

INSTRUCTOR'S SOLUTIONS MANUAL
TO ACCOMPANY

ATKINS'
**PHYSICAL
CHEMISTRY** EIGHTH EDITION

PETER ATKINS • CHARLES TRAPP
MARSHALL CADY • CARMEN GUINTA

**INSTRUCTOR'S SOLUTIONS
MANUAL TO ACCOMPANY**

**ATKINS'
PHYSICAL
CHEMISTRY**

Eighth Edition

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Preface

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

The solutions to the Problems in this edition rely more heavily on the mathematical and molecular modeling software that is now generally accessible to physical chemistry students, and this is particularly true for many of the new Problems which request the use of such software for their solutions. But almost all of the Exercises and many of the Problems can still be solved with a modern hand-held scientific calculator. When a quantum chemical calculation or molecular modeling process has been called for, we have usually provided the solution with PC Spartan Pro™ because of its common availability.

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

We have carefully cross-checked the solutions for errors and expect that most have been eliminated. We would be grateful to any readers who bring any remaining errors to our attention.

We warmly thank our publishers for their patience in guiding this complex, detailed project to completion.

P. W. A.
C. A. T.
M. P. C.
C. G

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PART 1 Equilibrium

1 The properties of gases

Answers to discussion questions

- D1.2** The partial pressure of a gas in a mixture of gases is the pressure the gas would exert if it occupied alone the same container as the mixture at the same temperature. 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.
- D1.4** The critical constants represent the state of a system at which the distinction between the liquid and vapor 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 vapor phases can no longer coexist, though fluids in the so-called supercritical region have both liquid and vapor characteristics. (See *Impact* I.4.1 for a more thorough discussion of the supercritical state.)
- D1.6** 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.

Solutions to exercises

- E1.1(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.

$$n = \frac{25 \text{ g}}{39.95 \text{ g mol}^{-1}} = 0.626 \text{ mol}$$

$$\text{so } p = \frac{(0.626 \text{ mol}) \times (8.31 \times 10^{-2} \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}) \times (30 + 273 \text{ K})}{1.5 \text{ dm}^3} = \boxed{10.5 \text{ bar}}$$

not 2.0 bar.

(b) The van der Waals equation is

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

$$\begin{aligned} \text{so } p = & \frac{(8.31 \times 10^{-2} \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}) \times (30 + 273 \text{ K})}{(1.53 \text{ dm}^3 / 0.626 \text{ mol}) - 3.20 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}} \\ & - \frac{(1.337 \text{ dm}^6 \text{ atm mol}^{-2}) \times (1.013 \text{ bar atm}^{-1})}{(1.5 \text{ dm}^3 / 0.626 \text{ mol})^2} = \boxed{10.4 \text{ bar}} \end{aligned}$$

E1.2(b) (a) Boyle's law applies:

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

and

$$p_i = \frac{p_f V_f}{V_i} = \frac{(1.97 \text{ bar}) \times (2.14 \text{ dm}^3)}{(2.14 + 1.80) \text{ dm}^3} = \boxed{1.07 \text{ bar}}$$

(b) The original pressure in bar is

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

E1.3(b) The relation between pressure and temperature at constant volume can be derived from the perfect gas law

$$pV = nRT \quad \text{so} \quad p \propto T \quad \text{and} \quad \frac{p_i}{T_i} = \frac{p_f}{T_f}$$

The final pressure, then, ought to be

$$p_f = \frac{p_i T_f}{T_i} = \frac{(125 \text{ kPa}) \times (11 + 273) \text{ K}}{(23 + 273) \text{ K}} = \boxed{120 \text{ kPa}}$$

E1.4(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

$$pV = nRT$$

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

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

- E1.5(b)** Identifying p_{ex} in the equation $p = p_{\text{ex}} + \rho gh$ [1.3] as the pressure at the top of the straw and p as the atmospheric pressure on the liquid, the pressure difference is

$$p - p_{\text{ex}} = \rho gh = (1.0 \times 10^3 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2}) \times (0.15 \text{ m}) \\ = \boxed{1.5 \times 10^3 \text{ Pa}} (= 1.5 \times 10^{-2} \text{ atm})$$

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

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

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

$$\rho gh = 13.55 \text{ g cm}^{-3} \times \left(\frac{1 \text{ kg}}{10^3 \text{ g}} \right) \times \left(\frac{10^6 \text{ cm}^3}{\text{m}^3} \right) \times 0.100 \text{ m} \times 9.806 \text{ m s}^{-2} = 1.33 \times 10^4 \text{ Pa}$$

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

- E1.7(b)** 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 .

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

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

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

$$\text{From Figure 1.1(a), } \left(\frac{pV_{\text{m}}}{T} \right)_{p=0} = \boxed{0.082 061 5 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}}$$

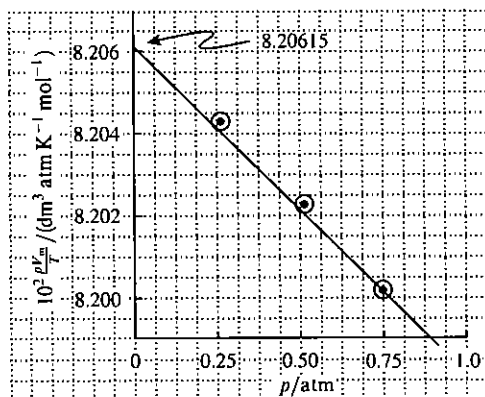


Figure 1.1(a)

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

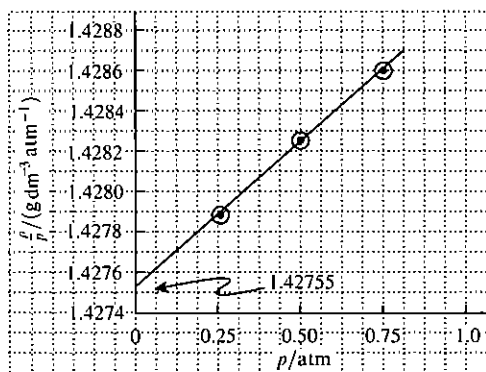


Figure 1.1(b)

$$\begin{aligned}
 M &= RT \left(\frac{\rho}{p}\right)_{p=0} = (0.082\,061\,5\text{ dm}^3\text{ atm mol}^{-1}\text{ K}^{-1}) \times (273.15\text{ K}) \times (1.42755\text{ g dm}^{-3}\text{ atm}^{-1}) \\
 &= \boxed{31.9987\text{ g mol}^{-1}}
 \end{aligned}$$

The value obtained for R deviates from the accepted value by 0.005 percent. 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.

E1.8(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

$$\begin{aligned}
 M &= \frac{RT\rho}{p} = \frac{(8.314\text{ Pa m}^3\text{ mol}^{-1}) \times [(100 + 273)\text{ K}] \times (0.6388\text{ kg m}^{-3})}{1.60 \times 10^4\text{ Pa}} \\
 &= 0.124\text{ kg mol}^{-1} = 124\text{ g mol}^{-1}
 \end{aligned}$$

The number of atoms per molecule is

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

suggesting a formula of $\boxed{\text{P}_4}$

E1.9(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 percent of the equilibrium vapor pressure at the given temperature and standard pressure.

$$p = (0.53) \times (2.69 \times 10^3 \text{ Pa}) = 1.43 \times 10^3 \text{ Pa}$$

$$\text{so } n = \frac{(1.43 \times 10^3 \text{ Pa}) \times (250 \text{ m}^3)}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (23 + 273) \text{ K}} = 1.45 \times 10^2 \text{ mol}$$

$$\text{or } m = (1.45 \times 10^2 \text{ mol}) \times (18.0 \text{ g mol}^{-1}) = 2.61 \times 10^3 \text{ g} = \boxed{2.61 \text{ kg}}$$

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

$$\begin{aligned} V &= \frac{n_J RT}{p_J} \quad n_{\text{Ne}} = \frac{0.225 \text{ g}}{20.18 \text{ g mol}^{-1}} \\ &= 1.115 \times 10^{-2} \text{ mol}, \quad p_{\text{Ne}} = 8.87 \text{ kPa}, \quad T = 300 \text{ K} \\ V &= \frac{(1.115 \times 10^{-2} \text{ mol}) \times (8.314 \text{ dm}^3 \text{ kPa K}^{-1} \text{ mol}^{-1}) \times 300 \text{ K}}{8.87 \text{ kPa}} = 3.137 \text{ dm}^3 \\ &= \boxed{3.14 \text{ dm}^3} \end{aligned}$$

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

$$\begin{aligned} n_{\text{CH}_4} &= \frac{0.320 \text{ g}}{16.04 \text{ g mol}^{-1}} = 1.995 \times 10^{-2} \text{ mol} \quad n_{\text{Ar}} = \frac{0.175 \text{ g}}{39.95 \text{ g mol}^{-1}} = 4.38 \times 10^{-3} \text{ mol} \\ n &= (1.995 + 0.438 + 1.115) \times 10^{-2} \text{ mol} = 3.548 \times 10^{-2} \text{ mol} \\ p &= \frac{nRT}{V} [1.8] = \frac{(3.548 \times 10^{-2} \text{ mol}) \times (8.314 \text{ dm}^3 \text{ kPa K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{3.137 \text{ dm}^3} \\ &= \boxed{28.2 \text{ kPa}} \end{aligned}$$

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

$$\begin{aligned} M &= \rho \frac{RT}{p} \quad [\text{Exercise 1.8(a)}] \\ \rho &= \frac{33.5 \text{ mg}}{250 \text{ cm}^3} = 0.1340 \text{ g dm}^{-3}, \quad p = 152 \text{ Torr}, \quad T = 298 \text{ K} \\ M &= \frac{(0.1340 \text{ g dm}^{-3}) \times (62.36 \text{ dm}^3 \text{ Torr K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{152 \text{ Torr}} = \boxed{16.14 \text{ g mol}^{-1}} \end{aligned}$$

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

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

At absolute zero, $V = 0$, or $0 = 20.00 \text{ dm}^3 + 0.0741 \text{ dm}^3 \text{ } ^\circ\text{C}^{-1} \times \theta(\text{abs. zero})$

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

which is close to the accepted value of $-273 \text{ } ^\circ\text{C}$.

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

$$n = 1.0 \text{ mol}$$

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

$$V = \text{(i) } 22.414 \text{ dm}^3; \text{ (ii) } 150 \text{ cm}^3$$

$$\begin{aligned} \text{(i)} \quad p &= \frac{(1.0 \text{ mol}) \times (8.206 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (273.15 \text{ K})}{22.414 \text{ dm}^3} \\ &= \boxed{1.0 \text{ atm}} \end{aligned}$$

$$\begin{aligned} \text{(ii)} \quad p &= \frac{(1.0 \text{ mol}) \times (8.206 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (500 \text{ K})}{0.150 \text{ dm}^3} \\ &= \boxed{270 \text{ atm}} \text{ (2 significant figures)} \end{aligned}$$

(b) From Table (1.6) for H_2S

$$a = 4.484 \text{ dm}^6 \text{ atm mol}^{-1} \quad b = 4.34 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$$

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

$$\begin{aligned} \text{(i)} \quad p &= \frac{(1.0 \text{ mol}) \times (8.206 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (273.15 \text{ K})}{22.414 \text{ dm}^3 - (1.0 \text{ mol}) \times (4.34 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1})} \\ &\quad - \frac{(4.484 \text{ dm}^6 \text{ atm mol}^{-1}) \times (1.0 \text{ mol})^2}{(22.414 \text{ dm}^3)^2} \\ &= \boxed{0.99 \text{ atm}} \end{aligned}$$

$$\begin{aligned} \text{(ii)} \quad p &= \frac{(1.0 \text{ mol}) \times (8.206 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (500 \text{ K})}{0.150 \text{ dm}^3 - (1.0 \text{ mol}) \times (4.34 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1})} \\ &\quad - \frac{(4.484 \text{ dm}^6 \text{ atm mol}^{-1}) \times (1.0 \text{ mol})^2}{(0.150 \text{ dm}^3)^2} \\ &= 185.6 \text{ atm} \approx \boxed{190 \text{ atm}} \text{ (2 significant figures).} \end{aligned}$$

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

$$1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}; \quad 1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}; \quad 1 \text{ dm}^6 = 10^{-6} \text{ m}^6; \quad 1 \text{ dm}^3 = 10^{-3} \text{ m}^3$$

Therefore,

$a = 1.32 \text{ atm dm}^6 \text{ mol}^{-2}$ becomes, after substitution of the conversions

$$a = \boxed{1.34 \times 10^{-1} \text{ kg m}^5 \text{ s}^{-2} \text{ mol}^{-2}}, \text{ and}$$

$b = 0.0436 \text{ dm}^3 \text{ mol}^{-1}$ becomes

$$b = \boxed{4.36 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}$$

E1.15(b) The compression factor is

$$Z = \frac{pV_m}{RT} = \frac{V_m}{V_m^o}$$

(a) Because $V_m = V_m^o + 0.12 V_m^o = (1.12)V_m^o$, we have $Z = \boxed{1.12}$ Repulsive forces dominate.

(b) The molar volume is

$$V = (1.12)V_m^o = (1.12) \times \left(\frac{RT}{p} \right)$$

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

E1.16(b) (a)
$$V_m^o = \frac{RT}{p} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{(200 \text{ bar}) \times (10^5 \text{ Pa bar}^{-1})}$$

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

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

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

with $x = V_m/(\text{dm}^3 \text{ mol}^{-1})$.

The coefficients in the equation are evaluated as

$$b + \frac{RT}{p} = (3.183 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}) + \frac{(8.206 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}) \times (298.15 \text{ K})}{(200 \text{ bar}) \times (1.013 \text{ atm bar}^{-1})}$$

$$= (3.183 \times 10^{-2} + 0.1208) \text{ dm}^3 \text{ mol}^{-1} = 0.1526 \text{ dm}^3 \text{ mol}^{-1}$$

$$\frac{a}{p} = \frac{1.360 \text{ dm}^6 \text{ atm mol}^{-2}}{(200 \text{ bar}) \times (1.013 \text{ atm bar}^{-1})} = 6.71 \times 10^{-3} (\text{dm}^3 \text{ mol}^{-1})^2$$

$$\frac{ab}{p} = \frac{(1.360 \text{ dm}^6 \text{ atm mol}^{-2}) \times (3.183 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1})}{(200 \text{ bar}) \times (1.013 \text{ atm bar}^{-1})} = 2.137 \times 10^{-4} (\text{dm}^3 \text{ mol}^{-1})^3$$

Thus, the equation to be solved is $x^3 - 0.1526x^2 + (6.71 \times 10^{-3})x - (2.137 \times 10^{-4}) = 0$.

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

$$x = 0.112 \quad \text{or} \quad V_m = \boxed{0.112 \text{ dm}^3 \text{ mol}^{-1}}$$

The difference is about 15 percent.

E1.17(b) The molar volume is obtained by solving $Z = pV_m/RT$ [1.17], for V_m , which yields

$$V_m = \frac{ZRT}{p} = \frac{(0.86) \times (0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{20 \text{ atm}} = 1.059 \text{ dm}^3 \text{ mol}^{-1}$$

(a) Then, $V = nV_m = (8.2 \times 10^{-3} \text{ mol}) \times (1.059 \text{ dm}^3 \text{ mol}^{-1}) = 8.7 \times 10^{-3} \text{ dm}^3 = \boxed{8.7 \text{ cm}^3}$

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

$$\begin{aligned} B &= V_m \left(\frac{pV_m}{RT} - 1 \right) = V_m \times (Z - 1) \\ &= (1.059 \text{ dm}^3 \text{ mol}^{-1}) \times (0.86 - 1) = \boxed{-0.15 \text{ dm}^3 \text{ mol}^{-1}} \end{aligned}$$

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

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

Similarly, $x_H = \boxed{0.37}$

(b) According to the perfect gas law

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

(c) The partial pressures are

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

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

E1.19(b) The critical volume of a van der Waals gas is

$$V_c = 3b$$

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

By interpreting b as the excluded volume of a mole of spherical molecules, we can obtain an estimate of molecular size. The centers of spherical particles are excluded from a sphere whose radius is the

diameter of those spherical particles (i.e. twice their radius); that volume times the Avogadro constant is the molar excluded volume b

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

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

The critical pressure is

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

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

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

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

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

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

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

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

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

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

In the limit of large molar volume, we have

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

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

- (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

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

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

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

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

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

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

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

- E1.22(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 Solving for n from the perfect gas equation [1.8] yields $n = pV/RT$ and $n = m/M$, hence $\rho = m/V = Mp/RT$. Rearrangement yields the desired relation, that is $\boxed{\rho = \frac{RT}{M} p}$, or $\frac{p}{\rho} = \frac{RT}{M}$, and $M = \frac{RT}{p/\rho}$

Draw up the following table and then plot p/ρ versus p to find the zero pressure limit of p/ρ where all gases behave ideally.

$$\rho/(\text{g dm}^{-3}) = \rho/(\text{kg m}^{-3});$$

$$1 \text{ Torr} = (1 \text{ Torr}) \times \left(\frac{1 \text{ atm}}{760 \text{ Torr}} \right) \times \left(\frac{1.013 \times 10^5 \text{ Pa}}{1 \text{ atm}} \right) = 133.3 \text{ Pa}$$

p/Torr	91.74	188.98	277.3	452.8	639.3	760.0
$p/(10^4 \text{ Pa})$	1.223	2.519	3.696	6.036	8.522	10.132
$\rho/(\text{kg m}^{-3})$	0.225	0.456	0.664	1.062	1.468	1.734
$(p/\rho) (10^4 \text{ m}^2 \text{ s}^{-2})$	5.44	5.52	5.56	5.68	5.81	5.84

$\frac{p}{\rho}$ is plotted in Figure 1.2. A straight line fits the data rather well. The extrapolation to $p = 0$ yields an intercept of $5.40 \times 10^4 \text{ m}^2 \text{ s}^{-2}$. Then

$$M = \frac{RT}{5.40 \times 10^4 \text{ m}^2 \text{ s}^{-2}} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{5.40 \times 10^4 \text{ m}^2 \text{ s}^{-2}} = 0.0459 \text{ kg mol}^{-1} = \boxed{45.9 \text{ g mol}^{-1}}$$

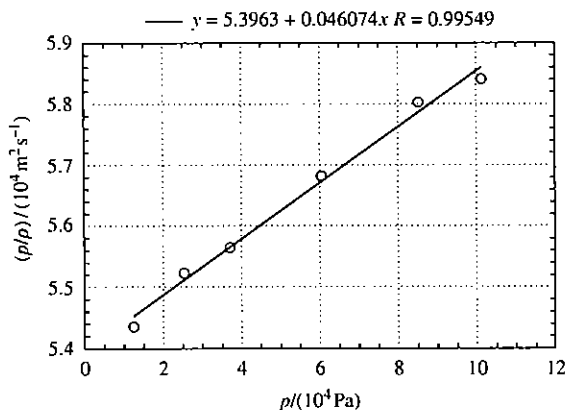


Figure 1.2

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

P1.4 The mass of displaced gas is ρV , where V is the volume of the bulb and ρ is the density of the gas. The balance condition for the two gases is $m(\text{bulb}) = \rho V(\text{bulb})$, $m(\text{bulb}) = \rho' V(\text{bulb})$

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

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

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

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

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

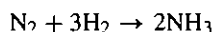
In experiment 2, $p = 427.22 \text{ Torr}$, $p' = 293.10 \text{ Torr}$; hence

$$M' = \frac{427.22 \text{ Torr}}{293.10 \text{ Torr}} \times 70.014 \text{ g mol}^{-1} = 102.0 \text{ g mol}^{-1}$$

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

$M \approx 102 \text{ g mol}^{-1}$. The molecules CH_2FCF_3 or CHF_2CHF_2 have $M \approx 102 \text{ g mol}^{-1}$.

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



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

$$p = \frac{nRT}{V} = (1.66 \text{ mol}) \times \left(\frac{(8.206 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (273.15 \text{ K})}{22.4 \text{ dm}^3} \right) = 1.66 \text{ atm}$$

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

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

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

P1.8 From definition of Z [1.16] and the virial equation [1.19], Z may be expressed in virial form as

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

Since $V_m = RT/p$ [assumption of perfect gas], $1/V_m = p/RT$; hence upon substitution, and dropping terms beyond the second power of $(1/V_m)$

$$\begin{aligned} Z &= 1 + B \left(\frac{p}{RT} \right) + C \left(\frac{p}{RT} \right)^2 \\ Z &= 1 + (-21.7 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}) \times \left(\frac{100 \text{ atm}}{(0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})} \right) \\ &\quad + (1.200 \times 10^{-3} \text{ dm}^6 \text{ mol}^{-2}) \times \left(\frac{100 \text{ atm}}{(0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})} \right)^2 \\ Z &= 1 - (0.0968) + (0.0239) = \boxed{0.927} \\ V_m &= (0.927) \times \left(\frac{RT}{p} \right) = (0.927) \times \left(\frac{(0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})}{100 \text{ atm}} \right) = \boxed{0.208 \text{ dm}^3} \end{aligned}$$

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

P1.10 Since $B'(T_B) = 0$ at the Boyle temperature (Section 1.3b): $B'(T_B) = a + b e^{-c/T_B^2} = 0$

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

P1.12 From Table 1.6 $T_c = \left(\frac{2}{3} \right) \times \left(\frac{2a}{3bR} \right)^{1/2}$, $p_c = \left(\frac{1}{12} \right) \times \left(\frac{2aR}{3b^3} \right)^{1/2}$
 $\left(\frac{2a}{3bR} \right)^{1/2}$ may be solved for from the expression for p_c and yields $\left(\frac{12bp_c}{R} \right)$. Thus

$$\begin{aligned} T_c &= \left(\frac{2}{3} \right) \times \left(\frac{12p_c b}{R} \right) = \left(\frac{8}{3} \right) \times \left(\frac{p_c V_c}{R} \right) \\ &= \left(\frac{8}{3} \right) \times \left(\frac{(40 \text{ atm}) \times (160 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1})}{8.206 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}} \right) = \boxed{210 \text{ K}} \\ v_{\text{mol}} &= \frac{b}{N_A} = \left(\frac{1}{3} \right) \times \left(\frac{V_c}{N_A} \right) = \frac{160 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}}{(3) \times (6.022 \times 10^{23} \text{ mol}^{-1})} = 8.86 \times 10^{-29} \text{ m}^3 \\ v_{\text{mol}} &= \frac{4\pi}{3} r^3 \\ r &= \left(\frac{3}{4\pi} \times (8.86 \times 10^{-29} \text{ m}^3) \right)^{1/3} = \boxed{0.28 \text{ nm}} \end{aligned}$$

Solutions to theoretical problems

P1.14

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

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

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

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

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

can Z be less than one. If we ignore terms beyond b/V_m , the conditions are simply stated as

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

Thus $Z < 1$ when attractive forces predominate, and $Z > 1$ when size effects (short-range repulsions) predominate.

P1.16

The Dieterici equation of state is listed in Table 1.7. At the critical point the derivatives of p with respect to (wrt) V_m equal zero along the isotherm for which $T = T_c$. This means that $(\partial p / \partial V_m)_T = 0$ and $(\partial^2 p / \partial V_m^2)_T = 0$ at the critical point.

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

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

Each of these equations is evaluated at the critical point giving the three equations:

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

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

Solving the middle equation for T_c , substitution of the result into the last equation, and solving for V_c yields the result: $V_c = 2b$ or $b = V_c/2$ (The solution $V_c = b$ is rejected because there is a singularity in the Dieterici equation at the point $V_m = b$.) Substitution of $V_c = 2b$ into the middle equation and

solving for T_c gives the result: $T_c = a/4bR$ or $a = 2RT_cV_c$. Substitution of $V_c = 2b$ and $T_c = a/4bR$ into the first equation gives:

$$p_c = \frac{1}{4} \left(\frac{a}{b^2} \right) e^{-2}$$

The equations for V_c , T_c , p_c are substituted into the equation for the critical compression factor (eqn 1.23) to give: $Z_c = p_c V_c / RT_c = 2e^{-2} = 0.2707$. This is significantly lower than the critical compression factor that is predicted by the van der Waals equation (eqn 1.21a): $Z_c(\text{vdW}) = p_c V_c / RT_c = 3/8 = 0.3750$. Experimental values for Z_c are summarized in Table 1.5 where it is seen that the Dieterici equation prediction is often better.

P1.18
$$\frac{pV_m}{RT} = 1 + B'p + C'p^2 + \dots \quad [1.18]$$

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

whence $B'p + C'p^2 + \dots = \frac{B}{V_m} + \frac{C}{V_m^2} + \dots$

Now multiply through by V_m , replace pV_m by $RT\{1 + (B/V_m) + \dots\}$, and equate coefficients of

powers of $\frac{1}{V_m}$: $B'RT + \frac{BB'RT + C'R^2T^2}{V_m} + \dots = B + \frac{C}{V_m} + \dots$

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

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

P1.20 Write $V_m = f(T, p)$; then $dV_m = \left(\frac{\partial V_m}{\partial T} \right)_p dT + \left(\frac{\partial V_m}{\partial p} \right)_T dp$

Restricting the variations of T and p to those which leave V_m constant, that is $dV_m = 0$, we obtain

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

From the equation of state

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

Substituting

$$\left(\frac{\partial V_m}{\partial T} \right)_p = - \frac{\left(\frac{R}{V_m} + \frac{b}{V_m^2} \right)}{\left(-\frac{RT}{V_m^2} - \frac{2(a + bT)}{V_m^3} \right)} = + \frac{\left(R + \frac{b}{V_m} \right)}{\left(\frac{RT}{V_m} + \frac{2(a + bT)}{V_m^2} \right)}$$

From the equation of state $\frac{(a + bT)}{V_m^2} = p - \frac{RT}{V_m}$

$$\text{Then } \left(\frac{\partial V_m}{\partial T}\right)_p = \frac{\left(R + \frac{b}{V_m}\right)}{\frac{RT}{V_m} + 2\left(p - \frac{RT}{V_m}\right)} = \frac{\left(R + \frac{b}{V_m}\right)}{2p - \frac{RT}{V_m}} = \boxed{\frac{RV_m + b}{2pV_m - RT}}$$

P1.22 $Z = V_m/V_m^\circ$, where V_m° = the molar volume of a perfect gas

From the given equation of state

$$V_m = b + \frac{RT}{p} = b + V_m^\circ \text{ then } Z = \frac{b + V_m^\circ}{V_m^\circ} = 1 + \frac{b}{V_m^\circ}$$

For $V_m = 10b$, $10b = b + V_m^\circ$ or $V_m^\circ = 9b$

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

P1.24 The virial equation is

$$pV_m = RT \left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right) \quad \text{or}$$

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

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

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

A plot of the data in the third column against that of the fourth column is shown in Figure 1.3. The data fit a straight line reasonably well, and the y -intercept is very close to 1. The regression yields

$$B = \boxed{-1.32 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}}$$

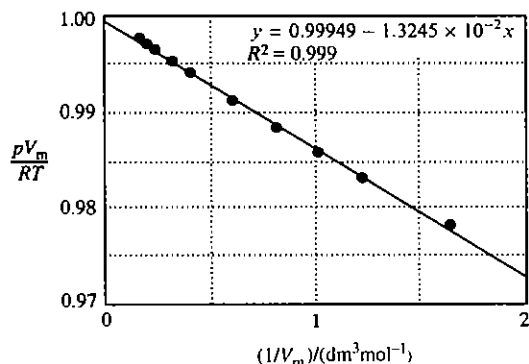


Figure 1.3

- (b) A quadratic function fits the data somewhat better (Figure 1.4) with a slightly better correlation coefficient and a y-intercept closer to 1. This fit implies that truncation of the virial series after the term with C is more accurate than after just the B term. The regression then yields

$$B = \boxed{-1.51 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}} \quad \text{and} \quad C = \boxed{1.07 \times 10^{-3} \text{ dm}^6 \text{ mol}^{-2}}$$

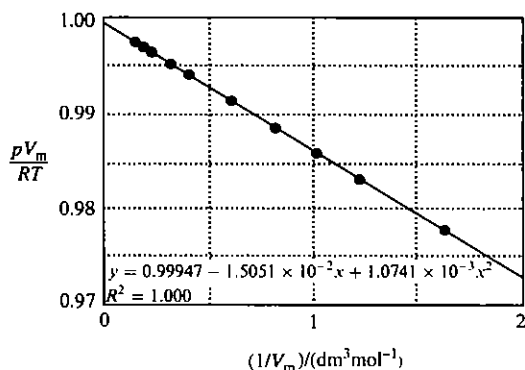


Figure 1.4

Solutions to applications

P1.26 The perfect gas law is

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

At mid-latitudes

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

In the ozone hole

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

The corresponding concentrations are

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

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

respectively.

