following table based on the third and last equations of *Justification* 24.12

N	4	6	8	10	20
$P(6\lambda)_{\text{Exact}}$	0	0.016	0.0313	0.0439	0.0739
$P(6\lambda)_{\text{Approx.}}$	0.004	0.162	0.0297	0.0417	0.0725

N	30	40	60	100
$P(6\lambda)_{\text{Exact}}$	0.0806	0.0807	0.0763	0.0666
$P(6\lambda)_{\text{Approx.}}$	0.0799	0.0804	0.0763	0.0666

The points are plotted in Fig. 24.1.

The discrepancy is less than 0.1 per cent when $\boxed{N > 60}$

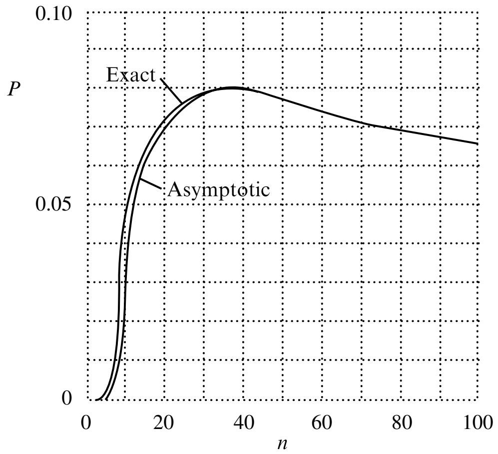


Figure 24.1

Solutions to applications

P24.33 The work required for a mass, m, to go from a distance r from the centre of a planet of mass m' to infinity is

$$w = \int_r^\infty F\,\mathrm{d}r$$

where F is the force of gravity and is given by Newton's law of universal gravitation, which is

$$F = \frac{Gmm'}{r^2}$$

G is the gravitational constant (not to be confused with g). Then

$$w' = \int_r^\infty \frac{Gmm'}{r^2}\,\mathrm{d}r = \frac{Gmm'}{r}$$

Since according to Newton's second law of motion, $F = mg$, we may make the identification

$$g = \frac{Gm'}{r^2}$$

Thus, $w = grm$. This is the kinetic energy that the particle must have in order to escape the planet's gravitational attraction at a distance r from the planet's centre; hence $w = \frac{1}{2}mv^2 = mgr$

$$v_\mathrm{e} = (2g\,R_\mathrm{p})^{1/2} \quad [R_\mathrm{p} = \text{radius of planet}]$$

which is the escape velocity.

(a) $v_\mathrm{e} = [(2) \times (9.81\,\mathrm{m\,s^{-2}}) \times (6.37 \times 10^6\,\mathrm{m})]^{1/2} = \boxed{11.2\,\mathrm{km\,s^{-1}}}$

(b) $g(\text{Mars}) = \dfrac{m(\text{Mars})}{m(\text{Earth})} \times \dfrac{R(\text{Earth})^2}{R(\text{Mars})^2} \times g(\text{Earth}) = (0.108) \times \left(\dfrac{6.37}{3.38}\right)^2 \times (9.81\,\mathrm{m\,s^{-2}})$

$$= 3.76\,\mathrm{m\,s^{-2}}$$

Hence, $v_\mathrm{e} = [(2) \times (3.76\,\mathrm{m\,s^{-2}}) \times (3.38 \times 10^6\,\mathrm{m})]^{1/2} = \boxed{5.0\,\mathrm{km\,s^{-1}}}$

Since $\bar{c} = \left(\dfrac{8RT}{\pi M}\right)^{1/2}$, $T = \dfrac{\pi M \bar{c}^2}{8R}$

and we can draw up the following table

$10^{-3}\,T/\mathrm{K}$	H_2	He	O_2	
Earth	11.9	23.7	190	$[\bar{c} = 11.2\,\mathrm{km\,s^{-1}}]$
Mars	2.4	4.8	38	$[\bar{c} = 5.0\,\mathrm{km\,s^{-1}}]$

In order to calculate the proportion of molecules that have speeds exceeding the escape velocity, v_e, we must integrate the Maxwell distribution [24.4] from v_e to infinity.

$$P = \int_{v_\mathrm{e}}^{\infty} f(v)\mathrm{d}v = \int_{v_\mathrm{e}}^{\infty} 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \mathrm{e}^{-mv^2/2kT}\mathrm{d}v \left[\frac{M}{R} = \frac{m}{k}\right]$$

This integral cannot be evaluated analytically and must be expressed in terms of the error function. We proceed as follows.

Defining $\beta = \dfrac{m}{2kT}$ and $y^2 = \beta v^2$ gives $v = \beta^{-1/2}y$, $v^2 = \beta^{-1}y^2$, $v_\mathrm{e} = \beta^{-1/2}y_\mathrm{e}$,

$$\begin{aligned} y_\mathrm{e} &= \beta^{1/2}v_\mathrm{e}, \quad \text{and} \quad \mathrm{d}v = \beta^{-1/2}\mathrm{d}y \\ P &= 4\pi\left(\frac{\beta}{\pi}\right)^{3/2}\beta^{-1}\beta^{-1/2}\int_{\beta^{1/2}v_\mathrm{e}}^{\infty} y^2\mathrm{e}^{-y^2}\mathrm{d}y = \frac{4}{\pi^{1/2}}\int_{\beta^{1/2}v_\mathrm{e}}^{\infty} y^2\mathrm{e}^{-y^2}\mathrm{d}y \\ &= \frac{4}{\pi^{1/2}}\left[\int_0^{\infty} y^2\mathrm{e}^{-y^2}\mathrm{d}y - \int_0^{\beta^{1/2}v_\mathrm{e}} y^2\mathrm{e}^{-y^2}\mathrm{d}y\right] \end{aligned}$$

The first integral can be evaluated analytically; the second cannot.

$$\int_0^{\infty} y^2\mathrm{e}^{-y^2}\mathrm{d}y = \frac{\pi^{1/2}}{4}, \text{ hence}$$

$$P = 1 - \frac{2}{\pi^{1/2}}\int_0^{\beta^{1/2}v_\mathrm{e}} y\mathrm{e}^{-y^2}(2y\,\mathrm{d}y) = 1 - \frac{2}{\pi^{1/2}}\int_0^{\beta^{1/2}v_\mathrm{e}} y\,\mathrm{d}(-\mathrm{e}^{-y^2})$$

This integral may be evaluated by parts

$$P = 1 - \frac{2}{\pi^{1/2}}\left[y(-\mathrm{e}^{-y^2})\Big|_0^{\beta^{1/2}v_\mathrm{e}} - \int_0^{\beta^{1/2}v_\mathrm{e}}(-\mathrm{e}^{-y^2})\,\mathrm{d}y\right]$$

$$\begin{aligned} P &= 1 + 2\left(\frac{\beta}{\pi}\right)^{1/2} v_\mathrm{e}\mathrm{e}^{-\beta v_\mathrm{e}^2} - \frac{2}{\pi^{1/2}}\int_0^{\beta^{1/2}v_\mathrm{e}}\mathrm{e}^{-y^2}\mathrm{d}y = 1 + 2\left(\frac{\beta}{\pi}\right)^{1/2} v_\mathrm{e}\mathrm{e}^{-\beta v_\mathrm{e}^2} - \mathrm{erf}(\beta^{1/2}v_\mathrm{e}) \\ &= \mathrm{erfc}(\beta^{1/2}v_\mathrm{e}) + 2\left(\frac{\beta}{\pi}\right)^{1/2} v_\mathrm{e}\mathrm{e}^{-\beta v_\mathrm{e}^2} \quad [\mathrm{erfc}(z) = 1 - \mathrm{erf}(z)] \end{aligned}$$

From $\beta = \dfrac{m}{2kT} = \dfrac{M}{2RT}$ and $v_\mathrm{e} = (2gR_\mathrm{p})^{1/2}$

$$\beta^{1/2}v_\mathrm{e} = \left(\frac{MgR_\mathrm{p}}{RT}\right)^{1/2}$$

For H_2 on Earth at 240 K

$$\beta^{1/2}v_\mathrm{e} = \left(\frac{(0.002016\,\mathrm{kg\,mol^{-1}}) \times (9.807\,\mathrm{m\,s^{-2}}) \times (6.37 \times 10^{6}\,\mathrm{m})}{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (240\,\mathrm{K})}\right)^{1/2} = 7.94$$

$$P = \mathrm{erfc}(7.94) + 2\left(\frac{7.94}{\pi^{1/2}}\right)e^{-(7.94)^2} = (2.9 \times 10^{-29}) + (3.7 \times 10^{-27}) = \boxed{3.7 \times 10^{-27}}$$

at 1500 K

$$\beta^{1/2}v_\mathrm{e} = \left(\frac{(0.002016\,\mathrm{kg\,mol^{-1}}) \times (9.807\,\mathrm{m\,s^{-2}}) \times (6.37 \times 10^{6}\,\mathrm{m})}{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (1500\,\mathrm{K})}\right)^{1/2} = 3.18$$

$$P = \mathrm{erfc}(3.18) + 2\left(\frac{3.18}{\pi^{1/2}}\right)e^{-(3.18)^2} = (6.9 \times 10^{-6}) + (1.4\overline{6} \times 10^{-4}) = \boxed{1.5 \times 10^{-4}}$$

For H_2 on Mars at 240 K

$$\beta^{1/2}v_\mathrm{e} = \left(\frac{(0.002016\,\mathrm{kg\,mol^{-1}}) \times (3.76\,\mathrm{m\,s^{-2}}) \times (3.38 \times 10^{6}\,\mathrm{m})}{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (240\,\mathrm{K})}\right)^{1/2} = 3.58$$

$$P = \mathrm{erfc}(3.58) + 2\left(\frac{3.58}{\pi^{1/2}}\right)\mathrm{e}^{-(3.58)^2} = (4.13 \times 10^{-7}) + (1.1\overline{0} \times 10^{-5}) = \boxed{1.1 \times 10^{-5}}$$

at 1500 K, $\beta^{1/2}v_\mathrm{e} = 1.43$

$$P = \mathrm{erfc}(1.43) + (1.128) \times (1.43) \times \mathrm{e}^{-(1.43)^2} = 0.0431 + 0.20\overline{9} = \boxed{0.25}$$

For He on Earth at 240 K

$$\beta^{1/2}v_\mathrm{e} = \left(\frac{(0.004003\,\mathrm{kg\,mol^{-1}}) \times (9.807\,\mathrm{m\,s^{-2}}) \times (6.37 \times 10^{6}\,\mathrm{m})}{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (240\,\mathrm{K})}\right)^{1/2} = 11.1\overline{9}$$

$$P = \mathrm{erfc}(11.2) + (1.128) \times (11.2) \times \mathrm{e}^{-(11.2)^2} = 0 + (4 \times 10^{-54}) = \boxed{4 \times 10^{-54}}$$

at 1500 K, $\beta^{1/2}v_\mathrm{e} = 4.48$

$$P = \mathrm{erfc}(4.48) + (1.128) \times (4.48) \times \mathrm{e}^{-(4.48)^2} = (2.36 \times 10^{-10}) + (9.7\overline{1} \times 10^{-9})$$

$$= \boxed{1.0 \times 10^{-8}}$$

For He on Mars at 240 K

$$\beta^{1/2}v_\mathrm{e} = \left(\frac{(0.004003\,\mathrm{kg\,mol^{-1}}) \times (3.76\,\mathrm{m\,s^{-2}}) \times (3.38 \times 10^{6}\,\mathrm{m})}{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (240\,\mathrm{K})}\right)^{1/2} = 5.05$$

$$P = \mathrm{erfc}(5.05) + (1.128) \times (5.05) \times \mathrm{e}^{-(5.05)^2} = (9.21 \times 10^{-13}) + (4.7\overline{9} \times 10^{-11})$$

$$= \boxed{4.9 \times 10^{-11}}$$

at 1500 K, $\beta^{1/2}v_\mathrm{e} = 2.02$

$$P = \mathrm{erfc}(2.02) + (1.128) \times (2.02) \times \mathrm{e}^{-(2.02)^2} = (4.28 \times 10^{-3}) + (0.040\overline{1}) = \boxed{0.044}$$

For O_2 on Earth it is clear that $P \approx 0$ at both temperatures.

For O_2 on Mars at 240 K, $\beta^{1/2}v_e = 14.3$

$$P = \text{erfc}(14.3) + (1.128) \times (14.3) \times e^{-(14.3)^2} = 0 + (2.5 \times 10^{-88}) = \boxed{2.5 \times 10^{-88}} \approx 0$$

at 1500 K, $\beta^{1/2}v_e = 5.71$

$$P = \text{erfc}(5.71) + (1.128) \times (5.71) \times e^{-(5.71)^2} = (6.7 \times 10^{-6}) + (4.46 \times 10^{-14})$$
$$= \boxed{4.5 \times 10^{-14}}$$

Based on these numbers alone, it would appear that H_2 and He would be depleted from the atmosphere of both Earth and Mars only after many (millions?) years; that the rate on Mars, though still slow, would be many orders of magnitude larger than on Earth; that O_2 would be retained on Earth indefinitely; and that the rate of O_2 depletion on Mars would be very slow (billions of years?), though not totally negligible. The temperatures of both planets may have been higher in past times than they are now.

In the analysis of the data, we must remember that the proportions, P, are not rates of depletion, though the rates should be roughly proportional to P.

The results of the calculations are summarized in the following table

	240 K			1500 K		
	H_2	He	O_2	H_2	He	O_2
P(Earth)	3.7×10^{-27}	4×10^{-54}	0	1.5×10^{-4}	1.0×10^{-8}	0
P(Mars)	1.1×10^{-5}	4.9×10^{-11}	0	0.25	0.044	4.5×10^{-14}

25 The rates of chemical reactions

Solutions to exercises

Discussion questions

E25.1(b) The determination of a rate law is simplified by the isolation method in which the concentrations of all the reactants except one are in large excess. If B is in large excess, for example, then to a good approximation its concentration is constant throughout the reaction. Although the true rate law might be $\nu = k[A][B]$, we can approximate [B] by $[B]_0$ and write

$$\nu = k'[A] \quad k' = k[B]_0 \ [25.8]$$

which has the form of a first-order rate law. Because the true rate law has been forced into first-order form by assuming that the concentration of B is constant, it is called a pseudofirst-order rate law. The dependence of the rate on the concentration of each of the reactants may be found by isolating them in turn (by having all the other substances present in large excess), and so constructing a picture of the overall rate law.

In the method of initial rates, which is often used in conjunction with the isolation method, the rate is measured at the beginning of the reaction for several different initial concentrations of reactants. We shall suppose that the rate law for a reaction with A isolated is $\nu = k[A]^a$; then its initial rate, ν_0 is given by the initial values of the concentration of A, and we write $\nu_0 = k[A]_0^a$. Taking logarithms gives:

$$\log\ \nu_0 = \log\ k + a\log[A]_0 \ [25.9]$$

For a series of initial concentrations, a plot of the logarithms of the initial rates against the logarithms of the initial concentrations of A should be a straight lime with slope a.

The method of initial rates might not reveal the full rate law, for the products may participate in the reaction and affect the rate. For example, products participate in the synthesis of HBr, where the full rate law depends on the concentration of HBr. To avoid this difficulty, the rate law should be fitted to the data throughout the reaction. The fitting may be done, in simple cases at least, by using a proposed rate law to predict the concentration of any component at any time, and comparing it with the data.

Because rate laws are differential equations, we must integrate them if we want to find the concentrations as a function of time. Even the most complex rate laws may be integrated numerically. However, in a number of simple cases analytical solutions are easily obtained, and prove to be very useful. These are summarized in Table 25.3. In order to determine the rate law, one plots the right hand side of the integrated rate laws shown in the table against t in order to see which of them results in a straight line through the origin. The one that does is the correct rate law.

E25.2(b) The rate-determining step is not just the slowest step: it must be slow *and* be a crucial gateway for the formation of products. If a faster reaction can also lead to products, then the slowest step is irrelevant because the slow reaction can then be side-stepped. The rate-determining step is like a slow ferry crossing between two fast highways: the overall rate at which traffic can reach its destination is determined by the rate at which it can make the ferry crossing.

If the first step in a mechanism is the slowest step with the highest activation energy, then it is rate-determining, and the overall reaction rate is equal to the rate of the first step because all subsequent steps are so fast that once the first intermediate is formed it results immediately in the formation of products. Once over the initial barrier, the intermediates cascade into products. However, a rate-determining step may also stem from the low concentration of a crucial reactant or catalyst and need not correspond to the step with highest activation barrier. A rate-determining step arising from the low activity of a crucial enzyme can sometimes be identified by determining whether or not the reactants and products for that step are in equilibrium: if the reaction is not at equilibrium it suggests that the step may be slow enough to be rate-determining.

E25.3(b) The parameter A, which corresponds to the intercept of the line at $1/T = 0$ (at infinite temperature), is called the pre-exponential factor or the frequency factor. The parameter E_a, which is obtained from the slope of the line $(-E_a/R)$, is called the activation energy. Collectively, the two quantities are called the Arrhenius parameters.

The temperature dependence of some reactions is not Arrhenius-like, in the sense that a straight line is not obtained when $\ln k$ is plotted against $1/T$. However, it is still possible to define an activation energy as

$$E_a = RT^2\left(\frac{\mathrm{d}\ln k}{\mathrm{d}T}\right)$$

This definition reduces to the earlier one (as the slope of a straight line) for a temperature-independent activation energy. However, this latter definition is more general, because it allows E_a to be obtained from the slope (at the temperature of interest) of a plot of $\ln k$ against $1/T$ even if the Arrhenius plot is not a straight line. Non-Arrhenius behaviour is sometimes a sign that quantum mechanical tunnelling is playing a significant role in the reaction.

E25.4(b) The expression $k = k_a k_b\,[\mathrm{A}]/(k_b + k'_a[\mathrm{A}])$ for the effective rate constant of a unimolecular reaction $\mathrm{A} \rightarrow \mathrm{P}$ is based on the validity of the assumption of the existence of the pre-equilibrium $\mathrm{A} + \mathrm{A} \rightleftarrows \mathrm{A}^* + \mathrm{A}(k_a, k'_a)$. This can be a good assumption if both k_a and k'_a are much larger than k_b. The expression for the effective rate-constant, k, can be rearranged to

$$\frac{1}{k} = \frac{k'_a}{k_a k_b} + \frac{1}{k_a[\mathrm{A}]}$$

Hence, a test of the theory is to plot $1/k$ against 1/[A], and to expect a straight line. Another test is based on the prediction from the Lindemann–Hinshelwood mechanism that as the concentration (and therefore the partial pressure) of A is reduced, the reaction should switch to overall second order kinetics. Whereas the mechanism agrees in general with the switch in order of unimolecular reactions, it does not agree in detail. A typical graph of $1/k$ against 1/[A] has a pronounced curvature, corresponding to a larger value of k (a smaller value of $1/k$) at high pressures (low 1/[A]) than would be expected by extrapolation of the reasonably linear low pressure (high 1/[A]) data.

Numerical exercises

E25.5(b) Rate of reaction $= -\dfrac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -\dfrac{1}{3}\dfrac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = \dfrac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = \dfrac{1}{2}\dfrac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = 1.00\,\mathrm{mol\,L^{-1}\,s^{-1}}$ so

Rate of consumption of A = $\boxed{1.0\,\mathrm{mol\,L^{-1}\,s^{-1}}}$

Rate of consumption of B = $\boxed{3.0\,\mathrm{mol\,L^{-1}\,s^{-1}}}$

Rate of formation of C = $\boxed{1.0\,\mathrm{mol\,L^{-1}\,s^{-1}}}$

Rate of formation of D = $\boxed{2.0\,\mathrm{mol\,L^{-1}\,s^{-1}}}$

E25.6(b) Rate of consumption of B $= -\dfrac{d[B]}{dt} = 1.00\,\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}$.

$$\text{Rate of reaction} = -\frac{1}{3}\frac{d[B]}{dt} = \boxed{0.33\,\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}} = \frac{d[C]}{dt} = \frac{1}{2}\frac{d[D]}{dt} = -\frac{d[A]}{dt}$$

Rate of formation of C $= \boxed{0.33\,\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}}$

Rate of formation of D $= \boxed{0.66\,\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}}$

Rate of consumption of A $= \boxed{0.33\,\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}}$

E25.7(b) The dimensions of k are

$$\frac{\text{dim of } v}{(\text{dim of [A]}) \times (\text{dim of [B]})^2} = \frac{\text{amount} \times \text{length}^{-3} \times \text{time}^{-1}}{(\text{amount} \times \text{length}^{-3})^3}$$
$$= \text{length}^6 \times \text{amount}^{-2} \times \text{time}^{-1}$$

In mol, L, s units, the units of k are $\boxed{\text{L}^2\,\text{mol}^{-2}\,\text{s}^{-1}}$

(a) $v = -\dfrac{d[A]}{dt} = k[A][B]^2$ so $\boxed{\dfrac{d[A]}{dt} = -k[A][B]^2}$

(b) $v = \dfrac{d[C]}{dt}$ so $\boxed{\dfrac{d[C]}{dt} = k[A][B]^2}$

E25.8(b) The dimensions of k are

$$\frac{\text{dim of } v}{\text{dim of [A]} \times \text{dim of [B]} \times (\text{dim of [C] })^{-1}} = \frac{\text{amount} \times \text{length}^{-3} \times \text{time}^{-1}}{(\text{amount} \times \text{length}^{-3})} = \text{time}^{-1}$$

The units of k are $\boxed{\text{s}^{-1}}$

$$v = \frac{d[C]}{dt} = \boxed{k[A][B][C]^{-1}}$$

E25.9(b) The rate law is

$$v = kp^a = kp_0(1-f)^a$$

where a is the reaction order, and f the fraction reacted (so that $1-f$ is the fraction remaining). Thus

$$\frac{v_1}{v_2} = \frac{kp_0(1-f_1)^a}{kp_0(1-f_2)^a} = \left(\frac{1-f_1}{1-f_2}\right)^a \quad \text{and} \quad a = \frac{\ln(v_1/v_2)}{\ln\left(\frac{1-f_1}{1-f_2}\right)} = \frac{\ln(9.71/7.67)}{\ln\left(\frac{1-0.100}{1-0.200}\right)} = \boxed{2.00}$$

E25.10(b) The half-life changes with concentration, so we know the reaction order is not 1. That the half-life increases with decreasing concentration indicates a reaction order <1. Inspection of the data shows the half-life roughly proportional to concentration, which would indicate a reaction order of 0 according to Table 25.3.

More quantitatively, if the reaction order is 0, then

$$t_{1/2} \propto p \quad \text{and} \quad \frac{t_{1/2}^{(1)}}{t_{1/2}^{(2)}} = \frac{p_1}{p_2}$$

We check to see if this relationship holds

$$\frac{t_{1/2}^{(1)}}{t_{1/2}^{(2)}} = \frac{340\,\text{s}}{178\,\text{s}} = 1.91 \quad \text{and} \quad \frac{p_1}{p_2} = \frac{55.5\,\text{kPa}}{28.9\,\text{kPa}} = 1.92$$

so the reaction order is $\boxed{0}$

E25.11(b) The rate law is

$$v = -\frac{1}{2}\frac{\text{d}[\text{A}]}{\text{d}t} = k[\text{A}]$$

The half-life formula in the text, however, is based on a rate constant for the rate of change of the reactant. That is, it would be accurate to say

$$t_{1/2} = \frac{\ln 2}{k'}$$

provided the k' here referred to a rate law

$$-\frac{\text{d}[\text{A}]}{\text{d}t} = k'[\text{A}] = 2k[\text{A}] \quad \text{so} \quad t_{1/2} = \frac{\ln 2}{2(2.78 \times 10^{-7}\,\text{s}^{-1})} = \boxed{1.80 \times 10^6\,\text{s}}$$

The concentration of our reactant (pressure in this case) is

$$[\text{A}] = [\text{A}]_0 \text{e}^{-2kt}$$

(a) Therefore, after 10 h, we have

$$[\text{A}] = (32.1\,\text{kPa}) \exp[-2 \times (2.78 \times 10^{-7}\,\text{s}^{-1}) \times (3.6 \times 10^4\,\text{s})] = \boxed{31.5\,\text{kPa}}$$

(b) and after 50 h, we have

$$[\text{A}] = (32.1\,\text{kPa}) \exp[-2 \times (2.78 \times 10^{-7}\,\text{s}^{-1}) \times (1.8 \times 10^5\,\text{s})] = \boxed{29.0\,\text{kPa}}$$

E25.12(b) From Table 25.3, we see that for A + 2B → P the integrated rate law is

$$kt = \frac{1}{[\text{B}]_0 - 2[\text{A}]_0} \ln\left[\frac{[\text{A}]_0([\text{B}]_0 - 2x)}{([\text{A}]_0 - x)[\text{B}]_0}\right]$$

(a) Substituting the data after solving for k

$$k = \frac{1}{(3.6 \times 10^3\,\text{s}) \times (0.080 - 2 \times 0.075) \times (\text{mol}\,\text{L}^{-1})} \times \ln\left[\frac{0.075 \times (0.080 - 0.060)}{(0.075 - 0.030) \times 0.080}\right]$$
$$= \boxed{3.4\overline{7} \times 10^{-3}\,\text{L}\,\text{mol}^{-1}\,\text{s}^{-1}}$$

(b) The half-life in terms of A is

$$t_{1/2}(\mathrm{A}) = \frac{1}{k([\mathrm{B}]_0 - 2[\mathrm{A}]_0)} \ln\left[\frac{[\mathrm{A}]_0\left([\mathrm{B}]_0 - \frac{2[\mathrm{A}]_0}{2}\right)}{\left(\frac{[\mathrm{A}]_0[\mathrm{B}]_0}{2}\right)}\right]$$

which reduces to

$$\begin{aligned} t_{1/2}(\mathrm{A}) &= \frac{1}{k([\mathrm{B}]_0 - 2[\mathrm{A}]_0)} \ln\left(2 - \frac{2[\mathrm{A}]_0}{[\mathrm{B}]_0}\right) \\ &= \frac{1}{(3.4\overline{7} \times 10^{-3}\,\mathrm{L\,mol^{-1}\,s^{-1}}) \times (-0.070\,\mathrm{mol\,L^{-1}})} \times \ln\left(2 - \frac{0.150}{0.080}\right) \\ &= 85\overline{61}\,\mathrm{s} = \boxed{2.4\,\mathrm{h}} \end{aligned}$$

The half-life in terms of B is

$$t_{1/2}(\mathrm{B}) = \frac{1}{k([\mathrm{B}]_0 - 2[\mathrm{A}]_0)} \ln\left[\frac{[\mathrm{A}]_0\left([\mathrm{B}]_0 - \frac{[\mathrm{B}]_0}{2}\right)}{\left([\mathrm{A}]_0 - \frac{[\mathrm{B}]_0}{4}\right)[\mathrm{B}]_0}\right]$$

which reduces to

$$\begin{aligned} t_{1/2}(\mathrm{B}) &= \frac{1}{k([\mathrm{B}]_0 - 2[\mathrm{A}]_0)} \ln\left(\frac{[\mathrm{A}]_0/2}{[\mathrm{A}]_0 - [\mathrm{B}]_0/4}\right) \\ &= \frac{1}{(3.4\overline{7} \times 10^{-3}\,\mathrm{L\,mol^{-1}\,s^{-1}}) \times (-0.070\,\mathrm{mol\,L^{-1}})} \times \ln\left(\frac{0.075/2}{0.075 - (0.080/4)}\right) \\ &= 15\overline{76}\,\mathrm{s} = \boxed{0.44\,\mathrm{h}} \end{aligned}$$

E25.13(b) The dimensions of a second-order rate constant are

$$\frac{\text{dim of } v}{(\text{dim of [A] })^2} = \frac{\text{amount} \times \text{length}^{-3} \times \text{time}^{-1}}{(\text{amount} \times \text{length}^{-3})^2} = \text{length}^3 \times \text{amount}^{-1} \times \text{time}^{-1}$$

In molecule, m, s units, the units of k are $\boxed{\mathrm{m^3\,molecule^{-1}\,s^{-1}}}$

The dimensions of a second-order rate constant in pressure units are

$$\frac{\text{dim of } v}{(\text{dim of } p)^2} = \frac{\text{pressure} \times \text{time}^{-1}}{(\text{pressure})^2} = \text{pressure}^{-1} \times \text{time}^{-1}$$

In SI units, the pressure unit is $\mathrm{N\,m^{-2}} = \mathrm{Pa}$, so the units of k are $\boxed{\mathrm{Pa^{-1}\,s^{-1}}}$

The dimensions of a third-order rate constant are

$$\frac{\text{dim of } v}{(\text{dim of [A]})^3} = \frac{\text{amount} \times \text{length}^{-3} \times \text{time}^{-1}}{(\text{amount} \times \text{length}^{-3})^3} = \text{length}^6 \times \text{amount}^{-2} \times \text{time}^{-1}$$

In molecule, m, s units, the units of k are $\boxed{\mathrm{m^6\,molecule^{-2}\,s^{-1}}}$

The dimensions of a third-order rate constant in pressure units are

$$\frac{\text{dim of } v}{(\text{dim of } p)^3} = \frac{\text{pressure} \times \text{time}^{-1}}{(\text{pressure})^3} = \text{pressure}^{-2} \times \text{time}^{-1}$$

In SI units, the pressure unit is $\mathrm{N\,m^{-2}} = \mathrm{Pa}$, so the units of k are $\boxed{\mathrm{Pa^{-2}\,s^{-1}}}$

E25.14(b) The integrated rate law is

$$kt = \frac{1}{[\mathrm{B}]_0 - 2[\mathrm{A}]_0} \ln \frac{[\mathrm{A}]_0([\mathrm{B}]_0 - 2[\mathrm{C}])}{([\mathrm{A}]_0 - [\mathrm{C}])[\mathrm{B}]_0}$$

Solving this for [C] yields

$$[\mathrm{C}] = \frac{[\mathrm{A}]_0[\mathrm{B}]_0\{\exp[kt([\mathrm{B}]_0 - 2[\mathrm{A}]_0)] - 1\}}{[\mathrm{B}]_0 \exp[kt([\mathrm{B}]_0 - 2[\mathrm{A}]_0)] - 2[\mathrm{A}]_0}$$

(a)

$$[\mathrm{C}]/(\mathrm{mol\,L^{-1}}) = \frac{(0.025) \times (0.150)}{(0.150) \times \exp[(0.21\,\mathrm{s^{-1}}) \times (10\,\mathrm{s}) \times (0.150 - 2 \times 0.025)] - 2(0.025)} \times \{\exp[(0.21\,\mathrm{s^{-1}}) \times (10\,\mathrm{s}) \times (0.150 - 2 \times 0.025)] - 1\}$$

$$[\mathrm{C}] = \boxed{6.5 \times 10^{-3}\,\mathrm{mol\,L^{-1}}}$$

(b)

$$[\mathrm{C}]/(\mathrm{mol\,L^{-1}}) = \frac{(0.025) \times (0.150)}{(0.150) \times \exp[(0.21\,\mathrm{s^{-1}}) \times (600\,\mathrm{s}) \times (0.150 - 2 \times 0.025)] - 2(0.025)} \times \{\exp[(0.21\,\mathrm{s^{-1}}) \times (600\,\mathrm{s}) \times (0.150 - 2 \times 0.025)] - 1\}$$

$$[\mathrm{C}] = \boxed{0.025\,\mathrm{mol\,L^{-1}}}$$

E25.15(b) The rate law is

$$v = -\frac{1}{2}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k[\mathrm{A}]^3$$

which integrates to

$$2kt = \frac{1}{2}\left(\frac{1}{[\mathrm{A}]^2} - \frac{1}{[\mathrm{A}]_0^2}\right) \quad \text{so} \quad t = \frac{1}{4k}\left(\frac{1}{[\mathrm{A}]^2} - \frac{1}{[\mathrm{A}]_0^2}\right)$$

$$t = \left(\frac{1}{4(3.50 \times 10^{-4}\,\mathrm{L^2\,mol^{-2}\,s^{-1}})}\right) \times \left(\frac{1}{(0.021\,\mathrm{mol\,L^{-1}})^2} - \frac{1}{(0.077\,\mathrm{mol\,L^{-1}})^2}\right)$$

$$= \boxed{1.5 \times 10^6\,\mathrm{s}}$$

E25.16(b) The rate constant is given by

$$k = A \exp\left(\frac{-E_\mathrm{a}}{RT}\right)$$

so at 30°C it is

$$1.70 \times 10^{-2}\,\mathrm{L\,mol^{-1}\,s^{-1}} = A \exp\left(\frac{-E_\mathrm{a}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times [(24 + 273)\,\mathrm{K}]}\right)$$

and at 50°C it is

$$2.01\times10^{-2}\,\mathrm{L\,mol^{-1}\,s^{-1}}=A\exp\left(\frac{-E_a}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times[(37+273)\,\mathrm{K}]}\right)$$