P1.28

$$n = \frac{pV}{RT} [1.8], \quad V = \frac{4\pi}{3} r^3 = \frac{4\pi}{3} \times (3.0 \text{ m})^3 = 113 \text{ m}^3 = \text{volume of balloon}$$

$$p = 1.0 \text{ atm}, \quad T = 298 \text{ K}$$

$$(a) \quad n = \frac{(1.0 \text{ atm}) \times (113 \times 10^3 \text{ dm}^3)}{(8.206 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} = \boxed{4.62 \times 10^3 \text{ mol}}$$

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

$$\text{Then } m(\text{H}_2) = nM(\text{H}_2) = (4.62 \times 10^3 \text{ mol}) \times (2.02 \text{ g mol}^{-1}) = 9.33 \times 10^3 \text{ g}$$

$$\text{Mass of displaced air} = (113 \text{ m}^3) \times (1.22 \text{ kg m}^{-3}) = 1.38 \times 10^2 \text{ kg}$$

$$\text{Therefore, the payload is } (138 \text{ kg}) - (9.33 \text{ kg}) = \boxed{1.3 \times 10^2 \text{ kg}}$$

$$(c) \text{ For helium, } m = nM(\text{He}) = (4.62 \times 10^3 \text{ mol}) \times (4.00 \text{ g mol}^{-1}) = 18 \text{ kg}$$

$$\text{The payload is now } 138 \text{ kg} - 18 \text{ kg} = \boxed{1.2 \times 10^2 \text{ kg}}$$

P1.30

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

$$p_J = x_J p$$

The perfect gas law is

$$pV = nRT \quad \text{so} \quad \frac{n_J}{V} = \frac{p_J}{RT} = \frac{x_J p}{RT}$$

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

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

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

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

2 The First Law

Answers to discussion questions

D2.2 Rewrite the two expressions as follows:

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

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

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

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

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

D2.6 One can use the general expression for π_T given in *Further Information 2.2* (and proved in Section 3.8, eqn 3.48) to derive its specific form for a van der Waals gas as given in Exercise 2.30(a), that is, $\pi_T = a/V_m^2$. (The derivation is carried out in Example 3.6.) For an isothermal expansion in a van der Waals gas $dU_m = (a/V_m)^2$. Hence $\Delta U_m = -a(1/V_{m,2} - 1/V_{m,1})$. See this derivation in the solution to Exercise 2.30(a). This formula corresponds to what one would expect for a real gas. As the molecules get closer and closer the molar volume gets smaller and smaller and the energy of attraction gets larger and larger.

Solutions to exercises

E2.1(b) The physical definition of work is $dw = -F dz$ [2.4]

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

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

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

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

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

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

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

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

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

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

$$w = -nRT \ln \left(\frac{V_f}{V_i} \right) \text{ [2.11]}$$

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

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

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

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

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

$$pV = nRT$$

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

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

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

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

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

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

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

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

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

$$\begin{aligned}
 q &= \int C_V dT \approx C_V \Delta T = (2.5) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (2.00 \text{ mol}) \times (356 - 277) \text{ K} \\
 &= \boxed{3.28 \times 10^3 \text{ J}} \\
 \Delta U &= q + w = \boxed{3.28 \times 10^3 \text{ J}}
 \end{aligned}$$

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

(b) $w = -nRT \ln \left(\frac{V_f}{V_i} \right) \quad [2.11]$

$$\begin{aligned}
 w &= - \left(\frac{6.56 \text{ g}}{39.95 \text{ g mol}^{-1}} \right) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (305 \text{ K}) \times \ln \frac{(2.5 + 18.5) \text{ dm}^3}{18.5 \text{ dm}^3} \\
 &= \boxed{-52.8 \text{ J}}
 \end{aligned}$$

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

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

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

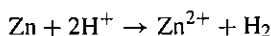
$$w = -p_{\text{ex}} \Delta V \quad [2.8] \quad \text{where} \quad \Delta V = V_{\text{liq}} - V_{\text{vap}} \approx -V_{\text{vap}} \quad \text{because} \quad V_{\text{liq}} \ll V_{\text{vap}}$$

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

$$w \approx nRT = (2.00 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (64 + 273) \text{ K} = \boxed{5.60 \times 10^3 \text{ J}}$$

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

E2.7(b) The reaction is



so it liberates 1 mol of $\text{H}_2(\text{g})$ for every 1 mol Zn used. Work at constant pressure is

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

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

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

$$\begin{aligned}
 q &= \int C_p dT = \int_{0+273\text{ K}}^{100+273\text{ K}} [20.17 + (0.4001)T/\text{K}] dT \text{ J K}^{-1} \\
 &= \left[(20.17)T + \frac{1}{2}(0.4001) \times \left(\frac{T^2}{\text{K}} \right) \right]_{273\text{ K}}^{373\text{ K}} \text{ J K}^{-1} \\
 &= \left[(20.17) \times (373 - 273) + \frac{1}{2}(0.4001) \times (373^2 - 273^2) \right] \text{ J} = \boxed{14.9 \times 10^3 \text{ J}} = \Delta H \\
 w &= -p\Delta V = -nR\Delta T = -(1.00 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (100 \text{ K}) = \boxed{-831 \text{ J}} \\
 \Delta U &= q + w = (14.9 - 0.831) \text{ kJ} = \boxed{14.1 \text{ kJ}}
 \end{aligned}$$

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

E2.9(b) For reversible adiabatic expansion

$$T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/c} \quad [2.28a]$$

where

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

so the final temperature is

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

E2.10(b) Reversible adiabatic work is

$$w = C_V \Delta T \quad [2.27] = n(C_{p,m} - R) \times (T_f - T_i)$$

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

$$T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/c} \quad [2.28a] \quad \text{where} \quad c = \frac{C_{V,m}}{R} = \frac{C_{p,m} - R}{R} = 2.503$$

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

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

E2.11(b) For reversible adiabatic expansion

$$p_f V_f^\gamma = p_i V_i^\gamma \quad [2.29] \quad \text{so} \quad p_f = p_i \left(\frac{V_i}{V_f} \right)^\gamma = (8.73 \text{ Torr}) \times \left(\frac{500 \times 10^{-3} \text{ dm}^3}{3.0 \text{ dm}^3} \right)^{1.3} = \boxed{8.5 \text{ Torr}}$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$p_f V_f^\gamma = p_i V_i^\gamma \quad \text{where} \quad \gamma = \frac{C_{p,m}}{C_{V,m}} = \frac{C_{p,m}}{C_{p,m} - R} = \frac{20.8 \text{ J K}^{-1} \text{ mol}^{-1}}{(20.8 - 8.31) \text{ J K}^{-1} \text{ mol}^{-1}} = 1.67$$

Find V_i from the perfect gas law:

$$V_i = \frac{nRT_i}{p_i} = \frac{(1.5 \text{ mol})(8.31 \text{ J K}^{-1} \text{ mol}^{-1})(315 \text{ K})}{230 \times 10^3 \text{ Pa}} = 0.0171 \text{ m}^3$$

$$\text{so } V_f = V_i \left(\frac{p_i}{p_f} \right)^{1/\gamma} = (0.0171 \text{ m}^3) \left(\frac{230 \text{ kPa}}{170 \text{ kPa}} \right)^{1/1.67} = \boxed{0.0205 \text{ m}^3}.$$

Find the final temperature from the perfect gas law:

$$T_f = \frac{p_f V_f}{nR} = \frac{(170 \times 10^3 \text{ Pa}) \times (0.0205 \text{ m}^3)}{(1.5 \text{ mol})(8.31 \text{ J K}^{-1} \text{ mol}^{-1})} = \boxed{279 \text{ K}}$$

Adiabatic work is (eqn 2.27)

$$w = C_V \Delta T = (20.8 - 8.31) \text{ J K}^{-1} \text{ mol}^{-1} \times 1.5 \text{ mol} \times (279 - 315) \text{ K} = \boxed{-6.7 \times 10^2 \text{ J}}$$

E2.16(b) At constant pressure

$$q = \Delta H = n \Delta_{\text{vap}} H^\ominus = (0.75 \text{ mol}) \times (32.0 \text{ kJ mol}^{-1}) = \boxed{24.0 \text{ kJ}}$$

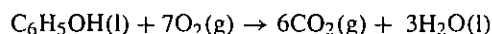
and $w = -p \Delta V \approx -p V_{\text{vapor}} = -nRT = -(0.75 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (260 \text{ K})$

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

$$\Delta U = w + q = 24.0 - 1.6 \text{ kJ} = \boxed{22.4 \text{ kJ}}$$

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.

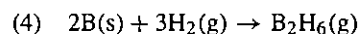
E2.17(b) The reaction is



$$\Delta_c H^\ominus = 6 \Delta_f H^\ominus(\text{CO}_2) + 3 \Delta_f H^\ominus(\text{H}_2\text{O}) - \Delta_f H^\ominus(\text{C}_6\text{H}_5\text{OH}) - 7 \Delta_f H^\ominus(\text{O}_2)$$

$$= [6(-393.15) + 3(-285.83) - (-165.0) - 7(0)] \text{ kJ mol}^{-1} = \boxed{-3053.6 \text{ kJ mol}^{-1}}$$

E2.18(b) We need $\Delta_f H^\ominus$ for the reaction

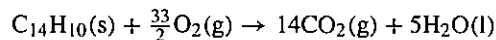


$$\text{reaction}(4) = \text{reaction}(2) + 3 \times \text{reaction}(3) - \text{reaction}(1)$$

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

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

E2.19(b) For anthracene the reaction is



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

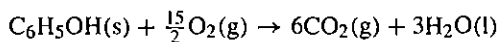
$$\Delta_c U^\ominus = -7061 \text{ kJ mol}^{-1} - \left(-\frac{5}{2} \times 8.3 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}\right)$$

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

$$|q| = |q_V| = |n \Delta_c U^\ominus| = \left(\frac{2.25 \times 10^{-3} \text{ g}}{172.23 \text{ g mol}^{-1}}\right) \times (7055 \text{ kJ mol}^{-1}) = 0.0922 \text{ kJ}$$

$$C = \frac{|q|}{\Delta T} = \frac{0.0922 \text{ kJ}}{1.35 \text{ K}} = 0.0683 \text{ kJ K}^{-1} = \boxed{68.3 \text{ J K}^{-1}}$$

When phenol is used the reaction is



$$\Delta_{\text{c}}H^{\ominus} = -3054 \text{ kJ mol}^{-1} \text{ [Table 2.5]}$$

$$\begin{aligned}\Delta_{\text{c}}U &= \Delta_{\text{c}}H - \Delta n_{\text{g}}RT, \quad \Delta n_{\text{g}} = -\frac{3}{2} \\ &= (-3054 \text{ kJ mol}^{-1}) + \left(\frac{3}{2}\right) \times (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \\ &= -3050 \text{ kJ mol}^{-1}\end{aligned}$$

$$|q| = \left(\frac{135 \times 10^{-3} \text{ g}}{94.12 \text{ g mol}^{-1}}\right) \times (3050 \text{ kJ mol}^{-1}) = 4.375 \text{ kJ}$$

$$\Delta T = \frac{|q|}{C} = \frac{4.375 \text{ kJ}}{0.0683 \text{ kJ K}^{-1}} = \boxed{+64.1 \text{ K}}$$

COMMENT. In this case $\Delta_{\text{c}}U^{\ominus}$ and $\Delta_{\text{c}}H^{\ominus}$ differed by about 0.1 percent. Thus, to within 3 significant figures, it would not have mattered if we had used $\Delta_{\text{c}}H^{\ominus}$ instead of $\Delta_{\text{c}}U^{\ominus}$, but for very precise work it would.

E2.20(b) The reaction is $\text{AgBr}(\text{s}) \rightarrow \text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq})$

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

E2.21(b) The combustion products of graphite and diamond are the same, so the transition $\text{C}(\text{gr}) \rightarrow \text{C}(\text{d})$ is equivalent to the combustion of graphite plus the reverse of the combustion of diamond, and

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

E2.22(b) (a) reaction(3) = (-2) × reaction(1) + reaction(2) and $\Delta n_{\text{g}} = -1$

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

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

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

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

$$\begin{aligned}\Delta_{\text{f}}H^{\ominus}(\text{HI}) &= \frac{1}{2} (52.96 \text{ kJ mol}^{-1}) = \boxed{26.48 \text{ kJ mol}^{-1}} \\ \Delta_{\text{f}}H^{\ominus}(\text{H}_2\text{O}) &= \frac{1}{2} (-483.64 \text{ kJ mol}^{-1}) = \boxed{-241.82 \text{ kJ mol}^{-1}}\end{aligned}$$

E2.23(b) $\Delta_r H^\ominus = \Delta_r U^\ominus + RT \Delta n_g$ [2.21]
 $= -772.7 \text{ kJ mol}^{-1} + (5) \times (8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})$
 $= \boxed{-760.3 \text{ kJ mol}^{-1}}$

E2.24(b) Combine the reactions in such a way that the combination is the desired formation reaction. The enthalpies of the reactions are then combined in the same way as the equations to yield the enthalpy of formation.

	$\Delta_r H^\ominus / (\text{kJ mol}^{-1})$
$\frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{NO}(\text{g})$	+ 90.25
$\text{NO}(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{NOCl}(\text{g})$	$-\frac{1}{2}(75.5)$
$\frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{NOCl}(\text{g})$	+ 52.5

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

E2.25(b) According to Kirchhoff's law [2.36]

$$\Delta_r H^\ominus(100^\circ\text{C}) = \Delta_r H^\ominus(25^\circ\text{C}) + \int_{25^\circ\text{C}}^{100^\circ\text{C}} \Delta_r C_p^\ominus dT$$

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

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

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

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

Combining this expression with our original integral, we have

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

Now for the pieces

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

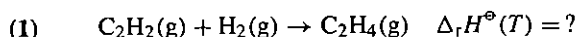
$$\Delta_r a = [2(75.29) - 2(27.28) - (29.96)] \text{ J K}^{-1} \text{ mol}^{-1} = 0.06606 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\Delta_r b = [2(0) - 2(3.29) - (4.18)] \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1} = -10.76 \times 10^{-6} \text{ kJ K}^{-2} \text{ mol}^{-1}$$

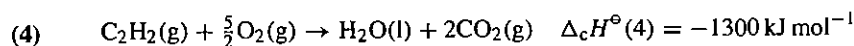
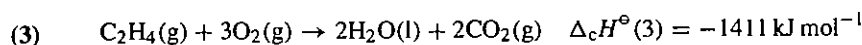
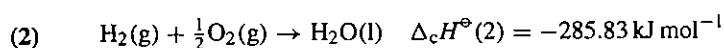
$$\Delta_r c = [2(0) - 2(0.50) - (-1.67)] \times 10^5 \text{ J K mol}^{-1} = 67 \text{ kJ K mol}^{-1}$$

$$\begin{aligned}\Delta_r H^\ominus(100^\circ\text{C}) &= \left[-571.66 + (373 - 298) \times (0.06606) + \frac{1}{2}(373^2 - 298^2) \right. \\ &\quad \left. \times (-10.76 \times 10^{-6}) - (67) \times \left(\frac{1}{373} - \frac{1}{298} \right) \right] \text{kJ mol}^{-1} \\ &= \boxed{-566.93 \text{ kJ mol}^{-1}}\end{aligned}$$

E2.26(b) The hydrogenation reaction is



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



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

(a) Hence, at 298 K:

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

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

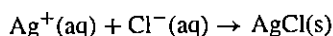
(b) At 348 K:

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

$$\begin{aligned}\Delta_r C_p &= \sum_j \nu_j C_{p,m}^\ominus(j) \quad [2.37] = C_{p,m}^\ominus(\text{C}_2\text{H}_4, \text{g}) - C_{p,m}^\ominus(\text{C}_2\text{H}_2, \text{g}) - C_{p,m}^\ominus(\text{H}_2, \text{g}) \\ &= (43.56 - 43.93 - 28.82) \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} = -29.19 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_r H^\ominus(348 \text{ K}) &= (-175 \text{ kJ mol}^{-1}) - (29.19 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (50 \text{ K}) \\ &= \boxed{-176 \text{ kJ mol}^{-1}}\end{aligned}$$

E2.27(b) NaCl, AgNO₃, and NaNO₃ are strong electrolytes; therefore the net ionic equation is



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

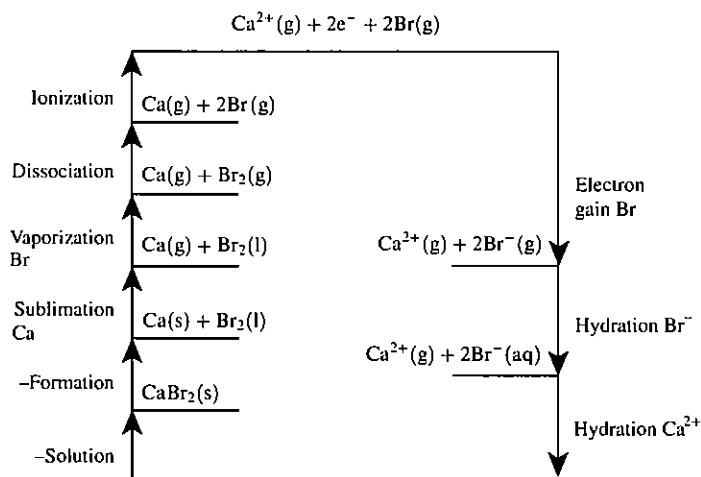


Figure 2.1

E2.28(b) The cycle is shown in Figure 2.1.

$$\begin{aligned}
 -\Delta_{\text{hyd}} H^{\circ}(\text{Ca}^{2+}) &= -\Delta_{\text{soln}} H^{\circ}(\text{CaBr}_2) - \Delta_{\text{f}} H^{\circ}(\text{CaBr}_2, \text{s}) + \Delta_{\text{sub}} H^{\circ}(\text{Ca}) \\
 &\quad + \Delta_{\text{vap}} H^{\circ}(\text{Br}_2) + \Delta_{\text{diss}} H^{\circ}(\text{Br}_2) + \Delta_{\text{ion}} H^{\circ}(\text{Ca}) \\
 &\quad + \Delta_{\text{ion}} H^{\circ}(\text{Ca}^{+}) + 2\Delta_{\text{eg}} H^{\circ}(\text{Br}) + 2\Delta_{\text{hyd}} H^{\circ}(\text{Br}^{-}) \\
 &= [-(-103.1) - (-682.8) + 178.2 + 30.91 + 192.9 \\
 &\quad + 589.7 + 1145 + 2(-331.0) + 2(-337)] \text{ kJ mol}^{-1} \\
 &= \boxed{1587 \text{ kJ mol}^{-1}}
 \end{aligned}$$

so $\Delta_{\text{hyd}} H^{\circ}(\text{Ca}^{2+}) = \boxed{-1587 \text{ kJ mol}^{-1}}$

E2.29(b) The Joule–Thomson coefficient μ is the ratio of temperature change to pressure change under conditions of isenthalpic expansion. So

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

E2.30(b) The internal energy is a function of temperature and volume, $U_{\text{m}} = U_{\text{m}}(T, V_{\text{m}})$, so

$$dU_{\text{m}} = \left(\frac{\partial U_{\text{m}}}{\partial T} \right)_{V_{\text{m}}} dT + \left(\frac{\partial U_{\text{m}}}{\partial V_{\text{m}}} \right)_T dV_{\text{m}} \quad \left[\pi_T = \left(\frac{\partial U_{\text{m}}}{\partial V} \right)_T \right]$$

For an isothermal expansion $dT = 0$; hence

$$\begin{aligned}
 dU_{\text{m}} &= \left(\frac{\partial U_{\text{m}}}{\partial V_{\text{m}}} \right)_T dV_{\text{m}} = \pi_T dV_{\text{m}} = \frac{a}{V_{\text{m}}^2} dV_{\text{m}} \\
 \Delta U_{\text{m}} &= \int_{V_{\text{m},1}}^{V_{\text{m},2}} dU_{\text{m}} = \int_{V_{\text{m},1}}^{V_{\text{m},2}} \frac{a}{V_{\text{m}}^2} dV_{\text{m}} = a \int_{1.00 \text{ dm}^3 \text{ mol}^{-1}}^{22.1 \text{ dm}^3 \text{ mol}^{-1}} \frac{dV_{\text{m}}}{V_{\text{m}}^2} = -\frac{a}{V_{\text{m}}} \Big|_{1.00 \text{ dm}^3 \text{ mol}^{-1}}^{22.1 \text{ dm}^3 \text{ mol}^{-1}} \\
 &= -\frac{a}{22.1 \text{ dm}^3 \text{ mol}^{-1}} + \frac{a}{1.00 \text{ dm}^3 \text{ mol}^{-1}} = \frac{21.1a}{22.1 \text{ dm}^3 \text{ mol}^{-1}} = 0.95475a \text{ dm}^{-3} \text{ mol}
 \end{aligned}$$

From Table 1.6, $a = 1.337 \text{ dm}^6 \text{ atm mol}^{-1}$

$$\begin{aligned}\Delta U_m &= (0.95475 \text{ mol dm}^3) \times (1.337 \text{ atm dm}^6 \text{ mol}^{-2}) \\ &= (1.2765 \text{ atm dm}^3 \text{ mol}^{-1}) \times (1.01325 \times 10^5 \text{ Pa atm}^{-1}) \times \left(\frac{1 \text{ m}^3}{10^3 \text{ dm}^3}\right) \\ &= 129 \text{ Pa m}^3 \text{ mol}^{-1} = \boxed{129 \text{ J mol}^{-1}}\end{aligned}$$

$$w = -\int p \, dV_m \quad \text{where} \quad p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \text{ for a van der Waals gas.}$$

Hence,

$$w = -\int \left(\frac{RT}{V_m - b} \right) dV_m + \int \frac{a}{V_m^2} dV_m = -q + \Delta U_m$$

Thus

$$\begin{aligned}q &= \int_{1.00 \text{ dm}^3 \text{ mol}^{-1}}^{22.1 \text{ dm}^3 \text{ mol}^{-1}} \left(\frac{RT}{V_m - b} \right) dV_m = RT \ln(V_m - b) \Big|_{1.00 \text{ dm}^3 \text{ mol}^{-1}}^{22.1 \text{ dm}^3 \text{ mol}^{-1}} \\ &= (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln \left(\frac{22.1 - 3.20 \times 10^{-2}}{1.00 - 3.20 \times 10^{-2}} \right) = \boxed{+7.7465 \text{ kJ mol}^{-1}}\end{aligned}$$

$$\text{and } w = -q + \Delta U_m = -(7747 \text{ J mol}^{-1}) + (129 \text{ J mol}^{-1}) = \boxed{-7618 \text{ J mol}^{-1}} = \boxed{-7.62 \text{ kJ mol}^{-1}}$$

E2.31(b) The expansion coefficient is

$$\begin{aligned}\alpha &= \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{V'(3.7 \times 10^{-4} \text{ K}^{-1} + 2 \times 1.52 \times 10^{-6} T \text{ K}^{-2})}{V} \\ &= \frac{V'[3.7 \times 10^{-4} + 2 \times 1.52 \times 10^{-6} (T/\text{K})] \text{ K}^{-1}}{V'[0.77 + 3.7 \times 10^{-4} (T/\text{K}) + 1.52 \times 10^{-6} (T/\text{K})^2]} \\ &= \frac{[3.7 \times 10^{-4} + 2 \times 1.52 \times 10^{-6} (310)] \text{ K}^{-1}}{0.77 + 3.7 \times 10^{-4} (310) + 1.52 \times 10^{-6} (310)^2} = \boxed{1.27 \times 10^{-3} \text{ K}^{-1}}\end{aligned}$$

E2.32(b) Isothermal compressibility is

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

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

$$\Delta p = \frac{0.0008}{2.21 \times 10^{-6} \text{ atm}^{-1}} = \boxed{3.6 \times 10^2 \text{ atm}}$$

E2.33(b) The isothermal Joule–Thomson coefficient is

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

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

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

$$\Delta H = -(41.2 \text{ J atm}^{-1} \text{ mol}^{-1}) \times (12.0 \text{ mol}) \times (-55 \text{ atm}) = \boxed{27.2 \times 10^3 \text{ J}}$$

Solutions to problems

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

Solutions to numerical problems

P2.2

$$w = -p_{\text{ex}} \Delta V \quad [2.8] \quad V_f = \frac{nRT}{p_{\text{ex}}} \gg V_i; \quad \text{so} \quad \Delta V \approx V_f$$