Dividing the two rate constants yields

$$\frac{1.70\times10^{-2}}{2.01\times10^{-2}}=\exp\left[\left(\frac{-E_a}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\right)\times\left(\frac{1}{297\,\mathrm{K}}-\frac{1}{310\,\mathrm{K}}\right)\right]$$

$$\text{so}\ \ln\left(\frac{1.70\times10^{-2}}{2.01\times10^{-2}}\right)=\left(\frac{-E_a}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\right)\times\left(\frac{1}{297\,\mathrm{K}}-\frac{1}{310\,\mathrm{K}}\right)$$

$$\text{and } E_a=-\left(\frac{1}{297\,\mathrm{K}}-\frac{1}{310\,\mathrm{K}}\right)^{-1}\ln\left(\frac{1.70\times10^{-2}}{2.01\times10^{-2}}\right)\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})$$

$$=9.9\times10^{3}\,\mathrm{J\,mol^{-1}}=\boxed{9.9\,\mathrm{kJ\,mol^{-1}}}$$

With the activation energy in hand, the prefactor can be computed from either rate constant value

$$A=k\exp\left(\frac{E_a}{RT}\right)=(1.70\times10^{-2}\,\mathrm{L\,mol^{-1}\,s^{-1}})\times\exp\left(\frac{9.9\times10^{3}\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(297\,\mathrm{K})}\right)$$

$$=\boxed{0.94\,\mathrm{L\,mol^{-1}\,s^{-1}}}$$

E25.17(b) **(a)** Assuming that the rate-determining step is the scission of a C—H bond, the ratio of rate constants for the tritiated versus protonated reactant should be

$$\frac{k_T}{k_H}=e^{-\lambda}\quad\text{where }\lambda=\frac{\hbar k_f^{1/2}}{2kT}\left(\frac{1}{\mu_{CH}^{1/2}}-\frac{1}{\mu_{CT}^{1/2}}\right)$$

The reduced masses will be roughly 1 u and 3 u respectively, for the protons and ^3H nuclei are far lighter than the rest of the molecule to which they are attached. So

$$\lambda=\frac{(1.0546\times10^{-34}\,\mathrm{J\,s})\times(450\,\mathrm{N\,m^{-1}})^{1/2}}{2\times(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}\times\left(\frac{1}{(1\,\mathrm{u})^{1/2}}-\frac{1}{(3\,\mathrm{u})^{1/2}}\right)\times(1.66\times10^{-27}\,\mathrm{kg\,u^{-1}})^{-1/2}$$

$$=2.8\quad\text{so}\quad\boxed{\frac{k_T}{k_H}=0.06\approx1/16}$$

(b) The analogous expression for ^{16}O and ^{18}O requires reduced masses for $C^{16}O$ and $C^{18}O$ bonds. These reduced masses could vary widely depending on the size of the whole molecule. I will use $^{12}C^{16}O$, for example

$$\mu_{16}=\frac{(16.0\,\mathrm{u})\times(12.0\,\mathrm{u})}{(16.0+12.0)\,\mathrm{u}}=6.86\,\mathrm{u}\quad\text{and}\quad\mu_{18}=\frac{(18.0\,\mathrm{u})\times(12.0\,\mathrm{u})}{(18.0+12.0)\,\mathrm{u}}=7.20\,\mathrm{u}$$

$$\lambda=\frac{(1.0546\times10^{-34}\,\mathrm{J\,s})\times(1750\,\mathrm{N\,m^{-1}})^{1/2}}{2\times(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}\times\left(\frac{1}{(6.86\,\mathrm{u})^{1/2}}-\frac{1}{(7.20\,\mathrm{u})^{1/2}}\right)\times(1.66\times10^{-27}\,\mathrm{kg\,u^{-1}})^{-1/2}$$

$$=0.12\quad\text{so}\quad\boxed{\frac{k_{18}}{k_{16}}=0.89}$$

E25.18(b) A reaction *n*th-order in A has the following rate law

$$-\frac{d[A]}{dt} = k[A]^n \quad \text{so} \quad \frac{d[A]}{[A]^n} = -k\,dt = [A]^{-n}\,d[A]$$

Integration yields

$$\frac{[A]^{1-n} - [A]_0^{1-n}}{1-n} = -kt$$

Let $t_{1/3}$ be the time at which $[A] = \frac{1}{3}[A]_0$, so

$$-kt_{1/3} = \frac{\left(\frac{1}{3}[A]_0\right)^{1-n} - [A]_0^{1-n}}{1-n} = \frac{[A]_0^{1-n}[\left(\frac{1}{3}\right)^{1-n} - 1]}{1-n}$$

and $t_{1/3} = \boxed{\dfrac{3^{n-1}-1}{k(n-1)}[A]_0^{1-n}}$

E25.19(b) The effective rate constant is related to the individual steps by

$$\frac{1}{k} = \frac{k'_a}{k_a k_b} + \frac{1}{k_a p} \quad \text{so} \quad \frac{1}{k_1} - \frac{1}{k_2} = \frac{1}{k_a}\left(\frac{1}{p_1} - \frac{1}{p_2}\right)$$

$$\begin{aligned} k_a &= \left(\frac{1}{p_1} - \frac{1}{p_2}\right)\left(\frac{1}{k_1} - \frac{1}{k_2}\right)^{-1} \\ &= \left(\frac{1}{1.09 \times 10^3\,\text{Pa}} - \frac{1}{25\,\text{Pa}}\right) \times \left(\frac{1}{1.7 \times 10^{-3}\,\text{s}^{-1}} - \frac{1}{2.2 \times 10^{-4}\,\text{s}^{-1}}\right)^{-1} \\ &= \boxed{9.9 \times 10^{-6}\,\text{s}^{-1}\,\text{Pa}^{-1}} \end{aligned}$$

E25.20(b) The equilibrium constant of the reaction is

$$K = \frac{k_f}{k_r} \quad \text{so} \quad k_f = Kk_r$$

The relaxation time for the temperature jump is

$$\tau = \{k_f + k_r([B] + [C])\}^{-1} \quad \text{so} \quad k_f = \tau^{-1} - k_r([B] + [C])$$

Setting these two expressions for k_f equal yields

$$Kk_r = \tau^{-1} - k_r([B] + [C]) \quad \text{so} \quad k_r = \frac{1}{\tau(K + [B] + [C])}$$

$$\begin{aligned} k_r &= \frac{1}{(3.0 \times 10^{-6}\,\text{s}) \times (2.0 \times 10^{-16} + 2.0 \times 10^{-4} + 2.0 \times 10^{-4})\,\text{mol}\,\text{L}^{-1}} \\ &= \boxed{8.3 \times 10^8\,\text{L}\,\text{mol}^{-1}\,\text{s}^{-1}} \end{aligned}$$

and $k_f = (2.0 \times 10^{-16}\,\text{mol}\,\text{L}^{-1}) \times (8.3 \times 10^8\,\text{L}\,\text{mol}^{-1}\,\text{s}^{-1}) = \boxed{1.7 \times 10^{-7}\,\text{s}^{-1}}$

Solutions to problems

Solutions to numerical problems

P25.2 The procedure is that described in solution to Problem 25.1. Visual inspection of the data seems to indicate that the half-life is roughly independent of the concentration. Therefore, we first try to fit the data to eqn 10*b*. As in Example 25.3 we plot $\ln\left(\frac{[A]}{[A]_0}\right)$ against time to see if a straight line is obtained. We draw up the following table ($A = (CH_3)_3CBr$)

t/h	0	3.15	6.20	10.00	18.30	30.80
$[A]/(10^{-2}\,\mathrm{mol\,L^{-1}})$	10.39	8.96	7.76	6.39	3.53	2.07
$\frac{[A]}{[A]_0}$	1	0.862	0.747	0.615	0.340	0.199
$\ln\left(\frac{[A]}{[A]_0}\right)$	0	−0.148	−0.292	−0.486	−1.080	−1.613
$\left(\frac{1}{[A]}\right)/(\mathrm{L\,mol^{-1}})$	9.62	11.16	12.89	15.65	28.3	48.3

The data are plotted in Fig. 25.1. The fit to a straight line is only fair. The least squares value of k is $0.0542\,\mathrm{h^{-1}} = \boxed{1.51 \times 10^{-5}\,\mathrm{s^{-1}}}$ with a correlation coefficient of 0.996. If we try to fit the data to eqn 12*b*, which corresponds to a second-order reaction, the fit is not as good. The correlation coefficient is 0.985. Thus we conclude that the reaction is most likely $\boxed{\text{first-order}}$. A more complex order, which is neither first nor second, is possible, but not likely. At 43.8 h

$$\ln\left(\frac{[A]}{[A]_0}\right) = -2.359$$

$$[A] = \boxed{9.82 \times 10^{-3}\,\mathrm{mol\,L^{-1}}}$$

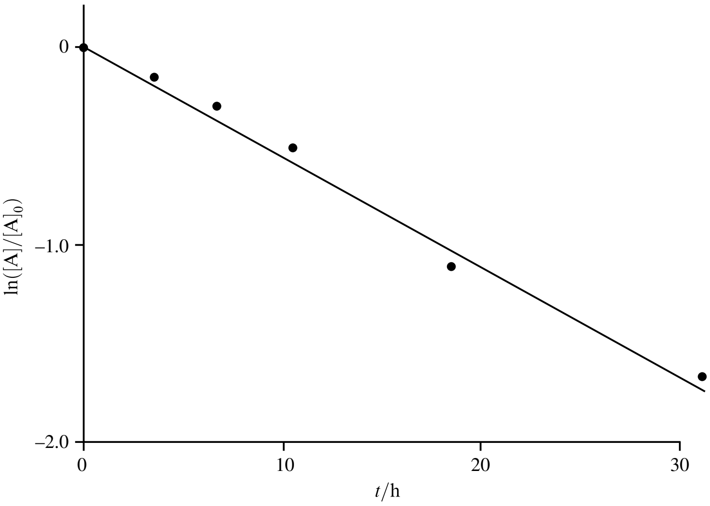


Figure 25.1

P25.4 Examination of the data shows that the half-life remains constant at about 2 minutes. Therefore, the reaction is $\boxed{\text{first-order}}$. This can be confirmed by fitting any two pairs of data to the integrated first-order rate law, solving for k from each pair, and checking to see that they are the same to within experimental error.

$$\ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right) = -kt \quad [10b, \mathrm{A} = \mathrm{N_2O_5}]$$

Solving for k,

$$k = \frac{\ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]}\right)}{t}$$

at $t = 1.00$ min, $[\mathrm{A}] = 0.705\,\mathrm{mol\,L^{-1}}$

$$k = \frac{\ln\left(\frac{1.000}{0.705}\right)}{1.00\,\mathrm{min}} = 0.350\,\mathrm{min^{-1}} = 5.83 \times 10^{-3}\,\mathrm{s^{-1}}$$

at $t = 3.00\,\mathrm{min}$, $[\mathrm{A}] = 0.399\,\mathrm{mol\,L^{-1}}$

$$k = \frac{\ln\left(\frac{1.000}{0.349}\right)}{3.00\,\mathrm{min}} = 0.351\,\mathrm{min^{-1}} = 5.85 \times 10^{-3}\,\mathrm{s^{-1}}$$

Values of k may be determined in a similar manner at all other times. The average value of k obtained is $\boxed{5.84 \times 10^{-3}\,\mathrm{s^{-1}}}$. The constancy of k, which varies only between 5.83 and $5.85 \times 10^{-3}\,\mathrm{s^{-1}}$ confirms that the reaction is $\boxed{\text{first-order}}$. A linear regression of ln[A] against t yields the same result.

$$t_{1/2} = \frac{\ln 2}{k}[11] = \frac{0.693}{5.84 \times 10^{-3}\,\mathrm{s^{-1}}} = 118.\overline{7}\,\mathrm{s} = \boxed{1.98\,\mathrm{min}}$$

P25.7 $[\mathrm{B}]_0 = \frac{1}{2}[\mathrm{A}]_0$; hence $[\mathrm{A}]_0 = 0.624\,\mathrm{mol\,L^{-1}}$. For the reaction $2\mathrm{A} \rightarrow \mathrm{B}$, $[\mathrm{A}] = [\mathrm{A}]_0 - 2[\mathrm{B}]$. We can therefore draw up the following table

t/s	0	600	1200	1800	2400
$[\mathrm{B}]/(\mathrm{mol\,L^{-1}})$	0	0.089	0.153	0.200	0.230
$[\mathrm{A}]/(\mathrm{mol\,L^{-1}})$	0.624	0.446	0.318	0.224	0.164

The data are plotted in Fig. 25.2(a).

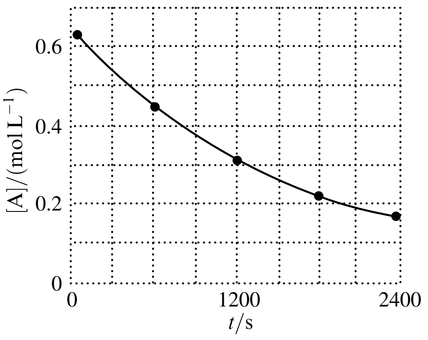


Figure 25.2(a)

We see that the half-life of A from its initial concentration is approximately 1200 s, and that its half-life from the concentration at 1200 s is also 1200 s. This indicates a first-order reaction. We confirm this conclusion by plotting the data accordingly, using

$$\ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]} = k_{\mathrm{A}}t \quad \text{if } \frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{A}}[\mathrm{A}]$$

First, draw up the table

t/s	0	600	1200	1800	2400
$\ln\dfrac{[\mathrm{A}]_0}{[\mathrm{A}]}$	0	0.34	0.67	1.02	1.34

and plot the points (Fig. 25.2(b)).

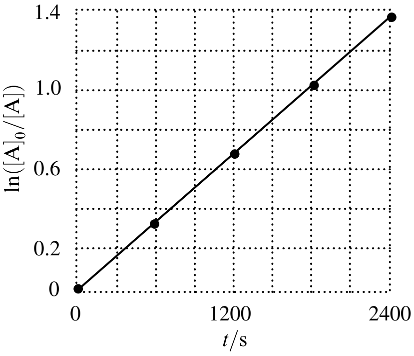


Figure 25.2(b)

The points lie as a straight line, which confirms $\boxed{\text{first-order}}$ kinetics. Since the slope of the line is 5.6×10^{-4}, we conclude that $k_{\mathrm{A}} = 5.6 \times 10^{-4}\,\mathrm{s}^{-1}$. To express the rate law in the form

$$v = k[\mathrm{A}]$$

we note that $v = -\frac{1}{2}\dfrac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -\left(\frac{1}{2}\right) \times (-k_{\mathrm{A}}[\mathrm{A}]) = \frac{1}{2}k_{\mathrm{A}}[\mathrm{A}]$

and hence $k = \frac{1}{2}k_{\mathrm{A}} = \boxed{2.8 \times 10^{-4}\,\mathrm{s}^{-1}}$

P25.8 The data do not extend much beyond one half-life; therefore, we cannot see whether the **half**-life is constant over the course of the reaction as a preliminary step in guessing a reaction order. In a first-order reaction, however, not only the half-life but any other similarly-defined fractional lifetime remains constant. (That is a property of the exponential function.) In this problem, we can see that the $^2\!/_3$-life is **not** constant. (It takes less than 1.6 ms for [ClO] to drop from the first recorded value ($8.49\,\mu\mathrm{mol\,L^{-1}}$) by more than $^1\!/_3$ of that value (to $5.79\,\mu\mathrm{mol\,L^{-1}}$); it takes more than 4.0 more ms for the concentration to drop by not even $^1\!/_3$ of **that** value (to $3.95\,\mu\mathrm{mol\,L^{-1}}$). So our working assumption is that the reaction is not first-order but second-order. Draw up the following table

t/ms	$[\mathrm{ClO}]/(\mu\mathrm{mol\,L^{-1}})$	$(1/[\mathrm{CLO}])/(\mathrm{L}\,\mu\mathrm{mol^{-1}})$
0.12	8.49	0.118
0.62	8.09	0.124
0.96	7.10	0.141
1.60	5.79	0.173
3.20	5.20	0.192
4.00	4.77	0.210
5.75	3.95	0.253

The plot of $(1/[\mathrm{ClO}])/(\mathrm{L}\,\mu\mathrm{mol^{-1}})$ vs. t/ms yields a good straight line; the linear least squares fit is:

$$(1/[\mathrm{ClO}]/(\mathrm{L}\,\mu\mathrm{mol^{-1}}) = 0.118 + 0.0237(t/\mathrm{ms}) \quad r^2 = 0.974$$

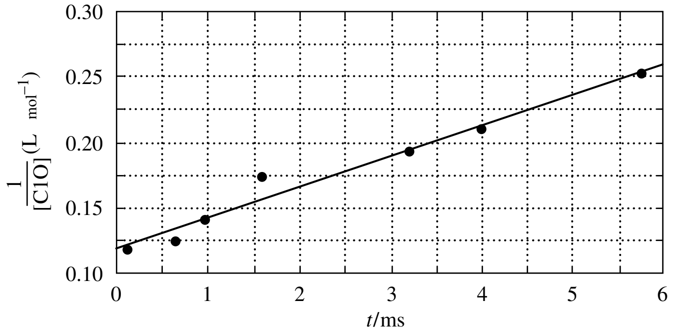


Figure 25.3

The rate constant is equal to the slope

$$k = 0.0237\,\mathrm{L\,\mu mol^{-1}\,ms^{-1}} = \boxed{2.37 \times 10^{7}\,\mathrm{L\,mol^{-1}\,s^{-1}}}$$

The lifetime or time constant is the time required for the concentration to drop to 1/e of its initial value. Use the integrated second-order rate law

$$\frac{1}{[\mathrm{ClO}]} - \frac{1}{[\mathrm{ClO}]_0} = kt$$

to solve for the time when $[\mathrm{ClO}] = [\mathrm{ClO}]_0/\mathrm{e}$

$$\frac{\mathrm{e}}{[\mathrm{ClO}]_0} - \frac{1}{[\mathrm{ClO}]_0} = kt$$

So $$t = \frac{\mathrm{e}-1}{k[\mathrm{ClO}]_0} = \frac{\mathrm{e}-1}{(2.37 \times 10^{-7}\,\mathrm{L\,mol^{-1}\,s^{-1}})(8.47 \times 10^{-6}\,\mathrm{mol\,L^{-1}})} = \boxed{8.56 \times 10^{-3}\,\mathrm{s}}.$$

Note: $[\mathrm{ClO}]_0$ was taken from the intercept of the best-fit equation

$$(1/[\mathrm{ClO}]_0)/(\mathrm{L\,\mu mol^{-1}}) = 0.118 \qquad \text{so} \qquad [\mathrm{ClO}]_0 = 8.47\,\mathrm{\mu mol\,L^{-1}}$$

P25.11 Using spreadsheet software to evaluate eqn 25.36, one can draw up a plot like the following. The curves in this plot represent the concentration of the intermediate [I] as a function of time. They are labeled with the ratio k_1/k_2, where $k_2 = 1\,\mathrm{s^{-1}}$ for all curves and k_1 varies. The thickest curve, labeled 10, corresponds to $k_1 = 10\,\mathrm{s^{-1}}$, as specified in part a of the problem. As the ratio k_1/k_2 gets smaller (or, as the problem puts it, the ratio k_2/k_1 gets larger), the concentration profile for I becomes lower, broader, and flatter; that is, [I] becomes more nearly constant over a longer period of time. This is the nature of the $\boxed{\text{steady-state approximation}}$, which becomes more and more valid as consumption of the intermediate becomes fast compared with its formation.

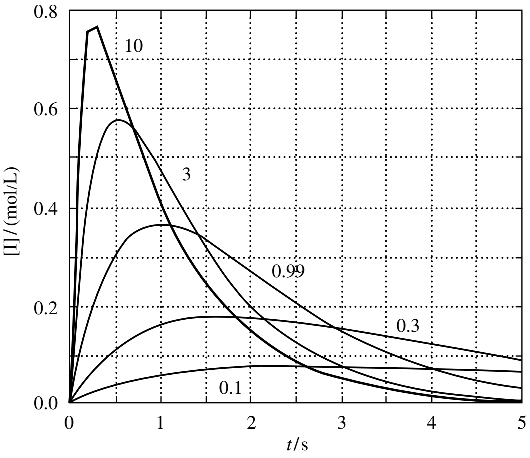


Figure 25.4

P25.13 $$E_a = \frac{R\ln\left(\frac{k'_{\text{eff}}}{k_{\text{eff}}}\right)}{\left(\frac{1}{T}-\frac{1}{T'}\right)}\text{[Exercise 25.16(a) from eqn 25.25]} = \frac{R\ln 3}{\frac{1}{343\,\text{K}}-\frac{1}{292\,\text{K}}} = \boxed{-18\,\text{kJ mol}^{-1}}$$

But $k_{\text{eff}} = kK_1K_2$ [Problem 25.12]

$$\ln k_{\text{eff}} = \ln k + \ln K_1 + \ln K_2$$

$$E_a = -R\frac{\text{d}\ln k_{\text{eff}}}{\text{d}(1/T)}[25.26] = E'_a + \Delta_r H_1 + \Delta_r H_2$$

since $\dfrac{\text{d}\ln K}{\text{d}(1/T)} = \dfrac{-\Delta_r H}{R}$[van't Hoff equation, Chapter 9] Therefore,

$$E'_a = E_a - \Delta_r H_1 - \Delta_r H_2 = [-(18) + (14) + (14)]\,\text{kJ mol}^{-1} = \boxed{+10\,\text{kJ mol}^{-1}}$$

P25.15 $$\frac{1}{k} = \frac{k'_a}{k_a k_b} + \frac{1}{k_a[\text{A}]}\ [25.63]$$

or, in terms of pressure of A

$$\frac{1}{k} = \frac{k'_a}{k_a k_b} + \frac{1}{k_a p}$$

and we expect a straight line when $\dfrac{1}{k}$ is plotted against $\dfrac{1}{p}$. We draw up the following table

p/Torr	84.1	11.0	2.89	0.569	0.120	0.067
$1/(p/\text{Torr})$	0.012	0.091	0.346	1.76	8.33	14.9
$10^{-4}/(k/\text{s}^{-1})$	0.336	0.448	0.629	1.17	2.55	3.30

These points are plotted in Fig. 25.5. There are marked deviations at low pressures, indicating that the Lindemann theory is deficient in that region.

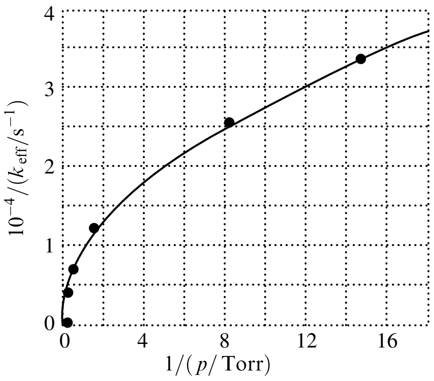


Figure 25.5

Solutions to theoretical problems

P25.18 We assume a pre-equilibrium (as the initial step is fast), and write

$$K = \frac{[\text{A}]^2}{[\text{A}_2]}, \quad \text{implying that} \quad [\text{A}] = K^{1/2}[\text{A}_2]^{1/2}$$

The rate-determining step then gives

$$v = \frac{\text{d}[\text{P}]}{\text{d}t} = k_2[\text{A}][\text{B}] = \boxed{k_2K^{1/2}[\text{A}_2]^{1/2}[\text{B}]} = k_{\text{eff}}[\text{A}_2]^{1/2}[\text{B}]$$

where $k_{\text{eff}} = k_2K^{1/2}$.

P25.20 $\dfrac{\text{d}[\text{P}]}{\text{d}t} = k[\text{A}][\text{B}]$

Let the initial concentrations be A_0, B_0, and $[\text{P}]_0 = 0$. Then, when an amount x of P is formed, the amount of A changes to $A_0 - 2x$ and that of B changes to $B_0 - 3x$. Therefore

$$\frac{\text{d}[\text{P}]}{\text{d}t} = \frac{\text{d}x}{\text{d}t} = k(A_0 - 2x)(B_0 - 3x) \quad \text{with } x = 0 \text{ at } t = 0.$$

$$\int_0^t k\,\text{d}t = \int_0^x \frac{\text{d}x}{(A_0 - 2x) \times (B_0 - 3x)}$$

$$= \int_0^x \left(\frac{6}{2B_0 - 3A_0}\right) \times \left(\frac{1}{3(A_0 - 2x)} - \frac{1}{2(B_0 - 3x)}\right)\text{d}x$$

$$= \left(\frac{-1}{(2B_0 - 3A_0)}\right) \times \left(\int_0^x \frac{\text{d}x}{x - (1/2)A_0} - \int_0^x \frac{\text{d}x}{x - (1/3)B_0}\right)$$

$$kt = \left(\frac{-1}{(2B_0 - 3A_0)}\right) \times \left[\ln\left(\frac{x - \frac{1}{2}A_0}{-\frac{1}{2}A_0}\right) - \ln\left(\frac{x - \frac{1}{3}B_0}{-\frac{1}{3}B_0}\right)\right]$$

$$= \left(\frac{-1}{2B_0 - 3A_0}\right)\ln\left(\frac{(2x - A_0)B_0}{A_0(3x - B_0)}\right)$$

$$= \boxed{\left(\frac{1}{(3A_0 - 2B_0)}\right)\ln\left(\frac{(2x - A_0)B_0}{A_0(3x - B_0)}\right)}$$

P25.23 $$kt = \left(\frac{1}{n-1}\right) \times \left(\frac{1}{[\mathrm{A}]^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right) \text{ [Exercise 25.18(a), } n \neq 1]$$

At $t = t_{1/2}, kt_{1/2} = \left(\frac{1}{n-1}\right)\left[\left(\frac{2}{A_0}\right)^{n-1} - \left(\frac{1}{A_0}\right)^{n-1}\right]$

At $t = t_{3/4}$, $[\mathrm{A}] = \frac{3}{4}[\mathrm{A}]_0$

$$kt_{3/4} = \left(\frac{1}{n-1}\right)\left[\left(\frac{4}{3A_0}\right)^{n-1} - \left(\frac{1}{A_0}\right)^{n-1}\right]$$

Hence, $\boxed{\dfrac{t_{1/2}}{t_{3/4}} = \dfrac{2^{n-1}-1}{\left(\frac{4}{3}\right)^{n-1} - 1}}$

P25.24 Let the forward rates be written as

$$r_1 = k_1[\mathrm{A}], \qquad r_2 = k_2[\mathrm{B}], \qquad r_3 = k_3[\mathrm{C}]$$

and the reverse rates as

$$r_1' = k_1'[\mathrm{B}], \qquad r_2' = k_2'[\mathrm{C}], \qquad r_3' = k_3'[\mathrm{D}]$$

The net rates are then

$$R_1 = k_1[\mathrm{A}] - k_1'[\mathrm{B}], \qquad R_2 = k_2[\mathrm{B}] - k_2'[\mathrm{C}], \qquad R_3 = k_3[\mathrm{C}] - k_3'[\mathrm{D}]$$

But $[\mathrm{A}] = [\mathrm{A}]_0$ and $[\mathrm{D}] = 0$, so that the steady-state equations for the rates of the intermediates are

$$k_1[\mathrm{A}]_0 - k_1'[\mathrm{B}] = k_2[\mathrm{B}] - k_2'[\mathrm{C}] = k_3[\mathrm{C}]$$

From the second of these equations we find

$$[\mathrm{C}] = \frac{k_2[\mathrm{B}]}{k_2' + k_3}$$

After inserting this expression for [C] into the first of the steady-state equations we obtain

$$[\mathrm{B}] = [\mathrm{A}]_0 \times \frac{k_1}{k_2 + k_1' - \left(\frac{k_2'k_2}{k_2'+k_3}\right)}$$

Thus, at the steady state

$$\boxed{R_1 = R_2 = R_3 = [\mathrm{A}]_0 k_1 \times \left(1 - \frac{k_1'}{k_2 + k_1' - \left(\frac{k_2'k_2}{k_2'+k_3}\right)}\right)}$$

P25.25 $v = k([\mathrm{A}]_0 - x)([\mathrm{B}]_0 + x)$

$$\frac{\mathrm{d}v}{\mathrm{d}x} = k([\mathrm{A}]_0 - x) - k([\mathrm{B}]_0 + x)$$

The extrema correspond to $\dfrac{\mathrm{d}v}{\mathrm{d}x} = 0$, or

$$[\mathrm{A}]_0 - x = [\mathrm{B}]_0 + x \quad \text{or} \quad 2x = [\mathrm{A}]_0 - [\mathrm{B}]_0 \quad \text{or} \quad x = \frac{[\mathrm{A}]_0 - [\mathrm{B}]_0}{2}$$

Substitute into v to obtain

$$v_{\max} = k\left(\frac{[\mathrm{A}]_0}{2} + \frac{[\mathrm{B}]_0}{2}\right) \times \left(\frac{[\mathrm{B}]_0}{2} + \frac{[\mathrm{A}]_0}{2}\right) = \boxed{k\left(\frac{[\mathrm{A}]_0 + [\mathrm{B}]_0}{2}\right)^2}$$

Since v and x cannot be negative in the reaction,

$$\boxed{[\mathrm{B}]_0 \le [\mathrm{A}]_0}$$

To see the variation of v with x, let $[\mathrm{B}]_0 = [\mathrm{A}]_0$. The rate equation becomes

$$v = k([\mathrm{A}]_0 - x)([\mathrm{A}]_0 + x) = k([\mathrm{A}]_0^2 - x^2) = k[\mathrm{A}]_0^2 - kx^2$$

or $\dfrac{v}{k[\mathrm{A}]_0^2} = \left(1 - \dfrac{x^2}{[\mathrm{A}]_0^2}\right) = \left(1 + \dfrac{x}{[\mathrm{A}]_0}\right)\left(1 - \dfrac{x}{[\mathrm{A}]_0}\right)$

Thus we plot $\dfrac{v}{k[\mathrm{A}]_0^2}$ against $\left(1 - \dfrac{x^2}{[\mathrm{A}]_0^2}\right)$ from $\dfrac{x}{[\mathrm{A}]_0} = 0$

The plot is shown in Fig. 25.6 in which $X = \dfrac{x}{[\mathrm{A}]_0}$. $\boxed{\dfrac{x}{[\mathrm{A}]_0} \le 1 \text{ corresponds to reality}}$

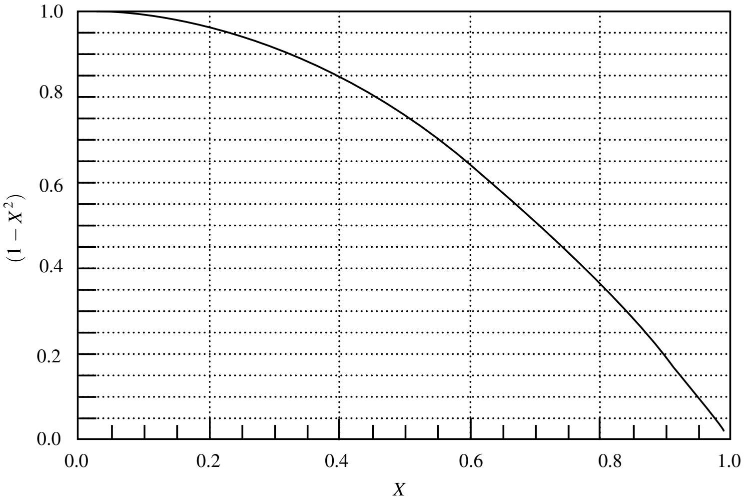


Figure 25.6

P25.26 For A → B → C

$$[\mathrm{I}] = \frac{k_\mathrm{a}}{k_\mathrm{b} - k_\mathrm{a}}(\mathrm{e}^{-k_\mathrm{a}t} - \mathrm{e}^{-k_\mathrm{b}t})[\mathrm{A}]_0 \ [25.36]$$

$$\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t} = \frac{k_\mathrm{a}}{k_\mathrm{b} - k_\mathrm{a}}(k_\mathrm{b}\mathrm{e}^{-k_\mathrm{b}t} - k_\mathrm{a}\mathrm{e}^{-k_\mathrm{a}t})$$

[I] reaches a maximum when d[I]/dt=0. This occurs when t satisfies the equation

$$k_\mathrm{b}\mathrm{e}^{-k_\mathrm{b}t_\mathrm{max}} - k_\mathrm{a}\mathrm{e}^{-k_\mathrm{a}t_\mathrm{max}} = 0$$

$$k_\mathrm{b}\mathrm{e}^{-k_\mathrm{b}t_\mathrm{max}}\left(1 - \frac{k_\mathrm{a}\mathrm{e}^{-(k_\mathrm{a}-k_\mathrm{b})t_\mathrm{max}}}{k_\mathrm{b}}\right) = 0$$

$$1 - \frac{k_\mathrm{a}}{k_\mathrm{b}}\mathrm{e}^{-(k_\mathrm{a}-k_\mathrm{b})t_\mathrm{max}} = 0$$

$$\mathrm{e}^{-(k_\mathrm{a}-k_\mathrm{b})t_\mathrm{max}} = k_\mathrm{b}/k_\mathrm{a}$$

$$-(k_\mathrm{a} - k_\mathrm{b})t_\mathrm{max} = \ln(k_\mathrm{b}/k_\mathrm{a})$$

$$t_\mathrm{max} = \frac{\ln(k_\mathrm{b}/k_\mathrm{a})}{(k_\mathrm{b} - k_\mathrm{a})} = \frac{(k_\mathrm{a}/k_\mathrm{b})\ln(k_\mathrm{a}/k_\mathrm{b})}{k_\mathrm{a}\left(\frac{k_\mathrm{a}}{k_\mathrm{b}} - 1\right)}$$

For $k_\mathrm{a} = 1.0\,\mathrm{min}^{-1}$, the times at which [I] is a maximum are

$k_\mathrm{a}/k_\mathrm{b}$	5	1	0.5
t_max/min	$\boxed{2.01}$	$\boxed{1}$	$\boxed{0.693}$

The evaluation for t_max when $k_\mathrm{a}/k_\mathrm{b} = 1$ requires special care. Imagine $k_\mathrm{a}/k_\mathrm{b} > 0$ and take $\lim\limits_{k_\mathrm{a}/k_\mathrm{b}\to 1}$ (t_max). In this limit the value of $\left(\frac{k_\mathrm{a}}{k_\mathrm{b}} - 1\right)$ in the denominator becomes very small (call this value x) and can be viewed as being part of the Taylor series expansion of $\ln(1 + x)$

$$\ln(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} + \cdots \approx x$$

$$\lim_{k_\mathrm{a}/k_\mathrm{b}\to 1}(t_\mathrm{max}) = \frac{1}{k_\mathrm{a}} \lim_{k_\mathrm{a}/k_\mathrm{b}\to 1}\left\{\frac{(k_\mathrm{a}/k_\mathrm{b})\ln(k_\mathrm{a}/k_\mathrm{b})}{\ln(k_\mathrm{a}/k_\mathrm{b})}\right\} = \frac{1}{k_\mathrm{a}}$$

Plots of $\frac{[\mathrm{I}]}{[\mathrm{A}]_0}$ for $k_\mathrm{a}/k_\mathrm{b} = 5$, 1, and 0.5 are shown in Fig. 25.6.