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

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

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

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

P2.4

The virial expression for pressure up to the second coefficient is

$$p = \left(\frac{RT}{V_m} \right) \left(1 + \frac{B}{V_m} \right) \quad [1.19]$$

$$w = - \int_i^f p dV = -n \int_i^f \left(\frac{RT}{V_m} \right) \times \left(1 + \frac{B}{V_m} \right) dV_m = -nRT \ln \left(\frac{V_{m,f}}{V_{m,i}} \right) + nBRT \left(\frac{1}{V_{m,f}} - \frac{1}{V_{m,i}} \right)$$

From the data,

$$nRT = (70 \times 10^{-3} \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (373 \text{ K}) = 217 \text{ J}$$

$$V_{m,i} = \frac{5.25 \text{ cm}^3}{70 \times 10^{-3} \text{ mol}} = 75.0 \text{ cm}^3 \text{ mol}^{-1}, \quad V_{m,f} = \frac{6.29 \text{ cm}^3}{70 \times 10^{-3} \text{ mol}} = 89.9 \text{ cm}^3 \text{ mol}^{-1}$$

$$\begin{aligned} \text{and so } B \left(\frac{1}{V_{m,f}} - \frac{1}{V_{m,i}} \right) &= (-28.7 \text{ cm}^3 \text{ mol}^{-1}) \times \left(\frac{1}{89.9 \text{ cm}^3 \text{ mol}^{-1}} - \frac{1}{75.0 \text{ cm}^3 \text{ mol}^{-1}} \right) \\ &= 6.34 \times 10^{-2} \end{aligned}$$

Therefore,

$$w = (-217 \text{ J}) \times \ln \left(\frac{6.29}{5.25} \right) + (217 \text{ J}) \times (6.34 \times 10^{-2}) = (-39.2 \text{ J}) + (13.8 \text{ J}) = \boxed{-25 \text{ J}}$$

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

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

$$\begin{aligned} \Delta(pV) &= nRTB \Delta \left(\frac{1}{V_m} \right) = nRTB \left(\frac{1}{V_{m,f}} - \frac{1}{V_{m,i}} \right), \quad \text{as } \Delta T = 0 \\ &= (217 \text{ J}) \times (6.34 \times 10^{-2}) = 13.8 \text{ J} \end{aligned}$$

Therefore, $\Delta H = (83.5 \text{ J}) + (13.8 \text{ J}) = \boxed{+97 \text{ J}}$

P2.6

$$w = - \int_{V_1}^{V_2} p \, dV \quad \text{with} \quad p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \quad [\text{Table 1.7}]$$

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

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

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

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

and, after substitution

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

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

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

$$w_0 = -1.72 \times 10^3 \text{ J} = \boxed{-1.7 \text{ kJ}}$$

$$\begin{aligned} (b) \quad w &= w_0 - (1.0 \text{ mol})^2 \times [0 - (5.11 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})] \\ &\quad \times \left(\frac{1}{2.0 \text{ dm}^3} - \frac{1}{1.0 \text{ dm}^3} \right) = (-1.72 \times 10^3 \text{ J}) - (63 \text{ J}) = -1.78 \times 10^3 \text{ J} = \boxed{-1.8 \text{ kJ}} \end{aligned}$$

$$\begin{aligned}
 \text{(c)} \quad w &= w_0 - (1.0 \text{ mol})^2 \times (4.2 \text{ dm}^6 \text{ atm mol}^{-2}) \times \left(\frac{1}{2.0 \text{ dm}^3} - \frac{1}{1.0 \text{ dm}^3} \right) \\
 w &= w_0 + 2.1 \text{ dm}^3 \text{ atm} \\
 &= (-1.72 \times 10^3 \text{ J}) + (2.1 \text{ dm}^3 \text{ atm}) \times \left(\frac{1 \text{ m}}{10 \text{ dm}} \right)^3 \times \left(\frac{1.01 \times 10^5 \text{ Pa}}{1 \text{ atm}} \right) \\
 &= (-1.72 \times 10^3 \text{ J}) + (0.21 \times 10^3 \text{ J}) = \boxed{-1.5 \text{ kJ}}
 \end{aligned}$$

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

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

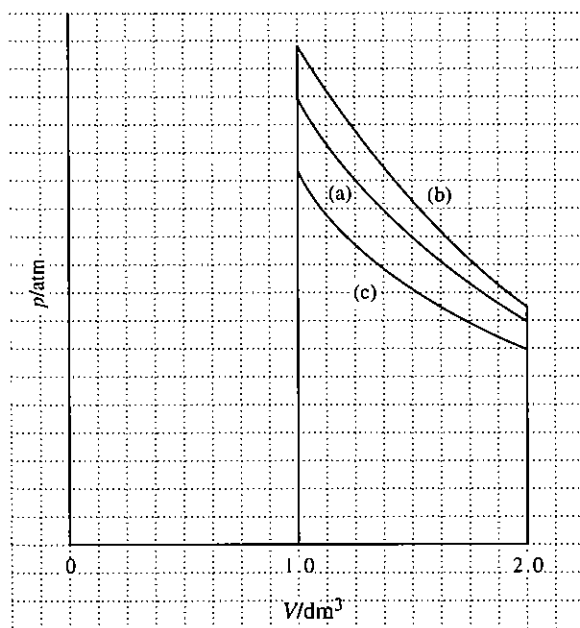


Figure 2.2

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

$$\Delta U = q_V$$

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

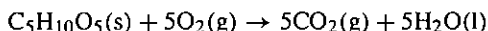
$$\Delta U = \left(\frac{0.825 \text{ g}}{122.12 \text{ g mol}^{-1}} \right) \times (-3251 \text{ kJ mol}^{-1}) = -21.96 \text{ kJ}$$

$$\text{Since } \Delta T = 1.940 \text{ K, } C = \frac{|q|}{\Delta T} = \frac{21.96 \text{ kJ}}{1.940 \text{ K}} = 11.32 \text{ kJ K}^{-1}$$

$$\text{For D-ribose, } \Delta U = -C\Delta T = -(11.32 \text{ kJ K}^{-1}) \times (0.910 \text{ K})$$

Therefore, $\Delta_r U = \frac{\Delta U}{n} = -(11.32 \text{ kJ K}^{-1}) \times (0.910 \text{ K}) \times \left(\frac{150.13 \text{ g mol}^{-1}}{0.727 \text{ g}} \right) = -2127 \text{ kJ mol}^{-1}$

The combustion reaction for D-ribose is



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

The enthalpy of formation is obtained from the sum

	$\Delta H / (\text{kJ mol}^{-1})$
$5\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_5\text{H}_{10}\text{O}_5(\text{s}) + 5\text{O}_2(\text{g})$	2130
$5\text{C}(\text{s}) + 5\text{O}_2(\text{g}) \rightarrow 5\text{CO}_2(\text{g})$	$5 \times (-393.51)$
$5\text{H}_2(\text{g}) + \frac{5}{2}\text{O}_2(\text{g}) \rightarrow 5\text{H}_2\text{O}(\text{l})$	$5 \times (-285.83)$
$5\text{C}(\text{s}) + 5\text{H}_2(\text{g}) + \frac{5}{2}\text{O}_2(\text{g}) \rightarrow \text{C}_5\text{H}_{10}\text{O}_5(\text{s})$	-1267

Hence $\Delta_f H = \boxed{-1267 \text{ kJ mol}^{-1}}$

P2.10

Data: methane–octane normal alkane combustion enthalpies

Species	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂	C ₆ H ₁₄	C ₈ H ₁₈
$\Delta_c H / (\text{kJ mol}^{-1})$	-890	-1560	-2220	-2878	-3537	-4163	-5471
$M / (\text{g mol}^{-1})$	16.04	30.07	44.10	58.13	72.15	86.18	114.23

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

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

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

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

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

$$R = 1.000$$

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

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

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

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

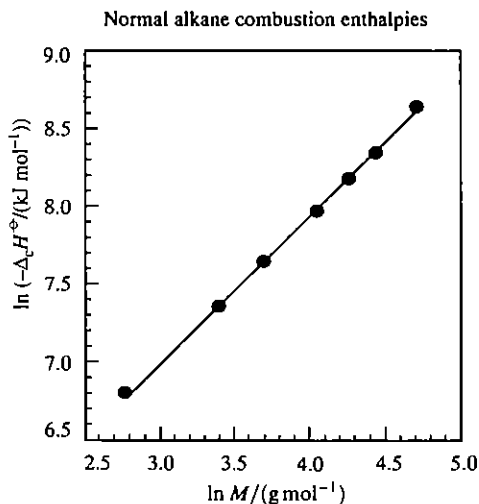
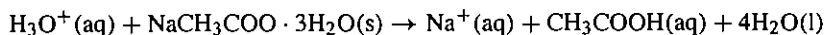


Figure 2.3

Percent error of prediction = 2.17 percent

P2.12



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

Application of eqns 2.14 and 2.19b gives:

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

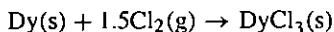
Application of eqn 2.32 gives:

$$\begin{aligned} \Delta_r H^\ominus &= \Delta_f H^\ominus(\text{Na}^+, \text{aq}) + \Delta_f H^\ominus(\text{CH}_3\text{COOH}, \text{aq}) + 3\Delta_f H^\ominus(\text{H}_2\text{O}, \text{l}) \\ &\quad - \Delta_f H^\ominus(\text{H}^+, \text{aq}) - \Delta_f H^\ominus(\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}, \text{s}) \end{aligned}$$

(where the water coefficient is 3 not 4 because one water in the chemical equation is part of the hydrated hydrogen ion). Solving for $\Delta_f H^\ominus(\text{Na}^+, \text{aq})$ and substituting $\Delta_f H^\ominus$ values found in Tables 2.5 and 2.7 gives:

$$\begin{aligned} \Delta_f H^\ominus(\text{Na}^+, \text{aq}) &= \Delta_r H^\ominus - \Delta_f H^\ominus(\text{CH}_3\text{COOH}, \text{aq}) - 3\Delta_f H^\ominus(\text{H}_2\text{O}, \text{l}) + \Delta_f H^\ominus(\text{H}^+, \text{aq}) \\ &\quad + \Delta_f H^\ominus(\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}, \text{s}) \\ \Delta_f H^\ominus(\text{Na}^+, \text{aq}) &= \{20.1 - (-485.76) - 3(-285.83) + (0) + (-1604)\} \text{ kJ mol}^{-1} \\ &= \boxed{241 \text{ kJ mol}^{-1}} \end{aligned}$$

P2.14 We must relate the formation of DyCl_3



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

$$\begin{aligned}\Delta_f H^\circ(\text{DyCl}_3, \text{s}) &= \Delta_r H^\circ(2) + 3\Delta_r H^\circ(3) - \Delta_r H^\circ(1), \\ \Delta_f H^\circ(\text{DyCl}_3, \text{s}) &= [-699.43 + 3(-158.31) - (-180.06)] \text{ kJ mol}^{-1} \\ &= \boxed{-994.30 \text{ kJ mol}^{-1}}\end{aligned}$$

P2.16 (a) $\Delta_r H^\circ = \Delta_f H^\circ(\text{SiH}_3\text{OH}) - \Delta_f H^\circ(\text{SiH}_4) - \frac{1}{2}\Delta_f H^\circ(\text{O}_2)$

$$= [-67.5 - 34.3 - \frac{1}{2}(0)] \text{ kJ mol}^{-1} = \boxed{-101.8 \text{ kJ mol}^{-1}}$$

(b) $\Delta_r H^\circ = \Delta_f H^\circ(\text{SiH}_2\text{O}) - \Delta_f H^\circ(\text{H}_2\text{O}) - \Delta_f H^\circ(\text{SiH}_4) - \Delta_f H^\circ(\text{O}_2)$

$$= [-23.5 + (-285.83) - 34.3 - 0] \text{ kJ mol}^{-1} = \boxed{-344.2 \text{ kJ mol}^{-1}}$$

(c) $\Delta_r H^\circ = \Delta_f H^\circ(\text{SiH}_2\text{O}) - \Delta_f H^\circ(\text{SiH}_3\text{OH}) - \Delta_f H^\circ(\text{H}_2)$

$$= [-23.5 - (-67.5) - 0] \text{ kJ mol}^{-1} = \boxed{44.0 \text{ kJ mol}^{-1}}$$

P2.18

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

$$\begin{aligned}\left(\frac{\partial H_m}{\partial p}\right)_T &= -\mu C_{p,m} [2.53] = -\left(\frac{2a}{RT} - b\right) \\ &= -\left(\frac{(2) \times (3.60 \text{ dm}^6 \text{ atm mol}^{-2})}{(0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})} - 0.044 \text{ dm}^3 \text{ mol}^{-1}\right) \\ &= -0.248\bar{3} \text{ dm}^3 \text{ mol}^{-1}\end{aligned}$$

$$\Delta H = \int_{p_i}^{p_f} dH = \int_{p_i}^{p_f} (-0.248\bar{3} \text{ dm}^3 \text{ mol}^{-1}) dp = -0.248\bar{3}(p_f - p_i) \text{ dm}^3 \text{ mol}^{-1}$$

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

$$p_i = \left(\frac{(0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{(20.0 \text{ dm}^3 \text{ mol}^{-1}) - (0.044 \text{ dm}^3 \text{ mol}^{-1})}\right) - \left(\frac{3.60 \text{ dm}^6 \text{ atm mol}^{-2}}{(20.0 \text{ dm}^3 \text{ mol}^{-1})^2}\right) = 1.22\bar{5} \text{ atm}$$

$$p_f = \left(\frac{(0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{(10.0 \text{ dm}^3 \text{ mol}^{-1}) - (0.044 \text{ dm}^3 \text{ mol}^{-1})}\right) - \left(\frac{3.60 \text{ dm}^6 \text{ atm mol}^{-2}}{(10.0 \text{ dm}^3 \text{ mol}^{-1})^2}\right) = 2.43\bar{8} \text{ atm}$$

$$\begin{aligned}\Delta H &= (-0.248\bar{3} \text{ dm}^3 \text{ mol}^{-1}) \times (2.43\bar{8} \text{ atm} - 1.225 \text{ atm}) \\ &= (-0.301 \text{ dm}^3 \text{ atm mol}^{-1}) \times \left(\frac{1 \text{ m}}{10 \text{ dm}}\right)^3 \times \left(\frac{1.013 \times 10^5 \text{ Pa}}{\text{atm}}\right) = \boxed{-30.5 \text{ J mol}^{-1}}\end{aligned}$$

Solutions to theoretical problems

P2.20 A function has an exact differential if its mixed partial derivatives are equal. That is, $f(x, y)$ has an exact differential if

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

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

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

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

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

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

P2.22

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

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

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

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

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

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

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

P2.24 Using the Euler's chain relation and the reciprocal identity [Further information 2.2]

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

Substituting into the given expression for $C_p - C_V$

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

Using the reciprocal identity again

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

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

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

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

P2.26

(a) $V = V(p, T)$; hence, $dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT$

Likewise $p = p(V, T)$, so $dp = \left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT$

(b) We use $\alpha = \left(\frac{1}{V}\right) \left(\frac{\partial V}{\partial T}\right)_p$ [2.43] and $\kappa_T = -\left(\frac{1}{V}\right) \left(\frac{\partial V}{\partial p}\right)_T$ [2.44] and obtain

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

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

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

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

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

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

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

P2.28

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

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

$$\begin{aligned} w &= -nR \times \left(\frac{T}{T_c} \right) T_c \times \ln \left(\frac{(V_2/V_c) - (nb/V_c)}{(V_1/V_c) - (nb/V_c)} \right) - \left(\frac{n^2 a}{V_c} \right) \times \left(\frac{V_c}{V_2} - \frac{V_c}{V_1} \right) \\ T_r &= \frac{T}{T_c}, \quad V_r = \frac{V}{V_c}, \quad T_c = \frac{8a}{27Rb}, \quad V_c = 3nb \quad [\text{Table 1.7}] \\ w &= - \left(\frac{8na}{27b} \right) \times (T_r) \times \ln \left(\frac{V_{r,2} - (1/3)}{V_{r,1} - (1/3)} \right) - \left(\frac{na}{3b} \right) \times \left(\frac{1}{V_{r,2}} - \frac{1}{V_{r,1}} \right) \end{aligned}$$

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

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

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

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

P2.30

$$\mu \equiv \left(\frac{\partial T}{\partial p} \right)_H \quad [2.51]$$

Use of Euler's chain relation [Further information 2.2] yields

$$\begin{aligned} \mu &= -\frac{(\partial H_m / \partial p)_T}{C_{p,m}} \quad [2.53] \\ \left(\frac{\partial H_m}{\partial p} \right)_T &= \left(\frac{\partial U_m}{\partial p} \right)_T + \left[\frac{\partial (pV_m)}{\partial p} \right]_T = \left(\frac{\partial U_m}{\partial V_m} \right)_T \left(\frac{\partial V_m}{\partial p} \right)_T + \left[\frac{\partial (pV_m)}{\partial p} \right]_T \end{aligned}$$

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

$$\begin{aligned} \left(\frac{\partial U_m}{\partial V_m} \right)_T &= \left(\frac{\partial U}{\partial V} \right)_T = \pi_T = \frac{a}{V_m^2} \quad [\text{Exercise 2.30}] \\ pV_m &= RT \left[1 + \frac{1}{RT} \left(b - \frac{a}{RT} \right) p + \dots \right] \end{aligned}$$

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

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

Since $(\partial H/\partial p)_T$ is in a sense a correction term, that is, it approaches zero for a perfect gas, little error will be introduced by the approximation, $(pV_m)^2 = (RT)^2$.

$$\text{Thus } (\partial H/\partial p)_T \approx (-a/RT) + (b - (a/RT)) = (b - (2a/RT)) \quad \text{and} \quad \mu = ((2a/RT) - b)/C_{p,m}$$

P2.32

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{1}{V (\partial T/\partial V)_p} \quad [\text{reciprocal identity, Further information 2.2}]$$

$$\alpha = \frac{1}{V} \times \frac{1}{(T/(V - nb)) - (2na/RV^3) \times (V - nb)} \quad [\text{Problem 2.31}]$$

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

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

$$\kappa_T = -\frac{1}{V} \times \frac{1}{(-nRT/(V - nb)^2) + (2n^2a/V^3)} \quad [\text{Problem 2.31}]$$

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

Then $\kappa_T/\alpha = (V - nb)/nR$, implying that $\kappa_T R = \alpha(V_m - b)$

Alternatively, from the definitions of α and κ_T above

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

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

$$= \frac{V - nb}{nR} \quad [\text{Problem 2.31}],$$

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

Hence, $\kappa_T R = \alpha(V_m - b)$

P2.34

Work with the left-hand side of the relation to be proved and show that after manipulation using the general relations between partial derivatives and the given equation for $(\partial U/\partial V)_T$, the right-hand side is produced.

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

P2.36

$$c = \left(\frac{RT\gamma}{M}\right)^{1/2}, \quad p = \rho \frac{RT}{M}, \quad \text{so} \quad \frac{RT}{M} = \frac{p}{\rho}; \quad \text{hence} \quad \boxed{c = \left(\frac{\gamma p}{\rho}\right)^{1/2}}$$

$$\text{For argon, } \gamma = \frac{5}{3}, \text{ so } c = \left(\frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \frac{5}{3}}{39.95 \times 10^{-3} \text{ kg mol}^{-1}} \right)^{1/2} = \boxed{322 \text{ m s}^{-1}}$$

Solutions to applications

P2.38

- (a) (i) One major limitation of Hooke's law is that it applies to displacements from a single equilibrium value of the end-to-end distance. In fact, if a DNA molecule or any other macromolecular chain that is susceptible to strong non-bonding intramolecular interactions is disturbed sufficiently from one equilibrium configuration, it is likely to settle into a different equilibrium configuration, a so-called "local minimum" in potential energy. Hooke's law is a good approximation for systems that have a single equilibrium configuration corresponding to a single minimum in potential energy. Another limitation is the assumption that it is just as easy (or as difficult) to move the ends away from each other in any direction. In fact, the intramolecular interactions would be quite different depending on whether one were displacing an end along the chain or outward from the chain. (See Figure 2.4.)

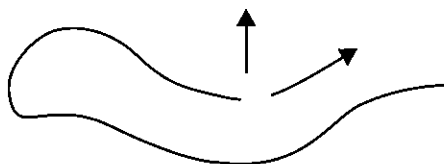


Figure 2.4

(ii) Work is $dw = -Fdx = +k_F x dx$. This integrates to

$$w = \int_0^{x_f} k_F x dx = \frac{1}{2} k_F x^2 \Big|_0^{x_f} = \boxed{\frac{1}{2} k_F x_f^2}$$

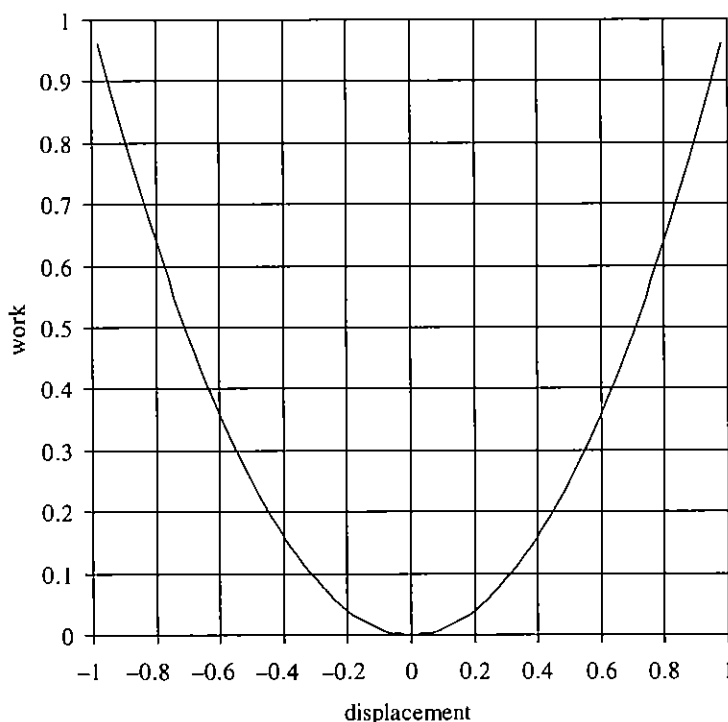


Figure 2.5

- (b) (i) One obvious limitation is that the model treats only displacements along the chain, not displacements that take an end away from the chain. (See Figure 2.4.)
(ii) The displacement is twice the persistence length, so

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

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

- (iii) Figure 2.6 displays a plot of force vs. displacement for Hooke's law and for the one-dimensional freely jointed chain. For small displacements the plots very nearly coincide. However, for large displacements, the magnitude of the force in the one-dimensional model grows much faster. In fact, in the one-dimensional model, the magnitude of the force approaches infinity for a finite displacement, namely a displacement the size of the chain itself ($|\nu| = 1$). (For Hooke's law, the force approaches infinity only for infinitely large displacements.)

(iv) Work is $dw = -F dx = \frac{kT}{2l} \ln \left(\frac{1+\nu}{1-\nu} \right) dx = \frac{kNT}{2} \ln \left(\frac{1+\nu}{1-\nu} \right) d\nu$

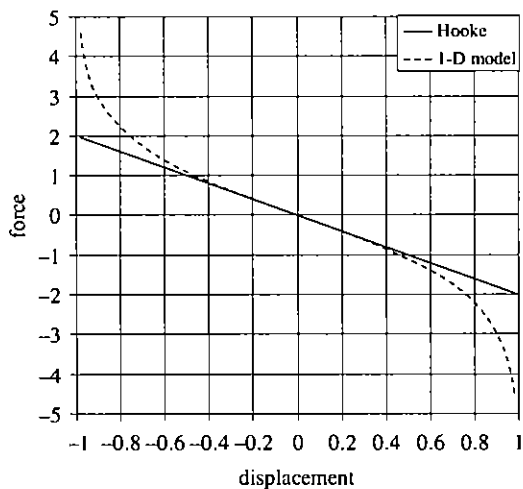


Figure 2.6

This integrates to

$$\begin{aligned}
 w &= \int_0^{v_f} \frac{kNT}{2} \ln \left(\frac{1+v}{1-v} \right) dv = \frac{kNT}{2} \int_0^{v_f} [\ln(1+v) - \ln(1-v)] dv \\
 &= \frac{kNT}{2} [(1+v) \ln(1+v) - v + (1-v) \ln(1-v) + v] \Big|_0^{v_f} \\
 &= \boxed{\frac{kNT}{2} [(1+v_f) \ln(1+v_f) + (1-v_f) \ln(1-v_f)]}
 \end{aligned}$$

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

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

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

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

$$\text{Therefore } w = \frac{kNT}{2} (2 \ln 2) = \boxed{kNT \ln 2}$$

(c) For $v \ll 1$, the natural log can be expanded: $\ln(1 + v) \approx v$ and $\ln(1 - v) \approx -v$. Therefore

$$\begin{aligned} |F| &= \frac{kT}{2l} \ln \left(\frac{1+v}{1-v} \right) = \frac{kT}{2l} [\ln(1+v) - \ln(1-v)] \\ &\approx \frac{kT}{2l} [v - (-v)] = \frac{vkT}{l} = \frac{nkT}{Nl} = \frac{xkT}{Nl^2} \end{aligned}$$

(d) Figure 2.6 above already suggested what the derivation in part (c) confirms: that the one-dimensional chain model and Hooke's law have the same behavior for small displacements. Part (c) allows us to identify kT/Nl^2 as the Hooke's law force constant.

P2.40 The needed data are the enthalpy of vaporization and heat capacity of water, available in the *Data section*.

$$C_{p,m}(\text{H}_2\text{O}, l) = 75.3 \text{ J K}^{-1} \text{ mol}^{-1} \quad \Delta_{\text{vap}}H^\circ(\text{H}_2\text{O}) = 44.0 \text{ kJ mol}^{-1}$$

$$n(\text{H}_2\text{O}) = \frac{65 \text{ kg}}{0.018 \text{ kg mol}^{-1}} = 3.6 \times 10^3 \text{ mol}$$

From $\Delta H = nC_{p,m}\Delta T$ we obtain

$$\Delta T = \frac{\Delta H}{nC_{p,m}} = \frac{1.0 \times 10^4 \text{ kJ}}{(3.6 \times 10^3 \text{ mol}) \times (0.0753 \text{ kJ K}^{-1} \text{ mol}^{-1})} = \boxed{+37 \text{ K}}$$

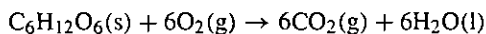
From $\Delta H = n\Delta_{\text{vap}}H^\circ = \frac{m}{M}\Delta_{\text{vap}}H^\circ$

$$m = \frac{M \times \Delta H}{\Delta_{\text{vap}}H^\circ} = \frac{(0.018 \text{ kg mol}^{-1}) \times (1.0 \times 10^4 \text{ kJ})}{44.0 \text{ kJ mol}^{-1}} = \boxed{4.09 \text{ kg}}$$

COMMENT. This estimate would correspond to about 30 glasses of water per day, which is much higher than the average consumption. The discrepancy may be a result of our assumption that evaporation of water is the main mechanism of heat loss.