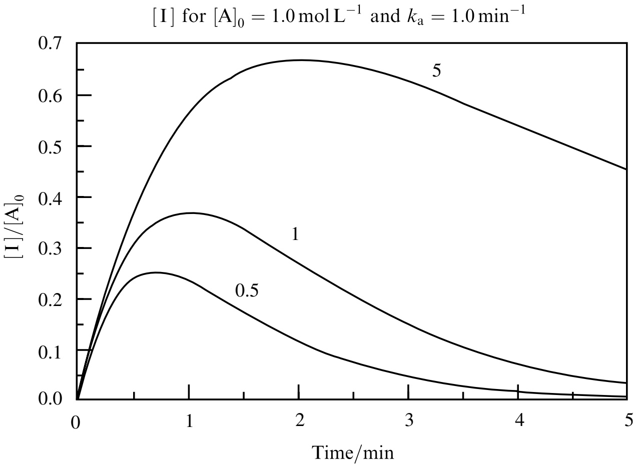


Figure 25.6(a)

For A + B → P

$$v = \frac{dx}{dt} = k[A][B] = k([A]_0 - x)([B]_0 - x)$$

$$\int_{x=0}^{x} \frac{dx}{([A]_0 - x)([B]_0 - x)} = \int_{t=0}^{t} k\,dt = kt$$

$$\int_{x=0}^{x} \frac{dx}{[A]_0[B]_0 - ([A]_0 + [B]_0)x + x^2} = kt$$

The integral on the left may be found in standard mathematics handbooks.

$$\int \frac{dz}{az^2 + bz + c} = \frac{1}{\sqrt{b^2 - 4ac}} \ln\left(\frac{2ax + b - \sqrt{b^2 - 4ac}}{2ax + b + \sqrt{b^2 - 4ac}}\right)$$

The transformations to our working equation are

$a \to 1$ $\qquad$ $b \to -([A]_0 + [B]_0)$

$c \to [A]_0[B]_0$ $\qquad$ $\sqrt{b^2 - 4ac} \to [A]_0 - [B]_0$

$b - \sqrt{b^2 - 4ac} \to -2[A]_0$

$b + \sqrt{b^2 - 4ac} \to -2[B]_0$

$$\frac{1}{[A]_0 - [B]_0} \ln\left(\frac{x - [A]_0}{x - [B]_0}\right)\Bigg]_{x=0}^{x} = kt$$

$$\frac{1}{[A]_0 - [B]_0} \left\{\ln\left(\frac{[A]_0 - x}{[B]_0 - x}\right) - \ln\left(\frac{[A]_0}{[B]_0}\right)\right\} = kt$$

$$\frac{1}{[A]_0 - [B]_0} \ln\left(\frac{[B]_0([A]_0 - x)}{[A]_0([B]_0 - x)}\right) = kt$$

This can also be written in the form

$$\boxed{\frac{1}{[B]_0 - [A]_0} \ln\left(\frac{[A]_0([B]_0 - x)}{[B]_0([A]_0 - x)}\right) = kt}$$

We will now solve this for x

$$\frac{[\mathrm{B}]_0 - x}{[\mathrm{A}]_0 - x} = \frac{[\mathrm{B}]_0}{[\mathrm{A}]_0}\mathrm{e}^{-\{([\mathrm{A}]_0-[\mathrm{B}]_0)kt\}} \equiv f(t)$$

$$[\mathrm{B}]_0 - x = [\mathrm{A}]_0 f(t) - f(t)x$$

$$(1 - f(t))x = [\mathrm{B}]_0 - [\mathrm{A}]_0 f(t)$$

$$\boxed{x = \frac{[\mathrm{B}]_0 - [\mathrm{A}]_0 f(t)}{1 - f(t)}} = \frac{[\mathrm{B}]_0 - [\mathrm{B}]_0\mathrm{e}^{-\{([\mathrm{A}]_0-[\mathrm{B}]_0)kt\}}}{1 - ([\mathrm{B}]_0/[\mathrm{A}]_0)\mathrm{e}^{-\{([\mathrm{A}]_0-[\mathrm{B}]_0)kt\}}}$$

Solutions to applications

P25.28 The first-order half-life is related to the rate constant by

$$t_{1/2} = \frac{\ln 2}{k} \quad \text{so} \quad k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{28.1\,\mathrm{y}} = 2.47 \times 10^{-2}\,\mathrm{y}^{-1}$$

The integrated rate law tells us

$$[^{90}\mathrm{Sr}] = [^{90}\mathrm{Sr}]_0\mathrm{e}^{-kt} \quad \text{so} \quad m = m_0\mathrm{e}^{-kt}$$

where m is the mass of ^{90}Sr.

(a) After 18 y: $m = (1.00\,\mu\mathrm{g}) \times \exp[-(2.47 \times 10^{-2}\,\mathrm{y}^{-1}) \times (18\,\mathrm{y})] = \boxed{0.642\,\mu\mathrm{g}}$

(b) After 70 y: $m = (1.00\,\mu\mathrm{g}) \times \exp[-(2.47 \times 10^{-2}\,\mathrm{y}^{-1}) \times (70\,\mathrm{y})] = \boxed{0.177\,\mu\mathrm{g}}$

P25.30 We assume a pre-equilibrium (as the initial step is fast), and write

$$K = \frac{[\text{unstable helix}]}{[\mathrm{A}][\mathrm{B}]}, \quad \text{implying that} \quad [\text{unstable helix}] = K[\mathrm{A}][\mathrm{B}]$$

The rate-determining step then gives

$$v = \frac{\mathrm{d}[\text{double helix}]}{\mathrm{d}t} = k_2[\text{unstable helix}] = k_2K[\mathrm{A}][\mathrm{B}] = \boxed{k[\mathrm{A}][\mathrm{B}]} \quad [k = k_2K]$$

The equilibrium constant is the outcome of the two processes

$$\mathrm{A} + \mathrm{B} \underset{k_1'}{\overset{k_1}{\rightleftarrows}} \text{unstable helix}, \quad K = \frac{k_1}{k_1'}$$

Therefore, with $v = k[\mathrm{A}][\mathrm{B}]$, $\boxed{k = \frac{k_1k_2}{k_1'}}$

P25.33 **(a)** The rate of reaction is

$$\begin{aligned} v &= k[\mathrm{CH_4}][\mathrm{OH}] \\ &= (1.13 \times 10^9\,\mathrm{L\,mol^{-1}\,s^{-1}}) \times \exp\left(\frac{-14.1 \times 10^3\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (263\,\mathrm{K})}\right) \\ &\quad \times (4.0 \times 10^{-8}\,\mathrm{mol\,L^{-1}}) \times (1.5 \times 10^{-15}\,\mathrm{mol\,L^{-1}}) = \boxed{1.1 \times 10^{-16}\,\mathrm{mol\,L^{-1}\,s^{-1}}} \end{aligned}$$

(b) The mass is the amount consumed (in moles) times the molar mass; the amount consumed is the rate of consumption times the volume of the "reaction vessel" times the time

$$\begin{aligned} m = MvVt &= (0.01604\,\mathrm{kg\,mol^{-1}}) \times (1.1 \times 10^{-16}\,\mathrm{mol\,L^{-1}\,s^{-1}}) \\ &\quad \times (4 \times 10^{21}\,\mathrm{L}) \times (365 \times 24 \times 3600\,\mathrm{s}) \\ &= \boxed{2.2 \times 10^{11}\,\mathrm{kg\ or\ 220\,Tg}} \end{aligned}$$

P25.35 The initial rate is

$$\begin{aligned} v_0 &= (3.6 \times 10^{6}\,\mathrm{L^3\,mol^{-3}\,s^{-1}}) \times (5 \times 10^{-4}\,\mathrm{mol\,L^{-1}})^2 \times (10^{-4.5}\,\mathrm{mol\,L^{-1}})^2 \\ &= \boxed{9 \times 10^{-10}\,\mathrm{mol\,L^{-1}\,s^{-1}}} \end{aligned}$$

The half-life for a second-order reaction is

$$t_{1/2} = \frac{1}{k'[\mathrm{HSO_3^-}]_0}$$

where k' is the rate constant in the expression

$$-\frac{\mathrm{d}[\mathrm{HSO_3^-}]}{\mathrm{d}t} = k'[\mathrm{HSO_3^-}]^2$$

Comparison to the given rate law and rate constant shows

$$\begin{aligned} k' = 2k[\mathrm{H^+}]^2 &= 2(3.6 \times 10^{6}\,\mathrm{L^3\,mol^{-3}\,s^{-1}}) \times (10^{-4.5}\,\mathrm{mol\,L^{-1}})^2 \\ &= 7.2 \times 10^{-3}\,\mathrm{L\,mol^{-1}\,s^{-1}} \end{aligned}$$

and $t_{1/2} = \dfrac{1}{(7.2 \times 10^{-3}\,\mathrm{L\,mol^{-1}\,s^{-1}}) \times (5 \times 10^{-4}\,\mathrm{mol\,L^{-1}})} = \boxed{2.\overline{8} \times 10^{5}\,\mathrm{s} = 3\,\mathrm{days}}$

26 The kinetics of complex reactions

Solutions to exercises

Discussion questions

E26.1(b) In the analysis of stepwise polymerization, the rate constant for the second-order condensation is assumed to be independent of the chain length and to remain constant throughout the reaction. It follows, then, that the degree of polymerization is given by

$$\langle n \rangle = 1 + kt[\mathrm{A}]_0$$

Therefore, the average molar mas can be controlled by adjusting the initial concentration of monomer and the length of time that the polymerization is allowed to proceed.

Chain polymerization is a complicated radical chain mechanism involving initiation, propagation, and termination steps (see Section 26.4 for the details of this mechanism). The derivation of the overall rate equation utilizes the steady state approximation and leads to the following expression for the average number of monomer units in the polymer chain:

$$\langle n \rangle = 2k[\mathrm{M}][\mathrm{I}]^{-1/2},$$

where $k = 1/2\ k_{\mathrm{P}}(fk_{\mathrm{i}}k_{\mathrm{t}})^{-1/2}$, with k_{P}, k_{i}, and k_{t}, being the rate constants for the propagation, initiation, and termination steps, and f is the fraction of radicals that successfully initiate a chain. We see that the average molar mass of the polymer is directly proportional to the monomer concentration, and inversely proportional to the square root of the initiator concentration and to the rate constant for initiation. Therefore, the slower the initiation of the chain, the higher the average molar mass of the polymer.

E26.2(b) Refer to eqns 26.26 and 26.27, which are the analogues of the Michaelis–Menten and Lineweaver–Burk equations (26.21 and 26.22), as well as to Fig. 26.12. There are three major modes of inhibition that give rise to distinctly different kinetic behaviour (Fig. 26.12). In competitive inhibition the inhibitor binds only to the active site of the enzyme and thereby inhibits the attachment of the substrate. This condition corresponds to $\alpha > 1$ and $\alpha' = 1$ (because ESI does not form). The slope of the Lineweaver–Burk plot increases by a factor of α relative to the slope for data on the uninhibited enzyme ($\alpha = \alpha' = 1$). The y-intercept does not change as a result of competitive inhibition. In uncompetitive inhibition, the inhibitor binds to a site of the enzyme that is removed from the active site, but only if the substrate is already present. The inhibition occurs because ESI reduces the concentration of ES, the active type of the complex. In this case $\alpha = 1$ (because EI does not form) and $\alpha' > 1$. The y- intercept of the Lineweaver–Burk plot increases by a factor of α' relative to the y-intercept for data on the uninhibited enzyme, but the slope does not change. In non-competitive inhibition, the inhibitor binds to a site other than the active site, and its presence reduces the ability of the substrate to bind to the active site. Inhibition occurs at both the E and ES sites. This condition corresponds to $\alpha > 1$ and $\alpha' > 1$. Both the slope and y-intercept of the Lineweaver–Burk plot increase upon addition of the inhibitor. Figure 26.12c shows the special case of $K_{\mathrm{I}} = K_{\mathrm{I}}'$ and $\alpha = \alpha'$, which results in intersection of the lines at the x-axis.

In all cases, the efficiency of the inhibitor may be obtained by determining K_{M} and $v_{\max}$ from a control experiment with uninhibited enzyme and then repeating the experiment with a known concentration of inhibitor. From the slope and y-intercept of the Lineweaver–Burk plot for the inhibited enzyme (eqn 26.27), the mode of inhibition, the values of α or α', and the values of K_{I}, or K_{I}' may be obtained.

E26.3(b) The steady-state approximation is applied to reactive intermediates in consecutive reactions and is the assumption that their concentrations do not change much with time. It is a good approximation if the rate constant for the reaction of the intermediate, in either the forward or backward direction, is large compared to the rate constant in the other direction. This approximation is applicable when chemical production and chemical consumption are closely balanced.

In the steady-state condition of a chemical reaction, a reactant or product is maintained at a constant concentration throughout the course of the reaction by supplying it to or withdrawing it from the reaction vessel. Steady-states are not equilibrium states in the thermodynamic sense and in fact are the other extreme from equilibrium.

Bistability is a condition in which two distinct, far from equilibrium, steady-states are chemically available to the reacting system. In some systems, bistability is a necessary condition for chemical oscillation to occur. Under the right conditions, the system may jump periodically between the two steady states as the reaction progresses. Refer to Figs 26.19 and 26.20 of the text for an illustration of the process. However, bistability alone is not a sufficient condition to achieve oscillation in an autocatalytic reaction. In order for the oscillation to occur, it is necessary to have a feedback mechanism involving a third species Z that reacts with the intermediates X and Y according to: $Y + Z \rightarrow X$ and $X + Z \rightarrow Y$. Thus Z reacts with X to produce Y and with Y to produce X. As a result the system can switch periodically between the upper and lower steady states.

E26.4(b) The shortening of the lifetime of an excited state is called quenching. Quenching effects may be studied by monitoring the emission from the excited state that is involved in the photochemical process. The addition of a quencher opens up an additional channel for the deactivation of the excited singlet state.

Three common mechanisms for bimolecular quenching of an excited singlet (or triplet) state are:

Collisional deactivation: $S^* + Q \rightarrow S + Q$
Energy transfer: $S^* + Q \rightarrow S + Q^*$
Electron transfer: $S^* + Q \rightarrow S^+ + Q^-$ or $S^- + Q^+$

Collisional quenching is particularly efficient when Q is a heavy species, such as iodide ion, which receives energy from S^* and then decays primarily by internal conversion to the ground state. Pure collisional quenching can be detected by the appearance of vibrational and rotational excitation in the spectrum of the acceptor.

In many cases, it is possible to prove that energy transfer is the predominant mechanism of quenching if the excited state of the acceptor fluoresces or phosphoresces at a characteristic wavelength. In a pulsed laser experiment, the rise in fluorescence intensity from Q^* with a characteristic time which is the same as that for the decay of the fluorescence of S^* is often taken as indication of energy transfer from S to Q.

Electron transfer can be studied by time-resolved spectroscopy (Section 17.7e). The oxidized and reduced products often have electronic absorption spectra distinct from those of their neutral parent compounds. Therefore, the rapid appearance of such known features in the absorption spectrum after excitation by a laser pulse may be taken as indication of quenching by electron transfer.

Numerical exercises

In the following exercises and problems, it is recommended that rate constants are labelled with the number of the step in the proposed reaction mechanism and that any reverse steps are labelled similarly but with a prime.

E26.5(b) The intermediates are NO and NO_3 and we apply the steady-state approximation to each of their concentrations

$$k_2[\mathrm{NO_2}][\mathrm{NO_3}] - k_3[\mathrm{NO}][\mathrm{N_2O_5}] = 0$$

$$k_1[\mathrm{N_2O_5}] - k_1'[\mathrm{NO_2}][\mathrm{NO_3}] - k_2[\mathrm{NO_2}][\mathrm{NO_3}] = 0$$

$$\text{Rate} = -\frac{1}{2}\frac{\mathrm{d}[\mathrm{N_2O_5}]}{\mathrm{d}t}$$

$$\frac{\mathrm{d}[\mathrm{N_2O_5}]}{\mathrm{d}t} = -k_1[\mathrm{N_2O_5}] + k_1'[\mathrm{NO_2}][\mathrm{NO_3}] - k_3[\mathrm{NO}][\mathrm{N_2O_5}]$$

From the steady state equations

$$k_3[\mathrm{NO}][\mathrm{N_2O_5}] = k_2[\mathrm{NO_2}][\mathrm{NO_3}]$$

$$[\mathrm{NO_2}][\mathrm{NO_3}] = \frac{k_1[\mathrm{N_2O_5}]}{k_1' + k_2}$$

Substituting,

$$\frac{\mathrm{d}[\mathrm{N_2O_5}]}{\mathrm{d}t} = -k_1[\mathrm{N_2O_5}] + \frac{k_1'k_1}{k_1' + k_2}[\mathrm{N_2O_5}] - \frac{k_2k_1}{k_1' + k_2}[\mathrm{N_2O_5}] = -\frac{2k_1k_2}{k_1' + k_2}[\mathrm{N_2O_5}]$$

$$\text{Rate} = \frac{k_1k_2}{k_1' + k_2}[\mathrm{N_2O_5}] = k[\mathrm{N_2O_5}]$$

E26.6(b)

$$\frac{\mathrm{d}[\mathrm{R}]}{\mathrm{d}t} = 2k_1[\mathrm{R_2}] - k_2[\mathrm{R}][\mathrm{R_2}] + k_3[\mathrm{R'}] - 2k_4[\mathrm{R}]^2$$

$$\frac{\mathrm{d}[\mathrm{R'}]}{\mathrm{d}t} = k_2[\mathrm{R}][\mathrm{R_2}] - k_3[\mathrm{R'}]$$

Apply the steady-state approximation to both equations

$$2k_1[\mathrm{R_2}] - k_2[\mathrm{R}][\mathrm{R_2}] + k_3[\mathrm{R'}] - 2k_4[\mathrm{R}]^2 = 0$$

$$k_2[\mathrm{R}][\mathrm{R_2}] - k_3[\mathrm{R'}] = 0$$

The second solves to $[\mathrm{R'}] = \dfrac{k_2}{k_3}[\mathrm{R}][\mathrm{R_2}]$

and then the first solves to $[\mathrm{R}] = \left(\dfrac{k_1}{k_4}[\mathrm{R_2}]\right)^{1/2}$

Therefore, $\dfrac{\mathrm{d}[\mathrm{R_2}]}{\mathrm{d}t} = -k_1[\mathrm{R_2}] - k_2[\mathrm{R_2}][\mathrm{R}] = \boxed{-k_1[\mathrm{R_2}] - k_2\left(\dfrac{k_1}{k_4}\right)^{1/2}[\mathrm{R_2}]^{3/2}}$

E26.7(b) **(a)** The figure suggests that a chain-branching explosion $\boxed{\text{does not occur}}$ at temperatures as low as 700 K. There may, however, be a thermal explosion regime at pressures in excess of 10^6 Pa.

(b) The lower limit seems to occur when

$$\log(p/\mathrm{Pa}) = 2.1 \quad \text{so} \quad p = 10^{2.1}\,\mathrm{Pa} = \boxed{1.3 \times 10^2\,\mathrm{Pa}}$$

There does not seem to be a pressure above which a steady reaction occurs. Rather the chain-branching explosion range seems to run into the thermal explosion range around

$$\log(p/\mathrm{Pa}) = 4.5 \quad \text{so} \quad p = 10^{4.5}\,\mathrm{Pa} = \boxed{3 \times 10^4\,\mathrm{Pa}}$$

E26.8(b) The rate of production of the product is

$$\frac{d[BH^+]}{dt} = k_2[HAH^+][B]$$

HAH^+ is an intermediate involved in a rapid pre-equilibrium

$$\frac{[HAH^+]}{[HA][H^+]} = \frac{k_1}{k_1'} \quad \text{so} \quad [HAH^+] = \frac{k_1[HA][H^+]}{k_1'}$$

and $\dfrac{d[BH^+]}{dt} = \boxed{\dfrac{k_1k_2}{k_1'}[HA][H^+][B]}$

This rate law can be made independent of $[H^+]$ if the source of H^+ is the acid HA, for then H^+ is given by another equilibrium

$$\frac{[H^+][A^-]}{[HA]} = K_a = \frac{[H^+]^2}{[HA]} \quad \text{so} \quad [H^+] = (K_a[HA])^{1/2}$$

and $\dfrac{d[BH^+]}{dt} = \boxed{\dfrac{k_1k_2K_a^{1/2}}{k_1'}[HA]^{3/2}[B]}$

E26.9(b) A_2 appears in the initiation step only.

$$\frac{d[A_2]}{dt} = -k_1[A_2]$$

Consequently, the rate of consumption of $[A_2]$ is first order in A_2 and the rate is independent of intermediate concentrations.

E26.10(b) The maximum velocity is $k_b[E]_0$ and the velocity in general is

$$v = k[E]_0 = \frac{k_b[S][E]_0}{K_M + [S]} \quad \text{so} \quad v_{max} = k_b[E]_0 = \frac{K_M + [S]}{[S]}v$$

$$v_{max} = \frac{(0.042 + 0.890)\,\text{mol L}^{-1}}{0.890\,\text{mol L}^{-1}}(2.45 \times 10^{-4}\,\text{mol L}^{-1}\,\text{s}^{-1}) = \boxed{2.57 \times 10^{-4}\,\text{mol L}^{-1}\,\text{s}^{-1}}$$

E26.11(b) The quantum yield tells us that each mole of photons absorbed causes 1.2×10^2 moles of A to react; the stoichiometry tells us that 1 mole of B is formed for every mole of A which reacts. From the yield of 1.77 mmol B, we infer that 1.77 mmol A reacted, caused by the absorption of $1.77 \times 10^{-3}\,\text{mol}/(1.2 \times 10^2\,\text{mol Einstein}^{-1}) = \boxed{1.5 \times 10^{-5}\ \text{moles of photons}}$

E26.12(b) The quantum efficiency is defined as the amount of reacting molecules n_A divided by the amount of photons absorbed n_{abs}. The fraction of photons absorbed f_{abs} is one minus the fraction transmitted f_{trans}; and the amount of photons emitted n_{photon} can be inferred from the energy of the light source (power P times time t) and the energy of the photons (hc/λ).

$$\begin{aligned}\Phi &= \frac{n_A hcN_A}{(1 - f_{trans})\lambda Pt} \\ &= \frac{(0.324\,\text{mol}) \times (6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^8\,\text{m s}^{-1}) \times (6.022 \times 10^{23}\,\text{mol}^{-1})}{(1 - 0.257) \times (320 \times 10^{-9}\,\text{m}) \times (87.5\,\text{W}) \times (28.0\,\text{min}) \times (60\,\text{s min}^{-1})} \\ &= \boxed{1.11}\end{aligned}$$

Solutions to problems

Solutions to numerical problems

P26.2 $O + Cl_2 \rightarrow ClO + Cl \quad p(Cl_2) \approx \text{constant}$ [Cl_2 at high pressure]

Therefore, the reaction is probably pseudo-first order, and

$$[O] \approx [O]_0 e^{-k't}$$

That being so, $\ln \dfrac{[O]_0}{[O]} = k't = k[Cl_2]t = k[Cl_2] \times \dfrac{d}{v}$

where $k' = [Cl_2]k$, v is the flow rate, and d is the distance along the tube. We draw up the following table

d/cm	0	2	4	6	8	10	12	14	16	18
$\ln \dfrac{[O]_0}{[O]}$	0.27	0.31	0.34	0.38	0.45	0.46	0.50	0.55	0.56	0.60

The points are plotted in Fig. 26.1.

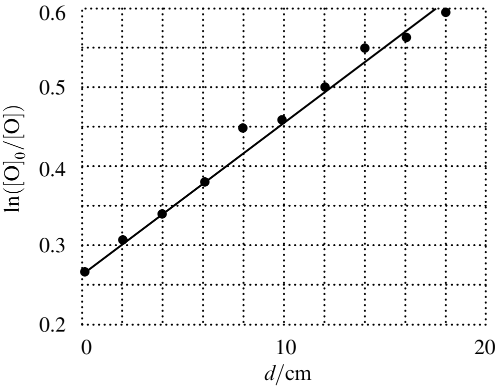


Figure 26.1

The slope is 0.0189, and so $\dfrac{k[Cl_2]}{v} = 0.0189\,\text{cm}^{-1}$.

Therefore, $k = \dfrac{(0.0189\,\text{cm}^{-1}) \times v}{[Cl_2]}$

$$= \frac{(0.0189\,\text{cm}^{-1}) \times (6.66 \times 10^2\,\text{cm s}^{-1})}{2.54 \times 10^{-7}\,\text{mol L}^{-1}} = \boxed{5.0 \times 10^7\,\text{L mol}^{-1}\,\text{s}^{-1}}$$

(There is a very fast $O + ClO \rightarrow Cl + O_2$ reaction, and so the answer given here is actually twice the true value.)

P26.5

$H_2 \rightarrow 2H\cdot$	initiation,	$v = v_{\text{init}}$
$H\cdot + O_2 \rightarrow \cdot OH + \cdot O\cdot$	branching,	$v = k_1[H\cdot][O_2]$
$\cdot O\cdot + H_2 \rightarrow \cdot OH + H\cdot$	branching,	$v = k_2[\cdot O\cdot][H_2]$
$H\cdot + O_2 \rightarrow HO_2\cdot$	propagation,	$v = k_3[H\cdot][O_2]$
$HO_2\cdot + H_2 \rightarrow H_2O + \cdot OH$	propagation,	$v = k_4[HO_2\cdot][H_2]$
$HO_2\cdot + \text{wall} \rightarrow \text{destruction}$	termination,	$v = k_5[HO_2\cdot]$
$H\cdot + M \rightarrow \text{destruction}$	termination,	$v = k_6[H\cdot][M]$

We identify the onset of explosion with the rapid increase in the concentration of radicals which we initially identify with [H·]. Then

$$v_{\text{rad}} = v_{\text{init}} - k_1[\text{H}\cdot][\text{O}_2] + k_2[\cdot\text{O}\cdot][\text{H}_2] - k_3[\text{H}\cdot][\text{O}_2] - k_6[\text{H}\cdot][\text{M}]$$

Intermediates are examined with the steady-state approximation.

$$\frac{\text{d}[\cdot\text{O}\cdot]}{\text{d}t} = k_1[\text{H}\cdot][\text{O}_2] - k_2[\cdot\text{O}\cdot][\text{H}_2] \approx 0$$

$$[\cdot\text{O}\cdot]_{\text{SS}} \approx \frac{k_1[\text{H}\cdot][\text{O}_2]}{k_2[\text{H}_2]}$$

Therefore,

$$\begin{aligned} v_{\text{rad}} &= v_{\text{init}} - k_1[\text{H}\cdot][\text{O}_2] + k_2\left(\frac{k_1[\text{H}\cdot][\text{O}_2]}{k_2[\text{H}_2]}\right)[\text{H}_2] - k_3[\text{H}\cdot][\text{O}_2] - k_6[\text{H}\cdot][\text{M}] \\ &= v_{\text{init}} - (k_3[\text{O}_2] + k_6[\text{M}])[\text{H}\cdot] \end{aligned}$$

The factor $(k_3[\text{O}_2] + k_6[\text{M}])$ is always positive and, therefore, v_{rad} always decreases for all values of [H·]. No explosion is possible according to this mechanism, or at least no exponential growth of [H·] is observed.

Let us try a second approach for which the concentration of radicals is identified with [·O·].

$$v_{\text{rad}} = k_1[\text{H}\cdot][\text{O}_2] - k_2[\cdot\text{O}\cdot][\text{H}_2]$$

Using the steady-state approximation to describe [H·], we find that

$$[\text{H}\cdot]_{\text{SS}} = \frac{v_{\text{init}} + k_2[\text{H}_2][\cdot\text{O}\cdot]}{(k_1 + k_3)[\text{O}_2] + k_6[\text{M}]}$$

$$v_{\text{rad}} = \frac{v_{\text{init}}k_1[\text{O}_2]}{(k_1 + k_3)[\text{O}_2] + k_6[\text{M}]} + \left\{\frac{k_1k_2[\text{H}_2][\text{O}_2]}{(k_1 + k_3)[\text{O}_2] + k_6[\text{M}]} - k_2[\text{H}_2]\right\}[\cdot\text{O}\cdot]$$

This has the form

$$v_{\text{rad}} = \frac{\text{d}[\cdot\text{O}\cdot]}{\text{d}t} = C_1 + \{C_2 - C_3\}[\cdot\text{O}\cdot]$$

where C_1, C_2, and C_3 are always positive. This means that the mechanism predicts exponential growth of radicals, and explosion, when $C_2 > C_3$. This will occur when $\dfrac{k_1[\text{O}_2]}{(k_1 + k_3)[\text{O}_2] + k_6[\text{M}]} > 1$. But this is not possible. So no exponential growth of [·O·] can occur. The proposed mechanism is inconsistent with the existence of an explosion on the assumption that the steady-state approximation can be applied to the intermediates H· and ·O·. It is, however, unlikely that the steady-state approximation can be applied to explosive reactions, and this is where the analysis breaks down.

P26.8 $\text{M} + h\nu_{\text{i}} \rightarrow \text{M}^*$, $\quad I_{\text{a}}$ [M = benzophenone]
$\text{M}^* + \text{Q} \rightarrow \text{M} + \text{Q}$, $\quad k_{\text{q}}$
$\text{M}^* \rightarrow \text{M} + h\nu_{\text{f}}$, $\quad k_{\text{f}}$

$$\frac{\text{d}[\text{M}^*]}{\text{d}t} = I_{\text{a}} - k_{\text{f}}[\text{M}^*] - k_{\text{q}}[\text{Q}][\text{M}^*] \approx 0 \text{ [steady state]}$$

and hence $[\text{M}^*] = \dfrac{I_{\text{a}}}{k_{\text{f}} + k_{\text{q}}[\text{Q}]}$

Then $I_f = k_f[M^*] = \dfrac{k_f I_a}{k_f + k_q[Q]}$

and so $\boxed{\dfrac{1}{I_f} = \dfrac{1}{I_a} + \dfrac{k_q[Q]}{k_f I_a}}$

If the exciting light is extinguished, $[M^*]$, and hence I_f, decays as $e^{-k_f t}$ in the absence of a quencher. Therefore we can measure $k_q/k_f I_a$ from the slope of $1/I_f$ plotted against [Q], and then use k_f to determine k_q.

We draw up the following table

$10^3[Q]/M$	1	5	10
$\dfrac{1}{I_f}$	2.4	4.0	6.3

The points are plotted in Fig. 26.2.