P2.42 (a) $q_V = -n\Delta_c U^\circ$; hence

(i) The complete aerobic oxidation is



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

$$\Delta_c H^\circ = \Delta_c U^\circ = \boxed{-2802 \text{ kJ mol}^{-1}}$$

$$\begin{aligned} \text{(ii)} \quad \Delta_c U^\circ &= \frac{-q_V}{n} = \frac{-C\Delta T}{n} = \frac{-MC\Delta T}{m} \text{ where } m \text{ is sample mass and } M \text{ molar mass} \\ \text{so } \Delta_c U^\circ &= -\frac{(180.16 \text{ g mol}^{-1}) \times (641 \text{ J K}^{-1}) \times (7.793 \text{ K})}{0.3212 \text{ g}} = \boxed{-2802 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{(iii)} \quad \Delta_c H^\circ &= 6\Delta_f H^\circ(\text{CO}_2, g) + 6\Delta_f H^\circ(\text{H}_2\text{O}, l) - \Delta_f H^\circ(\text{C}_6\text{H}_{12}\text{O}_6, s) - 6\Delta_f H^\circ(\text{O}_2, g) \\ \text{so } \Delta_f H^\circ(\text{C}_6\text{H}_{12}\text{O}_6, s) &= 6\Delta_f H^\circ(\text{CO}_2, g) + 6\Delta_f H^\circ(\text{H}_2\text{O}, l) - 6\Delta_f H^\circ(\text{O}_2, g) - \Delta_c H^\circ \\ \Delta_f H^\circ(\text{C}_6\text{H}_{12}\text{O}_6, s) &= [6(-393.51) + 6(-285.83) - 6(0) - (-2802)] \text{ kJ mol}^{-1} \\ &= \boxed{-1274 \text{ kJ mol}^{-1}} \end{aligned}$$

(b) The anaerobic glycolysis to lactic acid is



$$\begin{aligned}\Delta_r H^\ominus &= 2\Delta_f H^\ominus(\text{lactic acid}) - \Delta_f H^\ominus(\text{glucose}) \\ &= \{(2) \times (-694.0) - (-1274)\} \text{ kJ mol}^{-1} = -114 \text{ kJ mol}^{-1}\end{aligned}$$

Therefore, aerobic oxidation is more exothermic by 2688 kJ mol⁻¹ than glycolysis.

P2.44 The three possible fates of the radical are

- (a) $\text{tert-C}_4\text{H}_9 \rightarrow \text{sec-C}_4\text{H}_9$
- (b) $\text{tert-C}_4\text{H}_9 \rightarrow \text{C}_3\text{H}_6 + \text{CH}_3$
- (c) $\text{tert-C}_4\text{H}_9 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5$

The three corresponding enthalpy changes are

$$\begin{aligned}\text{(a)} \quad \Delta_r H^\ominus &= \Delta_f H^\ominus(\text{sec-C}_4\text{H}_9) - \Delta_f H^\ominus(\text{tert-C}_4\text{H}_9) = (67.5 - 51.3) \text{ kJ mol}^{-1} \\ &= \boxed{16.2 \text{ kJ mol}^{-1}}\end{aligned}$$

$$\begin{aligned}\text{(b)} \quad \Delta_r H^\ominus &= \Delta_f H^\ominus(\text{C}_3\text{H}_6) + \Delta_f H^\ominus(\text{CH}_3) - \Delta_f H^\ominus(\text{tert-C}_4\text{H}_9) \\ &= (20.42 + 145.49 - 51.3) \text{ kJ mol}^{-1} = \boxed{1146 \text{ kJ mol}^{-1}}\end{aligned}$$

$$\begin{aligned}\text{(c)} \quad \Delta_r H^\ominus &= \Delta_f H^\ominus(\text{C}_2\text{H}_4) + \Delta_f H^\ominus(\text{C}_2\text{H}_5) - \Delta_f H^\ominus(\text{tert-C}_4\text{H}_9) \\ &= (52.26 + 121.0 - 51.3) \text{ kJ mol}^{-1} = \boxed{122.0 \text{ kJ mol}^{-1}}\end{aligned}$$

P2.46 (a) The Joule–Thomson coefficient is related to the given data by

$$\begin{aligned}\mu &= -(1/C_p)(\partial H/\partial p)_T = -(-3.29 \times 10^3 \text{ J mol}^{-1} \text{ MPa}^{-1})/(110.0 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= \boxed{29.9 \text{ K MPa}^{-1}}\end{aligned}$$

(b) The Joule–Thomson coefficient is defined as

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

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

$$\Delta T = \mu \Delta p = (29.9 \text{ K MPa}^{-1}) \times [(0.5 - 1.5) \times 10^{-1} \text{ MPa}] = \boxed{-2.99 \text{ K}}$$

3 The Second Law

Answers to discussion questions

D3.2 The device proposed uses geothermal heat (energy) and appears to be similar to devices currently in existence for heating and lighting homes. As long as the amount of heat extracted from the hot source (the ground) is not less than the sum of the amount of heat discarded to the surroundings (by heating the home and operating the steam engine) and of the amount of work done by the engine to operate the heat pump, this device is possible; at least, it does not violate the first law of thermodynamics. However, the feasibility of the device needs to be tested from the point of view of the second law as well. There are various equivalent versions of the second law; 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 3; and therefore, that it cannot operate as described. However, we must carefully examine the exact wording of the second law. The key words are “sole result.” Another slightly different, 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.

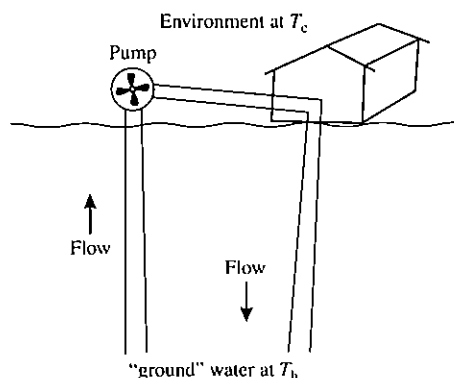


Figure 3.1 C_V and C_p are the temperature dependent heat capacities of water

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

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

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

$$\Delta E_{\text{ground}} = -C_V(T_h)\{T_h - T_c\}$$

$$\Delta E_{\text{environment}} = -C_V(T_h)\{T_h - T_c\}$$

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 .

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

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

$$\Delta S_{\text{ground}} = \frac{q_{\text{ground}}}{T_h} = \frac{-C_p(T_h)\{T_h - T_c\}}{T_h}$$

$$\Delta S_{\text{environment}} = \frac{q_{\text{environment}}}{T_c} = \frac{C_p(T_c)\{T_h - T_c\}}{T_c}$$

Adding terms and estimating that $C_p(T_h) \approx C_p(T_c) = C_p$, we find that

$$\Delta S_{\text{tot}} = C_p\{T_h - T_c\} \left\{ \frac{1}{T_c} - \frac{1}{T_h} \right\}$$

This expression satisfies the second law ($\Delta S_{\text{tot}} > 0$) only when $T_h > T_c$. 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 $T_h > T_c$, the resultant geothermal pump is feasible. However, the efficiency, given by eqn 3.10, must be high to compete with fossil fuels because high installation costs must be recovered during the lifetime of the apparatus.

$$E_{\text{rev}} = 1 - \frac{T_c}{T_h}$$

with $T_c \approx 273 \text{ K}$ and $T_h = 373 \text{ K}$ (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.

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

$$-dU - p_{\text{ex}}dV + dw_{\text{add}} + TdS \geq 0$$

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

$$dS \geq 0$$

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

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

$$dA \leq 0,$$

where A is defined as $U - TS$.

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

$$dG \leq 0,$$

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

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

D3.6 See the solution to Exercise 2.30(a) and Example 3.6, where it is demonstrated that $\pi_T = a/V_m^2$ for a van der Waals gas. Therefore, there is no dependence on b for a van der Waals gas. The internal pressure results from attractive interactions alone. For van der Waals gases and liquids with strong attractive forces (large a) at small volumes, the internal pressure can be very large.

D3.8 The 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

$$\Delta S = \int_i^f dq_{\text{rev}}/T$$

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

Solutions to exercises

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

E3.1(b)
$$\Delta S = \int \frac{dq_{\text{rev}}}{T} = \frac{q}{T}$$

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

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

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

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

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

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

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

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

For the first step

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

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

and for the second

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

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

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

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

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

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

$$\Delta S = \int_i^f \frac{dq_{\text{rev}}}{T} = \boxed{0}$$

$$\begin{aligned} \Delta U &= nC_{V,m} \Delta T = (2.00 \text{ mol}) \times (27.5 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 - 250) \text{ K} \\ &= 2750 \text{ J} = \boxed{+2.75 \text{ kJ}} \end{aligned}$$

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

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

$$C_{p,m} = C_{V,m} + R = (27.5 \text{ J K}^{-1} \text{ mol}^{-1} + 8.314 \text{ J K}^{-1} \text{ mol}^{-1}) = 35.814 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{So } \Delta H = (2.00 \text{ mol}) \times (35.814 \text{ J K}^{-1} \text{ mol}^{-1}) \times (+50 \text{ K}) = 3581.4 \text{ J} = \boxed{3.58 \text{ kJ}}$$

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

$$T_f = \frac{1}{2}(200^\circ\text{C} + 25^\circ\text{C}) = 112.5^\circ\text{C}$$

The heat capacity of each block is

$$C = mC_s \quad \text{where } C_s \text{ is the specific heat capacity}$$

$$\text{so } \Delta H \text{ (individual)} = mC_s\Delta T = 1.00 \times 10^3 \text{ g} \times 0.449 \text{ J K}^{-1} \text{ g}^{-1} \times (\pm 87.5 \text{ K}) = \pm 39 \text{ kJ}$$

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

$$\Delta S = mC_s \ln \left(\frac{T_f}{T_i} \right); 200^\circ\text{C} = 473.2 \text{ K}; 25^\circ\text{C} = 298.2 \text{ K}; 112.5^\circ\text{C} = 385.7 \text{ K}$$

$$\Delta S_1 = (1.00 \times 10^3 \text{ g}) \times (0.449 \text{ J K}^{-1} \text{ g}^{-1}) \times \ln \left(\frac{385.7}{298.2} \right) = 115.5 \text{ J K}^{-1}$$

$$\Delta S_2 = (1.00 \times 10^3 \text{ g}) \times (0.449 \text{ J K}^{-1} \text{ g}^{-1}) \times \ln \left(\frac{385.7}{473.2} \right) = -91.802 \text{ J K}^{-1}$$

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

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

$$\begin{aligned} \text{(b)} \quad w &= -p_{\text{ex}}\Delta V = -(1.5 \text{ atm}) \times \left(\frac{1.01 \times 10^5 \text{ Pa}}{\text{atm}} \right) \times (100.0 \text{ cm}^2) \times (15 \text{ cm}) \times \left(\frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \right) \\ &= -227.2 \text{ J} = -230 \text{ J} \end{aligned}$$

$$\text{(c)} \quad \Delta U = q + w = 0 - 230 \text{ J} = -230 \text{ J}$$

$$\text{(d)} \quad \Delta U = nC_{V,m}\Delta T$$

$$\begin{aligned} \Delta T &= \frac{\Delta U}{nC_{V,m}} = \frac{-227.2 \text{ J}}{(1.5 \text{ mol}) \times (28.8 \text{ J K}^{-1} \text{ mol}^{-1})} \\ &= -5.3 \text{ K} \end{aligned}$$

- (e) Entropy is a state function, so we can compute it by any convenient path. Although the specified transformation is adiabatic, a more convenient path is constant-volume cooling followed by isothermal expansion. The entropy change is the sum of the entropy changes of these two steps:

$$\Delta S = \Delta S_1 + \Delta S_2 = nC_{V,m} \ln \left(\frac{T_f}{T_i} \right) + nR \ln \left(\frac{V_f}{V_i} \right) \quad [3.19 \text{ and } 3.13]$$

$$T_f = 288.15 \text{ K} - 5.26 \text{ K} = 282.9 \text{ K}$$

$$\begin{aligned} V_i &= \frac{nRT}{p_i} = \frac{(1.5 \text{ mol}) \times (8.206 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (288.2 \text{ K})}{9.0 \text{ atm}} \\ &= 3.942 \text{ dm}^3 \end{aligned}$$

$$V_f = 3.942 \text{ dm}^3 + (100 \text{ cm}^2) \times (15 \text{ cm}) \times \left(\frac{1 \text{ dm}^3}{1000 \text{ cm}^3} \right)$$

$$= 3.942 \text{ dm}^3 + 1.5 \text{ dm}^3 = 5.44 \text{ dm}^3$$

$$\Delta S = (1.5 \text{ mol}) \times \left\{ (28.8 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left(\frac{282.9}{288.2} \right) \right.$$

$$\left. + (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left(\frac{5.44}{3.942} \right) \right\}$$

$$= 1.5 \text{ mol}(-0.5346 \text{ J K}^{-1} \text{ mol}^{-1} + 2.678 \text{ J K}^{-1} \text{ mol}^{-1}) = \boxed{3.2 \text{ J K}^{-1}}$$

E3.7(b) (a) $\Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{T_b} = \frac{35.27 \times 10^3 \text{ J mol}^{-1}}{(64.1 + 273.15) \text{ K}} = +104.58 \text{ J K}^{-1} = \boxed{104.6 \text{ J K}^{-1}}$

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

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

E3.8(b) (a) $\Delta_r S^\ominus = S_m^\ominus(\text{Zn}^{2+}, \text{aq}) + S_m^\ominus(\text{Cu}, \text{s}) - S_m^\ominus(\text{Zn}, \text{s}) - S_m^\ominus(\text{Cu}^{2+}, \text{aq})$

$$= [-112.1 + 33.15 - 41.63 + 99.6] \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{-21.0 \text{ J K}^{-1} \text{ mol}^{-1}}$$

(b) $\Delta_r S^\ominus = 12S_m^\ominus(\text{CO}_2, \text{g}) + 11S_m^\ominus(\text{H}_2\text{O}, \text{l}) - S_m^\ominus(\text{C}_{12}\text{H}_{22}\text{O}_{11}, \text{s}) - 12S_m^\ominus(\text{O}_2, \text{g})$

$$= [(12 \times 213.74) + (11 \times 69.91) - 360.2 - (12 \times 205.14)] \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= \boxed{+512.0 \text{ J K}^{-1} \text{ mol}^{-1}}$$

E3.9(b) (a) $\Delta_r H^\ominus = \Delta_f H^\ominus(\text{Zn}^{2+}, \text{aq}) - \Delta_f H^\ominus(\text{Cu}^{2+}, \text{aq})$

$$= -153.89 - 64.77 \text{ kJ mol}^{-1} = -218.66 \text{ kJ mol}^{-1}$$

$$\Delta_r G^\ominus = -218.66 \text{ kJ mol}^{-1} - (298.15 \text{ K}) \times (-21.0 \text{ J K}^{-1} \text{ mol}^{-1}) = \boxed{-212.40 \text{ kJ mol}^{-1}}$$

(b) $\Delta_r H^\ominus = \Delta_c H^\ominus = -5645 \text{ kJ mol}^{-1}$

$$\Delta_r G^\ominus = -5645 \text{ kJ mol}^{-1} - (298.15 \text{ K}) \times (512.0 \text{ J K}^{-1} \text{ mol}^{-1}) = \boxed{-5798 \text{ kJ mol}^{-1}}$$

E3.10(b) (a) $\Delta_r G^\ominus = \Delta_f G^\ominus(\text{Zn}^{2+}, \text{aq}) - \Delta_f G^\ominus(\text{Cu}^{2+}, \text{aq})$

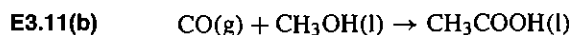
$$= -147.06 - 65.49 \text{ kJ mol}^{-1} = \boxed{-212.55 \text{ kJ mol}^{-1}}$$

(b) $\Delta_r G^\ominus = 12\Delta_f G^\ominus(\text{CO}_2, \text{g}) + 11\Delta_f G^\ominus(\text{H}_2\text{O}, \text{l}) - \Delta_f G^\ominus(\text{C}_{12}\text{H}_{22}\text{O}_{11}, \text{s}) - 12\Delta_f G^\ominus(\text{O}_2, \text{g})$

$$= [12 \times (-394.36) + 11 \times (-237.13) - (-1543) - 12 \times 0] \text{ kJ mol}^{-1}$$

$$= \boxed{-5798 \text{ kJ mol}^{-1}}$$

COMMENT. In each case these values of $\Delta_r G^\ominus$ agree closely with the calculated values in Exercise 3.9(b).

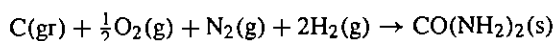


$$\begin{aligned}\Delta_r H^\ominus &= \sum_{\text{Products}} \nu \Delta_f H^\ominus - \sum_{\text{Reactants}} \nu \Delta_f H^\ominus \quad [2.32] \\ &= -484.5 \text{ kJ mol}^{-1} - (-238.66 \text{ kJ mol}^{-1}) - (-110.53 \text{ kJ mol}^{-1}) \\ &= -135.31 \text{ kJ mol}^{-1}\end{aligned}$$

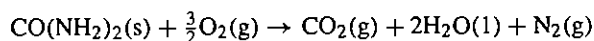
$$\begin{aligned}\Delta_r S^\ominus &= \sum_{\text{Products}} \nu S_m^\ominus - \sum_{\text{Reactants}} \nu S_m^\ominus \quad [3.21] \\ &= 159.8 \text{ J K}^{-1} \text{ mol}^{-1} - 126.8 \text{ J K}^{-1} \text{ mol}^{-1} - 197.67 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= -164.67 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_r G^\ominus &= \Delta_r H^\ominus - T \Delta_r S^\ominus \\ &= -135.31 \text{ kJ mol}^{-1} - (298 \text{ K}) \times (-164.67 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= -135.31 \text{ kJ mol}^{-1} + 49.072 \text{ kJ mol}^{-1} = \boxed{-86.2 \text{ kJ mol}^{-1}}\end{aligned}$$

E3.12(b) The formation reaction of urea is



The combustion reaction is



$$\Delta_c H = \Delta_f H^\ominus(\text{CO}_2, \text{g}) + 2\Delta_f H^\ominus(\text{H}_2\text{O, l}) - \Delta_f H^\ominus(\text{CO(NH}_2)_2, \text{s})$$

$$\begin{aligned}\Delta_f H^\ominus(\text{CO(NH}_2)_2, \text{s}) &= \Delta_f H^\ominus(\text{CO}_2, \text{g}) + 2\Delta_f H^\ominus(\text{H}_2\text{O, l}) - \Delta_c H(\text{CO(NH}_2)_2, \text{s}) \\ &= -393.51 \text{ kJ mol}^{-1} + (2) \times (-285.83 \text{ kJ mol}^{-1}) - (-632 \text{ kJ mol}^{-1}) \\ &= -333.17 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_r S^\ominus &= S_m^\ominus(\text{CO(NH}_2)_2, \text{s}) - S_m^\ominus(\text{C, gr}) - \frac{1}{2} S_m^\ominus(\text{O}_2, \text{g}) - S_m^\ominus(\text{N}_2, \text{g}) - 2S_m^\ominus(\text{H}_2, \text{g}) \\ &= 104.60 \text{ J K}^{-1} \text{ mol}^{-1} - 5.740 \text{ J K}^{-1} \text{ mol}^{-1} - \frac{1}{2}(205.138 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &\quad - 191.61 \text{ J K}^{-1} \text{ mol}^{-1} - 2(130.684 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= -456.687 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_r G^\ominus &= \Delta_r H^\ominus - T \Delta_r S^\ominus \\ &= -333.17 \text{ kJ mol}^{-1} - (298 \text{ K}) \times (-456.687 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= -333.17 \text{ kJ mol}^{-1} + 136.093 \text{ kJ mol}^{-1} \\ &= \boxed{-197 \text{ kJ mol}^{-1}}\end{aligned}$$

E3.13(b) (a) $\Delta S(\text{gas}) = nR \ln \left(\frac{V_f}{V_i} \right) [3.13] = \left(\frac{21 \text{ g}}{39.95 \text{ g mol}^{-1}} \right) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln 2$
 $= 3.029 \text{ J K}^{-1} = \boxed{3.0 \text{ J K}^{-1}}$

$$\Delta S(\text{surroundings}) = -\Delta S(\text{gas}) = \boxed{-3.0 \text{ J K}^{-1}} \text{ [reversible]}$$

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

(b) $\Delta S(\text{gas}) = \boxed{+3.0 \text{ J K}^{-1}}$ [S is a state function]

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

$$\Delta S(\text{total}) = \boxed{+3.0 \text{ J K}^{-1}}$$

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

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

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



$$\begin{aligned} \Delta_r G^\ominus &= 3\Delta_f G^\ominus(\text{CO}_2, \text{g}) + 4\Delta_f G^\ominus(\text{H}_2\text{O}, \text{l}) - \Delta_f G^\ominus(\text{C}_3\text{H}_8, \text{g}) - 0 \\ &= 3(-394.36 \text{ kJ mol}^{-1}) + 4(-237.13 \text{ kJ mol}^{-1}) - 1(-23.49 \text{ kJ mol}^{-1}) \\ &= -2108.11 \text{ kJ mol}^{-1} \end{aligned}$$

The maximum non-expansion work is $\boxed{2108.11 \text{ kJ mol}^{-1}}$ since $|w_{\text{add}}| = |\Delta G|$.

E3.15(b) (a) $\varepsilon = 1 - \frac{T_c}{T_h} [3.10] = 1 - \frac{500 \text{ K}}{1000 \text{ K}} = \boxed{0.500}$

(b) Maximum work $= \varepsilon |q_h| = (0.500) \times (1.0 \text{ kJ}) = \boxed{0.50 \text{ kJ}}$

(c) $\varepsilon_{\text{max}} = \varepsilon_{\text{rev}}$ and $|w_{\text{max}}| = |q_h| - |q_{c,\text{min}}|$

$$\begin{aligned} |q_{c,\text{min}}| &= |q_h| - |w_{\text{max}}| \\ &= 1.0 \text{ kJ} - 0.50 \text{ kJ} \\ &= \boxed{0.5 \text{ kJ}} \end{aligned}$$

E3.16(b) $\Delta G = nRT \ln \left(\frac{p_f}{p_i} \right) [3.56] = nRT \ln \left(\frac{V_i}{V_f} \right)$ [Boyle's law]

$$\Delta G = (2.5 \times 10^{-3} \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln \left(\frac{72}{100} \right) = \boxed{-2.0 \text{ J}}$$

E3.17(b) $\left(\frac{\partial G}{\partial T} \right)_p = -S$ [3.50]; hence $\left(\frac{\partial G_f}{\partial T} \right)_p = -S_f$, and $\left(\frac{\partial G_i}{\partial T} \right)_p = -S_i$

$$\begin{aligned} \Delta S &= S_f - S_i = - \left(\frac{\partial G_f}{\partial T} \right)_p + \left(\frac{\partial G_i}{\partial T} \right)_p = - \left(\frac{\partial (G_f - G_i)}{\partial T} \right)_p \\ &= - \left(\frac{\partial \Delta G}{\partial T} \right)_p = - \frac{\partial}{\partial T} \left(-73.1 \text{ J} + 42.8 \text{ J} \times \frac{T}{\text{K}} \right) \\ &= \boxed{-42.8 \text{ J K}^{-1}} \end{aligned}$$

E3.18(b) $dG = -S dT + V dp$ [3.49]; at constant T , $dG = V dp$; therefore

$$\Delta G = \int_{p_i}^{p_f} V dp$$

The change in volume of a condensed phase under isothermal compression is given by the isothermal compressibility (eqn 2.44).

$$\kappa_T = \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = 1.26 \times 10^{-9} \text{ Pa}^{-1}$$

This small isothermal compressibility (typical of condensed phases) tells us that we can expect a small change in volume from even a large increase in pressure. So we can make the following approximations to obtain a simple expression for the volume as a function of the pressure

$$\kappa_T \approx \frac{1}{V} \left(\frac{V - V_i}{p - p_i} \right) \approx \frac{1}{V_i} \left(\frac{V - V_i}{p} \right) \quad \text{so} \quad V = V_i(1 - \kappa_T p),$$

where V_i is the volume at 1 atm, namely the sample mass over the density, m/ρ .

$$\begin{aligned} \Delta G &= \int_{100 \text{ kPa}}^{100 \text{ MPa}} \frac{m}{\rho} (1 - \kappa_T p) dp \\ &= \frac{m}{\rho} \left(\int_{100 \text{ kPa}}^{100 \text{ MPa}} dp - \kappa_T \int_{100 \text{ kPa}}^{100 \text{ MPa}} p dp \right) \\ &= \frac{m}{\rho} \left(p \Big|_{100 \text{ kPa}}^{100 \text{ MPa}} - \frac{1}{2} \kappa_T p^2 \Big|_{100 \text{ kPa}}^{100 \text{ MPa}} \right) \\ &= \frac{25 \text{ g}}{0.791 \text{ g cm}^{-3}} \left(9.99 \times 10^7 \text{ Pa} - \frac{1}{2} (1.26 \times 10^{-9} \text{ Pa}^{-1}) \times (1.00 \times 10^{16} \text{ Pa}^2) \right) \\ &= 31.6 \text{ cm}^3 \times \left(\frac{1 \text{ m}}{100 \text{ cm}} \right)^3 \times 9.36 \times 10^7 \text{ Pa} \\ &= 2.96 \times 10^3 \text{ J} = \boxed{3.0 \text{ kJ}} \end{aligned}$$

E3.19(b) $\Delta G_m = G_{m,f} - G_{m,i} = RT \ln \left(\frac{p_f}{p_i} \right)$ [3.56]

$$= (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (323 \text{ K}) \times \ln \left(\frac{252.0}{92.0} \right) = \boxed{2.71 \text{ kJ mol}^{-1}}$$

E3.20(b) For an ideal gas, $G_m^O = G_m^\ominus + RT \ln \left(\frac{p}{p^\ominus} \right)$ [3.56 with $G_m = G_m^O$]

But for a real gas, $G_m = G_m^\ominus + RT \ln \left(\frac{f}{p^\ominus} \right)$ [3.58]

So $G_m - G_m^O = RT \ln \frac{f}{p}$ [3.58 minus 3.56]; $\frac{f}{p} = \phi$

$$= RT \ln \phi = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (290 \text{ K}) \times (\ln 0.68) = \boxed{-0.93 \text{ kJ mol}^{-1}}$$

E3.21(b) $\Delta G = nV_m \Delta p$ [3.55] $= V \Delta p$

$$\Delta G = (1.0 \text{ dm}^3) \times \left(\frac{1 \text{ m}^3}{10^3 \text{ dm}^3} \right) \times (200 \times 10^3 \text{ Pa}) = 200 \text{ Pa m}^3 = \boxed{200 \text{ J}}$$

E3.22(b) $\Delta G_m = RT \ln \left(\frac{p_f}{p_i} \right) = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (500 \text{ K}) \times \ln \left(\frac{100.0 \text{ kPa}}{50.0 \text{ kPa}} \right) = \boxed{+2.88 \text{ kJ mol}^{-1}}$

Solutions to problems

Solutions to numerical problems

P3.2 $\Delta S_m = \int_{T_1}^{T_2} \frac{C_{p,m} dT}{T}$ [3.18] $= \int_{T_1}^{T_2} \left(\frac{a + bT}{T} \right) dT = a \ln \left(\frac{T_2}{T_1} \right) + b(T_2 - T_1)$

$$a = 91.47 \text{ J K}^{-1} \text{ mol}^{-1}, \quad b = 7.5 \times 10^{-2} \text{ J K}^{-2} \text{ mol}^{-1}$$

$$\begin{aligned} \Delta S_m &= (91.47 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left(\frac{300 \text{ K}}{273 \text{ K}} \right) + (0.075 \text{ J K}^{-2} \text{ mol}^{-1}) \times (27 \text{ K}) \\ &= \boxed{10.7 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

P3.4 First, determine the final state in each section. In section B, the volume was halved at constant temperature, so the pressure was doubled: $p_{B,f} = 2p_{B,i}$. The piston ensures that the pressures are equal in both chambers, so $p_{A,f} = 2p_{B,i} = 2p_{A,i}$. From the perfect gas law

$$\frac{T_{A,f}}{T_{A,i}} = \frac{p_{A,f} V_{A,f}}{p_{A,i} V_{A,i}} = \frac{(2p_{A,i}) \times (3.00 \text{ dm}^3)}{(p_{A,i}) \times (2.00 \text{ dm}^3)} = 3.00 \quad \text{so} \quad T_{A,f} = 900 \text{ K}.$$

(a) $\Delta S_A = nC_{V,m} \ln \left(\frac{T_{A,f}}{T_{A,i}} \right)$ [3.19] $+ nR \ln \left(\frac{V_{A,f}}{V_{A,i}} \right)$ [3.13]

$$\begin{aligned} \Delta S_A &= (2.0 \text{ mol}) \times (20 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln 3.00 \\ &\quad + (2.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left(\frac{3.00 \text{ dm}^3}{2.00 \text{ dm}^3} \right) \\ &= \boxed{50.7 \text{ J K}^{-1}} \end{aligned}$$

$$\begin{aligned} \Delta S_B &= nR \ln \left(\frac{V_{B,f}}{V_{B,i}} \right) = (2.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left(\frac{1.00 \text{ dm}^3}{2.00 \text{ dm}^3} \right) \\ &= \boxed{-11.5 \text{ J K}^{-1}} \end{aligned}$$

(b) The Helmholtz free energy is defined as $A = U - TS$ [3.29]. Because section B is isothermal, $\Delta U = 0$ and $\Delta(TS) = T \Delta S$, so

$$\Delta A_B = -T_B \Delta S_B = -(300 \text{ K})(-11.5 \text{ J K}^{-1}) = 3.46 \times 10^3 \text{ J} = \boxed{+3.46 \text{ kJ}}$$

In Section A, we cannot compute $\Delta(TS)$, so we cannot compute ΔU . ΔA is indeterminate in both magnitude and sign. We know that in a perfect gas, U depends only on temperature; moreover, $U(T)$ is an increasing function of T , for $\partial U/\partial T = C$ (heat capacity), which is positive; since $\Delta T > 0$, $\Delta U > 0$ as well. But $\Delta(TS) > 0$ too, since both the temperature and the entropy increase.