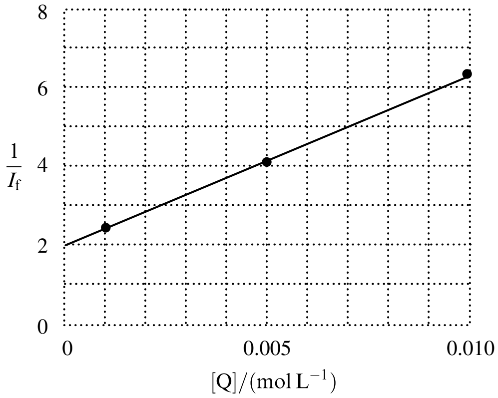


Figure 26.2

The intercept lies at 2.0, and so $I_a = \dfrac{1}{2.0} = 0.50$. The slope is 430, and so

$$\frac{k_q}{k_f I_a} = 430\,\text{L mol}^{-1}$$

Then, since $I_a = 0.50$ and $k_f = \dfrac{\ln 2}{t_{1/2}}$,

$$k_q = (0.50) \times (430\,\text{L mol}^{-1}) \times \left(\frac{\ln 2}{29 \times 10^{-6}\,\text{s}}\right) = \boxed{5.1 \times 10^6\,\text{L mol}^{-1}\,\text{s}^{-1}}$$

Solutions to theoretical problems

P26.11 $\dfrac{d[CH_3CH_3]}{dt} = -k_a[CH_3CH_3] - k_b[CH_3][CH_3CH_3] - k_d[CH_3CH_3][H] + k_e[CH_3CH_2][H]$

We apply the steady-state approximation to the three intermediates CH_3, CH_3CH_2, and H.

$$\frac{d[CH_3]}{dt} = 2k_a[CH_3CH_3] - k_b[CH_3CH_3][CH_3] = 0$$

which implies that $[CH_3] = \dfrac{2k_a}{k_b}$.

$$\frac{\mathrm{d}[\mathrm{CH_3CH_2}]}{\mathrm{d}t} = k_\mathrm{b}[\mathrm{CH_3}][\mathrm{CH_3CH_3}] - k_\mathrm{c}[\mathrm{CH_3CH_2}] + k_\mathrm{d}[\mathrm{CH_3CH_3}][\mathrm{H}] - k_\mathrm{e}[\mathrm{CH_3CH_2}][\mathrm{H}] = 0$$

$$\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t} = k_\mathrm{c}[\mathrm{CH_3CH_2}] - k_\mathrm{d}[\mathrm{CH_3CH_3}][\mathrm{H}] - k_\mathrm{e}[\mathrm{CH_3CH_2}][\mathrm{H}] = 0$$

These three equations give

$$[\mathrm{H}] = \frac{k_\mathrm{c}}{k_\mathrm{e} + k_\mathrm{d}\frac{[\mathrm{CH_3CH_3}]}{[\mathrm{CH_3CH_2}]}}$$

$$[\mathrm{CH_3CH_2}]^2 - \left(\frac{k_\mathrm{a}}{k_\mathrm{c}}\right)[\mathrm{CH_3CH_3}][\mathrm{CH_3CH_2}] - \left(\frac{k_\mathrm{a}k_\mathrm{d}}{k_\mathrm{c}k_\mathrm{e}}\right)[\mathrm{CH_3CH_3}]^2 = 0$$

or $[\mathrm{CH_3CH_2}] = \left\{\left(\frac{k_\mathrm{a}}{2k_\mathrm{c}}\right) + \left[\left(\frac{k_\mathrm{a}}{2k_\mathrm{c}}\right)^2 + \left(\frac{k_\mathrm{a}k_\mathrm{d}}{k_\mathrm{c}k_\mathrm{e}}\right)\right]^{1/2}\right\}[\mathrm{CH_3CH_3}]$

which implies that

$$[\mathrm{H}] = \frac{k_\mathrm{c}}{k_\mathrm{e} + \frac{k_\mathrm{d}}{\kappa}}, \quad \kappa = \left(\frac{k_\mathrm{a}}{2k_\mathrm{c}}\right) + \left[\left(\frac{k_\mathrm{a}}{2k_\mathrm{c}}\right)^2 + \left(\frac{k_\mathrm{a}k_\mathrm{d}}{k_\mathrm{c}k_\mathrm{e}}\right)\right]^{1/2}$$

If k_a is small in the sense that only the lowest order need be retained,

$$[\mathrm{CH_3CH_2}] \approx \left(\frac{k_\mathrm{a}k_\mathrm{d}}{k_\mathrm{c}k_\mathrm{e}}\right)^{1/2}[\mathrm{CH_3CH_3}]$$

$$[\mathrm{H}] \approx \frac{k_\mathrm{c}}{k_\mathrm{e} + k_\mathrm{d}\left(\frac{k_\mathrm{c}k_\mathrm{e}}{k_\mathrm{a}k_\mathrm{d}}\right)^{1/2}} \approx \left(\frac{k_\mathrm{a}k_\mathrm{c}}{k_\mathrm{d}k_\mathrm{e}}\right)^{1/2}$$

The rate of production of ethene is therefore

$$\frac{\mathrm{d}[\mathrm{CH_2CH_2}]}{\mathrm{d}t} = k_\mathrm{c}[\mathrm{CH_3CH_2}] = \left(\frac{k_\mathrm{a}k_\mathrm{c}k_\mathrm{d}}{k_\mathrm{e}}\right)^{1/2}[\mathrm{CH_3CH_3}]$$

The rate of production of ethene is equal to the rate of consumption of ethane (the intermediates all have low concentrations), so

$$\frac{\mathrm{d}[\mathrm{CH_3CH_3}]}{\mathrm{d}t} = -k[\mathrm{CH_3CH_3}], \quad k = \left(\frac{k_\mathrm{a}k_\mathrm{c}k_\mathrm{d}}{k_\mathrm{e}}\right)^{1/2}$$

Different orders may arise if the reaction is sensitized so that k_a is increased.

P26.12

$$\begin{array}{ll}
\mathrm{CH_3CHO} \rightarrow \cdot\mathrm{CH_3} + \cdot\mathrm{CHO}, & k_\mathrm{a} \\
\cdot\mathrm{CH_3} + \mathrm{CH_3\cdot CHO} \rightarrow \mathrm{CH_4} + \cdot\mathrm{CH_2CHO}, & k_\mathrm{b} \\
\cdot\mathrm{CH_2CHO} \rightarrow \mathrm{CO} + \cdot\mathrm{CH_3}, & k_\mathrm{c} \\
\cdot\mathrm{CH_3} + \cdot\mathrm{CH_3} \rightarrow \mathrm{CH_3CH_3}, & k_\mathrm{d}
\end{array}$$

$$\frac{\mathrm{d}[\mathrm{CH_4}]}{\mathrm{d}t} = k_\mathrm{b}[\mathrm{CH_3}][\mathrm{CH_3CHO}]$$

$$\frac{\mathrm{d}[\mathrm{CH_3CHO}]}{\mathrm{d}t} = -k_\mathrm{a}[\mathrm{CH_3CHO}] - k_\mathrm{b}[\mathrm{CH_3CHO}][\mathrm{CH_3}]$$

$$\frac{d[CH_3]}{dt} = k_a[CH_3CHO] - k_b[CH_3CHO][CH_3] + k_c[CH_2CHO] - 2k_d[CH_3]^2 = 0$$
$$\frac{d[CH_2CHO]}{dt} = k_b[CH_3][CH_3CHO] - k_c[CH_2CHO] = 0$$

Adding the last two equations gives

$$k_a[CH_3CHO] - 2k_d[CH_3]^2 = 0, \quad \text{or} \quad [CH_3] = \left(\frac{k_a}{2k_d}\right)^{1/2}[CH_3CHO]^{1/2}$$

Therefore

$$\frac{d[CH_4]}{dt} = k_b\left(\frac{k_a}{2k_d}\right)^{1/2}[CH_3CHO]^{3/2}$$
$$\frac{d[CH_3CHO]}{dt} = -k_a[CH_3CHO] - k_b\left(\frac{k_a}{2k_d}\right)^{1/2}[CH_3CHO]^{3/2}$$

Note that, to lowest-order in k_a,

$$\frac{d[CH_3CHO]}{dt} \approx -k_b\left(\frac{k_a}{2k_d}\right)^{1/2}[CH_3CHO]^{3/2}$$

and the reaction is three-halves order in CH_3CHO.

P26.14 **(a)** $$\overline{M}_n^3 = M^3\sum_n n^3P_n = M^3(1-p)\sum_n n^3p^{n-1} \quad [P_n = p^{n-1}(1-p), \text{Problem 26.13}]$$
$$= M^3(1-p)\frac{d}{dp}\sum_n n^2p^n = M^3(1-p)\frac{d}{dp}p\frac{d}{dp}p\frac{d}{dp}\sum_n p^n$$
$$= M^3(1-p)\frac{d}{dp}p\frac{d}{dp}p\frac{d}{dp}(1-p)^{-1} = \frac{M^3(1+4p+p^2)}{(1-p)^3}$$
$$\overline{M}_n^2 = \frac{M^2(1+p)}{(1-p)^2} \quad [\text{Problem 26.13}]$$
$$\text{Therefore, } \frac{\overline{M}_n^3}{\overline{M}_n^2} = \boxed{\frac{M(1+4p+p^2)}{1-p^2}}$$

(b) $$\langle n\rangle = \frac{1}{1-p}[26.8], \quad \text{so} \quad p = 1 - \frac{1}{\langle n\rangle}$$
$$\frac{\overline{M}_n^3}{\overline{M}_n^2} = \boxed{(6\langle n\rangle^2 - 6\langle n\rangle + 1)\langle n\rangle}$$

P26.16 $$\frac{d[A]}{dt} = -k[A]^2[OH] = -k[A]^3 \quad \text{because} \quad [A] = [OH].$$
$$\frac{d[A]^3}{[A]} = -k\,dt \quad \text{and} \quad \int_{[A]_0}^{[A]}\frac{d[A]}{[A]^3} = -k\int_0^t dt = -kt$$

since $\int \frac{dx}{x^3} = \frac{-1}{2x^2}$, the equation becomes

$$\frac{1}{[A]^2} - \frac{1}{[A]_0^2} = 2kt \quad \text{or} \quad [A] = [A]_0\,(1 + 2kt[A]_0)^{-1/2}$$

By eqn 26.8a the degree of polymerization, $\langle n\rangle$, is given by

$$\langle n\rangle = \frac{[\mathrm{A}]_0}{[\mathrm{A}]} = \boxed{(1+2kt[\mathrm{A}]_0)^{1/2}}$$

P26.18 $$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = k[\mathrm{A}][\mathrm{P}]^2$$

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(A_0 - x)(P_0 + x)^2 \quad [x = P - P_0]$$

$$kt = \int_0^x \frac{\mathrm{d}x}{(A_0 - x)(P_0 + x)^2}$$

Integrate by partial fractions (as in Problem 26.17)

$$\begin{aligned}
k_t &= \left(\frac{1}{A_0+P_0}\right)\int_0^x \left\{\left(\frac{1}{P_0+x}\right)^2 + \left(\frac{1}{A_0+P_0}\right)\left[\frac{1}{P_0+x} + \frac{1}{A_0-x}\right]\right\}\mathrm{d}x \\
&= \left(\frac{1}{A_0+P_0}\right)\left\{\left(\frac{1}{P_0} - \frac{1}{P_0+x}\right) + \left(\frac{1}{A_0+P_0}\right)\left[\ln\left(\frac{P_0+x}{P_0}\right) + \ln\left(\frac{A_0}{A_0-x}\right)\right]\right\} \\
&= \left(\frac{1}{A_0+P_0}\right)\left[\left(\frac{x}{P_0(P_0+x)}\right) + \left(\frac{1}{A_0+P_0}\right)\ln\left(\frac{(P_0+x)A_0}{P_0(A_0-x)}\right)\right]
\end{aligned}$$

Therefore, with $y = \dfrac{x}{[\mathrm{A}]_0}$ and $p = \dfrac{P_0}{A_0}$,

$$A_0(A_0+P_0)kt = \boxed{\left(\frac{y}{p(p+y)}\right) + \left(\frac{1}{1+p}\right)\ln\left(\frac{p+y}{p(1-y)}\right)}$$

As in Problem 26.6, the rate is maximum when

$$\begin{aligned}
\frac{\mathrm{d}v_{\mathrm{P}}}{\mathrm{d}t} &= 2k[\mathrm{A}][\mathrm{P}]\left(\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t}\right) + k\left(\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}\right)[\mathrm{P}]^2 \\
&= 2k[\mathrm{A}][\mathrm{P}]v_{\mathrm{P}} - k[\mathrm{P}]^2 v_{\mathrm{P}} = k[\mathrm{P}](2[\mathrm{A}] - [\mathrm{P}])v_{\mathrm{P}} = 0
\end{aligned}$$

That is, at $[\mathrm{A}] = \frac{1}{2}[\mathrm{P}]$

On substitution of this condition into the integrated rate law, we find

$$A_0(A_0+P_0)kt_{\max} = \left(\frac{2-p}{2p(1+p)}\right) + \left(\frac{1}{1+p}\right)\ln\frac{2}{p}$$

or $(A_0+P_0)^2 kt_{\max} = \boxed{\dfrac{2-p}{2p} + \ln\dfrac{2}{p}}$

P26.20 (i) $$\frac{\mathrm{d}[\mathrm{X}]}{\mathrm{d}t} = k_{\mathrm{a}}[\mathrm{A}][\mathrm{Y}] - k_{\mathrm{b}}[\mathrm{X}][\mathrm{Y}] + k_{\mathrm{c}}[\mathrm{A}][\mathrm{X}] - 2k_{\mathrm{d}}[\mathrm{X}]^2$$

(ii) $$\frac{\mathrm{d}[\mathrm{Y}]}{\mathrm{d}t} = -k_{\mathrm{a}}[\mathrm{A}][\mathrm{Y}] - k_{\mathrm{b}}[\mathrm{X}][\mathrm{Y}] - k_{\mathrm{e}}[\mathrm{Z}]$$

Express these differential equations as finite-difference equations

$$\text{(i)}\ \ \mathrm{X}(t_{\mathrm{i+1}}) = \mathrm{X}(t_{\mathrm{i}}) + \{k_{\mathrm{a}}[\mathrm{A}]\mathrm{Y}(t_{\mathrm{i}}) - k_{\mathrm{b}}\mathrm{X}(t_{\mathrm{i}})\mathrm{Y}(t_{\mathrm{i}}) + k_{\mathrm{c}}[\mathrm{A}]\mathrm{X}(t_{\mathrm{i}}) - 2k_{\mathrm{d}}\mathrm{X}^2(t_{\mathrm{i}})\}\Delta t$$

$$\text{(ii)}\ \ \mathrm{Y}(t_{\mathrm{i+1}}) = \mathrm{Y}(t_{\mathrm{i}}) + \{k_{\mathrm{c}}[\mathrm{Z}] - k_{\mathrm{a}}[\mathrm{A}]\mathrm{Y}(t_{\mathrm{i}}) - k_{\mathrm{b}}\mathrm{X}(t_{\mathrm{i}})\mathrm{Y}(t_{\mathrm{i}})\}\Delta t$$

Solve these equations by iteration.

P26.21

$$\mathrm{A} \to \mathrm{B} \quad \frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = \mathcal{I}_{\mathrm{a}}$$

$$\mathrm{B} \to \mathrm{A} \quad \frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = -k[\mathrm{B}]^2$$

In the photostationary state $\mathcal{I}_{\mathrm{a}} - k[\mathrm{B}]^2 = 0$. Hence,

$$[\mathrm{B}] = \boxed{\left(\frac{\mathcal{I}_{\mathrm{a}}}{k}\right)^{1/2}} \propto [\mathrm{A}]^{1/2} \quad [\text{because } \mathcal{I} \propto [\mathrm{A}]]$$

The illumination may increase the rate of the forward reaction without affecting the reverse reaction. Hence the position of equilibrium may be shifted toward products.

P26.23

$$\begin{array}{ll}
\mathrm{Cl_2} + h\nu \to 2\mathrm{Cl} & \mathcal{I}_{\mathrm{a}} \\
\mathrm{Cl} + \mathrm{CHCl_3} \to \mathrm{CCl_3} + \mathrm{HCl} & k_2 \\
\mathrm{CCl_3} + \mathrm{Cl_2} \to \mathrm{CCl_4} + \mathrm{Cl} & k_3 \\
2\mathrm{CCl_3} + \mathrm{Cl_2} \to 2\mathrm{CCl_4} & k_4
\end{array}$$

$$\text{(i)}\ \ \frac{\mathrm{d}[\mathrm{CCl_4}]}{\mathrm{d}t} = 2k_4[\mathrm{CCl_3}]^2[\mathrm{Cl_2}] + k_3[\mathrm{CCl_3}][\mathrm{Cl_2}]$$

$$\text{(ii)}\ \ \frac{\mathrm{d}[\mathrm{CCl_3}]}{\mathrm{d}t} = k_2[\mathrm{Cl}][\mathrm{CHCl_3}] - k_3[\mathrm{CCl_3}][\mathrm{Cl_2}] - 2k_4[\mathrm{CCl_3}]^2[\mathrm{Cl_2}] = 0$$

$$\text{(iii)}\ \ \frac{\mathrm{d}[\mathrm{Cl}]}{\mathrm{d}t} = 2\mathcal{I}_{\mathrm{a}} - k_2[\mathrm{Cl}][\mathrm{CHCl_3}] + k_3[\mathrm{CCl_3}][\mathrm{Cl_2}] = 0$$

$$\text{(iv)}\ \ \frac{\mathrm{d}[\mathrm{Cl_2}]}{\mathrm{d}t} = -\mathcal{I}_{\mathrm{a}} - k_3[\mathrm{CCl_3}][\mathrm{Cl_2}] - k_4[\mathrm{CCl_3}]^2[\mathrm{Cl_2}]$$

Therefore, $\mathcal{I}_{\mathrm{a}} = k_4[\mathrm{CCl_3}]^2[\mathrm{Cl_2}]$ [(ii) + (iii)]

which implies that

$$[\mathrm{CCl_3}] = \left(\frac{1}{k_4}\right)^{1/2}\left(\frac{\mathcal{I}_{\mathrm{a}}}{[\mathrm{Cl_2}]}\right)^{1/2}$$

Then, with (i),

$$\frac{\mathrm{d}[\mathrm{CCl_4}]}{\mathrm{d}t} = 2\mathcal{I}_{\mathrm{a}} + \frac{k_3\mathcal{I}_{\mathrm{a}}^{1/2}[\mathrm{Cl}]^{1/2}}{k_4^{1/2}}$$

When the pressure of chlorine is high, and the initiation rate is slow (in the sense that the lowest powers of $\mathcal{I}_{\mathrm{a}}$ dominate), the second term dominates the first, giving

$$\frac{\mathrm{d}[\mathrm{CCl_4}]}{\mathrm{d}t} = \frac{k_3\mathcal{I}_{\mathrm{a}}^{1/2}}{k_4^{1/2}}[\mathrm{Cl_2}]^{1/2} = \boxed{k\mathcal{I}_{\mathrm{a}}^{1/2}[\mathrm{Cl_2}]^{1/2}}$$

with $k = \dfrac{k_3}{k_4^{1/2}}$. It seems necessary to suppose that Cl + Cl recombination (which needs a third body) is unimportant.

Solutions to applications

P26.26 The mechanism considered is

$$\mathrm{E} + \mathrm{S} \underset{k'_\mathrm{a}}{\overset{k_\mathrm{a}}{\rightleftharpoons}} (\mathrm{ES}) \underset{k'_\mathrm{a}}{\overset{k_\mathrm{a}}{\rightleftharpoons}} \mathrm{P} + \mathrm{E}$$

We apply the steady-state approximation to [(ES)].

$$\frac{\mathrm{d[ES]}}{\mathrm{d}t} = k_\mathrm{a}[\mathrm{E}][\mathrm{S}] - k'_\mathrm{a}[(\mathrm{ES})] - k_\mathrm{b}[(\mathrm{ES})] + k'_\mathrm{b}[\mathrm{E}][\mathrm{P}] = 0$$

Substituting $[\mathrm{E}] = [\mathrm{E}]_0 - [(\mathrm{ES})]$ we obtain

$$k_\mathrm{a}([\mathrm{E}]_0 - [(\mathrm{ES})])[\mathrm{S}] - k'_\mathrm{a}[(\mathrm{ES})] - k_\mathrm{b}[(\mathrm{ES})] + k'_\mathrm{b}([\mathrm{E}]_0 - [(\mathrm{ES})])[\mathrm{P}] = 0$$

$$(-k_\mathrm{a}[\mathrm{S}] - k'_\mathrm{a} - k_\mathrm{b} - k'_\mathrm{b}[\mathrm{P}])[(\mathrm{ES})] + k_\mathrm{a}[\mathrm{E}]_0[\mathrm{S}] - k'_\mathrm{b}[\mathrm{E}]_0[\mathrm{P}] = 0$$

$$[(\mathrm{ES})] = \frac{k_\mathrm{a}[\mathrm{E}]_0[\mathrm{S}] + k'_\mathrm{b}[\mathrm{E}]_0[\mathrm{P}]}{k_\mathrm{a}[\mathrm{S}] + k'_\mathrm{a} + k_\mathrm{b} + k'_\mathrm{b}[\mathrm{P}]} = \frac{[\mathrm{E}]_0[\mathrm{S}] + \left(\frac{k'_\mathrm{b}}{k_\mathrm{a}}\right)[\mathrm{E}]_0[\mathrm{P}]}{K_\mathrm{M} + [\mathrm{S}] + \left(\frac{k'_\mathrm{b}}{k_\mathrm{a}}\right)[\mathrm{P}]} \qquad \left[K_\mathrm{M} = \frac{k'_\mathrm{a} + k_\mathrm{b}}{k_\mathrm{a}}\right]$$

$$\text{Then, } \frac{\mathrm{d[P]}}{\mathrm{d}t} = k_\mathrm{b}[(\mathrm{ES})] - k'_\mathrm{b}[\mathrm{P}][\mathrm{E}] = k_\mathrm{b}\frac{[\mathrm{E}]_0[\mathrm{S}] + \left(\frac{k'_\mathrm{b}}{k_\mathrm{a}}\right)[\mathrm{E}]_0[\mathrm{P}]}{K_\mathrm{M} + [\mathrm{S}] + \left(\frac{k'_\mathrm{b}}{k_\mathrm{a}}\right)[\mathrm{P}]} - k_{\mathrm{b}'}[\mathrm{P}]$$

$$\times\left([\mathrm{E}]_0 - \frac{[\mathrm{E}]_0[\mathrm{S}] + \left(\frac{k'_\mathrm{b}}{k_\mathrm{a}}\right)[\mathrm{E}]_0[\mathrm{P}]}{K_\mathrm{M} + [\mathrm{S}] + \left(\frac{k'_\mathrm{b}}{k_\mathrm{a}}\right)[\mathrm{P}]}\right)$$

$$= \frac{k_\mathrm{b}\left[[\mathrm{E}]_0[\mathrm{S}] + \left(\frac{k'_\mathrm{b}}{k_\mathrm{a}}\right)[\mathrm{E}]_0[\mathrm{P}]\right] - k'_\mathrm{b}[\mathrm{E}]_0[P]K_\mathrm{M}}{K_\mathrm{M} + [\mathrm{S}] + \left(\frac{k'_\mathrm{b}}{k_\mathrm{a}}\right)[\mathrm{P}]}$$

Substituting for K_M in the numerator and rearranging

$$\boxed{\frac{\mathrm{d[P]}}{\mathrm{d}t} = \frac{k_\mathrm{b}[\mathrm{E}]_0[\mathrm{S}] + \left(\frac{k'_\mathrm{a}k'_\mathrm{b}}{k_\mathrm{a}}\right)[\mathrm{E}]_0[\mathrm{P}]}{K_\mathrm{M} + [\mathrm{S}] + \left(\frac{k'_\mathrm{b}}{k_\mathrm{a}}\right)[\mathrm{P}]}}$$

For large concentrations of substrate, such that $[\mathrm{S}] \gg K_\mathrm{M}$ and $[\mathrm{S}] \gg [\mathrm{P}]$,

$$\boxed{\frac{\mathrm{d[P]}}{\mathrm{d}t} = k_\mathrm{b}[\mathrm{E}]_0}$$

which is the same as the unmodified mechanism. For $[\mathrm{S}] \gg K_\mathrm{M}$, but $[\mathrm{S}] \approx [\mathrm{P}]$

$$\boxed{\frac{\mathrm{d[P]}}{\mathrm{d}t} = k_\mathrm{b}[\mathrm{E}]_0\left\{\frac{[\mathrm{S}] - (k/k_\mathrm{b})[\mathrm{P}]}{[\mathrm{S}] + (k/k'_\mathrm{a})[\mathrm{P}]}\right\}} \qquad k = \frac{k'_\mathrm{a}k'_\mathrm{b}}{k_\mathrm{a}}$$

$$\text{For } [S] \to 0,\ \frac{\mathrm{d[P]}}{\mathrm{d}t} = \frac{-k'_\mathrm{a}k'_\mathrm{b}[\mathrm{E}]_0[\mathrm{P}]}{k'_\mathrm{a} + k_\mathrm{b} + k'_\mathrm{b}[\mathrm{P}]} = \boxed{\frac{-k'_\mathrm{a}[\mathrm{E}]_0[\mathrm{P}]}{k_\mathrm{P} + [\mathrm{P}]}}$$

where $k_\mathrm{P} = \dfrac{k'_\mathrm{a} + k_\mathrm{b}}{k'_\mathrm{b}}$

Comment. The negative sign in the expression for $\dfrac{\mathrm{d[P]}}{\mathrm{d}t}$ for the case $[\mathrm{S}] \to 0$ is to be interpreted to mean that the mechanism in this case is the reverse of the mechanism for the case $[\mathrm{P}] \to 0$. The roles of P and S are interchanged.

Question. Can you demonstrate the last statement in the comment above?

P26.28 $$\nu = \frac{\nu_{\max}}{1 + K_M\,[S]_0} \qquad [26.21]$$

Taking the inverse and multiplying by $\nu_{\max}\,\nu$, we find that

$$\nu_{\max} = \nu + K_{\mathrm{M}}\frac{\nu}{[\mathrm{S}]_0}$$

Thus,

$$\nu = \nu_{\max} - K_{\mathrm{M}}\frac{\nu}{[\mathrm{S}]_0} \quad \text{or} \quad \boxed{\frac{\nu}{[\mathrm{S}]_0} = \frac{\nu_{\max}}{K_{\mathrm{M}}} - \frac{\nu}{K_{\mathrm{M}}}}$$

The regression slope and intercept of the Eadie–Hofstee data plot of ν against $\nu/[\mathrm{S}]_0$ gives $-K_{\mathrm{M}}$ and $\nu_{\max}$, respectively. Alternatively, the regression slope and intercept of an Eadie–Hofstee data plot of $\nu/[\mathrm{S}]_0$ against ν gives $-1/K_{\mathrm{M}}$, and $\nu_{\max}/K_{\mathrm{M}}$, respectively. The slope and intercept of the latter plot can be used to in the calculation of K_{M} and $\nu_{\max}$.

P26.32 The rate of reaction is the rate at which ozone absorbs photons times the quantum yield. The rate at which ozone absorbs photons is the rate at which photons impinge on the ozone times the fraction of photons absorbed. That fraction is $1 - T$, where T is the transmittance. T is related to the absorbance A by

$$A = -\log T = \varepsilon c l \quad \text{so} \quad 1 - T = 1 - 10^{-\varepsilon c l}$$

$$1 - T = 1 - 10^{-\{(260\,\mathrm{L\,mol^{-1}\,cm^{-1}})\times(8\times10^{-9}\,\mathrm{mol\,L^{-1}})\times(10^5\,\mathrm{cm})\}} = 0.38$$

If we let F stand for the flux of photons (the rate at which photons impinge on our sample of ozone), then the rate of reaction is

$$\nu = \Phi(1-T)F = (0.94)\times(0.38)\times\frac{(1\times10^{14}\,\mathrm{cm^{-2}\,s^{-1}})\times(1000\,\mathrm{cm^3\,L^{-1}})}{(6.022\times10^{23}\,\mathrm{mol^{-1}})\times(10^5\,\mathrm{cm})}$$

$$= \boxed{5.9\times10^{-13}\,\mathrm{mol\,L^{-1}\,s^{-1}}}$$

27 Molecular reaction dynamics

Solutions to exercises

Discussion questions

E27.1(b) A reaction in solution can be regarded as the outcome of two stages: one is the encounter of two reactant species, which is followed by their reaction, the second stage, if they acquire their activation energy. If the rate-determining step is the former, then the reaction is said to be diffusion-controlled. If the rate-determining step is the latter, then the reaction is activation controlled. For a reaction of the form A + B → P that obeys the second-order rate law $\nu = k_2[\mathrm{A}][\mathrm{B}]$, in the diffusion-controlled regime,

$$k_2 = 4\pi R^* D N_\mathrm{A}$$

where D is the sum of the diffusion coefficients of the two reactant species and R^* is the distance at which reaction occurs. A further approximation is that each molecule obeys the Stokes–Einstein relation and Stokes' law, and then

$$k_2 \approx \frac{8RT}{3\eta}$$

where η is the viscosity of the medium. The result suggests that k_2 is independent of the radii of the reactants.

E27.2(b) In the kinetic salt effect, the rate of a reaction in solution is changed by modification of the ionic strength of the medium. If the reactant ions have the same sign of charge (as in cation/cation or anion/anion reactions), then an increase in ionic strength increases the rate constant. If the reactant ions have opposite signs (as in cation/anion reactions), then an increase in ionic strength decreases the rate constant. In the former case, the effect can be traced to the denser ionic atmosphere (see the Debye–Huckel theory) that forms round the newly formed and highly charged ion that constitutes the activated complex and the stronger interaction of that ion with the atmosphere. In the latter case, the ion corresponding to the activated complex has a lower charge than the reactants and hence it has a more diffuse ionic atmosphere and interacts with it more weakly. In the limit of low ionic strength the rate constant can be expected to follow the relation

$$\log k = \log k^\circ + 2Az_\mathrm{A}z_\mathrm{B}I^{1/2}$$

E27.3(b) Refer to Figs 27.21 and 27.22 of the text. The first of these figures shows an attractive potential energy surface, the second, a repulsive surface.

(a) Consider Fig. 27.21. If the original molecule is vibrationally excited, then a collision with an incoming molecule takes the system along the floor of the potential energy valley (trajectory C). This path is bottled up in the region of the reactants, and does not take the system to the saddle point. If, however, the same amount of energy is present solely as translational kinetic energy, then the system moves along a successful encounter trajectory C* and travels smoothly over the saddle point into products. We can therefore conclude that reactions with attractive potential energy surfaces proceed more efficiently if the energy is in relative translational motion. Moreover, the potential surface shows that once past the saddle point the trajectory runs up the steep wall of the product valley, and then rolls from side to side as it falls to the foot of the valley as the products separate. In other words, the products emerge in a vibrationally excited state.

(b) Now consider the repulsive surface (Fig. 27.22). On trajectory C the collisional energy is largely in translation. As the reactants approach, the potential energy rises. Their path takes them up the opposing face of the valley, and they are reflected back into the reactant region. This path corresponds to an unsuccessful encounter, even though the energy is sufficient for reaction. On a successful trajectory C*, some of the energy is in the vibration of the reactant molecule and the motion causes the trajectory to weave from side to side up the valley as it approaches the saddle point. This motion may be sufficient to tip the system round the corner to the saddle point and then on to products. In this case, the product molecule is expected to be in an unexcited vibrational state. Reactions with repulsive potential surfaces can therefore be expected to proceed more efficiently if the excess is present as vibrations.

Numerical exercises

E27.4(b) The collision frequency is

$$z = \frac{2^{1/2}\sigma\langle v\rangle p}{kT} \quad \text{where } \sigma = \pi d^2 = 4\pi r^2 \text{ and } \langle v\rangle = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

$$\text{so } z = \frac{2^{1/2}p}{kT}(4\pi r^2)\left(\frac{8RT}{\pi M}\right)^{1/2} = \frac{16pN_A r^2\pi^{1/2}}{(RTM)^{1/2}}$$

$$= \frac{16 \times (100 \times 10^3\,\text{Pa}) \times (6.022 \times 10^{23}\,\text{mol}^{-1}) \times (180 \times 10^{-12}\,\text{m})^2 \times (\pi)^{1/2}}{[(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K}) \times (28.01 \times 10^{-3}\,\text{kg mol}^{-1})]^{1/2}}$$

$$= \boxed{6.64 \times 10^9\,\text{s}^{-1}}$$

The collision density is

$$Z_{AA} = \frac{1}{2}zN/V = \frac{zp}{2kT} = \frac{(6.64 \times 10^9\,\text{s}^{-1}) \times (100 \times 10^3\,\text{Pa})}{2(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (298\,\text{K})} = \boxed{8.07 \times 10^{34}\,\text{m}^{-3}\,\text{s}^{-1}}$$

Raising the temperature at constant volume means raising the pressure in proportion to the temperature

$$Z_{AA} \propto \sqrt{T}$$

so the per cent increase in z and Z_{AA} due to a 10 K increase in temperature is $\boxed{1.6 \text{ per cent}}$, same as Exercise 27.4(a).

E27.5(b) The appropriate fraction is given by

$$f = \exp\left(\frac{-E_a}{RT}\right)$$

The values in question are

$$\textbf{(a)} \quad \text{(i)} \quad f = \exp\left(\frac{-15 \times 10^3\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (300\,\text{K})}\right) = \boxed{2.4 \times 10^{-3}}$$

$$\text{(ii)} \quad f = \exp\left(\frac{-15 \times 10^3\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (800\,\text{K})}\right) = \boxed{0.10}$$

$$\textbf{(b)} \quad \text{(i)} \quad f = \exp\left(\frac{-150 \times 10^3\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (300\,\text{K})}\right) = \boxed{7.7 \times 10^{-27}}$$

$$\text{(ii)} \quad f = \exp\left(\frac{-150 \times 10^3\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (800\,\text{K})}\right) = \boxed{1.6 \times 10^{-10}}$$

E27.6(b) A straightforward approach would be to compute $f = \exp\left(\frac{-E_a}{RT}\right)$ at the new temperature and compare it to that at the old temperature. An approximate approach would be to note that f changes from $f_0 = \exp\left(\frac{-E_a}{RT}\right)$ to $f = \exp\left(\frac{-E_a}{RT(1+x)}\right)$, where x is the fractional increase in the temperature. If x is small, the exponent changes from $\frac{-E_a}{RT}$ to approximately $\frac{-E_a}{RT}(1-x)$ and f changes from $\exp\left(\frac{-E_a}{RT}\right)$ to $\exp\left(\frac{-E_a(1-x)}{RT}\right) = \exp\left(\frac{-E_a}{RT}\right)\left[\exp\left(\frac{-E_a}{RT}\right)\right]^{-x} = f_0 f_0^{-x}$. Thus the new Boltzmann factor is the old one times a factor of f_0^{-x}. The factor of increase is

(a) (i) $f_0^{-x} = (2.4 \times 10^{-3})^{-10/300} = \boxed{1.2}$

(ii) $f_0^{-x} = (0.10)^{-10/800} = \boxed{1.03}$

(b) (i) $f_0^{-x} = (7.7 \times 10^{-27})^{-10/300} = \boxed{7.4}$

(ii) $f_0^{-x} = (1.6 \times 10^{-10})^{-10/800} = \boxed{1.3}$

E27.7(b) The reaction rate is given by

$$v = P\sigma\left(\frac{8k_BT}{\pi\mu}\right)^{1/2} N_A \exp(-E_a/RT)[D_2][Br_2]$$

so, in the absence of any estimate of the reaction probability P, the rate constant is

$$\begin{aligned} k &= \sigma\left(\frac{8k_BT}{\pi\mu}\right)^{1/2} N_A \exp(-E_a/RT) \\ &= [0.30 \times (10^{-9}\,\text{m})^2] \times \left(\frac{8(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (450\,\text{K})}{\pi(3.930\,\text{u}) \times (1.66 \times 10^{-27}\,\text{kg u}^{-1})}\right)^{1/2} \\ &\quad \times (6.022 \times 10^{23}\,\text{mol}^{-1}) \exp\left(\frac{-200 \times 10^3\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (450\,\text{K})}\right) \\ &= 1.71 \times 10^{-15}\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1} = \boxed{1.7 \times 10^{-12}\,\text{L mol}^{-1}\,\text{s}^{-1}} \end{aligned}$$

E27.8(b) The rate constant is

$$k_d = 4\pi R^* D N_A$$

where D is the sum of two diffusion constants. So

$$\begin{aligned} k_d &= 4\pi(0.50 \times 10^{-9}\,\text{m}) \times (2 \times 4.2 \times 10^{-9}\,\text{m}^2\,\text{s}^{-1}) \times (6.022 \times 10^{23}\,\text{mol}^{-1}) \\ &= \boxed{3.2 \times 10^7\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}} \end{aligned}$$

In more common units, this is

$$k_d = \boxed{3.2 \times 10^{10}\,\text{L mol}^{-1}\,\text{s}^{-1}}$$

E27.9(b) **(a)** A diffusion-controlled rate constant in decylbenzene is

$$k_d = \frac{8RT}{3\eta} = \frac{8 \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})}{3 \times (3.36 \times 10^{-3}\,\text{kg m}^{-1}\,\text{s}^{-1})} = \boxed{1.97 \times 10^6\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$$

(b) In concentrated sulfuric acid

$$k_d = \frac{8RT}{3\eta} = \frac{8 \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})}{3 \times (27 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}})} = \boxed{2.4 \times 10^{5}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}}$$

E27.10(b) The diffusion-controlled rate constant is

$$k_d = \frac{8RT}{3\eta} = \frac{8 \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})}{3 \times (0.601 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}})} = \boxed{1.10 \times 10^{7}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}}$$

In more common units, $k_d = \boxed{1.10 \times 10^{10}\,\mathrm{L\,mol^{-1}s^{-1}}}$

The recombination reaction has a rate of

$$v = k_d[\mathrm{A}][\mathrm{B}] \quad \text{with } [\mathrm{A}] = [\mathrm{B}]$$

so the half-life is given by

$$t_{1/2} = \frac{1}{k[\mathrm{A}]_0} = \frac{1}{(1.10 \times 10^{10}\,\mathrm{L\,mol^{-1}\,s^{-1}}) \times (1.8 \times 10^{-3}\,\mathrm{mol\,L^{-1}})} = \boxed{5.05 \times 10^{-8}\,\mathrm{s}}$$

E27.11(b) The reactive cross-section σ^* is related to the collision cross-section σ by

$$\sigma^* = P\sigma \quad \text{so} \quad P = \sigma^*/\sigma.$$

The collision cross-section σ is related to effective molecular diameters by

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

Now $\sigma_{AB} = \pi d_{AB}^2 = \pi\left[\frac{1}{2}(d_A + d_B)\right]^2 = \frac{1}{4}\left(\sigma_{AA}^{1/2} + \sigma_{BB}^{1/2}\right)^2$

$$\text{so } P = \frac{\sigma^*}{\frac{1}{4}\left(\sigma_{AA}^{1/2} + \sigma_{BB}^{1/2}\right)^2}$$

$$= \frac{8.7 \times 10^{-22}\,\mathrm{m}}{\frac{1}{4}[((0.88)^{1/2} + (0.40)^{1/2}) \times 10^{-9}\,\mathrm{m}]^2} = \boxed{2.22 \times 10^{-3}}$$

E27.12(b) The diffusion-controlled rate constant is

$$k_d = \frac{8RT}{3\eta} = \frac{8 \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (293\,\mathrm{K})}{3 \times (1.27 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}})} = 5.12 \times 10^{6}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$$

In more common units, $k_d = 5.12 \times 10^{9}\,\mathrm{L\,mol^{-1}\,s^{-1}}$

The recombination reaction has a rate of

$$v = k_d[\mathrm{A}][\mathrm{B}] = (5.12 \times 10^{9}\,\mathrm{L\,mol^{-1}\,s^{-1}}) \times (0.200\,\mathrm{mol\,L^{-1}}) \times (0.150\,\mathrm{mol\,L^{-1}})$$

$$= \boxed{1.54 \times 10^{8}\,\mathrm{mol\,L^{-1}\,s^{-1}}}$$

E27.13(b) The enthalpy of activation for a reaction in solution is

$$\Delta^{\ddagger}H = E_a - RT = (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (6134\,\mathrm{K}) - (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})$$

$$= 4.852 \times 10^4\,\mathrm{J\,mol^{-1}} = \boxed{48.52\,\mathrm{kJ\,mol^{-1}}}$$

The entropy of activation is

$$\Delta^{\ddagger}S = R\left(\ln\frac{A}{B} - 1\right) \quad \text{where } B = \frac{kRT^2}{hp^{\ominus}}$$

$$B = \frac{(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})^2}{(6.626 \times 10^{-34}\,\mathrm{J\,s}) \times (1.00 \times 10^5\,\mathrm{Pa})}$$

$$= 1.54 \times 10^{11}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$$

$$\text{so } \Delta^{\ddagger}S = (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \left(\ln\frac{8.72 \times 10^{12}\,\mathrm{L\,mol^{-1}\,s^{-1}}}{(1000\,\mathrm{L\,m^{-3}}) \times (1.54 \times 10^{11}\,\mathrm{m^3\,mol^{-1}\,s^{-1}})} - 1\right)$$

$$= \boxed{-32.2\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

Comment. In this connection, the enthalpy of activation is often referred to as 'energy' of activation.

E27.14(b) The Gibbs energy of activation is related to the rate constant by

$$k_2 = B\exp\left(\frac{-\Delta^{\ddagger}G}{RT}\right) \quad \text{where } B = \frac{kRT^2}{hp^{\ominus}} \quad \text{so} \quad \Delta^{\ddagger}G = -RT\ln\frac{k_2}{B}$$

$$k_2 = (6.45 \times 10^{13}\,\mathrm{L\,mol^{-1}\,s^{-1}})\mathrm{e}^{-\{(5375\,\mathrm{K})/(298\,\mathrm{K})\}} = 9.47 \times 10^5\,\mathrm{L\,mol^{-1}\,s^{-1}}$$

$$= 947\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$$

Using the value of B computed in Exercise 27.13(b), we obtain

$$\Delta^{\ddagger}G = -(8.3145 \times 10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K}) \times \ln\left(\frac{947\,\mathrm{m^3\,mol^{-1}\,s^{-1}}}{1.54 \times 10^{11}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}}\right)$$

$$= \boxed{46.8\,\mathrm{kJ\,mol^{-1}}}$$

E27.15(b) The entropy of activation for a bimolecular reaction in the gas phase is

$$\Delta^{\ddagger}S = R\left(\ln\frac{A}{B} - 2\right) \quad \text{where } B = \frac{kRT^2}{hp^{\ominus}}$$

$$B = \frac{(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times [(55 + 273)\,\mathrm{K}]^2}{(6.626 \times 10^{-34}\,\mathrm{J\,s}) \times (1.00 \times 10^5\,\mathrm{Pa})}$$

$$= 1.86 \times 10^{11}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$$

The rate constant is

$$k_2 = A\exp\left(\frac{-E_a}{RT}\right) \quad \text{so} \quad A = k_2\exp\left(\frac{E_a}{RT}\right)$$

$$A = (0.23\,\mathrm{m^3\,mol^{-1}\,s^{-1}}) \times \exp\left(\frac{49.6 \times 10^3\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (328\,\mathrm{K})}\right)$$

$$= 1.8 \times 10^7\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$$

$$\text{and } \Delta^{\ddagger}S = (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times \left(\ln\left(\frac{1.8\times 10^{7}\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}}{1.86\times 10^{11}\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}}\right) - 2\right)$$

$$= \boxed{-93\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

E27.16(b) The entropy of activation for a bimolecular reaction in the gas phase is

$$\Delta^{\ddagger}S = R\left(\ln\frac{A}{B} - 2\right) \quad \text{where } B = \frac{kRT^2}{hp^{\ominus}}$$

For the collision of structureless particles, the rate constant is

$$k_2 = N_A\left(\frac{8kT}{\pi\mu}\right)^{1/2}\sigma\exp\left(\frac{-\Delta E_0}{RT}\right)$$

so the prefactor is

$$A = N_A\left(\frac{8kT}{\pi\mu}\right)^{1/2}\sigma = 4N_A\left(\frac{RT}{\pi M}\right)^{1/2}\sigma$$

where we have used the fact that $\mu = \frac{1}{2}m$ for identical particles and $k/m = R/M$. So

$$\begin{aligned} A &= 4\times(6.022\times 10^{23}\,\text{mol}^{-1})\times\left(\frac{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(500\,\text{K})}{\pi\times(78\times 10^{-3}\,\text{kg mol}^{-1})}\right)^{1/2}\times(0.68\times 10^{-18}\,\text{m}^2) \\ &= 2.13\times 10^{8}\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1} \\ B &= \frac{(1.381\times 10^{-23}\,\text{J K}^{-1})\times(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(500\,\text{K})^2}{(6.626\times 10^{-34}\,\text{J s})\times(1.00\times 10^{5}\,\text{Pa})} \\ &= 4.33\times 10^{11}\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1} \end{aligned}$$

$$\text{and } \Delta^{\ddagger}S = (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times \left(\ln\left(\frac{2.13\times 10^{8}\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}}{4.33\times 10^{11}\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}}\right) - 2\right)$$

$$= \boxed{-80.0\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

E27.17(b) **(a)** The entropy of activation for a unimolecular gas-phase reaction is

$$\Delta^{\ddagger}S = R\left(\ln\frac{A}{B} - 1\right) \quad \text{where } B = 1.54\times 10^{11}\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1} \text{ [See Exercise 27.17(a)]}$$

$$\text{so } \Delta^{\ddagger}S = (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times\left(\ln\left(\frac{2.3\times 10^{13}\,\text{L mol}^{-1}\,\text{s}^{-1}}{(1000\,\text{L m}^{-3})\times(1.54\times 10^{11}\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1})}\right) - 1\right)$$

$$= \boxed{-24.1\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

(b) The enthalpy of activation is

$$\begin{aligned} \Delta^{\ddagger}H &= E_a - RT = 30.0\times 10^{3}\,\text{J mol}^{-1} - (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(298\,\text{K}) \\ &= 27.5\times 10^{3}\,\text{J mol}^{-1} = \boxed{27.5\,\text{kJ mol}^{-1}} \end{aligned}$$

(c) The Gibbs energy of activation is

$$\begin{aligned} \Delta^{\ddagger}G &= \Delta^{\ddagger}H - T\Delta^{\ddagger}S = 27.5\,\text{kJ mol}^{-1} - (298\,\text{K})\times(-24.1\times 10^{-3}\,\text{kJ K}^{-1}\,\text{mol}^{-1}) \\ &= \boxed{34.7\,\text{kJ mol}^{-1}} \end{aligned}$$

E27.18(b) The dependence of a rate constant on ionic strength is given by

$$\log k_2 = \log k_2^\circ + 2Az_Az_BI^{1/2}$$

At infinite dilution, $I = 0$ and $k_2 = k_2^\circ$, so we must find

$$\begin{aligned}\log k_2^\circ &= \log k_2 - 2Az_Az_BI^{1/2} = \log(1.55) - 2 \times (0.509) \times (+1) \times (+1) \times (0.0241)^{1/2} \\ &= 0.323 \quad \text{and} \quad \boxed{k_2^\circ = 1.08\,\mathrm{L^2\,mol^{-2}\,min^{-1}}}\end{aligned}$$

Solutions to problems

Solutions to numerical problems

P27.1

$$A = N_A\sigma^*\left(\frac{8kT}{\pi\mu}\right) \quad \text{[Section 27.1 and Exercise 27.16(a); } \mu = \tfrac{1}{2}m(\mathrm{CH_3})]$$

$$= (\sigma^*) \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}}) \times \left(\frac{(8) \times (1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K})}{(\pi) \times (1/2) \times (15.03\,\mathrm{u}) \times (1.6605 \times 10^{-27}\,\mathrm{kg/u})}\right)^{1/2}$$

$$= (5.52 \times 10^{26}) \times (\sigma^*\,\mathrm{mol^{-1}\,m\,s^{-1}})$$

(a) $$\sigma^* = \frac{2.4 \times 10^{10}\,\mathrm{mol^{-1}\,dm^3\,s^{-1}}}{5.52 \times 10^{26}\,\mathrm{mol^{-1}\,m\,s^{-1}}} = \frac{2.4 \times 10^{7}\,\mathrm{mol^{-1}\,m^3\,s^{-1}}}{5.52 \times 10^{26}\,\mathrm{mol^{-1}\,m\,s^{-1}}} = \boxed{4.4 \times 10^{-20}\,\mathrm{m^2}}$$

(b) Take $\sigma \approx \pi d^2$ and estimate d as 2 × bond length; therefore

$$\sigma = (\pi) \times (154 \times 2 \times 10^{-12}\,\mathrm{m})^2 = 3.0 \times 10^{-19}\,\mathrm{m^2}$$

Hence $P = \dfrac{\sigma^*}{\sigma} = \dfrac{4.3\bar{5} \times 10^{-20}}{3.0 \times 10^{-19}} = \boxed{0.15}$

P27.3 For radical recombination it has been found experimentally that $E_a \approx 0$. The maximum rate of recombination is obtained when $P = 1$ (or more), and then

$$k_2 = A = \sigma^*N_A\left(\frac{8kT}{\pi\mu}\right)^{1/2} = 4\sigma^*N_A\left(\frac{kT}{\pi m}\right)^{1/2} \quad \left[\mu = \tfrac{1}{2}m\right]$$

$$\sigma^* \approx \pi d^2 = \pi \times (308 \times 10^{-12}\,\mathrm{m})^2 = 3.0 \times 10^{-19}\,\mathrm{m^2}$$

Hence

$$\begin{aligned}k_2 &= (4) \times (3.0 \times 10^{-19}\,\mathrm{m^2}) \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}}) \\ &\quad \times \left(\frac{(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K})}{(\pi) \times (15.03\,\mathrm{u}) \times (1.6605 \times 10^{-27}\,\mathrm{kg/u})}\right)^{1/2} \\ &= 1.7 \times 10^{8}\,\mathrm{m^3\,mol^{-1}\,s^{-1}} = \boxed{1.7 \times 10^{11}\,\mathrm{M^{-1}\,s^{-1}}}\end{aligned}$$

The rate constant is for the rate law

$$v = k_2[\mathrm{CH_3}]^2$$

Therefore $\dfrac{\mathrm{d}[\mathrm{CH_3}]}{\mathrm{d}t} = -2k_2[\mathrm{CH_3}]^2$

and its solution is $\frac{1}{[CH_3]} - \frac{1}{[CH_3]_0} = 2k_2t$

For 90 per cent recombination, $[CH_3] = 0.10 \times [CH_3]_0$, which occurs when

$$2k_2t = \frac{9}{[CH_3]_0} \quad \text{or} \quad t = \frac{9}{2k_2[CH_3]_0}$$

The mole fractions of CH_3 radicals in which 10 mol% of ethane is dissociated is

$$\frac{(2) \times (0.10)}{1 + 0.10} = 0.18$$

The initial partial pressure of CH_3 radicals is thus

$$p_0 = 0.18\,p = 1.8 \times 10^4\,\text{Pa}$$

and $[CH_3]_0 = \frac{1.8 \times 10^4\,\text{Pa}}{RT}$

Therefore $t = \frac{9RT}{(2k_2) \times (1.8 \times 10^4\,\text{Pa})} = \frac{(9) \times (8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})}{(1.7 \times 10^8\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}) \times (3.6 \times 10^4\,\text{Pa})}$

$$= \boxed{3.6\,\text{ns}}$$

P27.6 Figure 27.1 shows that log k is proportional to the ionic strength for neutral molecules.

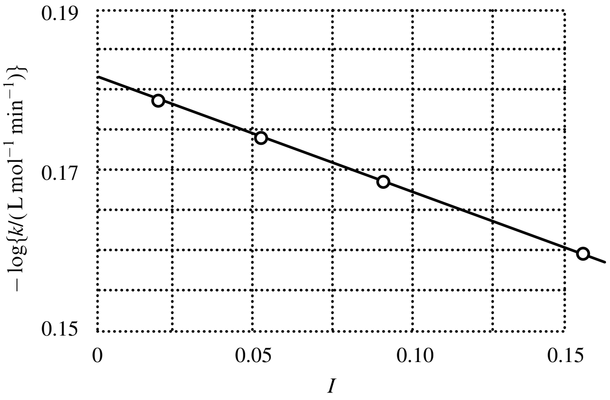


Figure 27.1

From the graph, the intercept at $I = 0$ is -0.182, so

$$k^\circ = \boxed{0.658\,\text{L mol}^{-1}\,\text{min}^{-1}}$$

Comment. In comparison to the effect of ionic strength on reactions in which two or more reactants are ions, the effect when only one is an ion is slight, in rough qualitative agreement with eqn 27.69.

P27.7 $\frac{\sigma^*}{\sigma} \approx \left(\frac{e^2}{4\pi\varepsilon_0 d(I - E_{ea})}\right)^2$ [Example 27.2]

Taking $\sigma = \pi d^2$ gives

$$\sigma^* \approx \pi\left(\frac{e^2}{4\pi\varepsilon_0[I(\text{M}) - E_{ea}(\text{X}_2)]}\right)^2 = \frac{6.5\,\text{nm}^2}{(I - E_{ea})/\text{eV}}$$

Thus, σ^* is predicted to increase as $I - E_{\mathrm{ea}}$ decreases. The data let us construct the following table

σ^*/nm^2	Cl_2	Br_2	I_2
Na	0.45	0.42	0.56
K	0.72	0.68	0.97
Rb	0.77	0.72	1.05
Cs	0.97	0.90	1.34

All values of σ^* in the table are smaller than the experimental ones, but they do show the correct trends down the columns. The variation with E_{ea} across the table is not so good, possibly because the electron affinities used here are poor estimates.

Question. Can you find better values of electron affinities and do they improve the horizontal trends in the table?

P27.10 $\mathrm{A} + \mathrm{A} \rightarrow \mathrm{A}_2 \quad \Delta v = -1$

$$\Delta^{\ddagger}S = R\left(\ln\left[\frac{A}{\left(\frac{kT}{h}\right)\times\left(\frac{RT}{p^{\ominus}}\right)}\right]+2\right) \quad [27.63]$$

$$= -(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \left[\ln\left[\frac{4.07\times 10^{5}\,\mathrm{M^{-1}\,s^{-1}}\left(\frac{\mathrm{m^3}}{10^3\,\mathrm{L}}\right)}{\frac{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(300\,\mathrm{K})^2\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})}{(6.626\times10^{-34}\,\mathrm{J\,s})\times(1.013\times10^{5}\,\mathrm{Pa})}}\right]+2\right]$$

$$= (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times [\ln(2.631\times10^{-9})+2]$$

$$\boxed{\Delta^{\ddagger}S = -148\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

$$\Delta^{\ddagger}H = E_{\mathrm{a}} - 2RT = 65.43\,\mathrm{kJ\,mol^{-1}} - 2\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(300\,\mathrm{K}) \times\left(\frac{10^{-3}\,\mathrm{kJ}}{\mathrm{J}}\right) \quad [27.60, 27.61]$$

$$\boxed{\Delta^{\ddagger}H = 60.44\,\mathrm{kJ\,mol^{-1}}}$$

$$\begin{aligned}
\Delta^{\ddagger}H &= \Delta^{\ddagger}U + \Delta^{\ddagger}(pV)\\
\Delta^{\ddagger}U &= \Delta^{\ddagger}H - \Delta^{\ddagger}(pV) = \Delta^{\ddagger}H - \Delta vRT\\
&= (60.44\,\mathrm{kJ\,mol^{-1}}) - (-1)\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(300\,\mathrm{K})\times\left(\frac{10^{-3}\,\mathrm{kJ}}{\mathrm{J}}\right)
\end{aligned}$$

$$\boxed{\Delta^{\ddagger}U = 62.9\,\mathrm{kJ\,mol^{-1}}}$$

$$\Delta^{\ddagger}G = \Delta^{\ddagger}H - T\Delta^{\ddagger}S = 60.44\,\mathrm{kJ\,mol^{-1}} - (300\,\mathrm{K})\times(-148\,\mathrm{J\,K^{-1}\,mol^{-1}})\times\left(\frac{10^{-3}\,\mathrm{kJ}}{\mathrm{J}}\right)$$

$$\boxed{\Delta^{\ddagger}G = 104.8\,\mathrm{kJ\,mol^{-1}}} \quad [27.59]$$

P27.12 **(a)** The multilinear hypothesis is

$$E_a = c_1\Delta G_b + c_2 I + c_3$$

where the constants c_1, c_2, and c_3 are independent of temperature. The substitutions $E_a = -RT\ln(k/A)$ and $\Delta G_b = -RT\ln(K_b)$ (eqns 25.25 and 9.19) give

$$-RT\ln\left(\frac{k}{A}\right) = -c_1RT\ln(K_b) + c_2I + c_3$$

c_3 may be eliminated by subtracting the analogous equation for the methylbenzene reference. Assuming that the pre-exponential A values for the reference and members of the series are comparable, the working equation becomes

$$-RT\ln\left(\frac{k}{k_{\text{toluene}}}\right) = -c_1RT\ln\left(\frac{K_b}{K_{b,\text{toluene}}}\right) + c_2(I - I_{\text{toluene}})$$

substituting $\Delta_p k = -\log\left(\dfrac{k}{k_{\text{toluene}}}\right)$, $\Delta_p K_b = -\log\left(\dfrac{K_b}{K_{b,\text{toluene}}}\right)$, $\Delta I = I - I_{\text{toluene}}$ gives

$$\Delta_p k = c_1\Delta_p k_b + \frac{c_2\Delta I}{RT\ln(10)} \tag{1}$$

The temperature dependence of $\Delta_p k$ depends upon $\Delta_p K_b$.

$$\begin{aligned} RT\ln(10)\Delta_p K_b &= \Delta G_b = \Delta H_b - T\Delta S_b \\ RT\ln(10)\Delta_p K_b &= \Delta\Delta H_b - T\Delta\Delta S_b \\ &= (cT-1)\Delta\Delta H_b \quad \text{(assuming that } \Delta\Delta S_b = C\Delta\Delta H_b\text{)} \end{aligned} \tag{2}$$

Evaluating the above equation at $T = T_0 = 273.15\,\text{K}$ gives

$$\Delta\Delta H_b^{\text{o}} = \frac{-RT_0\ln(10)\Delta_p K_b^{\text{o}}}{cT_0 - 1} \tag{3}$$

where $\Delta\Delta H_b(T_0) = \Delta\Delta H_b^{\text{o}}$ and $\Delta_p K_b(T_0) = \Delta_p K_b^{\text{o}}$. Assuming that ΔH_b is approximately independent of temperature gives $\Delta\Delta H_b = \Delta\Delta H_b^{\text{o}}$. Substitute equation (3) into (2) and substitute the result into equation (1) to get

$$\Delta_p k = \frac{a\,T_0(cT-1)\Delta_p K_b^{\text{o}}}{T(cT_0-1)} + \frac{b\Delta I}{RT\ln(10)}$$

where the symbols c_1 and c_2 have been replaced with the symbols a and b.

(b) The activation parameters for the ring destruction of p-xylene are determined with a linear regression analysis of the experimental data plotted as $\ln(k)$ versus $1/T$ (eqn 25.25 and Example 25.5). The regression first gives:

$$\text{slope} = -8.875\times10^3\,\text{K}$$

$$\text{intercept} = 25.53$$

$$E_a = -R \times \text{slope} = 73.8\,\text{kJ mol}^{-1}$$
$$A = e^{\text{intercept}}\,\text{L mol}^{-1}\text{s}^{-1} = 1.223 \times 10^{11}\,\text{L mol}^{-1}\text{s}^{-1}$$

$\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$ values for solution reactions may be calculated with the following equation (k is the Boltzmann constant in these equations).

$$\Delta^{\ddagger}H = E_a - RT \quad \text{and} \quad \Delta^{\ddagger}S = \text{R}\,\ln\left(\frac{hA}{K\text{e}kT}\right)$$

where the transmission coefficient K is assumed to equal 1. These equations may be deduced by modification of Sections 27.4 and 27.5 concepts to the solution phase. Eqn 27.42 becomes $[\text{C}^{\ddagger}] = K^{\ddagger}[\text{A}][\text{B}]$; eqn 27.44 becomes $k_2 = k^{\ddagger}K^{\ddagger} = k\nu K^{\ddagger}$ (eqn 27.45). Eqns 27.5 and 27.53 become $k_2 = K\nu(kT\overline{K}^{\ddagger}/h\nu) = KkT\overline{K}^{\ddagger}/h$.
Eqn 27.58 becomes $k_2 = (KkT/h)\,\text{e}^{-\Delta^{\ddagger}G/RT}$ and eqn 27.60 becomes
$k_2 = (K\,kT/h)\,\text{e}^{\Delta^{\ddagger}S/R}\text{e}^{-\Delta^{\ddagger}H/RT}$. According to the last equation,

$$\begin{aligned}\left(\frac{\partial \ln k_2}{\partial T}\right)_p &= \frac{1}{T} + \frac{1}{R}\left(\frac{\partial \Delta^{\ddagger}S}{\partial T}\right)_p + \frac{\Delta^{\ddagger}H}{RT^2} - \frac{1}{RT}\left(\frac{\partial \Delta^{\ddagger}H}{\partial T}\right)_p \\ &= \frac{1}{T} + \cancel{\frac{1}{R}\left(\frac{\partial \Delta^{\ddagger}S}{\partial T}\right)_p} + \frac{\Delta^{\ddagger}H}{RT^2} - \cancel{\frac{1}{RT}\left[T\left(\frac{\partial \Delta^{\ddagger}H}{\partial T}\right)_p\right]} \quad \text{(eqn 4.16)} \\ &= \frac{1}{T} + \frac{\Delta^{\ddagger}H}{RT^2}\end{aligned}$$

Substitution into the formal definition of activation energy (eqn 25.26) $E_a = RT^2(\partial \ln k_2/\partial T)_p$, gives $E_a = \Delta^{\ddagger}H + RT$ or $\Delta^{\ddagger}H = E_a - RT$. Subtitution of this condusion into the k_2 equation gives

$$\begin{aligned}k_2 &= (K\,RT/h)\text{e}^{\Delta^{\ddagger}S/R}\text{e}^{-\Delta^{\ddagger}H/RT} = (K\,kT/h)\text{e}^{\Delta^{\ddagger}S/R}\text{e}^{-(E_a-RT)/RT} \\ &= (K\text{e}\,kT/h)\text{e}^{\Delta^{\ddagger}S/R}\end{aligned}$$

Substituting of $k_2 = A\text{e}^{-E_a/RT}$ (eqn 25.25) and solving for $\Delta^{\ddagger}S$ gives the final result.

$$\Delta^{\ddagger}S = \text{R}\ln\left(\frac{hA}{Ke\,kT}\right)$$

T/K	$k/10^{-2}\,\text{L mol}^{-1}\text{s}^{-1}$	$\Delta^{\ddagger}H/\text{kJ mol}^{-1}$	$\Delta^{\ddagger}S/\text{J K}^{-1}\text{mol}^{-1}$
293.15	0.86	71.4	−40.8
303.15	2.5	71.3	−41.1
313.15	5.4	71.2	−41.4
323.15	13	71.1	−41.6
333.15	47	71.0	−41.9
343.15	59	70.9	−42.1

Entropy decreases upon formation of the transition state.

(c) The 6 temperatures at which rate constants are measured may be indexed as $i = 0, 1, 2, \ldots, 5$. The 7 arenes studied may be indexed as $j = 0, 1, 2, \ldots,\ 6$. $\Delta_p K,\ \Delta_p K_b^{\text{o}}$, and ΔI values may be calculated for each arene at each temperature. Methybenzene (toluene is the reference arene). The values for $\Delta_p k_{\text{exp}}(T)$ are calcluated with the arrhenius parameters. The constants a, b, and c that appear in the equation deduced in part (a) are determined by systematically altering their values so that the sum of the squares of errors (SSE) between $\Delta_p k_{\text{exp}}$ and the fitted equation $\Delta_p k_{\text{fit}}$ is minimized.

$$\mathrm{SSE}(a,b,c)=\sum_{j=0}^{6}\left[\sum_{i=0}^{5}\left(\Delta_p k_{\mathrm{exp}}(T_i)-\Delta_p k_{\mathrm{fit}}(a,b,c,T_i)\right)^2\right]_j$$

Mathematical software like mathcad's given/minerr solve block easily perform the minimization. We find a best fit when

$$\boxed{a=0.413 \quad b=-0.192 \quad c=1.39\times10^{-3}\,\mathrm{K}^{-1}}$$

The goodness of the fit may be graphically evaluated by plotting the ratio $\Delta_p k_{\mathrm{fit}}/\Delta_p k_{\mathrm{exp}}$ against $\Delta_\mathrm{p} K_{\mathrm{exp}}$ for the 7 arenes at a temperature of choice. A good fit gives a ratio of 1 to within experimental error. The following plot gives the ratio at 293.15 K.

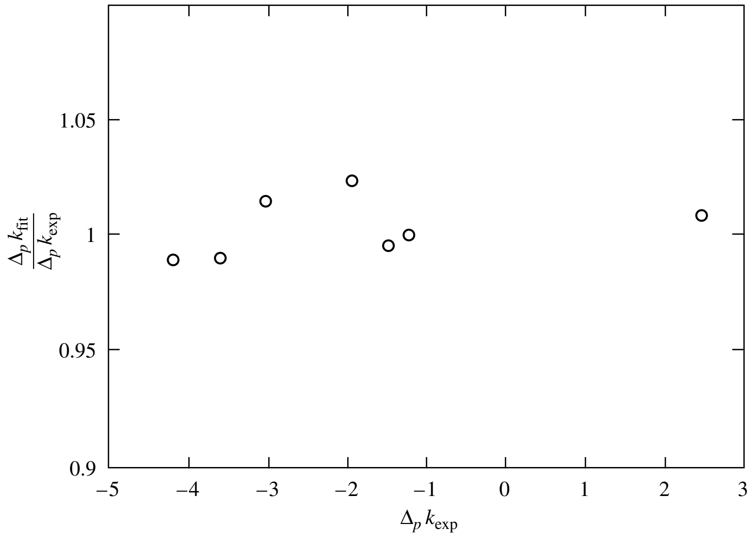


Figure 27.2

$\Delta_p k_{\mathrm{fit}}$ volumes are within about ±3% of the experimental values. This is a good fit, which confirms that the activation energy for arene distinction is multilinear in the basicity constant and the ionization energy. This is also evidence for the proposed arene ring oxidation mechanism.

Solutions to theoretical problems

P27.14 Programs for numerical integration using, for example, Simpson's rule are readily available for personal computers and hand-held calculators. Simplify the form of eqn 27.40 by writing

$$z^2=\frac{kx^2}{4D},\quad \tau=kt,\quad j=\left(\frac{A}{n_0}\right)\left(\frac{\pi D}{k}\right)^{1/2}[\mathrm{J}]^*$$

Then evaluate

$$j=\int_0^{\tau}\left(\frac{1}{\tau}\right)^{1/2}\mathrm{e}^{-z^2/\tau}\mathrm{e}^{-\tau}\,\mathrm{d}\tau+\left(\frac{1}{\tau}\right)^{1/2}\mathrm{e}^{-z^2/\tau}\mathrm{e}^{-\tau}$$

for various values of k.