(c) Likewise, under constant-temperature conditions

$$\Delta G = \Delta H - T\Delta S$$

In Section B, $\Delta H_B = 0$ (constant temperature, perfect gas), so

$$\Delta G_B = -T_B \Delta S_B = -(300 \text{ K}) \times (-11.5 \text{ J K}^{-1}) = 3.46 \times 10^3 \text{ J}$$

ΔG_A is indeterminate in both magnitude and sign.

$$(d) \Delta S(\text{total system}) = \Delta S_A + \Delta S_B = (50.7 - 11.5) \text{ J K}^{-1} = +39.2 \text{ J K}^{-1}$$

If the process has been carried out reversibly as assumed in the statement of the problem we can say

$$\Delta S(\text{system}) + \Delta S(\text{surroundings}) = 0$$

$$\text{Hence, } \Delta S(\text{surroundings}) = -39.2 \text{ J K}^{-1}$$

Question. Can you design this process such that heat is added to section A reversibly?

P3.6

	q	w	$\Delta U = \Delta H$	ΔS	ΔS_{sur}	ΔS_{tot}
Path (a)	2.74 kJ	-2.74 kJ	0	9.13 J K ⁻¹	-9.13 J K ⁻¹	0
Path (b)	1.66 kJ	-1.66 kJ	0	9.13 J K ⁻¹	-5.53 J K ⁻¹	3.60 J K ⁻¹

Path (a)

$$\begin{aligned} w &= -nRT \ln \left(\frac{V_f}{V_i} \right) [3.13] = -nRT \ln \left(\frac{p_i}{p_f} \right) [\text{Boyle's law}] \\ &= -(1.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K}) \times \ln \left(\frac{3.00 \text{ atm}}{1.00 \text{ atm}} \right) = -2.74 \times 10^3 \text{ J} \\ &= -2.74 \text{ kJ} \end{aligned}$$

$$\Delta H = \Delta U = 0 [\text{isothermal process in perfect gas}]$$

$$q = \Delta U - w = 0 - (-2.74 \text{ kJ}) = +2.74 \text{ kJ}$$

$$\Delta S = \frac{q_{\text{rev}}}{T} [\text{isothermal}] = \frac{2.74 \times 10^3 \text{ J}}{300 \text{ K}} = +9.13 \text{ J K}^{-1}$$

$$\Delta S_{\text{tot}} = 0 [\text{reversible process}]$$

$$\Delta S_{\text{tot}} = \Delta S_{\text{sur}} = \Delta S_{\text{tot}} - \Delta S = 0 - 9.13 \text{ J K}^{-1} = -9.13 \text{ J K}^{-1}$$

Path (b)

$$\begin{aligned}
 w &= -p_{\text{ex}}(V_f - V_i) = -p_{\text{ex}} \left(\frac{nRT}{p_f} - \frac{nRT}{p_i} \right) = -nRT \left(\frac{p_{\text{ex}}}{p_f} - \frac{p_{\text{ex}}}{p_i} \right) \\
 &= -(1.00 \text{ mol}) \times (8.314 \text{ J K}^{-1}) \times (300 \text{ K}) \times \left(\frac{1.00 \text{ atm}}{1.00 \text{ atm}} - \frac{1.00 \text{ atm}}{3.00 \text{ atm}} \right) \\
 &= -1.66 \times 10^3 \text{ J} = \boxed{-1.66 \text{ kJ}}
 \end{aligned}$$

$$\Delta H = \Delta U = \boxed{0} \text{ [isothermal process in perfect gas]}$$

$$q = \Delta U - w = 0 - (-1.66 \text{ kJ}) = \boxed{+1.66 \text{ kJ}}$$

$$\Delta S = \frac{q_{\text{rev}}}{T} \text{ [isothermal]} = \frac{2.74 \times 10^3 \text{ J}}{300 \text{ K}} = \boxed{+9.13 \text{ J K}^{-1}}$$

(Note: One can arrive at this by using q from Path (a) as the reversible path, or one can simply use ΔS from Path (a), realizing that entropy is a state function.)

$$\Delta S_{\text{sur}} = \frac{q_{\text{sur}}}{T_{\text{sur}}} = \frac{-q}{T_{\text{sur}}} = \frac{-1.66 \times 10^3 \text{ J}}{300 \text{ K}} = \boxed{-5.53 \text{ J K}^{-1}}$$

$$\Delta S_{\text{tot}} = \Delta S + \Delta S_{\text{sur}} = (9.13 - 5.53) \text{ J K}^{-1} = \boxed{+3.60 \text{ J K}^{-1}}$$

P3.8 ΔS depends on only the initial and final states, so we can use $\Delta S = nC_{p,m} \ln \frac{T_f}{T_i}$ [3.19]

$$\text{Since } q = nC_{p,m}(T_f - T_i), \quad T_f = T_i + \frac{q}{nC_{p,m}} = T_i + \frac{I^2 R t}{nC_{p,m}} \quad [q = ItV = I^2 R t]$$

$$\text{That is, } \Delta S = nC_{p,m} \ln \left(1 + \frac{I^2 R t}{nC_{p,m} T_i} \right)$$

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

$$\begin{aligned}
 \Delta S &= (7.87 \text{ mol}) \times (24.4 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left(1 + \frac{(1.00 \text{ A})^2 \times (1000 \Omega) \times (15.0 \text{ s})}{(7.87) \times (24.4 \text{ J K}^{-1}) \times (293 \text{ K})} \right) \\
 &= (192 \text{ J K}^{-1}) \times (\ln 1.27) = \boxed{+45.4 \text{ J K}^{-1}}
 \end{aligned}$$

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

For the second experiment, no change in state occurs for the copper hence, $\Delta S(\text{copper}) = 0$. However, for the water, considered as a large heat sink

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

P3.10 Consider the temperature as a function of pressure and enthalpy: $T = T(p, H)$

$$\text{so } dT = \left(\frac{\partial T}{\partial p} \right)_H dp + \left(\frac{\partial T}{\partial H} \right)_p dH$$

The Joule–Thomson expansion is a constant-enthalpy process (Section 2.12). Hence,

$$\begin{aligned}dT &= \left(\frac{\partial T}{\partial p}\right)_H dp = \mu dp \\ \Delta T &= \int_{p_i}^{p_f} \mu dp = \mu \Delta p \quad [\mu \text{ is constant}] \\ &= (0.21 \text{ K atm}^{-1}) \times (1.00 \text{ atm} - 100 \text{ atm}) = \boxed{-21 \text{ K}} \\ T_f &= T_i + \Delta T = (373 - 21) \text{ K} = 352 \text{ K} \quad [\text{Mean } T = 363 \text{ K}]\end{aligned}$$

Consider the entropy as a function of temperature and pressure: $S = S(T, p)$

$$\begin{aligned}\text{Therefore, } dS &= \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp \\ \left(\frac{\partial S}{\partial T}\right)_p &= \frac{C_p}{T} \quad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad [\text{Table 3.5}]\end{aligned}$$

$$\begin{aligned}\text{For } V_m &= \frac{RT}{p}(1 + Bp) \\ \left(\frac{\partial V_m}{\partial T}\right)_p &= \frac{R}{p}(1 + Bp)\end{aligned}$$

$$\begin{aligned}\text{Then } dS_m &= \frac{C_{p,m}}{T} dT - \frac{R}{p}(1 + Bp) dp \\ \text{or } dS_m &= \frac{C_{p,m}}{T} dT - \frac{R}{p} dp - RB dp\end{aligned}$$

Upon integration

$$\begin{aligned}\Delta S_m &= \int_1^2 dS_m = C_{p,m} \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{p_2}{p_1}\right) - RB(p_2 - p_1) \\ &= \frac{5}{2} R \ln\left(\frac{352}{373}\right) - R \ln\left(\frac{1}{100}\right) - R\left(-\frac{0.525 \text{ atm}^{-1}}{363}\right) \times (-99 \text{ atm}) \\ &= \boxed{+35.9 \text{ J K}^{-1} \text{ mol}^{-1}}\end{aligned}$$

P3.12

$$\Delta_r H^\ominus = \sum_{\text{products}} \nu_j \Delta_f H^\ominus(\text{J}) - \sum_{\text{reactants}} \nu_j \Delta_f H^\ominus(\text{J}) \quad [2.34]$$

$$\begin{aligned}\Delta_r H^\ominus(298 \text{ K}) &= 1 \times \Delta_f H^\ominus(\text{CO, g}) + 1 \times \Delta_f H^\ominus(\text{H}_2\text{O, g}) - 1 \times \Delta_f H^\ominus(\text{CO}_2, \text{g}) \\ &= \{-110.53 - 241.82 - (-393.51)\} \text{ kJ mol}^{-1} = \boxed{+41.16 \text{ kJ mol}^{-1}}\end{aligned}$$

$$\Delta_r S^\ominus = \sum_{\text{products}} \nu_j S_m^\ominus(\text{J}) - \sum_{\text{reactants}} \nu_j S_m^\ominus(\text{J}) \quad [3.21]$$

$$\begin{aligned}\Delta_r S^\ominus(298 \text{ K}) &= 1 \times S_m^\ominus(\text{CO, g}) + 1 \times S_m^\ominus(\text{H}_2\text{O, g}) - 1 \times S_m^\ominus(\text{CO}_2, \text{g}) - 1 \times S_m^\ominus(\text{H}_2, \text{g}) \\ &= (197.67 + 188.83 - 213.74 - 130.684) \text{ kJ mol}^{-1} = \boxed{+42.08 \text{ J K}^{-1} \text{ mol}^{-1}}\end{aligned}$$

$$\begin{aligned}
 \Delta_r H^\circ(398 \text{ K}) &= \Delta_r H^\circ(298 \text{ K}) + \int_{298 \text{ K}}^{398 \text{ K}} \Delta_r C_p dT \quad [2.36] \\
 &= \Delta_r H^\circ(298 \text{ K}) + \Delta_r C_p \Delta T \quad [\text{heat capacities constant}] \\
 \Delta_r C_p &= 1 \times C_{p,m}(\text{CO}, \text{g}) + 1 \times C_{p,m}(\text{H}_2\text{O}, \text{g}) - 1 \times C_{p,m}(\text{CO}_2, \text{g}) - 1 \times C_{p,m}(\text{H}_2, \text{g}) \\
 &= (29.14 + 33.58 - 37.11 - 28.824) \text{ J K}^{-1} \text{ mol}^{-1} = -3.21 \text{ J K}^{-1} \text{ mol}^{-1} \\
 \Delta_r H^\circ(398 \text{ K}) &= (41.16 \text{ kJ mol}^{-1}) + (-3.21 \text{ J K}^{-1} \text{ mol}^{-1}) \times (100 \text{ K}) = \boxed{+40.84 \text{ kJ mol}^{-1}}
 \end{aligned}$$

For each substance in the reaction

$$\Delta S_m = C_{p,m} \ln \left(\frac{T_f}{T_i} \right) = C_{p,m} \ln \left(\frac{398 \text{ K}}{298 \text{ K}} \right) \quad [3.19]$$

Thus

$$\begin{aligned}
 \Delta_r S^\circ(398 \text{ K}) &= \Delta_r S^\circ(298 \text{ K}) + \sum_{\text{products}} \nu_j C_{p,m}(j) \ln \left(\frac{T_f}{T_i} \right) - \sum_{\text{reactants}} \nu_j C_{p,m}(j) \ln \left(\frac{T_f}{T_i} \right) \\
 &= \Delta_r S^\circ(298 \text{ K}) + \Delta_r C_p \ln \left(\frac{398 \text{ K}}{298 \text{ K}} \right) \\
 &= (42.01 \text{ J K}^{-1} \text{ mol}^{-1}) + (-3.21 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left(\frac{398 \text{ K}}{298 \text{ K}} \right) \\
 &= (42.01 - 0.93) \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{+41.08 \text{ J K}^{-1} \text{ mol}^{-1}}
 \end{aligned}$$

COMMENT. Both $\Delta_r H^\circ$ and $\Delta_r S^\circ$ changed little over 100 K for this reaction. This is not an uncommon result.

P3.14 Draw up the following table and proceed as in Problem 3.11.

T/K	14.14	16.33	20.03	31.15	44.08	64.81
$(C_{p,m}/T) (\text{J K}^{-2} \text{ mol}^{-1})$	0.671	0.778	0.908	1.045	1.063	1.024

T/K	100.90	140.86	183.59	225.10	262.99	298.06
$(C_{p,m}/T) (\text{J K}^{-2} \text{ mol}^{-1})$	0.942	0.861	0.787	0.727	0.685	0.659

Plot $C_{p,m}$ against T (Figure 3.2(a)) and $C_{p,m}/T$ against T (Figure 3.2(b)), extrapolating to $T = 0$ with $C_{p,m} = aT^3$ fitted at $T = 14.14 \text{ K}$, which gives $a = 3.36 \text{ mJ K}^{-1} \text{ mol}^{-1}$. Integration by determining the area under the curve then gives

$$\begin{aligned}
 H_m^\circ(298 \text{ K}) - H_m^\circ(0) &= \int_0^{298 \text{ K}} C_{p,m} dT = \boxed{34.4 \text{ kJ mol}^{-1}} \\
 S_m(298 \text{ K}) &= S_m(0) + \int_0^{298 \text{ K}} \frac{C_{p,m}}{T} dT = S_m(0) + \boxed{243 \text{ J K}^{-1} \text{ mol}^{-1}}
 \end{aligned}$$

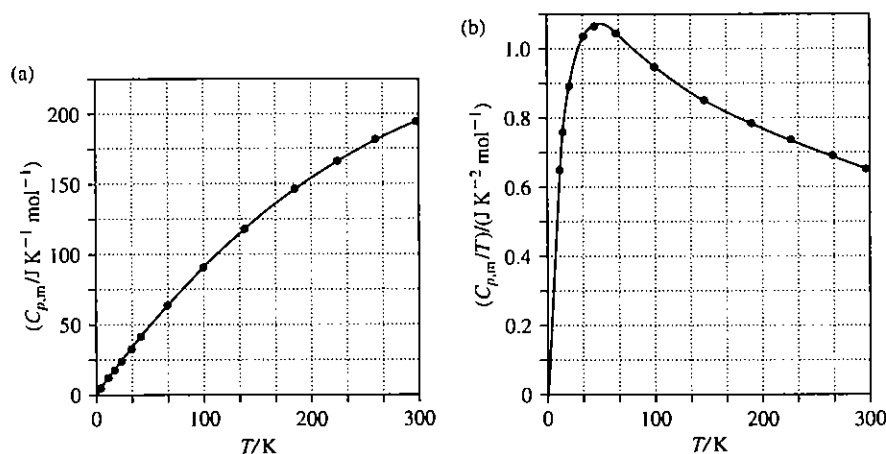


Figure 3.2

P3.16 The Gibbs–Helmholtz equation [3.52] may be recast into an analogous equation involving ΔG and ΔH , since

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = \left(\frac{\partial G_f}{\partial T}\right)_p - \left(\frac{\partial G_i}{\partial T}\right)_p$$

and $\Delta H = H_f - H_i$

Thus,

$$\left(\frac{\partial}{\partial T} \frac{\Delta_r G^\ominus}{T}\right)_p = -\frac{\Delta_r H^\ominus}{T^2}$$

$$d\left(\frac{\Delta_r G^\ominus}{T}\right) = \left(\frac{\partial}{\partial T} \frac{\Delta_r G^\ominus}{T}\right)_p dT \text{ [constant pressure]} = -\frac{\Delta_r H^\ominus}{T^2} dT$$

$$\begin{aligned} \Delta\left(\frac{\Delta_r G^\ominus}{T}\right) &= -\int_{T_c}^T \frac{\Delta_r H^\ominus}{T^2} dT \\ &\approx -\Delta_r H^\ominus \int_{T_c}^T \frac{dT}{T^2} = \Delta_r H^\ominus \left(\frac{1}{T} - \frac{1}{T_c}\right) \quad [\Delta_r H^\ominus \text{ assumed constant}] \end{aligned}$$

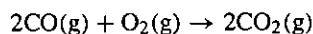
$$\text{Therefore, } \frac{\Delta_r G^\ominus(T)}{T} - \frac{\Delta_r G^\ominus(T_c)}{T_c} \approx \Delta_r H^\ominus \left(\frac{1}{T} - \frac{1}{T_c}\right)$$

$$\Delta_r G^\ominus(T) = \frac{T}{T_c} \Delta_r G^\ominus(T_c) + \left(1 - \frac{T}{T_c}\right) \Delta_r H^\ominus(T_c)$$

and so

$$= \tau \Delta_r G^\ominus(T_c) + (1 - \tau) \Delta_r H^\ominus(T_c) \quad \text{where } \tau = \frac{T}{T_c}$$

For the reaction



$$\Delta_r G^\ominus(T_c) = 2\Delta_f G^\ominus(\text{CO}_2, \text{g}) - 2\Delta_f G^\ominus(\text{CO}, \text{g})$$

$$= [2 \times (-394.36) - 2 \times (-137.17)] \text{ kJ mol}^{-1} = -514.38 \text{ kJ mol}^{-1}$$

$$\begin{aligned}\Delta_r H^\circ(T_c) &= 2\Delta_f H^\circ(\text{CO}_2, \text{g}) - 2\Delta_f H^\circ(\text{CO}, \text{g}) \\ &= [2 \times (-393.51) - 2 \times (-110.53)] \text{ kJ mol}^{-1} = -565.96 \text{ kJ mol}^{-1}\end{aligned}$$

Therefore, since $\tau = 375/298.15 = 1.258$

$$\begin{aligned}\Delta_r G^\circ(375 \text{ K}) &= \{(1.258) \times (-514.38) + (1 - 1.258) \times (-565.96)\} \text{ kJ mol}^{-1} \\ &= \boxed{-501 \text{ kJ mol}^{-1}}\end{aligned}$$

P3.18 A graphical integration of $\ln \phi = \int_0^p \left(\frac{Z-1}{p} \right) dp$ [3.60] is performed. We draw up the following table

p/atm	1	4	7	10	40	70	100
$10^3 \left(\frac{Z-1}{p} \right) / \text{atm}^{-1}$	-2.9	-3.01	-3.03	-3.04	-3.17	-3.19	-3.13

The points are plotted in Figure 3.3. The integral is the shaded area, which has the value -0.313 , so at 100 atm

$$\phi = e^{-0.313} = 0.73$$

and the fugacity of oxygen is $100 \text{ atm} \times 0.73 = \boxed{73 \text{ atm}}$

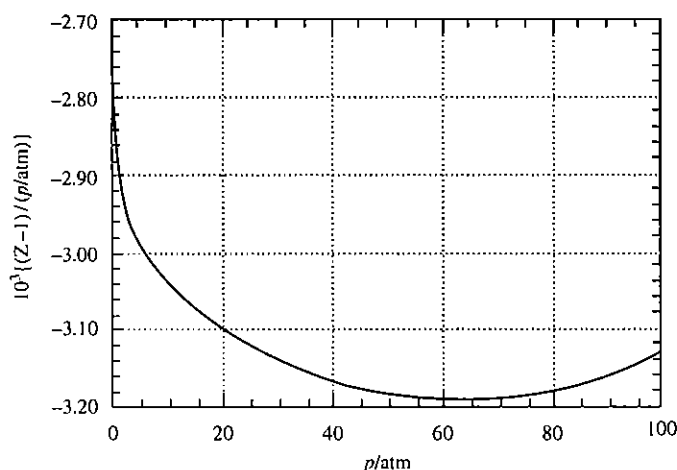


Figure 3.3

Solutions to theoretical problems

P3.20 Paths A and B in Figure 3.4 are the reversible adiabatic paths which are assumed to cross at state 1. Path C (dashed) is an isothermal path which connects the adiabatic paths at states 2 and 3. Now go round the cycle ($1 \rightarrow 2$, step 1; $2 \rightarrow 3$, step 2; $3 \rightarrow 1$, step 3).

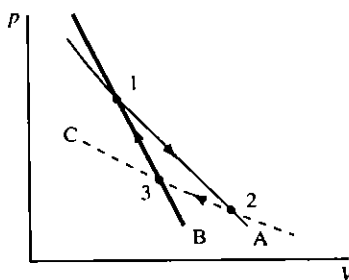


Figure 3.4

Step 1 $\Delta U_1 = q_1 + w_1 = w_1$ [$q_1 = 0$, adiabatic]

Step 2 $\Delta U_2 = q_2 + w_2 = 0$ [isothermal step, energy depends on temperature only]

Step 3 $\Delta U_3 = q_3 + w_3 = w_3$ [$q_3 = 0$, adiabatic]

For the cycle $\Delta U = 0 = w_1 + q_2 + w_2 + w_3$ or $w(\text{net}) = w_1 + w_2 + w_3 = -q_2$

But, $\Delta U_1 = -\Delta U_3$ [$\Delta T_1 = -\Delta T_2$]; hence $w_1 = -w_3$, and $w(\text{net}) = w_2 = -q_2$, or $-w(\text{net}) = q_2$.

Thus, a net amount of work has been done by the system from heat obtained from a heat reservoir at the temperature of step 2, without at the same time transferring heat from a hot to a cold reservoir. This violates the Kelvin statement of the Second Law. Therefore, the assumption that the two adiabatic reversible paths may intersect is disproven.

Question. May any adiabatic paths intersect, reversible or not?

P3.22
$$V = \left(\frac{\partial G}{\partial p} \right)_T [3.50] = \boxed{\frac{RT}{p} + B' + C'p + D'p^2}$$

which is the virial equation of state.

P3.24 We start from the fundamental relation

$$dU = T dS - p dV [3.43]$$

But, since $U = U(S, V)$, we may also write

$$dU = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV$$

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

$$dU = C_V dT$$

and

$$dS = \frac{dq_{\text{rev}}}{T} = \frac{C_V dT}{T}$$

$$\text{Then } \left(\frac{dU}{dS} \right)_V = \left(\frac{\partial U}{\partial S} \right)_V = \left(\frac{C_V dT}{\frac{C_V dT}{T}} \right) = T$$

For a reversible adiabatic (constant-entropy) change in a perfect gas

$$dU = dw = -pdV$$

$$\text{Therefore, } \left(\frac{\partial U}{\partial V} \right)_S = -p$$

P3.26

$$\alpha = \left(\frac{1}{V} \right) \times \left(\frac{\partial V}{\partial T} \right)_p \quad [3.8]; \quad \kappa_T = - \left(\frac{1}{V} \right) \times \left(\frac{\partial V}{\partial p} \right)_T \quad [3.14]$$

$$(a) \quad \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V \quad [\text{Maxwell relation}]$$

$$\left(\frac{\partial p}{\partial T} \right)_V = - \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial V} \right)_T \quad [\text{Euler chain relation, Further information 2.2}]$$

$$= - \frac{\left(\frac{\partial V}{\partial T} \right)_p}{\left(\frac{\partial V}{\partial p} \right)_T} \quad [\text{reciprocal identity, Further information 2.2}]$$

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

$$\left(\frac{\partial V}{\partial S} \right)_p = \left(\frac{\partial T}{\partial p} \right)_S \quad [\text{Maxwell relation}]$$

$$\left(\frac{\partial T}{\partial p} \right)_S = - \left(\frac{\partial T}{\partial S} \right)_p \left(\frac{\partial S}{\partial p} \right)_T \quad [\text{Euler chain}] = - \frac{\left(\frac{\partial S}{\partial p} \right)_T}{\left(\frac{\partial S}{\partial T} \right)_p} \quad [\text{reciprocal}]$$

First treat the numerator:

$$\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p \quad [\text{Maxwell relation}] = -\alpha V$$

As for the denominator, at constant p

$$dS = \left(\frac{\partial S}{\partial T} \right)_p dT \quad \text{and} \quad dS = \frac{dq_{\text{rev}}}{T} = \frac{dH}{T} = \frac{C_p dT}{T} \quad [dq_p = dH]$$

Therefore, $\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$ and $\left(\frac{\partial V}{\partial S}\right)_p = \boxed{\frac{\alpha TV}{C_p}}$

(b) $\left(\frac{\partial p}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S$ [Maxwell relation]

$$\begin{aligned} -\left(\frac{\partial T}{\partial V}\right)_S &= \frac{1}{\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial V}{\partial S}\right)_T} \text{ [Euler chain]} = \frac{\left(\frac{\partial S}{\partial V}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_V} \text{ [reciprocal]} \\ &= \frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial S}{\partial U}\right)_V \left(\frac{\partial U}{\partial T}\right)_V} \text{ [Maxwell relation]} = \frac{-\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial U}\right)_V \left(\frac{\partial U}{\partial T}\right)_V} \text{ [Euler chain]} \\ &= \frac{-\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial U}{\partial S}\right)_V}{\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial U}{\partial T}\right)_V} \text{ [reciprocal identity, twice]} = \boxed{\frac{\alpha T}{\kappa_T C_V}} \left[\left(\frac{\partial U}{\partial S}\right)_V = T \right] \end{aligned}$$

P3.28 First use an identity of partial derivatives that involves a change of variable

$$\left(\frac{\partial H}{\partial p}\right)_T = \left(\frac{\partial H}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_T + \left(\frac{\partial H}{\partial p}\right)_S$$

We will be able to identify some of these terms if we examine an expression for dH analogous to the fundamental equation [3.43]. From the definition of enthalpy, we have:

$$dH = dU + p dV + V dp = T dS - p dV + p dV + V dp = T dS + V dp$$

Compare this expression to the exact differential of H considered as a function of S and p :

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp$$

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 $pV = nRT$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p}, \text{ hence } \left(\frac{\partial H}{\partial p}\right)_T = \frac{-nRT}{p} + V = \boxed{0}$$

(b) For $p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$ [Table 1.7]

Because we cannot express V in closed form as a function of T , we solve for T as a function of V and evaluate

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

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

$$\left(\frac{\partial T}{\partial V}\right)_p = \frac{p}{nR} + \frac{na}{RV^2} - \frac{2na(V - nb)}{RV^3}$$

$$\text{Therefore, } \left(\frac{\partial H}{\partial p}\right)_T = \frac{-T}{\frac{p}{nR} + \frac{na}{RV^2} - \frac{2na(V - nb)}{RV^3}} + V$$

which yields after algebraic manipulation

$$\left(\frac{\partial H}{\partial p}\right)_T = \frac{nb - \left(\frac{2na}{RT}\right)\lambda^2}{1 - \left(\frac{2na}{RTV}\right)\lambda^2}, \lambda = 1 - \frac{nb}{V}$$

When $\frac{b}{V_m} \ll 1$, $\lambda \approx 1$ and

$$\frac{2na}{RTV} = \frac{2na}{RT} \times \frac{1}{V} \approx \frac{2na}{RT} \times \frac{p}{nRT} = \frac{2pa}{R^2T^2}$$

$$\text{Therefore, } \left(\frac{\partial H}{\partial p}\right)_T \approx \frac{nb - \left(\frac{2na}{RT}\right)}{1 - \left(\frac{2pa}{R^2T^2}\right)}$$

For argon, $a = 1.337 \text{ dm}^6 \text{ atm mol}^{-2}$, $b = 3.20 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$,

$$\frac{2na}{RT} = \frac{(2) \times (1.0 \text{ mol}) \times (1.337 \text{ dm}^6 \text{ atm mol}^{-2})}{(8.206 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} = 0.11 \text{ dm}^3$$

$$\frac{2pa}{R^2T^2} = \frac{(2) \times (10.0 \text{ atm}) \times (1.337 \text{ dm}^6 \text{ atm mol}^{-2})}{[(8.206 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})]^2} = 0.045$$

$$\text{Hence, } \left(\frac{\partial H}{\partial p}\right)_T \approx \frac{\{(3.20 \times 10^{-2}) - (0.11)\} \text{ dm}^3}{1 - 0.045} = -0.0817 \text{ dm}^3 = \boxed{-8.3 \text{ J atm}^{-1}}$$

$$\Delta H \approx \left(\frac{\partial H}{\partial p}\right)_T \Delta p \approx (-8.3 \text{ J atm}^{-1}) \times (1 \text{ atm}) = \boxed{-8 \text{ J}}$$

P3.30

$$\begin{aligned}
 \mu_J &= \left(\frac{\partial T}{\partial V} \right)_U \quad C_V = \left(\frac{\partial U}{\partial T} \right)_V \\
 \mu_J C_V &= \left(\frac{\partial T}{\partial V} \right)_U \left(\frac{\partial U}{\partial T} \right)_V = \frac{-1}{\left(\frac{\partial V}{\partial U} \right)_T} \quad [\text{Euler chain relation}] \\
 &= - \left(\frac{\partial U}{\partial V} \right)_T \quad [\text{reciprocal identity}] = p - T \left(\frac{\partial p}{\partial T} \right)_V \quad [3.48] \\
 \left(\frac{\partial p}{\partial T} \right)_V &= \frac{-1}{\left(\frac{\partial T}{\partial V} \right)_p \left(\frac{\partial V}{\partial p} \right)_T} \quad [\text{Euler chain}] = \frac{- \left(\frac{\partial V}{\partial T} \right)_p}{\left(\frac{\partial V}{\partial p} \right)_T} = \frac{\alpha}{\kappa_T}
 \end{aligned}$$

Therefore, $\boxed{\mu_J C_V = p - \frac{\alpha T}{\kappa_T}}$

P3.32

$$\kappa_S = - \left(\frac{1}{V} \right) \times \left(\frac{\partial V}{\partial p} \right)_S = - \frac{1}{V \left(\frac{\partial p}{\partial V} \right)_S}$$

The only constant-entropy changes of state for a perfect gas are reversible adiabatic changes, for which

$$pV^\gamma = \text{const}$$

$$\text{Then, } \left(\frac{\partial p}{\partial V} \right)_S = \left(\frac{\partial}{\partial V} \frac{\text{const}}{V^\gamma} \right)_S = -\gamma \times \left(\frac{\text{const}}{V^{\gamma+1}} \right) = \frac{-\gamma p}{V}$$

$$\text{Therefore, } \kappa_S = \frac{-1}{V \left(\frac{-\gamma p}{V} \right)} = \frac{+1}{\gamma p}$$

Hence, $\boxed{p\gamma\kappa_S = +1}$

P3.34

The starting point for the calculation is eqn 3.60. To evaluate the integral, we need an analytical expression for Z , which can be obtained from the equation of state.

- (a) We saw in Section 1.4 that the van der Waals coefficient a represents the attractions between molecules, so it may be set equal to zero in this calculation. When we neglect a in the van der Waals equation, that equation becomes

$$p = \frac{RT}{V_m - b}$$

and hence

$$Z = 1 + \frac{bp}{RT}$$

The integral in eqn 3.60 that we require is therefore

$$\ln \phi = \int_0^p \left(\frac{Z-1}{p} \right) dp = \int_0^p \left(\frac{b}{RT} \right) dp = \frac{bp}{RT}$$

Consequently, from eqns 3.60 and 3.59, the fugacity at the pressure p is

$$f = \boxed{pe^{bp/RT}}$$

From Table 1.6, $b = 3.71 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$, so $pb/RT = 1.516 \times 10^{-2}$, giving

$$f = (10.00 \text{ atm}) \times e^{0.01515} = \boxed{10.2 \text{ atm}}$$

COMMENT. The effect of the repulsive term (as represented by the coefficient b in the van der Waals equation) is to increase the fugacity above the pressure, and so the effective pressure of the gas—its “escaping tendency”—is greater than if it were perfect.

(b) When we neglect b in the van der Waals equation we have

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

and hence

$$Z = 1 - \frac{a}{RTV_m}$$

Then substituting into eqn 3.60 we get

$$\ln \phi = \int_0^p \left(\frac{Z - 1}{p} \right) dp = \int_0^p \frac{-a}{pRTV_m} dp$$

In order to perform this integration we must eliminate the variable V_m by solving for it in terms of p . Rewriting the expression for p in the form of a quadratic we have

$$V_m^2 - \frac{RT}{p} V_m + \frac{a}{p} = 0$$

The solution is

$$V_m = \frac{1}{2} \left(\frac{RT}{p} \pm \frac{1}{p} \sqrt{(RT)^2 - 4ap} \right)$$

Applying the approximation $(RT)^2 \gg 4ap$ we obtain

$$V_m = \frac{1}{2} \left(\frac{RT}{p} \pm \frac{RT}{p} \right)$$

Choosing the + sign we get

$$V_m = \frac{RT}{p} \text{ which is the perfect-gas volume.}$$

Then

$$\ln \phi = \int_0^p -\frac{a}{(RT)^2} dp = \boxed{-\frac{ap}{(RT)^2}}$$

For ammonia $a = 4.169 \text{ atm dm}^3 \text{ mol}^{-2}$

$$\ln \phi = -\frac{4.169 \text{ atm dm}^3 \text{ mol}^{-1} \times 10.00 \text{ atm}}{(0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K})^2} = -0.06965$$

$$\phi = 0.9237 = \frac{f}{p}$$

$$f = \phi p = 0.9237 \times 10.00 \text{ atm} = \boxed{9.237 \text{ atm}}$$

Solutions to applications

P3.36 Taking the hint, we have

$$\Delta_{\text{trs}} S^\ominus(25^\circ\text{C}) = \Delta S_{\text{i}} + \Delta S_{\text{ii}} + \Delta S_{\text{iii}}.$$

We are not given the heat capacity of either the folded or unfolded protein, but if we let $C_{p,\text{m}}$ be the heat capacity of the folded protein, the heat capacity of the unfolded protein is $C_{p,\text{m}} + 6.28 \text{ kJ K}^{-1} \text{ mol}^{-1}$. So for the heating and cooling steps, we have:

$$\Delta S_{\text{i}} = C_p \ln \left(\frac{T_{\text{f}}}{T_{\text{i}}} \right) = C_{p,\text{m}} \ln \left(\frac{348.7 \text{ K}}{298.2 \text{ K}} \right) [3.19]$$

$$\text{and } \Delta S_{\text{iii}} = (C_{p,\text{m}} + 6.28 \text{ kJ K}^{-1} \text{ mol}^{-1}) \ln \left(\frac{298.2 \text{ K}}{348.7 \text{ K}} \right)$$

$$\begin{aligned} \text{so } \Delta S_{\text{i}} + \Delta S_{\text{iii}} &= C_{p,\text{m}} \ln \left(\frac{348.7 \text{ K}}{298.2 \text{ K}} \right) + (C_{p,\text{m}} + 6.28 \text{ kJ K}^{-1} \text{ mol}^{-1}) \ln \left(\frac{298.2 \text{ K}}{348.7 \text{ K}} \right) \\ &= (6.28 \text{ kJ K}^{-1} \text{ mol}^{-1}) \ln \left(\frac{298.2 \text{ K}}{348.7 \text{ K}} \right) = -0.983 \text{ kJ K}^{-1} \text{ mol}^{-1} \end{aligned}$$

For the transition itself, use Trouton's rule (eqn 3.16):

$$\Delta S_{\text{ii}} = \frac{\Delta_{\text{trs}} H^\ominus}{T_{\text{trs}}} = \frac{509 \text{ kJ mol}^{-1}}{348.2 \text{ K}} = 1.460 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\text{Hence, } \Delta_{\text{trs}} S^\ominus = (1.460 - 0.983) \text{ kJ K}^{-1} \text{ mol}^{-1} = 0.477 \text{ kJ K}^{-1} \text{ mol}^{-1} = \boxed{477 \text{ J K}^{-1} \text{ mol}^{-1}}$$

P3.38 (a) At constant temperature,

$$\Delta_{\text{r}} G = \Delta_{\text{r}} H - T \Delta_{\text{r}} S \quad \text{so} \quad \Delta_{\text{r}} S = \frac{\Delta_{\text{r}} H - \Delta_{\text{r}} G}{T}$$

$$\text{and } \Delta_{\text{r}} S = \frac{[-20 - (-31)] \text{ kJ mol}^{-1}}{310 \text{ K}} = +0.035 \text{ kJ K}^{-1} \text{ mol}^{-1} = \boxed{+35 \text{ J K}^{-1} \text{ mol}^{-1}}$$

(b) The power density P is

$$P = \frac{|\Delta_{\text{r}} G|n}{V}$$

where n is the number of moles of ATP hydrolyzed per second

$$n = \frac{N}{N_A} = \frac{10^6 \text{ s}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 1.66 \times 10^{-18} \text{ mol s}^{-1}$$

and V is the volume of the cell

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi (10 \times 10^{-6} \text{ m})^3 = 4.19 \times 10^{-15} \text{ m}^3$$

$$\text{Thus } P = \frac{|\Delta_r G|n}{V} = \frac{(31 \times 10^3 \text{ J mol}^{-1}) \times (1.66 \times 10^{-18} \text{ mol s}^{-1})}{4.19 \times 10^{-15} \text{ m}^3} = \boxed{12 \text{ W m}^{-3}}$$

This is orders of magnitude less than the power density of a computer battery, which is about

$$P_{\text{battery}} = \frac{15 \text{ W}}{100 \text{ cm}^3} \times \left(\frac{100 \text{ cm}}{1 \text{ m}}\right)^3 = \boxed{1.5 \times 10^4 \text{ W m}^{-3}}$$

(c) Simply make a ratio of the magnitudes of the free energies

$$\frac{14.2 \text{ kJ (mol glutamine)}^{-1}}{31 \text{ kJ (mol ATP)}^{-1}} = \boxed{0.46 \frac{\text{mol ATP}}{\text{mol glutamine}}}$$

P3.40 The Gibbs–Helmholtz equation is

$$\frac{\partial}{\partial T} \left(\frac{\Delta G}{T} \right) = -\frac{\Delta H}{T^2}$$

so for a small temperature change

$$\Delta \left(\frac{\Delta_r G^\ominus}{T} \right) = \frac{\Delta_r H^\ominus}{T^2} \Delta T \quad \text{and} \quad \frac{\Delta_r G_2^\ominus}{T_2} = \frac{\Delta_r G_1^\ominus}{T_1} - \frac{\Delta_r H^\ominus}{T^2 \Delta T}$$

$$\text{so } \int d \frac{\Delta_r G^\ominus}{T} = - \int \frac{\Delta_r H^\ominus dT}{T^2} \quad \text{and} \quad \frac{\Delta_r G_{190}^\ominus}{T_{190}} = \frac{\Delta_r G_{220}^\ominus}{T_{220}} + \Delta_r H^\ominus \left(\frac{1}{T_{190}} - \frac{1}{T_{220}} \right)$$

$$\Delta_r G_{190}^\ominus = \Delta_r G_{220}^\ominus \frac{T_{190}}{T_{220}} + \Delta_r H^\ominus \left(1 - \frac{T_{190}}{T_{220}} \right)$$

For the monohydrate

$$\Delta_r G_{190}^\ominus = (46.2 \text{ kJ mol}^{-1}) \times \left(\frac{190 \text{ K}}{220 \text{ K}} \right) + (127 \text{ kJ mol}^{-1}) \times \left(1 - \frac{190 \text{ K}}{220 \text{ K}} \right),$$

$$\Delta_r G_{190}^\ominus = \boxed{57.2 \text{ kJ mol}^{-1}}$$

For the dihydrate

$$\Delta_r G_{190}^\ominus = (69.4 \text{ kJ mol}^{-1}) \times \left(\frac{190 \text{ K}}{220 \text{ K}} \right) + (188 \text{ kJ mol}^{-1}) \times \left(1 - \frac{190 \text{ K}}{220 \text{ K}} \right),$$

$$\Delta_r G_{190}^\ominus = \boxed{85.6 \text{ kJ mol}^{-1}}$$

For the trihydrate

$$\Delta_r G_{190}^\ominus = (93.2 \text{ kJ mol}^{-1}) \times \left(\frac{190 \text{ K}}{220 \text{ K}} \right) + (237 \text{ kJ mol}^{-1}) \times \left(1 - \frac{190 \text{ K}}{220 \text{ K}} \right),$$

$$\Delta_r G_{190}^\ominus = \boxed{112.8 \text{ kJ mol}^{-1}}$$

P3.42

In effect, we are asked to compute the maximum work extractable from a gallon of octane, assuming that the internal combustion engine is a reversible heat engine operating between the specified temperatures, and to equate that quantity of energy with gravitational potential energy of a 1000-kg mass. The efficiency is

$$\varepsilon = \frac{|w|}{|q_h|} [3.8] = \frac{|w|}{|\Delta H|} = \varepsilon_{\text{rev}} = 1 - \frac{T_c}{T_h} [3.10] \quad \text{so} \quad |w| = |\Delta H| \left(1 - \frac{T_c}{T_h} \right)$$

$$|\Delta H| = 5512 \times 10^3 \text{ J mol}^{-1} \times 1.00 \text{ gal} \times \frac{3.00 \times 10^3 \text{ g}}{1 \text{ gal}} \times \frac{1 \text{ mol}}{114.23 \text{ g}} = 1.448 \times 10^8 \text{ J}$$

$$\text{so } |w| = 1.448 \times 10^8 \text{ J} \times \left(1 - \frac{1073 \text{ K}}{2273 \text{ K}} \right) = 7.642 \times 10^7 \text{ J}$$

If this work is converted completely to potential energy, it could lift a 1000-kg object to a height h given by $|w| = mgh$, so

$$h = \frac{|w|}{mg} = \frac{7.642 \times 10^7 \text{ J}}{(1000 \text{ kg})(9.81 \text{ m s}^{-2})} = 7.79 \times 10^3 \text{ m} = \boxed{7.79 \text{ km}}$$

P3.44

(a) As suggested, relate the work to the temperature-dependent coefficient of performance [Impact I3.1]:

$$|dw| = \frac{|dq_c|}{c} = \frac{|C_p dT|}{\left(\frac{T}{T_h - T} \right)} = C_p \left| \frac{T_h dT}{T} - dT \right|$$

Integrating yields

$$|w| = C_p \left| T_h \int_{T_i}^{T_f} \frac{dT}{T} + \int_{T_i}^{T_f} dT \right| = C_p \left| T_h \ln \frac{T_f}{T_i} - (T_f - T_i) \right| = C_p \left(T_h \ln \frac{T_f}{T_i} - T_i + T_f \right)$$

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

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

The refrigerator must also remove the heat of fusion at the freezing temperature. For this isothermal process, the coefficient of performance does not change, so

$$\begin{aligned} |w|_{\text{freeze}} &= \frac{|q_c|}{c} = \frac{\Delta_{\text{fus}} H}{\left(\frac{T_c}{T_h - T_c} \right)} = \Delta_{\text{fus}} H \left(\frac{T_h - T_c}{T_c} \right) \\ &= 6.008 \times 10^3 \text{ J mol}^{-1} \times \frac{250 \text{ g}}{18.0 \text{ g mol}^{-1}} \times \left(\frac{293 - 273}{273} \right) = 6113 \text{ J} \end{aligned}$$

The total work is

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

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

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

4

Physical transformations of pure substances

Answers to discussion questions

- D4.2** Refer to Figure 4.9 of the text. 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.
- D4.4** 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 *Impact* I4.1). (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 vaporizes (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.
- D4.6** The Clapeyron equation is exact and applies rigorously to all first-order phase transitions. It shows how pressure and temperature vary with respect to each other (temperature or pressure) along the phase boundary line, and in that sense, it defines the phase boundary line.
- The Clausius–Clapeyron equation serves the same purpose, but it is not exact; its derivation involves approximations, in particular the assumptions that the perfect gas law holds and that the volume of condensed phases can be neglected in comparison to the volume of the gaseous phase. It applies only to phase transitions between the gaseous state and condensed phases.

Solutions to exercises

- E4.1(b)** Assume vapor is a perfect gas and $\Delta_{\text{vap}}H$ is independent of temperature

$$\ln \frac{p^*}{p} = + \frac{\Delta_{\text{vap}}H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right)$$

$$\begin{aligned}
 \frac{1}{T} &= \frac{1}{T^*} + \frac{R}{\Delta_{\text{vap}}H} \ln \frac{p^*}{p} \\
 &= \frac{1}{293.2 \text{ K}} + \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}{32.7 \times 10^3 \text{ J mol}^{-1}} \times \ln \left(\frac{58.0}{66.0} \right) \\
 &= 3.378 \times 10^{-3} \text{ K}^{-1} \\
 T &= \frac{1}{3.378 \times 10^{-3} \text{ K}^{-1}} = 296 \text{ K} = \boxed{23^\circ\text{C}}
 \end{aligned}$$

E4.2(b)

$$\begin{aligned}
 \frac{dp}{dT} &= \frac{\Delta_{\text{fus}}S}{\Delta_{\text{fus}}V} \\
 \Delta_{\text{fus}}S &= \Delta_{\text{fus}}V \left(\frac{dp}{dT} \right) \approx \Delta_{\text{fus}}V \frac{\Delta p}{\Delta T}
 \end{aligned}$$

assuming $\Delta_{\text{fus}}S$ and $\Delta_{\text{fus}}V$ independent of temperature.

$$\begin{aligned}
 \Delta_{\text{fus}}S &= (152.6 \text{ cm}^3 \text{ mol}^{-1} - 142.0 \text{ cm}^3 \text{ mol}^{-1}) \times \frac{(1.2 \times 10^6 \text{ Pa}) - (1.01 \times 10^5 \text{ Pa})}{429.26 \text{ K} - 427.15 \text{ K}} \\
 &= (10.6 \text{ cm}^3 \text{ mol}^{-1}) \times \left(\frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \right) \times (5.21 \times 10^5 \text{ Pa K}^{-1}) \\
 &= 5.52 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} = \boxed{5.5 \text{ J K}^{-1} \text{ mol}^{-1}} \\
 \Delta_{\text{fus}}H &= T_f \Delta S = (427.15 \text{ K}) \times (5.52 \text{ J K}^{-1} \text{ mol}^{-1}) \\
 &= \boxed{2.4 \text{ kJ mol}^{-1}}
 \end{aligned}$$

E4.3(b)

$$\begin{aligned}
 \text{Use } \int d \ln p &= \int \frac{\Delta_{\text{vap}}H}{RT^2} dT \\
 \ln p &= \text{constant} - \frac{\Delta_{\text{vap}}H}{RT}
 \end{aligned}$$

Terms with $1/T$ dependence must be equal, so

$$\begin{aligned}
 -\frac{3036.8 \text{ K}}{T/K} &= -\frac{\Delta_{\text{vap}}H}{RT} \\
 \Delta_{\text{vap}}H &= (3036.8 \text{ K})R = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (3036.8 \text{ K}) \\
 &= \boxed{25.25 \text{ kJ mol}^{-1}}
 \end{aligned}$$

E4.4(b) (a) $\log p = \text{constant} - \Delta_{\text{vap}}H/(RT(2.303))$

Thus

$$\begin{aligned}
 \Delta_{\text{vap}}H &= (1625 \text{ K}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (2.303) \\
 &= \boxed{31.11 \text{ kJ mol}^{-1}}
 \end{aligned}$$

(b) Normal boiling point corresponds to $p = 1.000 \text{ atm} = 760 \text{ Torr}$

$$\log(760) = 8.750 - \frac{1625}{T/\text{K}}$$

$$\frac{1625}{T/\text{K}} = 8.750 - \log(760)$$

$$T/\text{K} = \frac{1625}{8.750 - \log(760)} = 276.87$$

$$T_b = \boxed{276.9 \text{ K}}$$

E4.5(b)

$$\Delta T = \frac{\Delta_{\text{fus}} V}{\Delta_{\text{fus}} S} \times \Delta p = \frac{T_f \Delta_{\text{fus}} V}{\Delta_{\text{fus}} H} \times \Delta p = \frac{T_f \Delta p M}{\Delta_{\text{fus}} H} \times \Delta \left(\frac{1}{\rho} \right)$$

$$[T_f = -3.65 + 273.15 = 269.50 \text{ K}]$$

$$\Delta T = \frac{(269.50 \text{ K}) \times (99.9 \text{ MPa}) M}{8.68 \text{ kJ mol}^{-1}} \times \left(\frac{1}{0.789 \text{ g cm}^{-3}} - \frac{1}{0.801 \text{ g cm}^{-3}} \right)$$

$$= (3.1017 \times 10^6 \text{ K Pa J}^{-1} \text{ mol}) \times (M) \times (+0.01899 \text{ cm}^3/\text{g}) \times \left(\frac{\text{m}^3}{10^6 \text{ cm}^3} \right)$$

$$= (+5.889 \times 10^{-2} \text{ K Pa m}^3 \text{ J}^{-1} \text{ g}^{-1} \text{ mol}) M = (+5.889 \times 10^{-2} \text{ K g}^{-1} \text{ mol}) M$$

$$\Delta T = (46.07 \text{ g mol}^{-1}) \times (+5.889 \times 10^{-2} \text{ K g}^{-1} \text{ mol})$$

$$= +2.71 \text{ K}$$

$$T_f = 269.50 \text{ K} + 2.71 \text{ K} = \boxed{272 \text{ K}}$$

E4.6(b)

$$\frac{dm}{dt} = \frac{dn}{dt} \times M_{\text{H}_2\text{O}} \text{ where } n = \frac{q}{\Delta_{\text{vap}} H}$$

$$\frac{dn}{dt} = \frac{dq/dt}{\Delta_{\text{vap}} H} = \frac{(0.87 \times 10^3 \text{ W m}^{-2}) \times (10^4 \text{ m}^2)}{44.0 \times 10^3 \text{ J mol}^{-1}}$$

$$= 197.7 \text{ J s}^{-1} \text{ J}^{-1} \text{ mol}$$

$$= 200 \text{ mol s}^{-1}$$

$$\frac{dm}{dt} = (197.7 \text{ mol s}^{-1}) \times (18.02 \text{ g mol}^{-1})$$

$$= \boxed{3.6 \text{ kg s}^{-1}}$$

E4.7(b) The vapor pressure of ice at -5°C is 0.40 kPa. Therefore, the frost will sublime. A partial pressure of 0.40 kPa or more will ensure that the frost remains.