P27.16 $$K_a = \frac{[H^+][A^-]}{[HA]\gamma_{HA}}\gamma_\pm{}^2 \approx \frac{[H^+][A^-]\gamma_\pm{}^2}{[HA]}$$

Therefore, $[H^+] = \dfrac{[HA]K_a}{[A^-]\gamma_\pm^2}$

and $\log[H^+] = \log\ K_a + \log\dfrac{[HA]}{[A^-]} - 2\log\gamma_\pm = \log K_a + \log\dfrac{[HA]}{[A^-]} + 2AI^{1/2}$

Write $v = k_2[H^+][B]$

$$\begin{aligned}\text{then } \log v &= \log(k_2[B] + \log[H^+]\\ &= \log(k_2[B]) + \log\frac{[HA]}{[A^-]} + 2AI^{1/2} + \log K_a\\ &= \log v^\circ + 2AI^{1/2}, \quad v^\circ = k_2\frac{[B][HA]K_a}{[A^-]}\end{aligned}$$

That is, the logarithm of the rate should depend linearly on the square root of the ionic strength, $\boxed{\log v \propto I^{1/2}}$

P27.18 $$k_1 = \frac{kT}{h} \times \frac{q^\ddagger}{q}e^{-\beta\Delta E} \text{ [Problem 27.17]}$$

$$q^\ddagger = q_z^{\ddagger V} q_y^{\ddagger V} q_x^R \approx \left(\frac{kT}{h\nu^\ddagger}\right)^2 q^R$$

$$q^R \approx \frac{1.027}{\sigma} \times \frac{(T/K)^{3/2}}{(B/\text{cm}^{-1})^{3/2}} \text{ [Table 20.4, } A = B = C] \approx 80$$

$$q = q_z^V q_y^V q_x^V \approx \left(\frac{kT}{h\nu}\right)^3$$

Therefore, $k_1 \approx 80 \times \dfrac{\nu^3}{\nu^{\ddagger 2}}e^{-\beta\Delta E_0} \approx 80 \times 5.4 \times 10^4\ \text{s}^{-1}$[Problem 27.15] $= 4 \times 10^6\ \text{s}^{-1}$

Consequently, $D \approx (80) \times (2.7 \times 10^{-15}\ \text{m}^2\ \text{s}^{-1}) = \boxed{2 \times 10^{-13}\text{m}^2\ \text{s}^{-1}}$ if $\nu^\ddagger = \nu$ and $\boxed{9 \times 10^{-13}\ \text{m}^2\ \text{s}^{-1}}$ if $\nu^\ddagger = \frac{1}{2}\nu$.

P27.20 It follows that, since $\mathcal{N}_s$ and l are the same for the two experiments,

$$\frac{\sigma(CH_2F_2)}{\sigma(Ar)} = \frac{\ln 0.6}{\ln 0.9}\text{[Problem 27.17]} = \boxed{5}$$

CH_2F_2 is a polar molecule; Ar is not. CsCl is a polar ion pair and is scattered more strongly by the polar CH_2F_2.

Solutions to applications

P27.22 Collision theory gives for a rate constant with no energy barrier

$$k = P\sigma\left(\frac{8kT}{\pi\mu}\right)^{1/2} N_A \quad \text{so} \quad P = \frac{k}{\sigma N_A}\left(\frac{\pi\mu}{8kT}\right)^{1/2}$$

$$\begin{aligned}P &= \frac{k/(\mathrm{L\,mol^{-1}\,s^{-1}}) \times (10^{-3}\,\mathrm{m^3\,L^{-1}})}{(\sigma/\mathrm{nm^2}) \times (10^{-9}\,\mathrm{m})^2 \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}})} \\ &\quad \times \left(\frac{\pi \times (\mu/\mathrm{u}) \times (1.66 \times 10^{-27}\,\mathrm{kg})}{8 \times (1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K})}\right)^{1/2} \\ &= \frac{(6.61 \times 10^{-13})k/(\mathrm{L\,mol^{-1}\,s^{-1}})}{(\sigma/\mathrm{nm^2}) \times (\mu/\mathrm{u})^{1/2}}\end{aligned}$$

The collision cross-section is

$$\sigma_{\mathrm{AB}} = \pi d_{\mathrm{AB}}^2 \quad \text{where } d_{\mathrm{AB}} = \frac{1}{2}(d_{\mathrm{A}} + d_{\mathrm{B}}) = \frac{\sigma_{\mathrm{A}}^{1/2} + \sigma_{\mathrm{B}}^{1/2}}{2\pi^{1/2}} \quad \text{so} \quad \sigma_{\mathrm{AB}} = \frac{(\sigma_{\mathrm{A}}^{1/2} + \sigma_{\mathrm{B}}^{1/2})^2}{4}$$

The collision cross-section for O_2 is listed in the *Data Section*. We would not be far wrong if we took that of the ethyl radical to equal that of ethene; similarly, we will take that of cyclohexyl to equal that of benzene. For O_2 with ethyl

$$\begin{aligned}\sigma &= \frac{(0.40^{1/2} + 0.64^{1/2})^2}{4}\,\mathrm{nm^2} = 0.51\,\mathrm{nm^2} \\ \mu &= \frac{m_{\mathrm{O}} m_{\mathrm{e}}}{m_{\mathrm{O}} + m_{\mathrm{e}}} = \frac{(32.0\,\mathrm{u}) \times (29.1\,\mathrm{u})}{(32.0 + 29.1)\,\mathrm{u}} = 15.2\,\mathrm{u}\end{aligned}$$

$$\text{so } P = \frac{(6.61 \times 10^{-13}) \times (4.7 \times 10^9)}{(0.51) \times (15.2)^{1/2}} = \boxed{1.6 \times 10^{-3}}$$

For O_2 with cyclohexyl

$$\begin{aligned}\sigma &= \frac{(0.40^{1/2} + 0.88^{1/2})^2}{4}\,\mathrm{nm^2} = 0.62\,\mathrm{nm^2} \\ \mu &= \frac{m_{\mathrm{O}} m_{\mathrm{C}}}{m_{\mathrm{O}} + m_{\mathrm{C}}} = \frac{(32.0\,\mathrm{u}) \times (77.1\,\mathrm{u})}{(32.0 + 77.1)\,\mathrm{u}} = 22.6\,\mathrm{u}\end{aligned}$$

$$\text{so } P = \frac{(6.61 \times 10^{-13}) \times (8.4 \times 10^9)}{(0.62) \times (22.6)^{1/2}} = \boxed{1.8 \times 10^{-3}}$$

28 Processes at solid surfaces

Solutions to exercises

Discussion questions

E28.1(b) The motion of one section of a crystal past another (a dislocation) results in steps and terraces. See Figures 28.2 and 28.3 of the text. A special kind of dislocation is the screw dislocation shown in Fig. 28.3. Imagine a cut in the crystal, with the atoms to the left of the cut pushed up through a distance of one unit cell. The surface defect formed by a screw dislocation is a step, possibly with kinks, where growth can occur. The incoming particles lie in ranks on the ramp, and successive ranks reform the step at an angle to its initial position. As deposition continues the step rotates around the screw axis, and is not eliminated. Growth may therefore continue indefinitely. Several layers of deposition may occur, and the edges of the spirals might be cliffs several atoms high (Fig. 28.4).

Propagating spiral edges can also give rise to flat terraces (Fig. 28.5). Terraces are formed if growth occurs simultaneously at neighbouring left- and right-handed screw dislocations (Fig. 28.6). Successive tables of atoms may form as counter-rotating defects collide on successive circuits, and the terraces formed may then fill up by further deposition at their edges to give flat crystal planes.

E28.2(b) Consult the appropriate sections of the textbook (listed below) for the advantages and limitations of each technique.

AFM: 28.2(h) and Box 28.1; FIM: 28.5(c); LEED: 28.2(g); MBRS: 28.6(c); MBS: 28.2(i); SAM: 28.2(e); SEM: 28.2(h); and STM: 28.2(h).

E28.3(b) In the Langmuir–Hinshelwood mechanism of surface catalysed reactions, the reaction takes place by encounters between molecular fragments and atoms already adsorbed on the surface. We therefore expect the rate law to be second-order in the extent of surface coverage:

$$\mathrm{A}+\mathrm{B}\rightarrow\mathrm{P}\qquad \nu=k\theta_{\mathrm{A}}\theta_{\mathrm{B}}$$

Insertion of the appropriate isotherms for A and B then gives the reaction rate in terms of the partial pressures of the reactants. For example, if A and B follow Langmuir isotherms (eqn 28.5), and adsorb without dissociation, then it follows that the rate law is

$$\nu=\frac{kK_{\mathrm{A}}K_{\mathrm{B}}p_{\mathrm{A}}p_{\mathrm{B}}}{(1+K_{\mathrm{A}}p_{\mathrm{A}}+K_{\mathrm{B}}p_{\mathrm{B}})^2}$$

The parameters K in the isotherms and the rate constant k are all temperature dependent, so the overall temperature dependence of the rate may be strongly non-Arrhenius (in the sense that the reaction rate is unlikely to be proportional to $\exp(-E_{\mathrm{a}}/RT)$.

In the Eley-Rideal mechanism (ER mechanism) of a surface-catalysed reaction, a gas-phase molecule collides with another molecule already adsorbed on the surface. The rate of formation of product is expected to be proportional to the partial pressure, p_{B} of the non-adsorbed gas B and the extent of surface coverage, θ_{A}, of the adsorbed gas A. It follows that the rate law should be

$$\mathrm{A}+\mathrm{B}\rightarrow\mathrm{P}\qquad \nu=kp_{\mathrm{A}}\theta_{\mathrm{B}}$$

The rate constant, k, might be much larger than for the uncatalysed gas-phase reaction because the reaction on the surface has a low activation energy and the adsorption itself is often not activated.

If we know the adsorption isotherm for A, we can express the rate law in terms of its partial pressure, p_{A}. For example, if the adsorption of A follows a Langmuir isotherm in the pressure range of interest, then the rate law would be

$$\nu = \frac{kKp_A p_B}{1 + Kp_A}.$$

If A were a diatomic molecule that adsorbed as atoms, we would substitute the isotherm given in eqn 28.8 instead.

According to eqn 28.24, when the partial pressure of A is high (in the sense $Kp_A \gg l$, there is almost complete surface coverage, and the rate is equal to kp_B. Now the rate-determining step is the collision of B with the adsorbed fragments. When the pressure of A is low ($Kp_A \ll 1$), perhaps because of its reaction, the rate is equal to $kKp_A p_B$; and now the extent of surface coverage is important in the determination of the rate.

In the Mars van Krevelen mechanism of catalytic oxidation, for example in the partial oxidation of propene to propenal, the first stage is the adsorption of the propene molecule with loss of a hydrogen to form the allyl radical, $CH_2{=}CHCH_2$. An O atom in the surface can now transfer to this radical, leading to the formation of acrolein (propenal, $CH_2{=}CHCHO$) and its desorption from the surface. The H atom also escapes with a surface O atom, and goes on to form H_2O, which leaves the surface. The surface is left with vacancies and metal ions in lower oxidation states. These vacancies are attacked by O_2 molecules in the overlying gas, which then chemisorb as O_2^- ions, so reforming the catalyst. This sequence of events involves great upheavals of the surface, and some materials break up under the stress.

E28.4(b) Zeolites are microporous aluminosilictes, in which the surface effectively extends deep inside the solid. M^{n+} cations and H_2O molecules can bind inside the cavities, or pores, of the Al–O–Si framework (see Fig. 28.31 of the text). Small neutral molecules, such as CO_2, NH_3, and hydrocarbons (including aromatic compounds), can also adsorb to the internal surfaces and this partially accounts for the utility of zeolites as catalysts.

Like enzymes, a zeolite catalyst with a specific composition and structure is very selective toward certain reactants and products because only molecules of certain sizes can enter and exit the pores in which catalysis occurs. It is also possible that zeolites derive their selectivity from the ability to bind to stabilize only transition states that fit properly in the pores.

Numerical exercises

E28.5(b) The number collisions of gas molecules per unit surface area is

$$Z_W = \frac{N_A p}{(2\pi MRT)^{1/2}}$$

(a) For N_2

$$\text{(i)}\quad Z_W = \frac{(6.022 \times 10^{23}\,\text{mol}^{-1}) \times (10.0\,\text{Pa})}{(2\pi \times (28.013 \times 10^{-3}\,\text{kg mol}^{-1}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K}))^{1/2}}$$
$$= 2.88 \times 10^{23}\,\text{m}^{-2}\,\text{s}^{-1}$$
$$= \boxed{2.88 \times 10^{19}\,\text{cm}^{-2}\,\text{s}^{-1}}$$

$$\text{(ii)}\quad Z_W = \frac{(6.022 \times 10^{23}\,\text{mol}^{-1}) \times (0.150 \times 10^{-6}\,\text{Torr}) \times (1.01 \times 10^{5}\,\text{Pa}/760\,\text{Torr})}{(2\pi \times (28.013 \times 10^{-3}\,\text{kg mol}^{-1}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K}))^{1/2}}$$
$$= 5.75 \times 10^{17}\,\text{m}^{-2}\,\text{s}^{-1}$$
$$= \boxed{5.75 \times 10^{13}\,\text{cm}^{-2}\,\text{s}^{-1}}$$

(b) For methane

$$\text{(i)}\quad Z_W = \frac{(6.022\times10^{23}\,\text{mol}^{-1})\times(10.0\,\text{Pa})}{(2\pi\times(16.04\times10^{-3}\,\text{kg mol}^{-1})\times(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(298\,\text{K}))^{1/2}}$$

$$= 3.81\times10^{24}\,\text{m}^{-2}\,\text{s}^{-1}$$

$$= \boxed{3.81\times10^{20}\,\text{cm}^{-2}\,\text{s}^{-1}}$$

$$\text{(ii)}\quad Z_W = \frac{(6.022\times10^{23}\,\text{mol}^{-1})\times(0.150\times10^{-6}\,\text{Torr})\times(1.01\times10^{5}\,\text{Pa}/760\,\text{Torr})}{(2\pi\times(16.04\times10^{-3}\,\text{kg mol}^{-1})\times(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(298\,\text{K}))^{1/2}}$$

$$= 7.60\times10^{17}\,\text{m}^{-2}\,\text{s}^{-1}$$

$$= \boxed{7.60\times10^{13}\,\text{cm}^{-2}\,\text{s}^{-1}}$$

E28.6(b) The number of collisions of gas molecules per unit surface area is

$$Z_W = \frac{N_A p}{(2\pi MRT)^{1/2}} \quad \text{so} \quad p = \frac{Z_W A(2\pi MRT)^{1/2}}{N_A A}$$

$$p = \frac{(5.00\times10^{19}\,\text{s}^{-1})}{(6.022\times10^{23}\,\text{mol}^{-1})\times\pi\times(1/2\times2.0\times10^{-3}\,\text{m})^2}$$

$$\times(2\pi\times(28.013\times10^{-3}\,\text{kg mol}^{-1})\times(8.3145\,\text{J mol}^{-1}\,\text{K}^{-1})\times(525\,\text{K}))^{1/2}$$

$$= \boxed{7.3\times10^{2}\,\text{Pa}}$$

E28.7(b) The number of collisions of gas molecules per unit surface area is

$$Z_W = \frac{N_A p}{(2\pi MRT)^{1/2}}$$

so the rate of collision per Fe atom will be $Z_W A$ where A is the area per Fe atom. The exposed surface consists of faces of the bcc unit cell, with one atom per face. So the area per Fe is

$$A = c^2 \quad \text{and} \quad \text{rate} = Z_W A = \frac{N_A p c^2}{(2\pi MRT)^{1/2}}$$

where c is the length of the unit cell. So

$$\text{rate} = \frac{(6.022\times10^{23}\,\text{mol}^{-1})\times(24\,\text{Pa})\times(145\times10^{-12}\,\text{m})^2}{(2\pi\times(4.003\times10^{-3}\,\text{kg mol}^{-1})\times(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(100\,\text{K}))^{1/2}}$$

$$= \boxed{6.6\times10^{4}\,\text{s}^{-1}}$$

E28.8(b) The number of CO molecules adsorbed on the catalyst is

$$N = nN_A = \frac{pVN_A}{RT} = \frac{(1.00\,\text{atm})\times(4.25\times10^{-3}\,\text{L})\times(6.022\times10^{23}\,\text{mol}^{-1})}{(0.08206\,\text{L atm K}^{-1}\,\text{mol}^{-1})\times(273\,\text{K})}$$

$$= 1.14\times10^{20}$$

The area of the surface must be the same as that of the molecules spread into a monolayer, namely, the number of molecules times each one's effective area

$$A = Na = (1.14\times10^{20})\times(0.165\times10^{-18}\,\text{m}^2) = \boxed{18.8\,\text{m}^2}$$

E28.9(b) If the adsorption follows the Langmuir isotherm, then

$$\theta = \frac{Kp}{1+Kp} \quad \text{so} \quad K = \frac{\theta}{p(1-\theta)} = \frac{V/V_{\text{mon}}}{p(1-V/V_{\text{mon}})}$$

Setting this expression at one pressure equal to that at another pressure allows solution for V_{mon}

$$\frac{V_1/V_{\text{mon}}}{p_1(1-V_1/V_{\text{mon}})} = \frac{V_2/V_{\text{mon}}}{p_2(1-V_2/V_{\text{mon}})} \quad \text{so} \quad \frac{p_1(V_{\text{mon}}-V_1)}{V_1} = \frac{p_2(V_{\text{mon}}-V_2)}{V_2}$$

$$V_{\text{mon}} = \frac{p_1 - p_2}{p_1/V_1 - p_2/V_2} = \frac{(52.4-104)\,\text{kPa}}{(52.4/1.60 - 104/2.73)\,\text{kPa cm}^{-3}} = \boxed{9.7\,\text{cm}^3}$$

E28.10(b) The mean lifetime of a chemisorbed molecule is comparable to its half life:

$$t_{1/2} = \tau_0 \exp\left(\frac{E_{\text{d}}}{RT}\right) \approx (10^{-14}\,\text{s}) \exp\left(\frac{155\times 10^3\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\times(500\,\text{K})}\right) = \boxed{200\,\text{s}}$$

E28.11(b) The desorption rate constant is related to the mean lifetime (half-life) by

$$t = (\ln 2)/k_{\text{d}} \quad \text{so} \quad k_{\text{d}} = (\ln 2)/t$$

The desorption rate constant is related to its Arrhenius parameters by

$$k_{\text{d}} = A \exp\left(\frac{-E_{\text{d}}}{RT}\right) \quad \text{so} \quad \ln k_{\text{d}} = \ln A - \frac{E_{\text{d}}}{RT}$$

and $E_{\text{d}} = \dfrac{(\ln k_1 - \ln k_2)R}{T_2^{-1} - T_1^{-1}} = \dfrac{(\ln 1.35 - \ln 0)\times(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})}{(600\,\text{K})^{-1} - (1000\,\text{K})^{-1}}$

$$E_{\text{d}} = \boxed{3.7\times 10^3\,\text{J mol}^{-1}}$$

E28.12(b) The Langmuir isotherm is

$$\theta = \frac{Kp}{1+Kp} \quad \text{so} \quad p = \frac{\theta}{K(1-\theta)}$$

(a) $$p = \frac{0.20}{(0.777\,\text{kPa}^{-1})\times(1-0.20)} = \boxed{0.32\,\text{kPa}}$$

(b) $$p = \frac{0.75}{(0.777\,\text{kPa}^{-1})\times(1-0.75)} = \boxed{3.9\,\text{kPa}}$$

E28.13(b) The Langmuir isotherm is

$$\theta = \frac{Kp}{1+Kp}$$

We are looking for θ, so we must first find K or m_{mon}

$$K = \frac{\theta}{p(1-\theta)} = \frac{m/m_{\text{mon}}}{p(1-m/m_{\text{mon}})}$$

Setting this expression at one pressure equal to that at another pressure allows solution for m_{mon}

$$\frac{m_1/m_{\text{mon}}}{p_1(1-m_1/m_{\text{mon}})} = \frac{m_2/m_{\text{mon}}}{p_2(1-m_2/m_{\text{mon}})} \quad \text{so} \quad \frac{p_1(m_{\text{mon}}-m_1)}{m_1} = \frac{p_2(m_{\text{mon}}-m_2)}{m_2}$$

$$m_{\text{mon}} = \frac{p_1 - p_2}{p_1/m_1 - p_2/m_2} = \frac{(36.0-4.0)\,\text{kPa}}{(36.0/0.63 - 4.0/0.21)\,\text{kPa mg}^{-1}} = 0.84\,\text{mg}$$

So $\theta_1 = 0.63/0.84 = \boxed{0.75}$ and $\theta_2 = 0.21/0.84 = \boxed{0.25}$

E28.14(b) The mean lifetime of a chemisorbed molecule is comparable to its half-life

$$t_{1/2} = \tau_0 \exp\left(\frac{E_{\mathrm{d}}}{RT}\right)$$

(a) At 400 K:
$$t_{1/2} = (0.12 \times 10^{-12}\,\mathrm{s}) \exp\left(\frac{20 \times 10^3\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (400\,\mathrm{K})}\right) = \boxed{4.9 \times 10^{-11}\,\mathrm{s}}$$

At 800 K:
$$t_{1/2} = (0.12 \times 10^{-12}\,\mathrm{s}) \exp\left(\frac{20 \times 10^3\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (800\,\mathrm{K})}\right) = \boxed{2.4 \times 10^{-12}\,\mathrm{s}}$$

(b) At 400 K:
$$t_{1/2} = (0.12 \times 10^{-12}\,\mathrm{s}) \exp\left(\frac{200 \times 10^3\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (400\,\mathrm{K})}\right) = \boxed{1.6 \times 10^{13}\,\mathrm{s}}$$

At 800 K:
$$t_{1/2} = (0.12 \times 10^{-12}\,\mathrm{s}) \exp\left(\frac{200 \times 10^3\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (800\,\mathrm{K})}\right) = \boxed{1.4\,\mathrm{s}}$$

E28.15(b) The Langmuir isotherm is

$$\theta = \frac{Kp}{1+Kp} \quad \text{so} \quad p = \frac{\theta}{K(1-\theta)}$$

For constant fractional adsorption

$$pK = \text{constant} \quad \text{so} \quad p_1K_1 = p_2K_2 \ \text{ and } \ p_2 = p_1\frac{K_1}{K_2}$$

But $K \propto \exp\left(\frac{-\Delta_{\mathrm{ad}}H^{\ominus}}{RT}\right)$ so $\frac{K_1}{K_2} = \exp\left(\frac{-\Delta_{\mathrm{ad}}H^{\ominus}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)$

$$p_2 = p_1 \exp\left(\frac{-\Delta_{\mathrm{ad}}H^{\ominus}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)$$
$$= (8.86\,\mathrm{kPa}) \times \exp\left(\left(\frac{-12.2 \times 10^3\,\mathrm{J\,mol^{-1}}}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\right) \times \left(\frac{1}{298\,\mathrm{K}} - \frac{1}{318\,\mathrm{K}}\right)\right) = \boxed{6.50\,\mathrm{kPa}}$$

E28.16(b) The Langmuir isotherm would be

(a) $$\theta = \frac{Kp}{1+Kp}$$

(b) $$\theta = \frac{(Kp)^{1/2}}{1+(Kp)^{1/2}}$$

(c) $$\theta = \frac{(Kp)^{1/3}}{1+(Kp)^{1/3}}$$

A plot of θ versus p at low pressures (where the denominator is approximately 1) would show progressively weaker dependence on p for dissociation into two or three fragments.

E28.17(b) The Langmuir isotherm is

$$\theta = \frac{Kp}{1+Kp} \quad \text{so} \quad p = \frac{\theta}{K(1-\theta)}$$

For constant fractional adsorption

$$pK = \text{constant} \quad \text{so} \quad p_1K_1 = p_2K_2 \quad \text{and} \quad \frac{p_2}{p_1} = \frac{K_1}{K_2}$$

But $K \propto \exp\left(\frac{-\Delta_{\text{ad}}H^\ominus}{RT}\right)$ so $\frac{p_2}{p_1} = \exp\left(\frac{-\Delta_{\text{ad}}H^\ominus}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right)$

and $\Delta_{\text{ad}}H^\ominus = R\left(\frac{1}{T_1}-\frac{1}{T_2}\right)^{-1}\ln\frac{p_1}{p_2}$,

$$\begin{aligned}\Delta_{\text{ad}}H^\ominus &= (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times \left(\frac{1}{180\,\text{K}}-\frac{1}{240\,\text{K}}\right)^{-1} \times \left(\ln\frac{350\,\text{kPa}}{1.02\times10^3\,\text{kPa}}\right)\\ &= -6.40\times10^4\,\text{J mol}^{-1} = \boxed{-6.40\,\text{kJ mol}^{-1}}\end{aligned}$$

E28.18(b) The time required for a given quantity of gas to desorb is related to the activation energy for desorption by

$$t \propto \exp\left(\frac{E_{\text{d}}}{RT}\right) \quad \text{so} \quad \frac{t_1}{t_2} = \exp\left(\frac{E_{\text{d}}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right)$$

and $E_{\text{d}} = R\left(\frac{1}{T_1}-\frac{1}{T_2}\right)^{-1}\ln\frac{t_1}{t_2}$

$$\begin{aligned}E_{\text{d}} &= (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times \left(\frac{1}{873\,\text{K}}-\frac{1}{1012\,\text{K}}\right)^{-1} \times \left(\ln\frac{1856\,\text{s}}{8.44\,\text{s}}\right)\\ &= \boxed{2.85\times10^5\,\text{J mol}^{-1}}\end{aligned}$$

(a) The same desorption at 298 K would take

$$t = (1856\,\text{s}) \times \exp\left(\left(\frac{2.85\times10^5\,\text{J mol}^{-1}}{8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}}\right) \times \left(\frac{1}{298\,\text{K}}-\frac{1}{873\,\text{K}}\right)\right) = \boxed{1.48\times10^{36}\,\text{s}}$$

(b) The same desorption at 1500 K would take

$$\begin{aligned}t &= (8.44\,\text{s}) \times \exp\left(\left(\frac{2.85\times10^5\,\text{J mol}^{-1}}{8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}}\right) \times \left(\frac{1}{1500\,\text{K}}-\frac{1}{1012\,\text{K}}\right)\right)\\ &= \boxed{1.38\times10^{-4}\,\text{s}}\end{aligned}$$

Solutions to problems

Solutions to numerical problems

P28.2 Refer to Fig. 28.1.

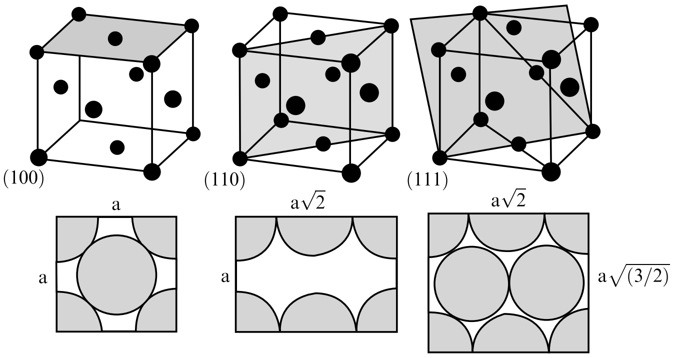


Figure 28.1

The (100) and (110) faces each expose two atoms, and the (111) face exposes four. The areas of the faces of each cell are **(a)** $(352\,\text{pm})^2 = 1.24 \times 10^{-15}\,\text{cm}^2$, **(b)** $\sqrt{2} \times (352\,\text{pm})^2 = 1.75 \times 10^{-15}\,\text{cm}^2$, and **(c)** $\sqrt{3} \times (352\,\text{pm})^2 = 2.15 \times 10^{-15}\,\text{cm}^2$. The numbers of atoms exposed per square centimetre are therefore

(a) $$\frac{2}{1.24 \times 10^{-15}\,\text{cm}^2} = \boxed{1.61 \times 10^{15}\,\text{cm}^{-2}}$$

(b) $$\frac{2}{1.75 \times 10^{-15}\,\text{cm}^2} = \boxed{1.14 \times 10^{15}\,\text{cm}^{-2}}$$

(c) $$\frac{4}{2.15 \times 10^{-15}\,\text{cm}^2} = \boxed{1.86 \times 10^{15}\,\text{cm}^{-2}}$$

For the collision frequencies calculated in Exercise 28.5(a), the frequency of collision per atom is calculated by dividing the values given there by the number densities just calculated. We can therefore draw up the following table

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

P28.4 $$\frac{V}{V_{\text{mon}}} = \frac{cz}{(1-z)\{1-(1-c)z\}} \quad \left[28.10, \text{BET isotherm}, z = \frac{p}{p^*}\right]$$

This rearranges to

$$\frac{z}{(1-z)V} = \frac{1}{cV_{\text{mon}}} + \frac{(c-1)z}{cV_{\text{mon}}}$$

Therefore a plot of the left-hand side against z should result in a straight line if the data obeys the

BET isotherm. We draw up the following tables

(a) 0°C, $p^* = 3222\,\text{Torr}$

p/Torr	105	282	492	594	620	755	798
$10^3 z$	32.6	87.5	152.7	184.4	192.4	234.3	247.7
$\dfrac{10^3 z}{(1-z)(V/\text{cm}^3)}$	3.04	7.10	12.1	14.1	15.4	17.7	20.0

(b) 18°C, $p^* = 6148\,\text{Torr}$

p/Torr	39.5	62.7	108	219	466	555	601	765
$10^3 z$	6.4	10.2	17.6	35.6	75.8	90.3	97.8	124.4
$\dfrac{10^3 z}{(1-z)(V/\text{cm}^3)}$	0.70	1.05	1.74	3.27	6.36	7.58	8.09	10.08

The points are plotted in Fig. 28.2, but we analyse the data by a least-squares procedure. The intercepts are at **(a)** 0.466 and **(b)** 0.303. Hence

$$\frac{1}{cV_{\text{mon}}} = \textbf{(a)}\ 0.466 \times 10^{-3}\,\text{cm}^{-3},\ \textbf{(b)}\ 0.303 \times 10^{-3}\,\text{cm}^{-3}$$

The slopes of the lines are **(a)** 76.10 and **(b)** 79.54. Hence

$$\frac{c-1}{cV_{\text{mon}}} = \textbf{(a)}\ 76.10 \times 10^{-3}\,\text{cm}^{-3},\ \textbf{(b)}\ 79.54 \times 10^{-3}\,\text{cm}^{-3}$$

Solving the equations gives

$$c - 1 = \textbf{(a)}\ 163.\overline{3},\ \textbf{(b)}\ 262.\overline{5}$$

and hence

$$c = \textbf{(a)}\ \boxed{164},\ \textbf{(b)}\ \boxed{264} \qquad V_{\text{mon}} = \textbf{(a)}\ \boxed{13.1\,\text{cm}^3},\ \textbf{(b)}\ \boxed{12.5\,\text{cm}^3}$$

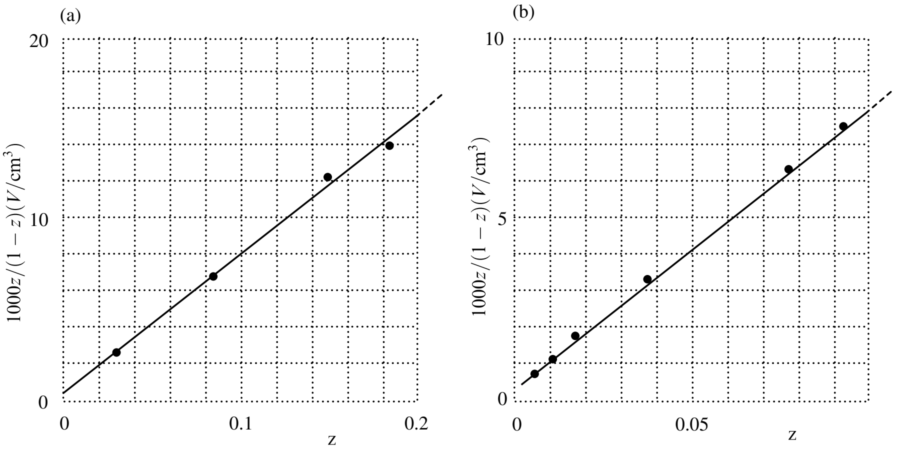


Figure 28.2

P28.7 We assume that the Langmuir isotherm applies.

$$\theta = \frac{Kp}{1+Kp}\ [28.5] \quad \text{and} \quad 1-\theta = \frac{1}{1+Kp}$$

For a strongly adsorbed species, $Kp \gg 1$ and $1-\theta = \dfrac{1}{Kp}$. Since the reaction rate is proportional to the pressure of ammonia and the fraction of sites left uncovered by the strongly adsorbed hydrogen product, we can write

$$\frac{\mathrm{d}p_{\mathrm{NH_3}}}{\mathrm{d}t} = -k_{\mathrm{c}}p_{\mathrm{NH_3}}(1-\theta) \approx \boxed{-\frac{k_{\mathrm{c}}p_{\mathrm{NH_3}}}{Kp_{\mathrm{H_2}}}}$$

To solve the rate law, we write

$$p_{\mathrm{H_2}} = \tfrac{3}{2}\{p_{0\mathrm{NH_3}} - p_{\mathrm{NH_3}}\} \quad \left[\mathrm{NH_3} \rightarrow \tfrac{1}{2}\mathrm{N_2} + \tfrac{3}{2}\mathrm{H_2}\right]$$

from which it follows that, with $p = p_{\mathrm{NH_3}}$

$$\frac{-\mathrm{d}p}{\mathrm{d}t} = \frac{kp}{p_0 - p}, \quad k = \frac{2k_{\mathrm{c}}}{3K}$$

This equation integrates as follows

$$\int_{p_0}^{p}\left(1 - \frac{p_0}{p}\right)\mathrm{d}p = k\int_0^t \mathrm{d}t$$

or $\boxed{\dfrac{p-p_0}{t} = k + \dfrac{p_0}{t}\ln\dfrac{p}{p_0}}$

We write $F' = \dfrac{p_0}{t}\ln\dfrac{p}{p_0}$, $G = \dfrac{p-p_0}{t}$

and obtain $G = k + F' = p_0F$

Hence, a plot of G against F' should give a straight line with intercept k at $F' = 0$. Alternatively, the difference $G - F'$ should be a constant, k. We draw up the following table

t/s	0	30	60	100	160	200	250
p/Torr	100	88	84	80	77	74	72
$G/(\mathrm{Torr\ s^{-1}})$		−0.40	−0.27	−0.20	−0.14	−0.13	−0.11
$F'/(\mathrm{Torr\ s^{-1}})$		−0.43	−0.29	−0.22	−0.16	−0.15	−0.13
$(G-F')/(\mathrm{Torr\ s^{-1}})$		0.03	0.02	0.02	0.02	0.02	0.02

Thus, the data fit the rate law, and we find $\boxed{k = 0.02\ \mathrm{Torr\ s^{-1}}}$.

P28.9 Taking the log of the isotherm gives

$$\ln c_{\mathrm{ads}} = \ln K + (\ln c_{\mathrm{sol}})/n$$

so a plot of $\ln c_{\mathrm{ads}}$ versus $\ln c_{\mathrm{sol}}$ would have a slope of $1/n_{\infty}$ and a y-intercept of $\ln K$. The transformed data and plot are shown in Fig. 28.3.

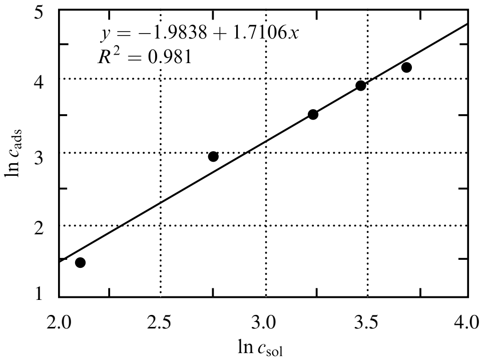


Figure 28.3

$c_{\mathrm{sol}}/(\mathrm{mg\,g^{-1}})$	8.26	15.65	25.43	31.74	40.00
$c_{\mathrm{ads}}/(\mathrm{mg\,g^{-1}})$	4.4	19.2	35.2	52.0	67.2
$\ln c_{\mathrm{sol}}$	2.11	2.75	3.24	3.46	3.69
$\ln c_{\mathrm{ads}}$	1.48	2.95	3.56	3.95	4.21

$$K = \mathrm{e}^{-1.9838}\,\mathrm{mg\,g^{-1}} = \boxed{0.138\,\mathrm{mg\,g^{-1}}} \quad \text{and} \quad n = 1/1.71 = \boxed{0.58}$$

In order to express this information in terms of fractional coverage, the amount of adsorbate corresponding to monolayer coverage must be known. This saturation point, however, has no special significance in the Freundlich isotherm (i.e. it does not correspond to any limiting case).

P28.11 The Langmuir isotherm is

$$\theta = \frac{Kp}{1+Kp} = \frac{n}{n_\infty} \quad \text{so} \quad n(1+Kp) = n_\infty Kp \quad \text{and} \quad \frac{p}{n} = \frac{p}{n_\infty} + \frac{1}{Kn_\infty}$$

So a plot of p/n against p should be a straight line with slope $1/n_\infty$ and y-intercept $1/Kn_\infty$. The transformed data and plot (Fig. 28.4) follow

p/kPa	31.00	38.22	53.03	76.38	101.97	130.47	165.06	182.41	205.75	219.91
$n/(\mathrm{mol\,kg^{-1}})$	1.00	1.17	1.54	2.04	2.49	2.90	3.22	3.30	3.35	3.36
$\dfrac{p/n}{\mathrm{kPa\,mol^{-1}\,kg}}$	31.00	32.67	34.44	37.44	40.95	44.99	51.26	55.28	61.42	65.45

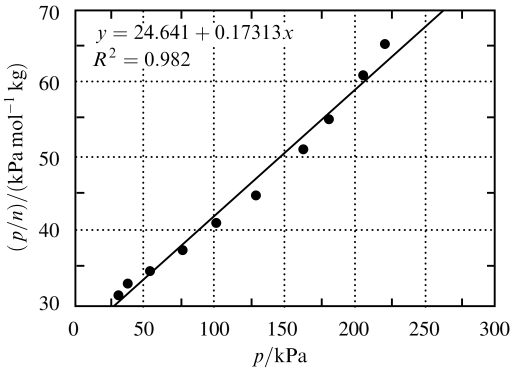


Figure 28.4

$$n_\infty = \frac{1}{0.17313\,\mathrm{mol^{-1}\,kg}} = \boxed{5.78\,\mathrm{mol\,kg^{-1}}}$$

The y-intercept is

$$b = \frac{1}{Kn_\infty} \quad \text{so} \quad K = \frac{1}{bn_\infty} = \frac{1}{(24.641\,\mathrm{kPa\,mol^{-1}\,kg}) \times (5.78\,\mathrm{mol\,kg^{-1}})}$$

$$K = 7.02 \times 10^{-3}\,\mathrm{kPa^{-1}} = \boxed{7.02\,\mathrm{Pa^{-1}}}$$

P28.12 For the Langmuir adsorption isotherm we must alter eqn 5 so that it describes adsorption from solution. This can be done with the transforms

$p \to$ concentration, c

$V \to$ amount adsorbed per gram adsorbent, s

Langmuir isotherm and regression analysis

$$\frac{c}{s} = \frac{c}{s_\infty} + \frac{1}{Ks_\infty}$$

$$\frac{1}{s_\infty} = 0.163\,\mathrm{g\,mmol^{-1}}, \quad \text{standard deviation} = 0.017\,\mathrm{g\,mmol^{-1}}$$

$$\frac{1}{Ks_\infty} = 35.6\,(\mathrm{mmol\,L^{-1}}) \times (\mathrm{g\,mmol^{-1}}), \text{ standard deviation} = 5.9\,(\mathrm{mmol\,L^{-1}}) \times (\mathrm{g\,mmol^{-1}})$$

$$\boxed{R\,(\text{Langmuir}) = 0.973}$$

$$K = \frac{0.163\,\mathrm{g\,mmol^{-1}}}{35.6\,(\mathrm{mmol\,L^{-1}}) \times (\mathrm{g\,mmol^{-1}})} = 0.0046\,\mathrm{L\,mmol^{-1}}$$

Freundlich isotherm and regression analysis

$$s = c_1 c^{1/c_2}$$

$$c_1 = 0.139, \quad \text{standard deviation} = 0.012$$

$$\frac{1}{c_2} = 0.539, \quad \text{standard deviation} = 0.003$$

$$\boxed{R\,(\text{Freundlich}) = 0.999\,94}$$

Temkin isotherm and regression analysis

$$s = c_1 \ln(c_2 c)$$

$$c_1 = 1.08, \quad \text{standard deviation} = 0.14$$

$$c_2 = 0.074, \quad \text{standard deviation} = 0.023$$

$$\boxed{R\,(\text{Temkin}) = 0.9590}$$

The correlation coefficients and standard deviations indicate that the $\boxed{\text{Freundlich isotherm}}$ provides the best fit of the data.

Solutions to theoretical problems

P28.17 $$\theta = \frac{Kp}{1+Kp}, \qquad \theta = \frac{V}{V_\infty}$$

$$p = \frac{\theta}{K(1-\theta)} = \frac{V}{K(V_\infty - V)}$$

$$\frac{\mathrm{d}p}{\mathrm{d}V} = \frac{1}{K(V_\infty - V)} + \frac{V}{K(V_\infty - V)^2} = \frac{V_\infty}{K(V_\infty - V)^2}$$

$$\begin{aligned}
\mathrm{d}\mu' &= -\left(\frac{RT}{\sigma}\right) V\,\mathrm{d}\ln p = \frac{-RT}{p\sigma} V\,\mathrm{d}p \\
&= -\left(\frac{RT}{\sigma}\right)\left(\frac{K(V_\infty - V)}{V}\right) V \left(\frac{V_\infty}{K(V_\infty - V)^2}\right)\mathrm{d}V \\
&= -\left(\frac{RT}{\sigma}\right)\left(\frac{V_\infty\,\mathrm{d}V}{V_\infty - V}\right)
\end{aligned}$$

Therefore, we can adopt any of several forms,

$$\mathrm{d}\mu' = -\frac{\left(\frac{RT}{\sigma}V_\infty\right)}{V_\infty - V}\mathrm{d}V = -\frac{\left(\frac{RT}{\sigma}\right)}{1-\theta}\mathrm{d}V = -\frac{\left(\frac{RTV_\infty}{\sigma}\right)}{1-\theta}\mathrm{d}\theta = \boxed{\frac{RTV_\infty}{\sigma}\,\mathrm{d}\ln(1-\theta)}$$

P28.18 For the Langmuir and BET isotherm tests we draw up the following table (using $p^* = 200\,\mathrm{kPa} = 1500\,\mathrm{Torr}$) [Examples 28.1 and 28.3]

p/Torr	100	200	300	400	500	600
$\frac{p}{V}\Big/(\mathrm{Torr\,cm^{-3}})$	5.59	6.06	6.38	6.58	6.64	6.57
$10^3 z$	67	133	200	267	333	400
$\frac{10^3 z}{(1-z)(V/\mathrm{cm^3})}$	4.01	4.66	5.32	5.98	6.64	7.30

$\frac{p}{V}$ is plotted against p in Fig. 28.5(a), and $\frac{10^3 z}{(1-z)V}$ is plotted against z in Fig. 28.5(b).

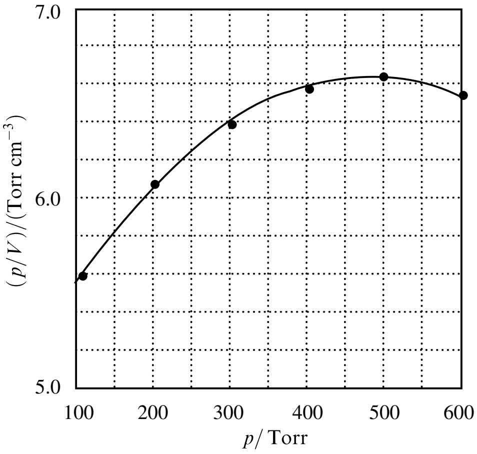


Figure 28.5(a)

We see that the $\boxed{\text{BET isotherm is a much better representation}}$ of the data than the Langmuir isotherm. The intercept in Fig. 28.5(b) is at 3.33×10^{-3}, and so $\dfrac{1}{cV_{\text{mon}}} = 3.33 \times 10^{-3}\,\text{cm}^{-3}$. The slope of the graph is 9.93, and so

$$\frac{c-1}{cV_{\text{mon}}} = 9.93 \times 10^{-3}\,\text{cm}^{-3}$$

Therefore, $c - 1 = 2.98$, and hence $\boxed{c = 3.98}$, $\boxed{V_{\text{mon}} = 75.4\,\text{cm}^3}$

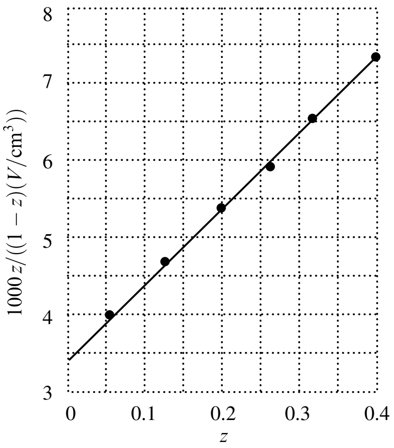


Figure 28.5(b)

P28.22 **(a)** K unit: $(\text{g}_{\text{R}}\,\text{L}^{-1})^{-1}$ [g_{R} = mass (grams) of rubber]

K_F unit: $(\text{mg})^{(1-1/n)} g_{\text{R}}^{-1} L^{-1/n}$

K_{L} unit: $(\text{mg}\,\text{L}^{-1})^{-1}$

M unit: $(\text{mg}\,\text{g}_{\text{R}}^{-1})$

(b) Linear sorption isotherm

$$q = Kc_{\text{eq}}$$

$K = \dfrac{q}{c_{\text{eq}}}$ so K is best determined as an average of all q/c_{eq} data pairs.

$\boxed{K_{\text{av}} = 0.126(\text{g}_{\text{R}}\,\text{L}^{-1})^{-1}}$, standard deviation $= 0.041(\text{g}_{\text{R}}\,\text{L}^{-1})^{-1}$

95 per cent confidence limit: $(0.083 - 0.169)(\text{g}_{\text{R}}\,\text{L}^{-1})^{-1}$

If this is done as a linear regression, the result is significantly different.

K (linear) $= 0.0813(\text{g}_{\text{R}}\,\text{L}^{-1})^{-1}$, standard deviation $= 0.0092(\text{g}_{\text{R}}\,\text{L}^{-1})^{-1}$

$\boxed{R\ (\text{linear}) = 0.9612}$

Freundlich sorption isotherm: $q = K_{\text{F}}c_{\text{eq}}^{1/n}$, using a power regression analysis, we find that

$\boxed{K_{\text{F}} = 0.164}$, standard deviation $= 0.317$

$$\frac{1}{n} = 0.877, \quad \text{standard deviation} = 0.113; \boxed{n = 1.14}$$

$$\boxed{R\,(\text{Freundlich}) = 0.9682}$$

Langmuir sorption isotherm

$$q = \frac{K_\mathrm{L} M c_\mathrm{eq}}{1 + K_\mathrm{L} c_\mathrm{eq}}$$

$$\frac{1}{q} = \left(\frac{1}{K_\mathrm{L} M}\right)\left(\frac{1}{c_\mathrm{eq}}\right) + \frac{1}{M}$$

$$\frac{1}{K_\mathrm{L} M} = 8.089\,\mathrm{g_R\,L^{-1}}, \quad \text{standard deviation} = 1.031; \quad K_\mathrm{L} = -0.00053(\mathrm{g_R L^{-1}})^{-1}$$

$$\frac{1}{M} = -0.0043\,\mathrm{g_R\,mg^{-1}}, \quad \text{standard deviation} = 0.1985; \quad M = \boxed{-233\,\mathrm{mg\,g_R^{-1}}}$$

$$\boxed{R\,(\text{Langmuir}) = 0.9690}$$

All regression fits have nearly the same correlation coefficient so that cannot be used to determine which is the best fit. However, the Langmuir isotherm give a negative value for K_L. If K_L is to represent an equilibrium constant, which must be positive, the Langmuir description must be rejected. The standard deviation of the slope of the Freundlich isotherm is twice as large as the slope itself. This would seem to be unfavourable. Thus, the $\boxed{\text{linear description seems to be the best}}$, but not excellent choice. However, the Freundlich isotherm is usually preferred for this kind of system, even though that choice is not supported by the data in this case.

(c) $$\frac{q_\text{rubber}}{q_\text{charcoal}} = \frac{0.164\,c_\mathrm{eq}^{1.14}}{c_\mathrm{eq}^{1.6}} = \boxed{0.164\,c_\mathrm{eq}^{-0.46}}$$

The sorption efficiency of ground rubber is much less than that of activated charcoal and drops significantly with increasing concentration. The only advantage of the ground rubber is its exceedingly low cost relative to activated charcoal, which might convert to a lower cost per gram of contaminant adsorbed.

29 Dynamics of electron transfer

Solutions to exercises

Discussion questions

E29.1(b) No solution.

E29.2(b) The net current density at an electrode is j; j_0 is the exchange current density; α is the transfer coefficient; f is the ratio F/RT; and η is the overpotential.

(a) $j = j_0 f\eta$ is the current density in the low overpotential limit.

(b) $j = j_0 \mathrm{e}^{(1-\alpha)f\eta}$ applies when the overpotential is large and positive.

(c) $j = -j_0 \mathrm{e}^{-\alpha f\eta}$ applies when the overpotential is large and negative.

E29.3(b) In cyclic voltammetry, the current at a working electrode is monitored as the applied potential difference is changed back and forth at a constant rate between pre-set limits (Figs 29.20 and 29.21). As the potential difference approaches $E^{\ominus}$ (Ox, Red) for a solution that contains the reduced component (Red), current begins to flow as Red is oxidized. When the potential difference is swept beyond $E^{\ominus}$ (Ox, Red), the current passes through a maximum and then falls as all the Red near the electrode is consumed and converted to Ox, the oxidized form. When the direction of the sweep is reversed and the potential difference passes through $E^{\ominus}$ (Ox, Red), current flows in the reverse direction. This current is caused by the reduction of the Ox formed near the electrode on the forward sweep. It passes through the maximum as Ox near the electrode is consumed. The forward and reverse current maxima bracket $E^{\ominus}$ (Ox, Red), so the species present can be identified. Furthermore, the forward and reverse peak currents are proportional to the concentration of the couple in the solution, and vary with the sweep rate. If the electron transfer at the electrode is rapid, so that the ratio of the concentrations of Ox and Red at the electrode surface have their equilibrium values for the applied potential (that is, their relative concentrations are given by the Nernst equation), the voltammetry is said to be *reversible*. In this case, the peak separation is independent of the sweep rate and equal to $(59\,\mathrm{mV})/n$ at room temperature, where n is the number of electrons transferred. If the rate of electron transfer is low, the voltammetry is said to be *irreversible*. Now, the peak separation is greater than $(59\,\mathrm{mV})/n$ and increases with increasing sweep rate. If homogeneous chemical reactions accompany the oxidation or reduction of the couple at the electrode, the shape of the voltammogram changes, and the observed changes give valuable information about the kinetics of the reactions as well as the identities of the species present.

E29.4(b) Corrosion is an electrochemical process. We will illustrate it with the example of the rusting of iron, but the same principles apply to other corrosive processes. The electrochemical basis of corrosion in the presence of water and oxygen is revealed by comparing the standard potentials of the metal reduction, such as

$$\mathrm{Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)} \qquad E^{\ominus} = -0.44\,\mathrm{V}$$

with the values for one of the following half-reactions

In acidic solution

(a) $\mathrm{2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)} \qquad E^{\ominus} = 0\,\mathrm{V}$

(b) $\mathrm{4\,H^+(aq) + O_2(g) + 4\,e^- \rightarrow 2H_2O(l)} \qquad E^{\ominus} = +1.23\,\mathrm{V}$

In basic solution:

(c) $\mathrm{2H_2O(l) + O_2(g) + 4\,e^- \rightarrow 4OH^-(aq)} \qquad E^{\ominus} = +0.40\,\mathrm{V}$

Because all three redox couples have standard potentials more positive than $E^{\ominus}(\mathrm{Fe^{2+}/Fe})$, all three can drive the oxidation of iron to iron(II). The electrode potentials we have quoted are standard values, and they change with the pH of the medium. For the first two

$$\begin{aligned} E(\mathrm{a}) &= E^{\ominus}(\mathrm{a}) + (RT/F)\ln \mathrm{a}(\mathrm{H^+}) = -(0.059\,\mathrm{V})\mathrm{pH} \\ E(\mathrm{b}) &= E^{\ominus}(\mathrm{b}) + (RT/F)\ln \mathrm{a}(\mathrm{H^+}) = 1.23\,\mathrm{V} - (0.059\,\mathrm{V})\mathrm{pH} \end{aligned}$$

These expressions let us judge at what pH the iron will have a tendency to oxidize (see Chapter 10). A thermodynamic discussion of corrosion, however, only indicates whether a tendency to corrode exists. If there is a thermodynamic tendency, we must examine the kinetics of the processes involved to see whether the process occurs at a significant rate. The effect of the exchange current density on the corrosion rate can be seen by considering the specific case of iron in contact with acidified water. Thermodynamically, either the hydrogen or oxygen reduction reaction (a) or (b) is effective. However, the exchange current density of reaction (b) on iron is only about $10^{-14}\,\mathrm{A\,cm^{-2}}$, whereas for (a) it is $10^{-6}\,\mathrm{A\,cm^{-2}}$. The latter therefore dominates kinetically, and iron corrodes by hydrogen evolution in acidic solution. For corrosion reactions with similar exchange current densities, eqn 29.62 predicts that the rate of corrosion is high when E is large. That is, rapid corrosion can be expected when the oxidizing and reducing couples have widely differing electrode potentials.

Several techniques for inhibiting corrosion are available. First, from eqn 62 we see that the rate of corrosion depends on the surfaces exposed: if either A or A' is zero, then the corrosion current is zero. This interpretation points to a trivial, yet often effective, method of slowing corrosion: cover the surface with some impermeable layer, such as paint, which prevents access of damp air. Paint also increases the effective solution resistance between the cathode and anode patches on the surface.

Another form of surface coating is provided by galvanizing, the coating of an iron object with zinc. Because the latter's standard potential is $-0.76\,\mathrm{V}$, which is more negative than that of the iron couple, the corrosion of zinc is thermodynamically favoured and the iron survives (the zinc survives because it is protected by a hydrated oxide layer).

Another method of protection is to change the electric potential of the object by pumping in electrons that can be used to satisfy the demands of the oxygen reduction without involving the oxidation of the metal. In cathodic protection, the object is connected to a metal with a more negative standard potential (such as magnesium, $-2.36\,\mathrm{V}$). The magnesium acts as a sacrificial anode, supplying its own electrons to the iron and becoming oxidized to $\mathrm{Mg^{2+}}$ in the process.

Numerical exercises

E29.5(b) Equation 29.14 holds for a donor–acceptor pair separated by a constant distance, assuming that the reorganization energy is constant:

$$\ln k_{\mathrm{et}} = -\frac{(\Delta_{\mathrm{r}}G^{\ominus})^2}{4\lambda RT} - \frac{\Delta_{\mathrm{r}}G^{\ominus}}{2RT} + \text{constant},$$

or equivalently

$$\ln k_{\mathrm{et}} = -\frac{(\Delta_{\mathrm{r}}G^{\ominus})^2}{4\lambda kT} - \frac{\Delta_{\mathrm{r}}G^{\ominus}}{2kT} + \text{constant},$$

if energies are expressed as molecular rather than molar quantities. Two sets of rate constants and reaction Gibbs energies can be used to generate two equation (eqn 29.14 applied to the two sets) in two unknowns: λ and the constant.

$$\ln k_{\text{et},\,1} + \frac{(\Delta_r G_1^{\ominus})^2}{4\lambda kT} + \frac{\Delta_r G_1^{\ominus}}{2kT} = \text{constant} = \ln k_{\text{et},2} + \frac{(\Delta_r G_2^{\ominus})^2}{4\lambda kT} + \frac{\Delta_r G_2^{\ominus}}{2kT},$$

$$\text{so}\ \frac{(\Delta_r G_1^{\ominus})^2 - (\Delta_r G_2^{\ominus})^2}{4\lambda kT} = \ln\frac{k_{\text{et},2}}{k_{\text{et},1}} + \frac{\Delta_r G_2^{\ominus} - \Delta_r G_1^{\ominus}}{2kT}$$

$$\text{and}\ \ \lambda = \frac{(\Delta_r G_1^{\ominus})^2 - (\Delta_r G_2^{\ominus})^2}{4\left(kT\ln\frac{k_{\text{et},2}}{k_{\text{et},1}} + \frac{\Delta_r G_2^{\ominus} - \Delta_r G_1^{\ominus}}{2}\right)},$$

$$\lambda = \frac{(-0.665\,\text{eV})^2 - (-0.975\,\text{eV})^2}{\frac{4(1.381\times10^{-23}\ \text{J K}^{-1})(298\ \text{K})}{1.602\times10^{-19}\ \text{J eV}^{-1}}\ln\frac{3.33\times10^6}{2.02\times10^5} - 2(0.975 - 0.665)\ \text{eV}} = \boxed{1.53\underline{1}\ \text{eV}}$$

If we knew the activation Gibbs energy, we could use eqn 29.12 to compute $\langle \mathrm{H_{DA}} \rangle$ from either rate constant, and we *can* compute the activation Gibbs energy from eqn 29.4:

$$\Delta^{\ddagger}G = \frac{(\Delta_r G^{\ominus} + \lambda)^2}{4\lambda} = \frac{[(-0.665 + 1.53\underline{1})\text{eV}]^2}{4(1.53\underline{1}\ \text{eV})} = 0.122\ \text{eV}.$$

$$\text{Now}\qquad k_{\text{et}} = \frac{2\langle \mathrm{H_{DA}}\rangle^2}{h}\left(\frac{\pi^3}{4\lambda kT}\right)^{1/2}\exp\left(\frac{-\Delta^{\ddagger}G}{kT}\right),$$

$$\text{so}\qquad \langle \mathrm{H_{DA}}\rangle = \left(\frac{hk_{\text{et}}}{2}\right)^{1/2}\left(\frac{4\lambda kT}{\pi^3}\right)^{1/4}\exp\left(\frac{\Delta^{\ddagger}G}{2kT}\right),$$

$$\langle \mathrm{H_{DA}}\rangle = \left(\frac{(6.626\times10^{-34}\ \text{J s})(2.02\times10^5\ \text{s}^{-1})}{2}\right)^{1/2}$$
$$\times\left(\frac{4(1.53\underline{1}\,\text{eV})(1.602\times10^{-19}\,\text{J eV}^{-1})(1.381\times10^{-23}\,\text{J K}^{-1})(298\,\text{K})}{\pi^3}\right)^{1/4}$$
$$\times\exp\left(\frac{(0.122\,\text{eV})(1.602\times10^{-19}\,\text{J eV}^{-1})}{2(1.381\times10^{-23}\,\text{J K}^{-1})(298\,\text{K})}\right) = \boxed{9.39\times10^{-24}\ \text{J}}$$

E29.6(b) Equation 29.13 applies. In E29.6(a), we found the parameter β to equal 12 nm^{-1}, so:

$$\ln k_{\text{et}}/\text{s}^{-1} = -\beta r + \text{constant}\quad \text{so}\quad \text{constant} = \ln k_{\text{et}}/\text{s}^{-1} + \beta r,$$

and constant $= \ln 2.02\times10^5 + (12\,\text{nm}^{-1})(1.11\,\text{nm}) = 25$.

Taking the exponential of eqn 29.13 yields:

$$k_{\text{et}} = \text{e}^{-\beta r + \text{constant}}\ \text{s}^{-1} = \text{e}^{-(12/\text{nm})(1.48\,\text{nm})+25}\ \text{s}^{-1} = \boxed{1.4\times10^3\ \text{s}^{-1}}.$$

E29.7(b) Disregarding signs, the electric field is the gradient of the electrical potential

$$\mathcal{E} = \frac{\text{d}\Delta\phi}{\text{d}x} \approx \frac{\Delta\phi}{d} = \frac{\sigma}{\varepsilon} = \frac{\sigma}{\varepsilon_r\varepsilon_0} = \frac{0.12\,\text{C m}^{-2}}{(48)\times(8.854\times10^{-12}\,\text{J}^{-1}\,\text{C}^2\text{m}^{-1})} = \boxed{2.8\times10^8\ \text{V m}^{-1}}$$

E29.8(b) In the high overpotential limit

$$j = j_0 e^{(1-\alpha)f\eta} \quad \text{so} \quad \frac{j_1}{j_2} = e^{(1-\alpha)f(\eta_1-\eta_2)} \quad \text{where } f = \frac{F}{RT} = \frac{1}{25.69\,\text{mV}}$$

The overpotential η_2 is

$$\eta_2 = \eta_1 + \frac{1}{f(1-\alpha)}\ln\frac{j_2}{j_1} = 105\,\text{mV} + \left(\frac{25.69\,\text{mV}}{1-0.42}\right)\times\ln\left(\frac{7255\,\text{mA cm}^{-2}}{17.0\,\text{mA cm}^{-2}}\right)$$

$$= \boxed{37\bar{3}\,\text{mV}}$$

E29.9(b) In the high overpotential limit

$$j = j_0 e^{(1-\alpha)f\eta} \quad \text{so} \quad j_0 = j e^{(\alpha-1)f\eta}$$

$$j_0 = (17.0\,\text{mA cm}^{-2}) \times e^{\{(0.42-1)\times(105\,\text{mV})/(25.69\,\text{mV})\}} = \boxed{1.6\,\text{mA cm}^{-2}}$$

E29.10(b) In the high overpotential limit

$$j = j_0 e^{(1-\alpha)f\eta} \quad \text{so} \quad \frac{j_1}{j_2} = e^{(1-\alpha)f(\eta_1-\eta_2)} \quad \text{and} \quad j_2 = j_1 e^{(1-\alpha)f(\eta_2-\eta_1)}.$$

So the current density at 0.60 V is

$$j_2 = (1.22\,\text{mA cm}^{-2}) \times e^{\{(1-0.50)\times(0.60\,\text{V}-0.50\,\text{V})/(0.02569\,\text{V})\}} = \boxed{8.5\,\text{mA cm}^{-2}}$$

Note. The exercise says the data refer to the same material and at the same temperature as the previous exercise (29.10(a)), yet the results for the current density at the same overpotential differ by a factor of over 5!

E29.11(b) **(a)** The Butler–Volmer equation gives

$$\begin{aligned} j &= j_0\left(e^{(1-\alpha)f\eta} - e^{-\alpha f\eta}\right) \\ &= (2.5\times10^{-3}\,\text{A cm}^{-2}) \times \left(e^{\{(1-0.58)\times(0.30\,\text{V})/(0.02569\,\text{V})\}} - e^{-\{(0.58)\times(0.30\,\text{V})/(0.02569\,\text{V})\}}\right) \\ &= \boxed{0.34\,\text{A cm}^{-2}} \end{aligned}$$

(b) According to the Tafel equation

$$\begin{aligned} j &= j_0 e^{(1-\alpha)f\eta} \\ &= (2.5\times10^{-3}\,\text{A cm}^{-2})e^{\{(1-0.58)\times(0.30\,\text{V})/(0.02569\,\text{V})\}} = \boxed{0.34\,\text{A cm}^{-2}} \end{aligned}$$

The validity of the Tafel equation improves as the overpotential increases.

E29.12(b) The limiting current density is

$$j_{\text{lim}} = \frac{zFDc}{\delta}$$

but the diffusivity is related to the ionic conductivity (Chapter 24)

$$D = \frac{\lambda RT}{z^2F^2} \quad \text{so} \quad j_{\text{lim}} = \frac{c\lambda}{\delta z f}$$

$$j_{\text{lim}} = \frac{(1.5\,\text{mol m}^{-3})\times(10.60\times10^{-3}\,\text{S m}^2\,\text{mol}^{-1})\times(0.02569\,\text{V})}{(0.32\times10^{-3}\,\text{m})\times(+1)}$$

$$= \boxed{1.3\,\text{A m}^{-2}}$$

E29.13(b) For the iron electrode $E^{\ominus} = -0.44\,\mathrm{V}$ (Table 10.7) and the Nernst equation for this electrode (Section 10.5) is

$$E = E^{\ominus} - \frac{RT}{\nu F}\ln\left(\frac{1}{[\mathrm{Fe}^{2+}]}\right) \qquad \nu = 2$$

Since the hydrogen overpotential is 0.60 V evolution of H_2 will begin when the potential of the Fe electrode reaches $-0.60\,\mathrm{V}$. Thus

$$-0.60\,\mathrm{V} = -0.44\,\mathrm{V} + \frac{0.02569\,\mathrm{V}}{2}\ln[\mathrm{Fe}^{2+}]$$

$$\ln[\mathrm{Fe}^{2+}] = \frac{-0.16\,\mathrm{V}}{0.0128\,\mathrm{V}} = -12.\overline{5}$$

$$[\mathrm{Fe}^{2+}] = \boxed{4\times10^{-6}\,\mathrm{mol\,L^{-1}}}$$

Comment. Essentially all Fe^{2+} has been removed by deposition before evolution of H_2 begins.