E4.8(b) (a) According to Trouton's rule (Section 3.3(b), eqn 3.16)

$$\Delta_{\text{vap}} H = (85 \text{ J K}^{-1} \text{ mol}^{-1}) \times T_b = (85 \text{ J K}^{-1} \text{ mol}^{-1}) \times (342.2 \text{ K}) = \boxed{29.1 \text{ kJ mol}^{-1}}$$

(b) Use the Clausius–Clapeyron equation [Exercise 4.8(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

$$\ln p_1 = - \left(\frac{29.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times \left(\frac{1}{298.2 \text{ K}} - \frac{1}{342.2 \text{ K}} \right) = -1.509$$

$$p_1 = \boxed{0.22 \text{ atm}} = 168 \text{ Torr}$$

At 60°C ,

$$\ln p_1 = - \left(\frac{29.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times \left(\frac{1}{333.2 \text{ K}} - \frac{1}{342.2 \text{ K}} \right) = -0.276$$

$$p_1 = \boxed{0.76 \text{ atm}} = 576 \text{ Torr}$$

E4.9(b)

$$\Delta T = T_{\text{fus}}(10 \text{ MPa}) - T_{\text{fus}}(0.1 \text{ MPa}) = \frac{T_{\text{fus}} \Delta \rho M}{\Delta_{\text{fus}} H} \Delta \left(\frac{1}{\rho} \right) \quad [\text{See Exercise 4.5(b)}]$$

$$\Delta_{\text{fus}} H = 6.01 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta T &= \left\{ \frac{(273.15 \text{ K}) \times (9.9 \times 10^6 \text{ Pa}) \times (18 \times 10^{-3} \text{ kg mol}^{-1})}{6.01 \times 10^3 \text{ J mol}^{-1}} \right\} \\ &\quad \times \left\{ \frac{1}{9.98 \times 10^2 \text{ kg m}^{-3}} - \frac{1}{9.15 \times 10^2 \text{ kg m}^{-3}} \right\} \\ &= -0.74 \text{ K} \end{aligned}$$

$$T_{\text{fus}}(10 \text{ MPa}) = 273.15 \text{ K} - 0.74 \text{ K} = \boxed{272.41 \text{ K}}$$

E4.10(b)

$$\Delta_{\text{vap}} H = \Delta_{\text{vap}} U + \Delta_{\text{vap}}(pV)$$

$$\Delta_{\text{vap}} H = 43.5 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{vap}}(pV) = p \Delta_{\text{vap}} V = p(V_{\text{gas}} - V_{\text{liq}}) = pV_{\text{gas}} = RT \quad [\text{per mole, perfect gas}]$$

$$\Delta_{\text{vap}}(pV) = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (352 \text{ K}) = 2927 \text{ J mol}^{-1}$$

$$\begin{aligned} \text{Fraction} &= \frac{\Delta_{\text{vap}}(pV)}{\Delta_{\text{vap}} H} = \frac{2.927 \text{ kJ mol}^{-1}}{43.5 \text{ kJ mol}^{-1}} \\ &= \boxed{6.73 \times 10^{-2}} = 6.73 \text{ percent} \end{aligned}$$

Solutions to problems

Solutions to numerical problems

P4.2

Use the definite integral form of the Clausius–Clapeyron equation [Solution to Exercise 4.8(b)].

$$\ln \left(\frac{p_2}{p_1} \right) = \frac{\Delta_{\text{vap}} H}{R} \times \left(\frac{1}{T_1} - \frac{1}{T_2} \right); \quad T_1 = \text{normal boiling point}; \quad p_1 = 1.000 \text{ atm}$$

$$\ln(p_2/\text{atm}) = \left(\frac{20.25 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times \left(\frac{1}{244.0 \text{ K}} - \frac{1}{313.2 \text{ K}} \right) = 2.206$$

$$p_2 = \boxed{9.07 \text{ atm}} \approx 9 \text{ atm}$$

COMMENT. Three significant figures are not really warranted in this answer because of the approximations employed.

P4.4

$$\begin{aligned}
 \text{(a)} \quad \left(\frac{\partial \mu(l)}{\partial T} \right)_p - \left(\frac{\partial \mu(s)}{\partial T} \right)_p &= -S_m(l) + S_m(s) \text{ [Section 4.7, eqn 13]} \\
 &= -\Delta_{\text{fus}} S = \frac{-\Delta_{\text{fus}} H}{T_f}; \quad \Delta_{\text{fus}} H = 6.01 \text{ kJ mol}^{-1} \text{ [Table 2.3]} \\
 &= \frac{-6.01 \text{ kJ mol}^{-1}}{273.15 \text{ K}} = \boxed{-22.0 \text{ J K}^{-1} \text{ mol}^{-1}}
 \end{aligned}$$

$$\begin{aligned}
 \text{(b)} \quad \left(\frac{\partial \mu(g)}{\partial T} \right)_p - \left(\frac{\partial \mu(l)}{\partial T} \right)_p &= -S_m(g) + S_m(l) = -\Delta_{\text{vap}} S \\
 &= \frac{-\Delta_{\text{vap}} H}{T_b} = \frac{-40.6 \text{ kJ mol}^{-1}}{373.15 \text{ K}} = \boxed{-109.0 \text{ J K}^{-1} \text{ mol}^{-1}}
 \end{aligned}$$

$$\begin{aligned}
 \text{(c)} \quad \Delta \mu &\approx \left(\frac{\partial \mu}{\partial T} \right)_p \Delta T = -S_m \Delta T \text{ [4.1]} \\
 \Delta \mu(l) - \Delta \mu(s) &= \mu(l, -5^\circ \text{C}) - \mu(l, 0^\circ \text{C}) - \mu(s, -5^\circ \text{C}) + \mu(s, 0^\circ \text{C}) \\
 &= \mu(l, -5^\circ \text{C}) - \mu(s, -5^\circ \text{C}) \text{ } [\mu(l, 0^\circ \text{C}) = \mu(s, 0^\circ \text{C})] \\
 &\approx -\{S_m(l) - S_m(s)\} \Delta T \approx -\Delta_{\text{fus}} S \Delta T \\
 &= -(5 \text{ K}) \times (-22.0 \text{ J K}^{-1} \text{ mol}^{-1}) = \boxed{+110 \text{ J mol}^{-1}}
 \end{aligned}$$

Since, $\mu(l, -5^\circ \text{C}) > \mu(s, -5^\circ \text{C})$, there is a thermodynamic tendency to freeze.

P4.6

$$\frac{dp}{dT} = \frac{\Delta_{\text{fus}} S}{\Delta_{\text{fus}} V} \text{ [4.6]} = \frac{\Delta_{\text{fus}} H}{T \Delta_{\text{fus}} V}$$

$$\Delta T = \int_{T_{m,1}}^{T_{m,2}} dT = \int_{p_{\text{top}}}^{p_{\text{bot}}} \frac{T_m \Delta_{\text{fus}} V}{\Delta_{\text{fus}} H} dp$$

$$\Delta T \approx \frac{T_m \Delta_{\text{fus}} V}{\Delta_{\text{fus}} H} \times \Delta p \text{ } [T_m, \Delta_{\text{fus}} H, \text{ and } \Delta_{\text{fus}} V \text{ assumed constant}]$$

$$\Delta p = p_{\text{bot}} - p_{\text{top}} = \rho g h$$

Therefore

$$\begin{aligned}
 \Delta T &= \frac{T_m \rho g h \Delta_{\text{fus}} V}{\Delta_{\text{fus}} H} \\
 &= \frac{(234.3 \text{ K}) \times (13.6 \times 10^3 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2}) \times (10 \text{ m}) \times (0.517 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})}{2.292 \times 10^3 \text{ J mol}^{-1}} \\
 &= 0.070 \text{ K}
 \end{aligned}$$

Therefore, the freezing point changes to $\boxed{234.4 \text{ K}}$

P4.8

$$\frac{d \ln p}{dT} = \frac{\Delta_{\text{vap}} H}{RT^2} \text{ [4.11]}, \text{ yields upon indefinite integration}$$

$$\ln p = \text{constant} - \frac{\Delta_{\text{vap}} H}{RT}$$

Therefore, plot $\ln p$ against $1/T$ and identify $-\Delta_{\text{vap}}H/R$ as its slope. Construct the following table

$\theta/^{\circ}\text{C}$	0	20	40	50	70	80	90	100
T/K	273	293	313	323	343	353	363	373
$1000\text{ K}/T$	3.66	3.41	3.19	3.10	2.92	2.83	2.75	2.68
$\ln(p/\text{kPa})$	0.652	1.85	2.87	3.32	4.13	4.49	4.83	5.14

The points are plotted in Figure 4.1. The slope is -4569 K , so

$$\frac{-\Delta_{\text{vap}}H}{R} = -4569\text{ K}, \quad \text{or} \quad \Delta_{\text{vap}}H = \boxed{+38.0\text{ kJ mol}^{-1}}$$

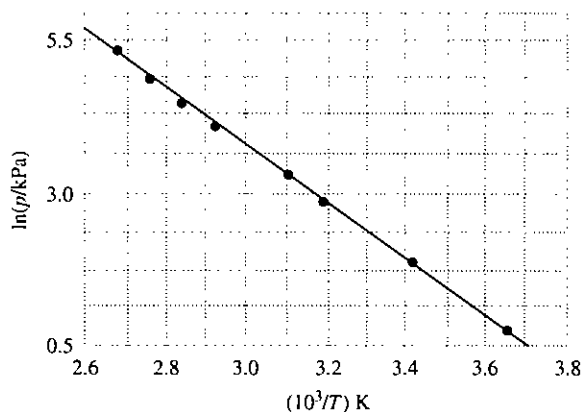


Figure 4.1

The normal boiling point occurs at $p = 760\text{ Torr}$, or at $\ln(p/\text{Torr}) = 6.633$, which from the figure corresponds to $1000\text{ K}/T \approx 2.80$. Therefore, $T_b = \boxed{357\text{ K } (84^{\circ}\text{C})}$. The accepted value is 83°C .

P4.10 The equations describing the coexistence curves for the three states are

(a) Solid–liquid boundary

$$p = p^* + \frac{\Delta_{\text{fus}}H}{\Delta_{\text{fus}}V} \ln \frac{T}{T^*} \quad [4.8]$$

(b) Liquid–vapor boundary

$$p = p^* e^{-\chi}, \quad \chi = \frac{\Delta_{\text{vap}}H}{R} \times \left(\frac{1}{T} - \frac{1}{T^*} \right) \quad [4.12]$$

(c) Solid–vapor boundary

$$p = p^* e^{-\chi}, \quad \chi = \frac{\Delta_{\text{sub}}H}{R} \times \left(\frac{1}{T} - \frac{1}{T^*} \right) \quad [\text{similar to 4.12}]$$

We need $\Delta_{\text{sub}}H = \Delta_{\text{fus}}H + \Delta_{\text{vap}}H = 41.4 \text{ kJ mol}^{-1}$

$$\Delta_{\text{fus}}V = M \times \left(\frac{1}{\rho(l)} - \frac{1}{\rho(s)} \right) = \left(\frac{78.11 \text{ g mol}^{-1}}{\text{g cm}^{-3}} \right) \times \left(\frac{1}{0.879} - \frac{1}{0.891} \right) = +1.197 \text{ cm}^3 \text{ mol}^{-1}$$

After insertion of these numerical values into the above equations, we obtain

$$\begin{aligned} \text{(a)} \quad p &= p^* + \left(\frac{10.6 \times 10^3 \text{ J mol}^{-1}}{1.197 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}} \right) \ln \frac{T}{T^*} \\ &= p^* + 8.855 \times 10^9 \text{ Pa} \times \ln \frac{T}{T^*} = p^* + (6.64 \times 10^7 \text{ Torr}) \ln \frac{T}{T^*} \quad (1 \text{ Torr} = 133.322 \text{ Pa}) \end{aligned}$$

This line is plotted as *a* in Figure 4.2, starting at $(p^*, T^*) = (36 \text{ Torr}, 5.50^\circ\text{C} (278.65 \text{ K}))$.

$$\begin{aligned} \text{(b)} \quad \chi &= \left(\frac{30.8 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times \left(\frac{1}{T} - \frac{1}{T^*} \right) = (3705 \text{ K}) \times \left(\frac{1}{T} - \frac{1}{T^*} \right) \\ p &= p^* e^{-3705 \text{ K} \times (1/T - 1/T^*)} \end{aligned}$$

This equation is plotted as line *b* in Figure 4.2, starting from $(p^*, T^*) = (36 \text{ Torr}, 5.50^\circ\text{C} (278.65 \text{ K}))$.

$$\begin{aligned} \text{(c)} \quad \chi &= \left(\frac{41.4 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times \left(\frac{1}{T} - \frac{1}{T^*} \right) = (4980 \text{ K}) \times \left(\frac{1}{T} - \frac{1}{T^*} \right) \\ p &= p^* e^{-4980 \text{ K} \times (1/T - 1/T^*)} \end{aligned}$$

These points are plotted as line *c* in Figure 4.2, starting at $(36 \text{ Torr}, 5.50^\circ\text{C})$.

The lighter lines in Figure 4.2 represent extensions of lines *b* and *c* into regions where the liquid and solid states respectively are not stable.

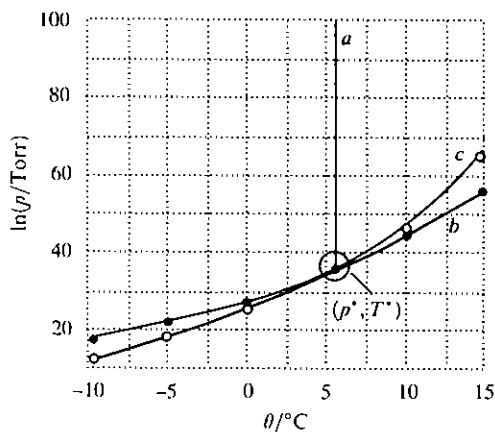


Figure 4.2

P4.12 The slope of the solid–vapor coexistence curve is given by

$$\frac{dp}{dT} = \frac{\Delta_{\text{sub}}H^\ominus}{T \Delta_{\text{sub}}V^\ominus} \quad \text{so} \quad \Delta_{\text{sub}}H^\ominus = T \Delta_{\text{sub}}V^\ominus \frac{dp}{dT}$$

The slope can be obtained by differentiating the coexistence curve graphically (Figure 4.3)

$$\frac{dp}{dT} = 4.41 \text{ Pa K}^{-1}$$

according to the exponential best fit of the data. The change in volume is the volume of the vapor

$$V_m = \frac{RT}{p} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (150 \text{ K})}{26.1 \text{ Pa}} = 47.8 \text{ m}^3$$

So

$$\Delta_{\text{sub}} H^\ominus = (150 \text{ K}) \times (47.8 \text{ m}^3) \times (4.41 \text{ Pa K}^{-1}) = 3.16 \times 10^4 \text{ J mol}^{-1} = \boxed{31.6 \text{ kJ mol}^{-1}}$$

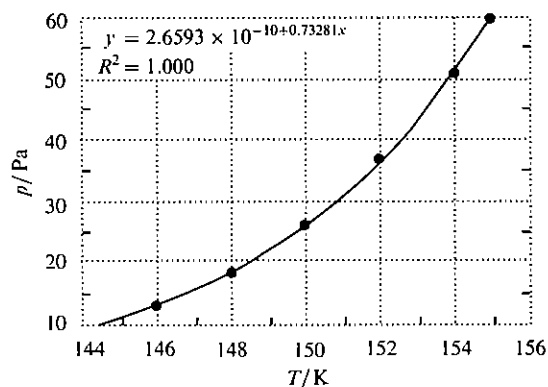


Figure 4.3

Solutions to theoretical problems

P4.14 $dH = C_p dT + V dp$ implying that $d\Delta H = \Delta C_p dT + \Delta V dp$

However, along a phase boundary dp and dT are related by

$$\frac{dp}{dT} = \frac{\Delta H}{T \Delta V} \quad [\text{Clapeyron equation, e.g. 4.6, 4.7, or 4.10}]$$

Therefore,

$$d\Delta H = \left(\Delta C_p + \Delta V \times \frac{\Delta H}{T \Delta V} \right) dT = \left(\Delta C_p + \frac{\Delta H}{T} \right) dT \quad \text{and} \quad \frac{dH}{dT} = \Delta C_p + \frac{\Delta H}{T}$$

Then, since

$$\frac{d}{dT} \left(\frac{\Delta H}{T} \right) = \frac{1}{T} \frac{d\Delta H}{dT} - \frac{\Delta H}{T^2} = \frac{1}{T} \left(\frac{d\Delta H}{dT} - \frac{\Delta H}{T} \right)$$

substituting the first result gives

$$\frac{d}{dT} \left(\frac{\Delta H}{T} \right) = \frac{\Delta C_p}{T}$$

Therefore,

$$d \left(\frac{\Delta H}{T} \right) = \frac{\Delta C_p dT}{T} = \boxed{\Delta C_p d \ln T}$$

P4.16

$$p = p_0 e^{-Mgh/RT} \text{ [Impact 11.1]}$$

$$p = p^* e^{-\chi} \quad \chi = \frac{\Delta_{\text{vap}} H}{R} \times \left(\frac{1}{T} - \frac{1}{T^*} \right) \quad [4.12]$$

Let $T^* = T_b$ the normal boiling point; then $p^* = 1$ atm. Let $T = T_h$, the boiling point at the altitude h . Take $p_0 = 1$ atm. Boiling occurs when the vapor (p) is equal to the ambient pressure, that is, when $p(T) = p(h)$, and when this is so, $T = T_h$. Therefore, since $p_0 = p^*$, $p(T) = p(h)$ implies that

$$e^{-Mgh/RT} = \exp \left\{ -\frac{\Delta_{\text{vap}} H}{R} \times \left(\frac{1}{T_h} - \frac{1}{T_b} \right) \right\}$$

It follows that

$$\frac{1}{T_h} = \frac{1}{T_b} + \frac{Mgh}{T \Delta_{\text{vap}} H}$$

where T is the ambient temperature and M the molar mass of the air. For water at 3000 m, using $M = 29 \text{ g mol}^{-1}$

$$\begin{aligned} \frac{1}{T_h} &= \frac{1}{373 \text{ K}} + \frac{(29 \times 10^{-3} \text{ kg mol}^{-1}) \times (9.81 \text{ m s}^{-2}) \times (3.000 \times 10^3 \text{ m})}{(293 \text{ K}) \times (40.7 \times 10^3 \text{ J mol}^{-1})} \\ &= \frac{1}{373 \text{ K}} + \frac{1}{1.397 \times 10^4 \text{ K}} \end{aligned}$$

Hence, $T_h = \boxed{363 \text{ K}} (90^\circ \text{C})$.

P4.18

$$(1) \quad V = V(T, p)$$

$$\begin{aligned} dV &= \left(\frac{\partial V}{\partial T} \right)_p dT + \left(\frac{\partial V}{\partial p} \right)_T dp \\ \left(\frac{\partial V}{\partial T} \right)_p &= \alpha V, \quad \left(\frac{\partial V}{\partial p} \right)_T = -\kappa_T V \end{aligned}$$

hence, $dV = \alpha V dT - \kappa_T V dp$

This equation applies to both phases 1 and 2, and since V is continuous through a second-order transition

$$\alpha_1 dT - \kappa_{T,1} dp = \alpha_2 dT - \kappa_{T,2} dp$$

$$\text{Solving for } \frac{dp}{dT} \text{ yields } \frac{dp}{dT} = \frac{\alpha_2 - \alpha_1}{\kappa_{T,2} - \kappa_{T,1}}$$

$$(2) \quad S_m = S_m(T, p)$$

$$\begin{aligned} dS_m &= \left(\frac{\partial S_m}{\partial T} \right)_p dT + \left(\frac{\partial S_m}{\partial p} \right)_T dp \\ \left(\frac{\partial S_m}{\partial T} \right)_p &= \frac{C_{p,m}}{T} \text{ [Problem 3.26]} \quad \left(\frac{\partial S_m}{\partial p} \right)_T = - \left(\frac{\partial V_m}{\partial T} \right)_p \text{ [Maxwell relation]} \\ &= -\alpha V_m \end{aligned}$$

$$\text{Thus, } dS_m = \frac{C_{p,m}}{T} dT - \alpha V_m dp$$

This relation applies to both phases. For second-order transitions both S_m and V_m are continuous through the transition, $S_{m,1} = S_{m,2}$, $V_{m,1} = V_{m,2} = V_m$, so that

$$\frac{C_{p,m,1}}{T} dT - \alpha_1 V_m dp = \frac{C_{p,m,2}}{T} dT - \alpha_2 V_m dp$$

$$\text{Solving for } \frac{dp}{dT} \text{ yields } \boxed{\frac{dp}{dT} = \frac{C_{p,m,2} - C_{p,m,1}}{TV_m(\alpha_2 - \alpha_1)}}$$

The Clapeyron equation cannot apply because both ΔV and ΔS are zero through a second-order transition, resulting in an indeterminate form 0/0.

Solutions to applications

P4.20 (a) $\Delta G_m = (n-4)\Delta_{hb}H_m - (n-2)T_m\Delta_{hb}S_m$ (1)

The enthalpy term is justified by $n-4$ independent hydrogen bonds for which each requires $\Delta_{hb}H_m$ of heat to break during melting dissociation. The entropy term is justified by $n-2$ highly ordered, but independent, structures for which each experiences an entropy increase of $\Delta_{hb}S_m$ during the melting process. According to [3.39], the enthalpy and entropy terms give a Gibbs energy change of $\Delta G = \Delta H - T\Delta S$ for a constant temperature process. Eqn (1) above has this necessary form.

(b) $\Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}}$ [3.16] yields $T_{trs} = \frac{\Delta_{trs}H}{\Delta_{trs}S}$ which here becomes

$$T_m = \frac{(n-4)\Delta_{hb}H_m}{(n-2)\Delta_{hb}S_m}$$

(c) See Figure 4.4

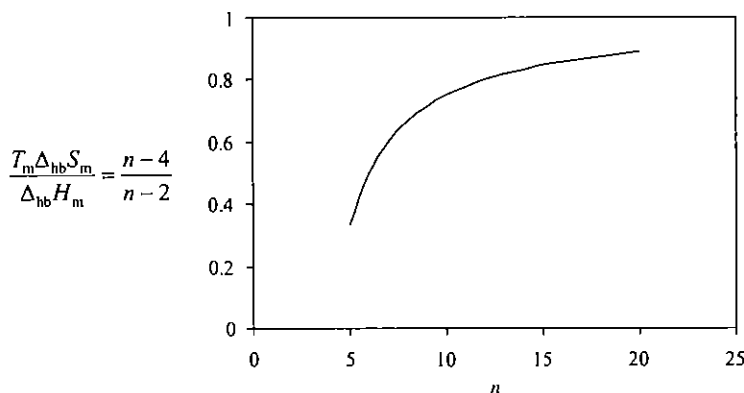


Figure 4.4

$$\begin{aligned} \text{Consider } \frac{1}{T_m} \frac{dT_m}{dn} &= \frac{\Delta_{hb}H_m}{T_m \Delta_{hb}S_m} \frac{d(T_m \Delta_{hb}S_m / \Delta_{hb}H_m)}{dn} = \left(\frac{n-2}{n-4} \right) \frac{d}{dn} \left(\frac{n-4}{n-2} \right) \\ &= \left(\frac{n-2}{n-4} \right) \left(\frac{2}{(n-2)^2} \right) = \frac{2}{(n-4)(n-2)} \end{aligned}$$

This expression will be less than 1% when $2/((n-4)(n-2)) \lesssim 0.01$ or when n equals, or is larger than the value given by $n^2 - 6n + 8 = 200$. The positive root of this quadratic is $n \cong 17$. T_m changes by about 1% or less upon addition of another amino acid residue when the polypeptide consists of 17 or more residues.

P4.22 (a) The phase boundary is plotted in Figure 4.5.

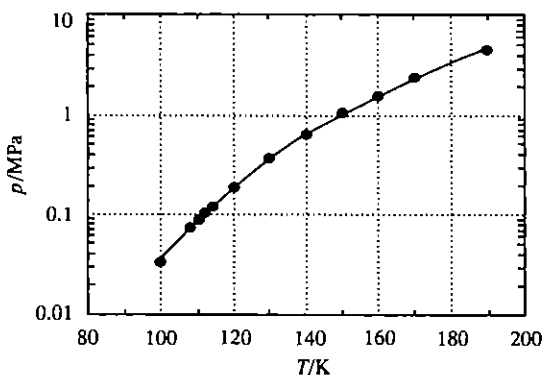


Figure 4.5

(b) The standard boiling point is the temperature at which the liquid is in equilibrium with the standard pressure of 1 bar (0.1 MPa). Interpolation of the plotted points gives $T_b = 112 \text{ K}$

(c) The slope of the liquid–vapor coexistence curve is given by

$$\frac{dp}{dT} = \frac{\Delta_{\text{vap}}H}{T\Delta_{\text{vap}}V} \quad \text{so} \quad \Delta_{\text{vap}}H = (T\Delta_{\text{vap}}V) \frac{dp}{dT}$$

The slope can be obtained graphically or by fitting the points nearest the boiling point. Then $dp/dT = 8.14 \times 10^{-3} \text{ MPa K}^{-1}$, so

$$\Delta_{\text{vap}}H = (112 \text{ K}) \times \left(\frac{(8.89 - 0.0380) \text{ dm}^3 \text{ mol}^{-1}}{1000 \text{ dm}^3 \text{ m}^3} \right) \times (8.14 \text{ k Pa K}^{-1}) = 8.07 \text{ kJ mol}^{-1}$$

5

Simple mixtures

Answers to discussion questions

- D5.2** For a component in an ideal solution, Raoult's law is: $p = xp^*$. For real solutions, the activity, a , replaces the mole fraction, x , and Raoult's law becomes $p = ap^*$.
- D5.4** 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 Figure 5.21 of the text. Both of these effects can be explained by the lowering of the vapor 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.
- D5.6** 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 γ_{\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 *Further Information 5.1* 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 $\ln \gamma_{\pm}$.