E29.14(b) The zero-current potential of the electrode is given by the Nernst equation

$$E = E^{\ominus} - \frac{RT}{\nu F}\ln Q = E^{\ominus} - \frac{1}{f}\ln\frac{a(\mathrm{Fe}^{2+})}{a(\mathrm{Fe}^{3+})} = 0.77\,\mathrm{V} - \frac{1}{f}\ln\frac{a(\mathrm{Fe}^{2+})}{a(\mathrm{Fe}^{3+})}$$

The Butler–Volmer equation gives

$$j = j_0\left(\mathrm{e}^{(1-\alpha)f\eta} - \mathrm{e}^{-\alpha f\eta}\right) = j_0\left(\mathrm{e}^{(0.42)f\eta} - \mathrm{e}^{-0.58f\eta}\right)$$

where η is the overpotential, defined as the working potential E' minus the zero-current potential E.

$$\eta = E' - 0.77\,\mathrm{V} + \frac{1}{f}\ln\frac{a(\mathrm{Fe}^{2+})}{a(\mathrm{Fe}^{3+})} = E' - 0.77\,\mathrm{V} + \frac{1}{f}\ln r,$$

where r is the ratio of activities; so

$$\begin{aligned} j = j_0\big(&\mathrm{e}^{(0.42)E'/f}\mathrm{e}^{\{(0.42)\times(-0.77\,\mathrm{V})/(0.02569\,\mathrm{V})\}}r^{0.42} \\ &- \mathrm{e}^{(-0.58)E'/f}\mathrm{e}^{\{(-0.58)\times(-0.77\,\mathrm{V})/(0.02569\,\mathrm{V})\}}r^{-0.58}\big) \end{aligned}$$

Specializing to the condition that the ions have equal activities yields

$$j = \boxed{(2.5\,\mathrm{mA\,cm^{-2}})\times[\mathrm{e}^{(0.42)E'/f}\times(3.4\overline{1}\times10^{-6}) - \mathrm{e}^{(-0.58)E'/f}\times(3.5\overline{5}\times10^{7})]}$$

E29.15(b) *Note*. The exercise did not supply values for j_0 or α. Assuming $\alpha = 0.5$, only j/j_0 is calculated. From Exercise 29.14(b)

$$\begin{aligned} j &= j_0\left(\mathrm{e}^{(0.50)E'/f}\mathrm{e}^{-(0.50)E^{\ominus}/f}r^{0.50} - \mathrm{e}^{(-0.50)E'/f}\mathrm{e}^{(0.50)E^{\ominus}/f}r^{-0.50}\right) \\ &= 2j_0\sinh\left[\tfrac{1}{2}fE' - \tfrac{1}{2}fE^{\ominus} + \tfrac{1}{2}\ln r\right], \end{aligned}$$

so, if the working potential is set at 0.50 V, then

$$j = 2j_0\sinh\left[\tfrac{1}{2}(0.91\,\mathrm{V})/(0.02569\,\mathrm{V}) + \tfrac{1}{2}\ln r\right]$$

$$j/j_0 = 2\sinh\left(8.4\overline{8} + \tfrac{1}{2}\ln r\right)$$

At $r = 0.1$: $j/j_0 = 2\sinh\left(8.4\overline{8} + \tfrac{1}{2}\ln 0.10\right) = 1.5\times10^{3}\,\mathrm{mA\,cm^{-2}} = \boxed{1.5\,\mathrm{A\,cm^{-2}}}$

At $r = 1$: $j/j_0 = 2\sinh(8.4\overline{8} + 0.0) = 4.8 \times 10^3 \text{ mA cm}^{-2} = \boxed{4.8 \text{ A cm}^{-2}}$

At $r = 10$: $j/j_0 = 2\sinh\left(8.4\overline{8} + \frac{1}{2}\ln 10\right) = 1.5 \times 10^4 \text{ mA cm}^{-2} = \boxed{15 \text{ A cm}^{-2}}$

E29.16(b) The potential needed to sustain a given current depends on the activities of the reactants, but the *over*potential does not. The Butler–Volmer equation says

$$j = j_0(\mathrm{e}^{(1-\alpha)f\eta} - \mathrm{e}^{-\alpha f\eta})$$

This cannot be solved analytically for η, but in the high-overpotential limit, it reduces to the Tafel equation

$$j = j_0\mathrm{e}^{(1-\alpha)f\eta} \quad \text{so} \quad \eta = \frac{1}{(1-\alpha)f}\ln\frac{j}{j_0} = \frac{0.02569 \text{ V}}{1 - 0.75}\ln\frac{15 \text{ mA cm}^{-2}}{4.0 \times 10^{-2} \text{ mA cm}^{-2}}$$

$$\eta = \boxed{0.61 \text{ V}}$$

This is a sufficiently large overpotential to justify use of the Tafel equation.

E29.17(b) The number of singly charged particles transported per unit time per unit area at equilibrium is the exchange current density divided by the charge

$$N = \frac{j_0}{e}$$

The frequency f of participation per atom on an electrode is

$$f = Na$$

where a is the effective area of an atom on the electrode surface.

For the Cu, $H_2|H^+$ electrode

$$N = \frac{j_0}{e} = \frac{1.0 \times 10^{-6} \text{ A cm}^{-2}}{1.602 \times 10^{-19} \text{ C}} = \boxed{6.2 \times 10^{12} \text{ s}^{-1} \text{ cm}^{-2}}$$

$$f = Na = (6.2 \times 10^{12} \text{ s}^{-1} \text{ cm}^{-2}) \times (260 \times 10^{-10} \text{ cm})^2$$

$$= \boxed{4.2 \times 10^{-3} \text{ s}^{-1}}$$

For the $\text{Pt}|\text{Ce}^{4+}, \text{Ce}^{3+}$ electrode

$$N = \frac{j_0}{e} = \frac{4.0 \times 10^{-5} \text{ A cm}^{-2}}{1.602 \times 10^{-19} \text{ C}} = \boxed{2.5 \times 10^{14} \text{ s}^{-1} \text{ cm}^{-2}}$$

The frequency f of participation per atom on an electrode is

$$f = Na = (2.5 \times 10^{14} \text{ s}^{-1} \text{ cm}^{-2}) \times (260 \times 10^{-10} \text{ cm})^2 = \boxed{0.17 \text{ s}^{-1}}$$

E29.18(b) The resistance R of an ohmic resistor is

$$R = \frac{\text{potential}}{\text{current}} = \frac{\eta}{jA}$$

where A is the surface area of the electrode. The overpotential in the low overpotential limit is

$$\eta = \frac{j}{fj_0} \quad \text{so} \quad R = \frac{1}{fj_0A}$$

(a) $$R = \frac{0.02569\,\text{V}}{(5.0\times10^{-12}\,\text{A cm}^{-2})\times(1.0\,\text{cm}^2)} = 5.1\times10^{9}\,\Omega = \boxed{5.1\,\text{G}\Omega}$$

(b) $$R = \frac{0.02569\,\text{V}}{(2.5\times10^{-3}\,\text{A cm}^{-2})\times(1.0\,\text{cm}^2)} = \boxed{10\,\Omega}$$

E29.19(b) No reduction of cations to metal will occur until the cathode potential is dropped below the zero-current potential for the reduction of Ni^{2+} (−0.23 V at unit activity). Deposition of Ni will occur at an appreciable rate after the potential drops significantly below this value; however, the deposition of Fe will begin (albeit slowly) after the potential is brought below −0.44 V. If the goal is to deposit pure Ni, then the Ni will be deposited rather slowly at just above −0.44 V; then the Fe can be deposited rapidly by dropping the potential well below −0.44 V.

E29.20(b) As was noted in Exercise 29.10(a), an overpotential of 0.6 V or so is necessary to obtain significant deposition or evolution, so H_2 is evolved from acid solution at a potential of about −0.6 V. The reduction potential of Cd^{2+} is more positive than this (−0.40 V), so Cd will deposit (albeit slowly) from Cd^{2+} before H_2 evolution.

E29.21(b) Zn can be deposited if the H^+ discharge current is less than about 1 mA cm^{-2}. The exchange current, according to the high negative overpotential limit, is

$$j = j_0 e^{-\alpha f \eta}$$

At the standard potential for reduction of Zn^{2+}(−0.76 V)

$$j = (0.79\,\text{mA cm}^{-2})\times e^{-\{(0.5)\times(-0.76\,\text{V})/(0.02569\,\text{V})\}} = 2.1\times10^{9}\,\text{mA cm}^{-2}$$

$\boxed{\text{much too large to allow deposition}}$. (That is, H_2 would begin being evolved, and fast, long before Zn began to deposit.)

E29.22(b) Fe can be deposited if the H^+ discharge current is less than about 1 mA cm^{-2}. The exchange current, according to the high negative overpotential limit, is

$$j = j_0 e^{-\alpha f \eta}$$

At the standard potential for reduction of Fe^{2+}(−0.44 V)

$$j = (1\times10^{-6}\,\text{A cm}^{-2})\times e^{-\{(0.5)\times(-0.44\,\text{V})/(0.02569\,\text{V})\}} = 5.2\times10^{-3}\,\text{A cm}^{-2}$$

$\boxed{\text{a bit too large to allow deposition}}$. (That is, H_2 would begin being evolved at a moderate rate before Fe began to deposit.)

E29.23(b) The lead acid battery half-cells are

$$Pb^{4+} + 2e^- \rightarrow Pb^{2+} \qquad 1.67\,\text{V}$$

and $Pb^{2+} + 2e^- \rightarrow Pb \qquad -0.13\,\text{V}$,

for a total of $E^\ominus = \boxed{1.80\,\text{V}}$. Power is

$$P = IV = (100\times10^{-3}\,\text{A})\times(1.80\,\text{V}) = \boxed{0.180\,\text{W}}$$

if the cell were operating at its zero-current potential yet producing 100 mA.

E29.24(b) The thermodynamic limit to the zero-current potential under standard conditions is the standard potential $E^\ominus$, which is related to the standard Gibbs energy by

$$\Delta_r G^\ominus = -\nu F E^\ominus \quad \text{so} \quad E = \frac{-\Delta_r G^\ominus}{\nu F}$$

The reaction is

$$\begin{aligned} &C_3H_8(g) + 7O_2(g) \to 3CO_2(g) + 4H_2O(l) \quad \text{with } \nu = 14 \\ &\Delta_r G^\ominus = 3\Delta_f G^\ominus(CO_2) + 4\Delta_f G^\ominus(H_2O) - \Delta_f G^\ominus(C_3H_8) - 7\Delta_f G^\ominus(O_2) \\ &\qquad = (3 \times (-394.36) + 4 \times (-237.13) - (-23.49) - 0)\,\text{kJ mol}^{-1} = -1319.4\,\text{kJ mol}^{-1} \end{aligned}$$

$$\text{so } E^\ominus = \frac{1319.39 \times 10^3\,\text{J mol}^{-1}}{14 \times (96485\,\text{C mol}^{-1})} = \boxed{0.97675\,\text{V}}$$

E29.25(b) Two electrons are lost in the corrosion of each zinc atom, so the number of zinc atoms lost is half the number of electrons which flow per unit time, i.e. half the current divided by the electron charge. The volume taken up by those zinc atoms is their number divided by their number density; their number density is their mass density divided by molar mass times Avogadro's number. Dividing the volume of the corroded zinc over the surface from which they are corroded gives the linear corrosion rate; this affects the calculation by changing the current to the current density. So the rate of corrosion is

$$\begin{aligned} \text{rate} &= \frac{jM}{2e\rho N_A} = \frac{(1.0\,\text{A m}^{-2}) \times (65.39 \times 10^{-3}\,\text{kg mol}^{-1})}{2(1.602 \times 10^{-19}\,\text{C}) \times (7133\,\text{kg m}^{-3}) \times (6.022 \times 10^{23}\,\text{mol}^{-1})} \\ &= 4.8 \times 10^{-11}\,\text{m s}^{-1} \\ &= (4.8 \times 10^{-11}\,\text{m s}^{-1}) \times (10^3\,\text{mm m}^{-1}) \times (3600 \times 24 \times 365\,\text{s y}^{-1}) \\ &= \boxed{1.5\,\text{mm y}^{-1}} \end{aligned}$$

Solutions to problems

Solutions to numerical problems

P29.3 $$E = E^\ominus + \frac{RT}{zF}\ln a(M^+)$$

Deposition may occur when the potential falls to below E and so simultaneous deposition will occur if the two potentials are the same; hence the relative activities are given by

$$E^\ominus(\text{Sn}, \text{Sn}^{2+}) + \frac{RT}{2F}\ln a(\text{Sn}^{2+}) = E^\ominus(\text{Pb}, \text{Pb}^{2+}) + \frac{RT}{2F}\ln a(\text{Pb}^{2+})$$

$$\text{or } \ln\frac{a(\text{Sn}^{2+})}{a(\text{Pb}^{2+})} = \left(\frac{2F}{RT}\right)\{E^\ominus(\text{Pb}, \text{Pb}^{2+}) - E^\ominus(\text{Sn}, \text{Sn}^{2+})\} = \frac{(2) \times (-0.126 + 0.136)\,\text{V}}{0.0257\,\text{V}} = 0.78$$

That is, we require $\boxed{a(\text{Sn}^{2+}) \approx 2.2a(\text{Pb}^{2+})}$

P29.8 $$r_D = \left(\frac{\varepsilon RT}{2\rho F^2 I b^\ominus}\right)^{1/2} \quad [22.50]$$

where $I = \frac{1}{2}\sum_i z_i^2(b_i/b^\ominus)$, $b^\ominus = 1\,\text{mol kg}^{-1}$ [10.18]

For NaCl: $Ib^{\ominus} = b_{\mathrm{NaCl}} \approx [\mathrm{NaCl}]$ assuming 100 per cent dissociation.

For $\mathrm{Na_2SO_4}$: $Ib^{\ominus} = \frac{1}{2}\left((1)^2(2b_{\mathrm{Na_2SO_4}}) + (2)^2 b_{\mathrm{Na_2SO_4}}\right)$

$= 3b_{\mathrm{Na_2SO_4}} \approx 3[\mathrm{Na_2SO_4}]$ assuming 100 per cent dissociation.

$$\begin{aligned} r_{\mathrm{D}} &\approx \left(\frac{78.54 \times (8.854 \times 10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}}) \times (8.315\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298.15\,\mathrm{K})}{2 \times (1.00\,\mathrm{g\,cm^{-3}}) \times \left(\frac{10^{-3}\,\mathrm{kg}}{\mathrm{g}}\right) \times \left(\frac{10^{6}\,\mathrm{cm^3}}{\mathrm{m^3}}\right) \times (96485\,\mathrm{C\,mol^{-1}})^2}\right)^{1/2} \times \left(\frac{1}{Ib^{\ominus}}\right)^{1/2} \\ &\approx \frac{3.043 \times 10^{-10}\,\mathrm{m\,mol^{1/2}\,kg^{-1/2}}}{(Ib^{\ominus})^{1/2}} \\ &\approx \frac{304.3\,\mathrm{pm\,mol^{1/2}\,kg^{-1/2}}}{(Ib^{\ominus})^{1/2}} \end{aligned}$$

These equations can be used to produce the graph of r_{D} against b_{salt} shown in Fig. 29.1. Note the contraction of the double layer with increasing ionic strength.

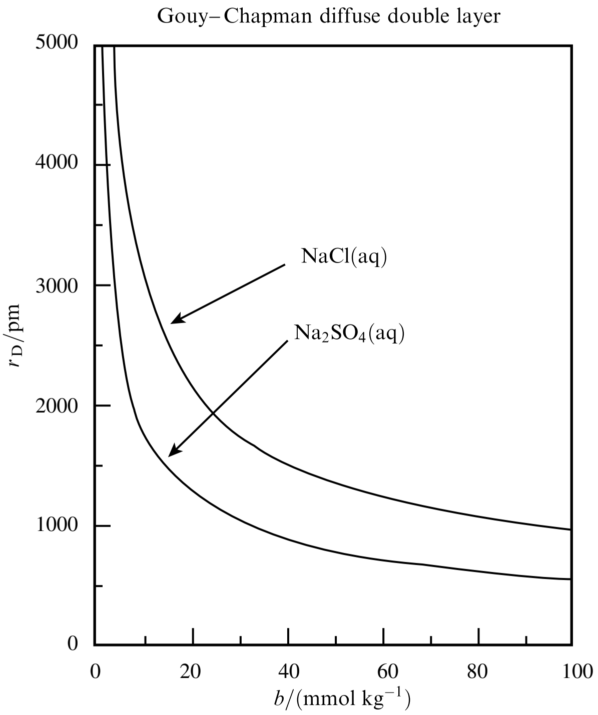


Figure 29.1

P29.9 This problem differs somewhat from the simpler one-electron transfers considered in the text. In place of $\mathrm{Ox} + \mathrm{e^-} \rightarrow \mathrm{Red}$ we have here

$$\mathrm{In^{3+}} + 3\mathrm{e^-} \rightarrow \mathrm{In}$$

namely, a three-electron transfer. Therefore eqns 29.25, 29.26, and all subsequent equations including the Butler–Volmer equation [29.35] and the Tafel equations [29.38–29.41] need to be modified by including the factor z (in this case 3) in the equation. Thus, in place of eqn 29.26, we have

$$\Delta^{\ddagger}G_{\mathrm{c}} = \Delta^{\ddagger}G_{\mathrm{c}}(0) + z\alpha F\Delta\phi$$

and in place of eqns 29.39 and 29.41

$$\ln j = \ln j_0 + z(1-\alpha)f\eta \quad \text{anode}$$

$$\ln(-j) = \ln j_0 - z\alpha f\eta \quad \text{cathode}$$

We draw up the following table

$j/(\mathrm{A\,m^{-2}})$	$-E/\mathrm{V}$	η/V	$\ln(j/(\mathrm{A\,m^{-2}}))$
0	0.388	0	
0.590	0.365	0.023	−0.5276
1.438	0.350	0.038	0.3633
3.507	0.335	0.053	1.255

We now do a linear regression of $\ln j$ against η with the following results (see Fig. 29.2)

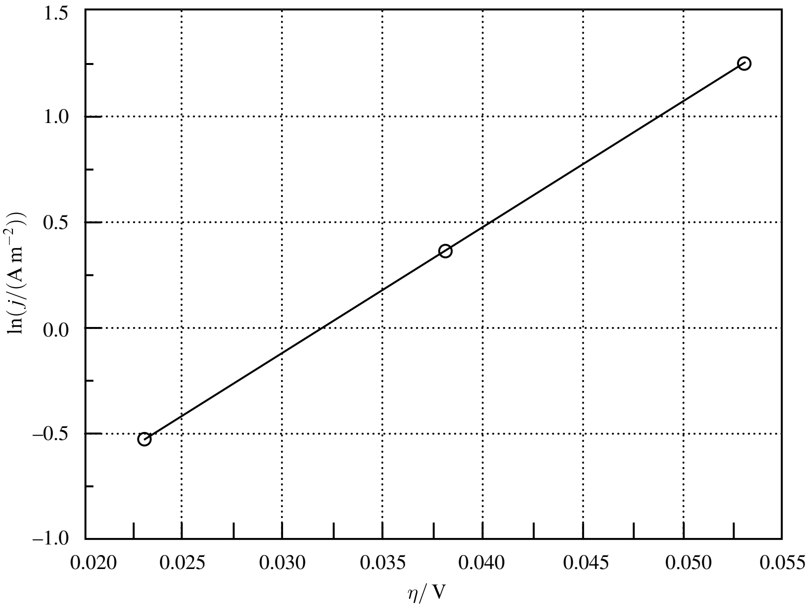


Figure 29.2

$$z(1-\alpha)f = 59.42\,\mathrm{V^{-1}}, \qquad \text{standard deviation} = 0.0154$$

$$\ln j_0 = -1.894, \qquad \text{standard deviation} = 0.0006$$

$$R = 1 \text{ (almost exact)}$$

Thus, although there are only three data points, the fit to the Tafel equation is almost exact. Solving for α from $z(1-\alpha)f = 59.42\,\mathrm{V^{-1}}$, we obtain

$$\alpha = 1 - \frac{59.42\,\mathrm{V^{-1}}}{3f} = 1 - \left(\frac{59.42\,\mathrm{V^{-1}}}{3}\right) \times (0.025262\,\mathrm{V})$$

$$= 0.49\overline{96} = \boxed{0.50}$$

which matches the usual value of α exactly.

$$j_0 = \mathrm{e}^{-1.894} = \boxed{0.150\,\mathrm{A\,m^{-2}}}$$

The cathodic current density is obtained from

$$\begin{aligned}\ln(-j_\mathrm{c}) &= \ln j_0 - z\alpha f\eta \quad \eta = 0.023\,\mathrm{V} \text{ at } -E/\mathrm{V} = 0.365\\ &= -1.894 - (3 \times 0.49\overline{96} \times 0.023)/(0.025\,262)\\ &= -3.2\overline{59}\\ -j_\mathrm{c} &= \mathrm{e}^{-3.2\overline{59}} = 0.038\overline{4}\,\mathrm{A\,m^{-2}}\\ j_\mathrm{c} &= \boxed{-0.038\,\mathrm{A\,m^{-2}}}\end{aligned}$$

P29.12 At large positive values of the overpotential the current density is anodic.

$$\begin{aligned}j &= j_0\left[\mathrm{e}^{(1-\alpha)f\eta} - \mathrm{e}^{-\alpha f\eta}\right] \quad [29.35]\\ &\approx j_0\mathrm{e}^{(1-\alpha)f\eta} = j_\mathrm{a} \quad [29.34]\\ \ln j &= \ln j_0 + (1-\alpha)f\eta\end{aligned}$$

Performing a linear regression analysis of $\ln j$ against η, we find

$$\begin{aligned}&\ln(j_0/(\mathrm{mA\,m^{-2}})) = -10.826, \quad \text{standard deviation} = 0.287\\ &(1-\alpha)f = 19.550\,\mathrm{V^{-1}}, \quad \text{standard deviation} = 0.355\\ &\boxed{R = 0.999\,01}\\ &j_0 = \mathrm{e}^{-10.826}\mathrm{mA\,m^{-2}} = \boxed{2.00 \times 10^{-5}\mathrm{mA\,m^{-2}}}\\ &\alpha = 1 - \frac{19.550\,\mathrm{V^{-1}}}{f} = 1 - \frac{19.550\,\mathrm{V^{-1}}}{(0.025693\,\mathrm{V})^{-1}}\\ &\boxed{\alpha = 0.498}\end{aligned}$$

The linear regression explains 99.90 per cent of the variation in a $\ln j$ against η plot and standard deviations are low. There are $\boxed{\text{no}}$ deviations from the Tafel equation/plot.

Solutions to theoretical problems

P29.14 **(a)** First, assume that eqn 4 applies to the bimolecular processes under consideration in this problem. (Cf. P29.1.) Thus,

$$\Delta^\ddagger G_{11} = \frac{(\Delta_\mathrm{r}G_{11}^\ominus + \lambda_{11})^2}{4\lambda_{11}}, \quad \Delta^\ddagger G_{22} = \frac{\Delta_\mathrm{r}G_{22}^\ominus + \lambda_{22})^2}{4\lambda_{22}}, \quad \Delta^\ddagger G_{12} = \frac{(\Delta_\mathrm{r}G_{12}^\ominus + \lambda_{12})^2}{4\lambda_{12}}$$

Because the standard free energy for elctron self-exchange is zero, these simplify to:

$$\begin{aligned}\Delta^\ddagger G_{11} &= \frac{\lambda_{11}^2}{4\lambda_{11}} = \lambda_{11}/4 \quad \text{and} \quad \Delta^\ddagger G_{22} = \lambda_{22}/4.\\ \Delta^\ddagger G_{12} &= \frac{(\Delta_\mathrm{r}G_{12}^\ominus)^2 + \lambda_{12}^2 + 2\lambda_{12}\Delta_\mathrm{r}G_{12}^\ominus}{4\lambda_{12}}\end{aligned}$$

(b) If $\Delta_r G^{\ominus}_{12} \ll \lambda_{12}$, then we may drop the quadratic term in the numerator, leaving:

$$\Delta^{\ddagger} G_{12} \approx \lambda_{12}/4 + \Delta_r G^{\ominus}_{12}/2.$$

Assume that $\lambda_{12} = (\lambda_{11} + \lambda_{22})/2$, so

$$\lambda_{12}/4 = (\lambda_{11}/4 + \lambda_{22}/4)/2 = (\Delta^{\ddagger} G_{11} + \Delta^{\ddagger} G_{22})/2.$$

Thus, we have:

$$\Delta^{\ddagger} G_{12} \approx (\Delta^{\ddagger} G_{11} + \Delta^{\ddagger} G_{22} + \Delta_r G^{\ominus}_{12})/2.$$

(c) According to activated complex theory, we can write for the self-exchange reactions:

$$k_{11} = \kappa_{11}\nu_{11} \exp\left(\frac{-\Delta^{\ddagger} G_{11}}{RT}\right) \quad \text{and} \quad k_{22} = \kappa_{22}\nu_{22} \exp\left(\frac{-\Delta^{\ddagger} G_{22}}{RT}\right).$$

(d) According to activated complex theory, we can write:

$$k_{12} = \kappa_{12}\nu_{12} \exp\left(\frac{-\Delta^{\ddagger} G_{12}}{RT}\right) \approx \kappa_{12}\nu_{12} \exp\left(\frac{-\Delta^{\ddagger} G_{11} - \Delta^{\ddagger} G_{22} - \Delta_r G^{\ominus}_{12}}{2RT}\right).$$

(e) Finally, we simplify by assuming that all $\kappa\nu$ terms are identical, so:

$$k_{12} \approx \left[\kappa\nu \exp\left(\frac{-\Delta^{\ddagger} G_{11}}{RT}\right) \kappa\nu \exp\left(\frac{-\Delta^{\ddagger} G_{22}}{RT}\right) \exp\left(\frac{-\Delta_r G^{\ominus}_{12}}{RT}\right)\right]^{1}/2.$$

The final exponential is the equilibrium constant; the first two exponentials with their factors of $\kappa\nu$ are electron self-exchange rate constants, so:

$$\boxed{k_{12} \approx (k_{11}k_{22}K)^{1/2}}.$$

P29.16 Let η oscillate between η_+ and η_- around a mean value η_0. Then η_- is large and positive (and $\eta_+ > \eta_-$),

$$j \approx j_0 e^{(1-\alpha)\eta f} = j_0 e^{(1/2)\eta f} \quad [\alpha = 0.5]$$

and η varies as depicted in Fig. 29.3(a).

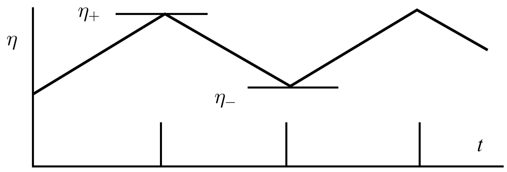


Figure 29.3(a)

Therefore, j is a chain of increasing and decreasing exponential functions,

$$j = j_0 e^{(\eta_- + \gamma t)f/2} \propto e^{-t/\tau}$$

during the increasing phase of η, where $\tau = \dfrac{2RT}{\gamma F}$, γ a constant, and

$$j = j_0 e^{(\eta_+ - \gamma t)f/2} \propto e^{-t/\tau}$$

during the decreasing phase. This is depicted in Fig. 29.3(b).

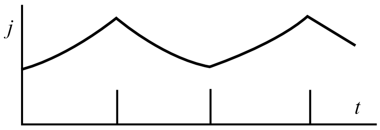


Figure 29.3(b)

P29.17

$$j = \left(\frac{cFD}{\delta}\right) \times (1 - e^{f\eta^c})[29.51;\, z = 1] = \boxed{j_L(1 - e^{F\eta^c/RT})}$$

The form of this expression is illustrated in Fig. 29.4.

For the anion current, the sign of η^c is changed, and the current of anions approaches its limiting value as η^c becomes more positive (Fig. 29.4).

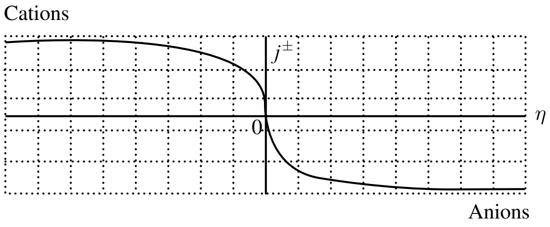


Figure 29.4

P29.19 Does eqn 29.13

$$\ln k_{\text{et}} = -\beta r + \text{constant}$$

apply to these data? Draw the follwing table:

r/nm	$k_{\text{et}}/\text{s}^{-1}$	$\ln k_{\text{et}}/\text{s}^{-1}$
0.48	1.58×10^{12}	28.1
0.95	3.98×10^{9}	22.1
0.96	1.00×10^{9}	20.7
1.23	1.58×10^{8}	18.9
1.35	3.98×10^{7}	17.5
2.24	6.31×10^{1}	4.14

and plot $\ln k_{\text{et}}$ vs. r

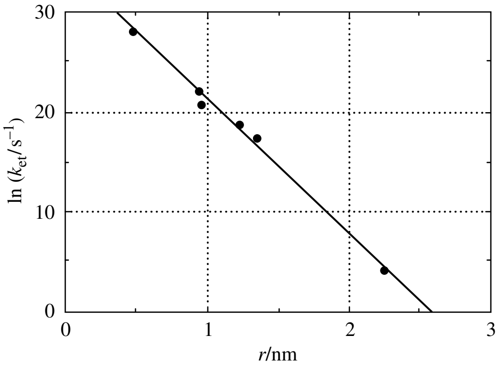


Figure 29.5

The data fall on a good straight line, so the equation $\boxed{\text{appears to apply}}$. The least squares linear fit equation is:

$$\ln k_{\rm et}/{\rm s} = 34.7 - 13.4r/{\rm nm} \quad r^2(\text{correlation coefficient}) = 0.991$$

so we identify $\boxed{\beta = 13.4\,{\rm nm}^{-1}}$.

P29.20 The theoretical treatment of section 29.1 applies only at relatively high temperatures. At temperatures above 130 K, the reaction in question is observed to follow a temperature dependence consistent with eqn 29.12, namely increasing rate with increasing temperature. Below 130 K, the temperature-dependent terms in eqn 29.12 are replaced by Frank–Condon factors; that is, temperature-dependent terms are replaced by temperature-independent wavefunction overlap integrals.

P29.21 **(a)** The electrode potentials of half-reactions (**a**), (**b**), and (**c**) are (Section 29.8)

(a) $E(\rm H_2, H^+) = -0.059\,V\,pH = (-7) \times (0.059\,V) = -0.14\,V$
(b) $E(\rm O_2, H^+) = (1.23\,V) - (0.059\,V)pH = +0.82\,V$
(c) $E(\rm O_2, OH^-) = (0.40\,V) + (0.059\,V)pOH = 0.81\,V$

$$E(\mathrm{M, M^+}) = E^\ominus(\mathrm{M, M^+}) + \left(\frac{0.059\,\mathrm{V}}{z_+}\right)\log 10^{-6} = E^\ominus(\mathrm{M, M^+}) - \frac{0.35\,\mathrm{V}}{z_+}$$

Corrosion will occur if E(a), E(b), or E(c) $> E(\rm M, M^+)$

(i) $E^\ominus(\rm Fe,\ Fe^{2+}) = -0.44\,V, \quad z_+ = 2$
$E(\rm Fe, Fe^{2+}) = (-0.44 - 0.18)\,V = -0.62\,V < E(\text{a, b, and c})$

(ii) $E(\mathrm{Cu, Cu^+}) = (0.52 - 0.35)\,\mathrm{V} = 0.17\,\mathrm{V}\begin{cases} > E(\mathrm{a}) \\ < E(\text{b and c})\end{cases}$

$E(\mathrm{Cu, Cu^{2+}}) = (0.34 - 0.18)\,\mathrm{V} = 0.16\,\mathrm{V}\begin{cases} > E(\mathrm{a}) \\ < E(\text{b and c})\end{cases}$

(iii) $E(\mathrm{Pb, Pb^{2+}}) = (-0.13 - 0.18)\,\mathrm{V} = -0.31\,\mathrm{V}\begin{cases} > E(\mathrm{a}) \\ < E(\text{b and c})\end{cases}$

(iv) $E(\rm Al, Al^{3+}) = (-1.66 - 0.12)\,V = -1.78\,V < E(\text{a, b, and c})$

(v) $E(\mathrm{Ag, Ag^+}) = (0.80 - 0.35)\,\mathrm{V} = 0.45\,\mathrm{V}\begin{cases} > E(\mathrm{a}) \\ < E(\text{b and c})\end{cases}$

(vi) $E(\rm Cr, Cr^{3+}) = (-0.74 - 0.12)\,V = -0.86\,V < E(\text{a, b, and c})$
(vii) $E(\rm Co, Co^{2+}) = (-0.28 - 0.15)\,V = -0.43\,V < E(\text{a, b, and c})$

Therefore, the metals with a thermodynamic tendency to corrode in moist conditions at pH = 7 are $\boxed{\text{Fe, Al, Co, Cr}}$ if oxygen is absent, but, if oxygen is present, all seven elements have a tendency to corrode.

(b) A metal has a thermodynamic tendency to corrosion in moist air if the zero-current potential for the reduction of the metal ion is more negative than the reduction potential of the half-reaction

$$\rm 4H^+ + O_2 + 4e^- \rightarrow 2H_2O \qquad E^\ominus = 1.23\,V$$

The zero-current cell potential is given by the Nernst equation

$$E = E^\ominus - \frac{RT}{\nu F}\ln Q = E^\ominus - \frac{RT}{\nu F}\ln\frac{[\mathrm{M}^{z+}]^{\nu/z}}{[\mathrm{H}^+]^\nu p(\mathrm{O_2})^{\nu/4}}$$

We are asked if a tendency to corrode exists at pH 7 ($[\mathrm{H}^+] = 10^{-7}$) in moist air ($p(\mathrm{O_2}) \approx$ 0.2 bar), and are to answer yes if $E \geq 0$ for a metal ion concentration of 10^{-6}, so for $\nu = 4$

and 2+ cations

$$E = 1.23\,\mathrm{V} - E^{\ominus}_{\mathrm{M}} - \frac{0.02569\,\mathrm{V}}{\nu} \ln \frac{(10^{-6})^2}{(1 \times 10^{-7})^4 \times (0.2)} = 0.983\,\mathrm{V} - E^{\ominus}_{\mathrm{M}}$$

In the following, $z = 2$

For Ni: $E^{\ominus} = 0.983\,\mathrm{V} - (-0.23\,\mathrm{V}) > 0$ $\boxed{\text{corrodes}}$

For Cd: $E^{\ominus} = 0.983\,\mathrm{V} - (-0.40\,\mathrm{V}) > 0$ $\boxed{\text{corrodes}}$

For Mg: $E^{\ominus} = 0.983\,\mathrm{V} - (-2.36\,\mathrm{V}) > 0$ $\boxed{\text{corrodes}}$

For Ti: $E^{\ominus} = 0.983\,\mathrm{V} - (-1.63\,\mathrm{V}) > 0$ $\boxed{\text{corrodes}}$

For Mn: $E^{\ominus} = 0.983\,\mathrm{V} - (-1.18\,\mathrm{V}) > 0$ $\boxed{\text{corrodes}}$

P29.22 $I_{\mathrm{corr}} = \overline{Aj_0}\mathrm{e}^{fE/4}$ [29.62]

with $E = -0.62 - (-0.94)\,\mathrm{V} = 0.32\,\mathrm{V}$ [as in Problem 29.21]

$$I_{\mathrm{corr}} \approx (0.25 \times 10^{-6}\,\mathrm{A}) \times (\mathrm{e}^{0.32/4\times 0.0257}) \approx \boxed{6\,\mu\mathrm{A}}$$