Solutions to exercises

E5.1(b) Total volume $V = n_A V_A + n_B V_B = n(x_A V_A + x_B V_B)$

Total mass $m = n_A M_A + n_B M_B$

$$= n(x_A M_A + (1 - x_A) M_B) \quad \text{where } n = n_A + n_B$$

$$\frac{m}{x_A M_A + (1 - x_A) M_B} = n$$

$$n = \frac{1.000 \text{ kg}(10^3 \text{ g/kg})}{(0.3713) \times (241.1 \text{ g/mol}) + (1 - 0.3713) \times (198.2 \text{ g/mol})} = 4.670\bar{1} \text{ mol}$$

$$\begin{aligned} V &= n(x_A V_A + x_B V_B) \\ &= (4.670\bar{1} \text{ mol}) \times [(0.3713) \times (188.2 \text{ cm}^3 \text{ mol}^{-1}) + (1 - 0.3713) \times (176.14 \text{ cm}^3 \text{ mol}^{-1})] \\ &= \boxed{843.5 \text{ cm}^3} \end{aligned}$$

E5.2(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 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 $(0.20) \times (96.87 \text{ g}) = 19.374 \text{ g}$ is ethanol and $(0.80) \times (96.87 \text{ g}) = 77.496 \text{ g}$ is water.

$$n_A = \frac{77.496 \text{ g}}{18.02 \text{ g mol}^{-1}} = 4.30 \text{ mol H}_2\text{O}$$

$$n_B = \frac{19.374 \text{ g}}{46.07 \text{ g mol}^{-1}} = 0.4205 \text{ mol ethanol}$$

$$\begin{aligned} \frac{V - n_B V_B}{n_A} &= V_A = \frac{100 \text{ cm}^3 - (0.4205 \text{ mol}) \times (52.2 \text{ cm}^3 \text{ mol}^{-1})}{4.30 \text{ mol}} \\ &= 18.15 \text{ cm}^3 \\ &= \boxed{18 \text{ cm}^3} \end{aligned}$$

E5.3(b) Check that $p_B/x_B = \text{a constant } (K_B)$

x_B	0.010	0.015	0.020
$(p_B/x_B)/\text{kPa}$	8.2×10^3	8.1×10^3	8.3×10^3

$$K_B = p/x, \text{ average value is } \boxed{8.2 \times 10^3 \text{ kPa}}$$

E5.4(b) In Exercise 5.3(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.

$$m(A) = 1000 \text{ g}, \text{ corresponding to } n(A) = \frac{1000 \text{ g}}{74.1 \text{ g mol}^{-1}} = 13.50 \text{ mol} \quad n(B) = 0.25 \text{ mol}$$

Therefore,

$$x_B = \frac{0.25 \text{ mol}}{0.25 \text{ mol} + 13.50 \text{ mol}} = 0.0182$$

using $K_B = 8.2 \times 10^3 \text{ kPa}$ [Exercise 5.3(b)]

$$p = 0.0182 \times 8.2 \times 10^3 \text{ kPa} = \boxed{1.5 \times 10^2 \text{ kPa}}$$

E5.5(b) We assume that the solvent, 2-propanol, is ideal and obeys Raoult's law.

$$x_A(\text{solvent}) = p/p^* = \frac{49.62}{50.00} = 0.9924$$

$$M_A(\text{C}_3\text{H}_8\text{O}) = 60.096 \text{ g mol}^{-1}$$

$$n_A = \frac{250 \text{ g}}{60.096 \text{ g mol}^{-1}} = 4.1600 \text{ mol}$$

$$x_A = \frac{n_A}{n_A + n_B} \quad n_A + n_B = \frac{n_A}{x_A}$$

$$n_B = n_A \left(\frac{1}{x_A} - 1 \right)$$

$$= 4.1600 \text{ mol} \left(\frac{1}{0.9924} - 1 \right) = 3.186 \times 10^{-2} \text{ mol}$$

$$M_B = \frac{8.69 \text{ g}}{3.186 \times 10^{-2} \text{ mol}} = 273 \text{ g mol}^{-1} = \boxed{270 \text{ g mol}^{-1}}$$

E5.6(b) $K_f = 6.94$ for naphthalene

$$M_B = \frac{\text{mass of B}}{n_B}$$

$$n_B = \text{mass of naphthalene} \cdot b_B$$

$$b_B = \frac{\Delta T}{K_f} \quad \text{so} \quad M_B = \frac{(\text{mass of B}) \times K_f}{(\text{mass of naphthalene}) \times \Delta T}$$

$$M_B = \frac{(5.00 \text{ g}) \times (6.94 \text{ K kg mol}^{-1})}{(0.250 \text{ kg}) \times (0.780 \text{ K})} = \boxed{178 \text{ g mol}^{-1}}$$

E5.7(b)

$$\Delta T = K_f b_B \quad \text{and} \quad b_B = \frac{n_B}{\text{mass of water}} = \frac{n_B}{V \rho}$$

$$\rho = 10^3 \text{ kg m}^{-3} \quad (\text{density of solution} \approx \text{density of water})$$

$$n_B = \frac{\Pi V}{RT} \quad \Delta T = K_f \frac{\Pi}{RT \rho} \quad K_f = 1.86 \text{ K mol}^{-1} \text{ kg}$$

$$\Delta T = \frac{(1.86 \text{ K kg mol}^{-1}) \times (99 \times 10^3 \text{ Pa})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (288 \text{ K}) \times (10^3 \text{ kg m}^{-3})} = 7.7 \times 10^{-2} \text{ K}$$

$$T_f = \boxed{-0.077^\circ\text{C}}$$

E5.8(b)

$$\Delta_{\text{mix}} G = nRT(x_A \ln x_A + x_B \ln x_B)$$

$$n_{\text{Ar}} = n_{\text{Ne}}, \quad x_{\text{Ar}} = x_{\text{Ne}} = 0.5, \quad n = n_{\text{Ar}} + n_{\text{Ne}} = \frac{pV}{RT}$$

$$\Delta_{\text{mix}} G = pV \left(\frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2} \right) = -pV \ln 2$$

$$= -(100 \times 10^3 \text{ Pa}) \times (250 \text{ cm}^3) \left(\frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \right) \ln 2$$

$$= -17.3 \text{ Pa m}^3 = -17.3 \text{ J}$$

$$\Delta_{\text{mix}} S = \frac{-\Delta_{\text{mix}} G}{T} = \frac{17.3 \text{ J}}{273 \text{ K}} = \boxed{6.34 \times 10^{-2} \text{ J K}^{-1}}$$

$$\text{E5.9(b)} \quad \Delta_{\text{mix}}G = nRT \sum_J x_J \ln x_J \quad [5.18]$$

$$\Delta_{\text{mix}}S = -nR \sum_J x_J \ln x_J \quad [5.19] = \frac{-\Delta_{\text{mix}}G}{T}$$

$$n = 1.00 \text{ mol} + 1.00 \text{ mol} = 2.00 \text{ mol}$$

$$x(\text{Hex}) = x(\text{Hep}) = 0.500$$

Therefore,

$$\begin{aligned} \Delta_{\text{mix}}G &= (2.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (0.500 \ln 0.500 + 0.500 \ln 0.500) \\ &= \boxed{-3.43 \text{ kJ}} \\ \Delta_{\text{mix}}S &= \frac{+3.43 \text{ kJ}}{298 \text{ K}} = \boxed{+11.5 \text{ J K}^{-1}} \end{aligned}$$

$\Delta_{\text{mix}}H$ for an ideal solution is zero as it is for a solution of perfect gases [7.20]. It can be demonstrated from

$$\Delta_{\text{mix}}H = \Delta_{\text{mix}}G + T\Delta_{\text{mix}}S = (-3.43 \times 10^3 \text{ J}) + (298 \text{ K}) \times (11.5 \text{ J K}^{-1}) = \boxed{0}$$

E5.10(b) Benzene and ethylbenzene form nearly ideal solutions, so

$$\Delta_{\text{mix}}S = -nR(x_A \ln x_A + x_B \ln x_B)$$

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 $x_B = 1 - x_A$ so

$$\Delta_{\text{mix}}S = -nR(x_A \ln x_A + (1 - x_A) \ln(1 - x_A))$$

$$\text{use } \frac{d \ln x}{dx} = \frac{1}{x}:$$

$$\begin{aligned} \frac{d}{dx}(\Delta_{\text{mix}}S) &= -nR(\ln x_A + 1 - \ln(1 - x_A) - 1) = -nR \ln \frac{x_A}{1 - x_A} \\ &= 0 \quad \text{when } x_A = \frac{1}{2} \end{aligned}$$

Thus the maximum entropy of mixing is attained by mixing equal molar amounts of two components.

$$\begin{aligned} \frac{n_B}{n_E} = 1 &= \frac{m_B/M_B}{m_E/M_E} \times \frac{m_E}{m_B} = \frac{M_E}{M_B} = \frac{106.169}{78.115} = 1.3591 \\ \frac{m_B}{m_E} &= \boxed{0.7358} \end{aligned}$$

E5.11(b) With concentrations expressed in molalities, Henry's law [5.26] becomes $p_B = b_B K$.

Solving for b , the molality, we have $b_B = p_B/K = x p_{\text{total}}/K$ and $p_{\text{total}} = p_{\text{atm}}$

For N_2 , $K = 1.56 \times 10^5 \text{ kPa kg mol}^{-1}$ [Table 5.1]

$$b = \frac{0.78 \times 101.3 \text{ kPa}}{1.56 \times 10^5 \text{ kPa kg mol}^{-1}} = \boxed{0.51 \text{ mmol kg}^{-1}}$$

For O_2 , $K = 7.92 \times 10^4 \text{ kPa kg mol}^{-1}$ [Table 5.1]

$$b = \frac{0.21 \times 101.3 \text{ kPa}}{7.92 \times 10^4 \text{ kPa kg mol}^{-1}} = \boxed{0.27 \text{ mmol kg}^{-1}}$$

E5.12(b)
$$b_{\text{B}} = \frac{p_{\text{B}}}{K} = \frac{2.0 \times 101.3 \text{ kPa}}{3.01 \times 10^3 \text{ kPa kg mol}^{-1}} = 0.067 \text{ mol kg}^{-1}$$

The molality will be about $0.067 \text{ mol kg}^{-1}$ and, since molalities and molar concentrations for dilute aqueous solutions are approximately equal, the molar concentration is about $\boxed{0.067 \text{ mol dm}^{-3}}$

E5.13(b) The procedure here is identical to Exercise 5.13(a).

$$\begin{aligned} \ln x_{\text{B}} &= \frac{\Delta_{\text{fus}} H}{R} \times \left(\frac{1}{T^*} - \frac{1}{T} \right) \quad [5.39; \text{B, the solute, is lead}] \\ &= \left(\frac{5.2 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times \left(\frac{1}{600 \text{ K}} - \frac{1}{553 \text{ K}} \right) \\ &= -0.088\bar{6}, \text{ implying that } x_{\text{B}} = 0.92 \end{aligned}$$

$$x_{\text{B}} = \frac{n(\text{Pb})}{n(\text{Pb}) + n(\text{Bi})}, \text{ implying that } n(\text{Pb}) = \frac{x_{\text{B}} n(\text{Bi})}{1 - x_{\text{B}}}$$

For 1 kg of bismuth, $n(\text{Bi}) = \frac{1000 \text{ g}}{208.98 \text{ g mol}^{-1}} = 4.785 \text{ mol}$

Hence, the amount of lead that dissolves in 1 kg of bismuth is

$$n(\text{Pb}) = \frac{(0.92) \times (4.785 \text{ mol})}{1 - 0.92} = 55 \text{ mol}, \text{ or } \boxed{11 \text{ kg}}$$

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 5.39 is based are not likely to apply. The answer above must then be considered an order of magnitude result only.

E5.14(b) Proceed as in Exercise 5.14(a). The data are plotted in Figure 5.1, and the slope of the line is $1.78 \text{ cm}/(\text{mg cm}^{-3}) = 1.78 \text{ cm}/(\text{g dm}^{-3}) = 1.78 \times 10^{-2} \text{ m}^4 \text{ kg}^{-1}$.

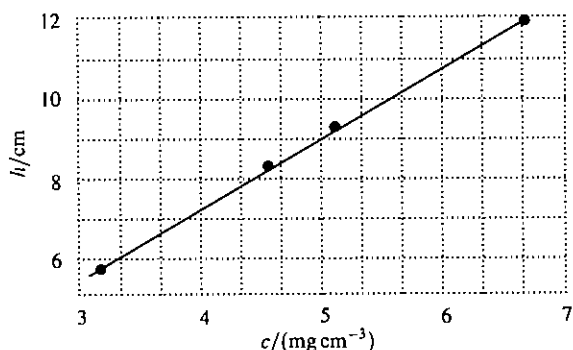


Figure 5.1

Therefore,

$$M = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293.15 \text{ K})}{(1.000 \times 10^3 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2}) \times (1.78 \times 10^{-2} \text{ m}^4 \text{ kg}^{-1})} = \boxed{14.0 \text{ kg mol}^{-1}}$$

E5.15(b) Let A = water and B = solute.

$$a_A = \frac{p_A}{p_A^*} [5.43] = \frac{0.02239 \text{ atm}}{0.02308 \text{ atm}} = \boxed{0.9701}$$

$$\gamma_A = \frac{a_A}{x_A} \quad \text{and} \quad x_A = \frac{n_A}{n_A + n_B}$$

$$n_A = \frac{0.920 \text{ kg}}{0.01802 \text{ kg mol}^{-1}} = 51.05 \text{ mol} \quad \text{and} \quad n_B = \frac{0.122 \text{ kg}}{0.241 \text{ kg mol}^{-1}} = 0.506 \text{ mol}$$

$$x_A = \frac{51.05}{51.05 + 0.506} = 0.990 \quad \text{and} \quad \gamma_A = \frac{0.9701}{0.990} = \boxed{0.980}$$

E5.16(b) B = Benzene $\mu_B(l) = \mu_B^*(l) + RT \ln x_B$ [5.25, ideal solution]

$$RT \ln x_B = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (353.3 \text{ K}) \times (\ln 0.30) = \boxed{-3536 \text{ J mol}^{-1}}$$

Thus, its chemical potential is lowered by this amount.

$$p_B = a_B p_B^* [5.43] = \gamma_B x_B p_B^* = (0.93) \times (0.30) \times (760 \text{ Torr}) = \boxed{212 \text{ Torr}}$$

Question. What is the lowering of the chemical potential in the nonideal solution with $\gamma = 0.93$?

E5.17(b)
$$y_A = \frac{p_A}{p_A + p_B} = \frac{p_A}{101.3 \text{ kPa}} = 0.314$$

$$p_A = (101.3 \text{ kPa}) \times (0.314) = 31.8 \text{ kPa}$$

$$p_B = 101.3 \text{ kPa} - 31.8 \text{ kPa} = 69.5 \text{ kPa}$$

$$a_A = \frac{p_A}{p_A^*} = \frac{31.8 \text{ kPa}}{73.0 \text{ kPa}} = \boxed{0.436}$$

$$a_B = \frac{p_B}{p_B^*} = \frac{69.5 \text{ kPa}}{92.1 \text{ kPa}} = \boxed{0.755}$$

$$\gamma_A = \frac{a_A}{x_A} = \frac{0.436}{0.220} = \boxed{1.98}$$

$$\gamma_B = \frac{a_B}{x_B} = \frac{0.755}{0.780} = \boxed{0.968}$$

E5.18(b) $I = \frac{1}{2} \sum_i (b_i/b^\ominus) z_i^2$ [5.71]

and for an M_pX_q salt, $b_+/b^\ominus = pb/b^\ominus$, $b_-/b^\ominus = qb/b^\ominus$, so

$$I = \frac{1}{2} (pz_+^2 + qz_-^2) b/b^\ominus$$

$$\begin{aligned} I &= I(\text{K}_3[\text{Fe}(\text{CN})_6]) + I(\text{KCl}) + I(\text{NaBr}) = \frac{1}{2} (3 + 3^2) \frac{b(\text{K}_3[\text{Fe}(\text{CN})_6])}{b^\ominus} + \frac{b(\text{KCl})}{b^\ominus} + \frac{b(\text{NaBr})}{b^\ominus} \\ &= (6) \times (0.040) + (0.030) + (0.050) = \boxed{0.320} \end{aligned}$$

Question. Can you establish that the statement in the comment following the solution to Exercise 5.18(a) holds for the solution of this exercise?

E5.19(b) $I = I(\text{KNO}_3) = \frac{b}{b^\ominus} (\text{KNO}_3) = 0.110$

Therefore, the ionic strengths of the added salts must be 0.890.

(a) $I(\text{KNO}_3) = \frac{b}{b^\ominus}$, so $b(\text{KNO}_3) = 0.890 \text{ mol kg}^{-1}$
and $(0.890 \text{ mol kg}^{-1}) \times (0.500 \text{ kg}) = 0.445 \text{ mol KNO}_3$
So $(0.445 \text{ mol}) \times (101.11 \text{ g mol}^{-1}) = 45.0 \text{ g KNO}_3$ must be added.

(b) $I(\text{Ba}(\text{NO}_3)_2) = \frac{1}{2} (2^2 + 2 \times 1^2) \frac{b}{b^\ominus} = 3 \frac{b}{b^\ominus} = 0.890$

$$b = \frac{0.890}{3} b^\ominus = 0.296\bar{7} \text{ mol kg}^{-1}$$

and $(0.296\bar{7} \text{ mol kg}^{-1}) \times (0.500 \text{ kg}) = 0.148\bar{4} \text{ mol Ba}(\text{NO}_3)_2$

So $(0.148\bar{4} \text{ mol}) \times (261.32 \text{ g mol}^{-1}) = \boxed{38.8 \text{ g Ba}(\text{NO}_3)_2}$

E5.20(b) Since the solutions are dilute, use the Debye-Hückel limiting law

$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2}$$

$$\begin{aligned} I &= \frac{1}{2} \sum_i z_i^2 (b_i/b^\ominus) = \frac{1}{2} \{1 \times (0.020) + 1 \times (0.020) + 4 \times (0.035) + 2 \times (0.035)\} \\ &= 0.125 \end{aligned}$$

$$\log \gamma_{\pm} = -1 \times 1 \times 0.509 \times (0.125)^{1/2} = -0.1799\bar{6}$$

(For NaCl) $\gamma_{\pm} = 10^{-0.1799\bar{6}} = \boxed{0.661}$

E5.21(b) The extended Debye–Hückel law is $\log \gamma_{\pm} = -\frac{A|z_+z_-|I^{1/2}}{1 + BI^{1/2}}$

Solving for B

$$B = -\left(\frac{1}{I^{1/2}} + \frac{A|z_+z_-|}{\log \gamma_{\pm}}\right) = -\left(\frac{1}{(b/b^{\circ})^{1/2}} + \frac{0.509}{\log \gamma_{\pm}}\right)$$

Draw up the following table

$b/(\text{mol kg}^{-1})$	5.0×10^{-3}	10.0×10^{-3}	50.0×10^{-3}
γ_{\pm}	0.927	0.902	0.816
B	1.32	1.36	1.29

$$B = \boxed{1.3}$$

Solutions to problems

Solutions to numerical problems

P5.2

$$\begin{aligned} V_A &= \left(\frac{\partial V}{\partial n_A}\right)_{n_B} [5.1, A = \text{NaCl(aq)}, B = \text{water}] = \left(\frac{\partial V}{\partial b}\right)_{n(\text{H}_2\text{O})} \text{mol}^{-1} [\text{with } b \equiv b/(\text{mol kg}^{-1})] \\ &= \left((16.62) + \frac{3}{2} \times (1.77) \times (b)^{1/2} + (2) \times (0.12b)\right) \text{cm}^3 \text{mol}^{-1} \\ &= 17.5 \text{cm}^3 \text{mol}^{-1} \text{ when } b = 0.100 \end{aligned}$$

For a solution consisting of 0.100 mol NaCl and 1.000 kg of water, corresponding to 55.49 mol H₂O, the total volume is given both by

$$\begin{aligned} V &= [(1003) + (16.62) + (0.100) \times (1.77) \times (0.100)^{3/2} + (0.12) \times (0.100)^2] \text{cm}^3 \\ &= 1004.7 \text{cm}^3 \end{aligned}$$

and by

$$V = n(\text{NaCl})V_{\text{NaCl}} + n(\text{H}_2\text{O})V_{\text{H}_2\text{O}} [5.3] = (0.100 \text{ mol}) \times (17.5 \text{cm}^3 \text{mol}^{-1}) + (55.49 \text{ mol}) \times V_{\text{H}_2\text{O}}$$

$$\text{Therefore, } V_{\text{H}_2\text{O}} = \frac{1004.7 \text{cm}^3 - 1.75 \text{cm}^3}{55.49 \text{mol}} = \boxed{18.07 \text{cm}^3 \text{mol}^{-1}}$$

COMMENT. Within four significant figures, this result is the same as the molar volume of pure water at 25 °C.

Question. How does the partial molar volume of NaCl(aq) in this solution compare to molar volume of pure solid NaCl?

P5.4 Let $m(\text{CuSO}_4)$, which is the mass of CuSO₄ dissolved in 100 g of solution, be represented by

$$w = \frac{100 m_B}{m_A + m_B} = \text{mass percent of CuSO}_4$$

where m_B is the mass of CuSO_4 and m_A is the mass of water. Then using

$$\rho = \frac{m_A + m_B}{V} \quad n_A = \frac{m_A}{M_A}$$

the procedure runs as follows

$$\begin{aligned} V_A &= \left(\frac{\partial V}{\partial n_A} \right)_{n_B} = \left(\frac{\partial V}{\partial m_A} \right)_B M_A \\ &= \frac{\partial}{\partial m_A} \left(\frac{m_A + m_B}{\rho} \right) \times M_A \\ &= \frac{M_A}{\rho} + (m_A + m_B) M_A \frac{\partial}{\partial m_A} \frac{1}{\rho} \\ \frac{\partial}{\partial m_A} \frac{1}{\rho} &= \left(\frac{\partial w}{\partial m_A} \right) \frac{\partial}{\partial w} \frac{1}{\rho} = \frac{-w}{m_A + m_B} \frac{\partial}{\partial w} \frac{1}{\rho} \end{aligned}$$

Therefore,

$$V_A = \frac{M_A}{\rho} - w M_A \frac{\partial}{\partial w} \frac{1}{\rho}$$

and hence

$$\frac{1}{\rho} = \frac{V_A}{M_A} + w \frac{d}{dw} \left(\frac{1}{\rho} \right)$$

Therefore, plot $1/\rho$ against w and extrapolate the tangent to $w = 100$ to obtain V_B/M_B . For the actual procedure, draw up the following table

w	5	10	15	20
$\rho/(\text{g cm}^{-3})$	1.051	1.107	1.167	1.230
$1/(\rho/\text{g cm}^{-3})$	0.951	0.903	0.857	0.813

The values of $1/\rho$ are plotted against w in Figure 5.2.

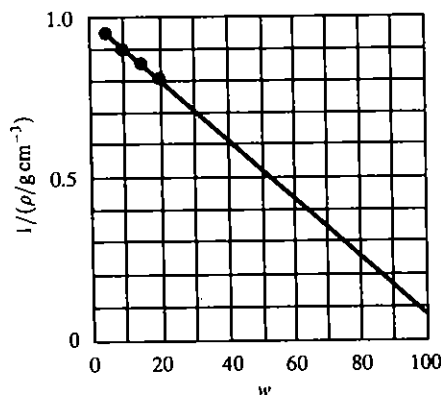


Figure 5.2

Four tangents are drawn to the curve at the four values of w . As the curve is a straight line to within the precision of the data, all four tangents are coincident and all four intercepts are equal at $0.075 \text{ g}^{-1} \text{ cm}^3$. Thus

$$V(\text{CuSO}_4) = 0.075 \text{ g}^{-1} \text{ cm}^3 \times 159.6 \text{ g mol}^{-1} = \boxed{12.0 \text{ cm}^3 \text{ mol}^{-1}}$$

P5.6

$$\Delta T = \frac{RT_f^{*2} x_B}{\Delta_{\text{fus}} H} [5.36], \quad x_B \approx \frac{n_B}{n(\text{CH}_3\text{COOH})} = \frac{n_B M(\text{CH}_3\text{COOH})}{1000 \text{ g}}$$

$$\begin{aligned} \text{Hence, } \Delta T &= \frac{n_B M R T_f^{*2}}{\Delta_{\text{fus}} H \times 1000 \text{ g}} = \frac{b_B M R T_f^{*2}}{\Delta_{\text{fus}} H} [b_B: \text{molality of solution}] \\ &= b_B \times \left(\frac{(0.06005 \text{ kg mol}^{-1}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (290 \text{ K})^2}{11.4 \times 10^3 \text{ J mol}^{-1}} \right) \\ &= 3.68 \text{ K} \times b_B / (\text{mol kg}^{-1}) \end{aligned}$$

Giving for b_B , the apparent molality,

$$b_B = \nu b_B^0 = \frac{\Delta T}{3.68 \text{ K}} \text{ mol kg}^{-1}$$

where b_B^0 is the actual molality and ν may be interpreted as the number of ions in solution per one formula unit of KCl. The apparent molar mass of KCl can be determined from the apparent molality by the relation

$$M_B(\text{apparent}) = \frac{b_B^0}{b_B} \times M_B^0 = \frac{1}{\nu} \times M_B^0 = \frac{1}{\nu} \times (74.56 \text{ g mol}^{-1})$$

where M_B^0 is the actual molar mass of KCl.

We can draw up the following table from the data.

$b_B^0 / (\text{mol kg}^{-1})$	0.015	0.037	0.077	0.295	0.602
$\Delta T / \text{K}$	0.115	0.295	0.470	1.381	2.67
$b_B / (\text{mol kg}^{-1})$	0.0312	0.0802	0.128	0.375	0.726
$\nu = b_B / b_B^0$	2.1	2.2	1.7	1.3	1.2
$M_B(\text{app}) / (\text{g mol}^{-1})$	26	34	44	57	62

A possible explanation is that the dissociation of KCl into ions is complete at the lower concentrations but incomplete at the higher concentrations. Values of ν greater than 2 are hard to explain, but they could be a result of the approximations involved in obtaining equation 5.36.

See the original reference for further information about the interpretation of the data.

P5.8

- (a) On a Raoult's law basis, $a = p/p^*$, $a = \gamma x$, and $\gamma = p/xp^*$. On a Henry's law basis, $a = p/K$, and $\gamma = p/xK$. The vapor pressures of the pure components are given in the table of data and are: $p_I^* = 47.12 \text{ kPa}$, $p_A^* = 37.38 \text{ kPa}$.

- (b) The Henry's law constants are determined by plotting the data and extrapolating the low concentration data to $x = 1$. The data are plotted in Figure 5.3. K_A and K_I are estimated as graphical tangents at $x_I = 1$ and $x_I = 0$, respectively. The values obtained are: $K_A = 60.0 \text{ kPa}$ and $K_I = 62.0 \text{ kPa}$

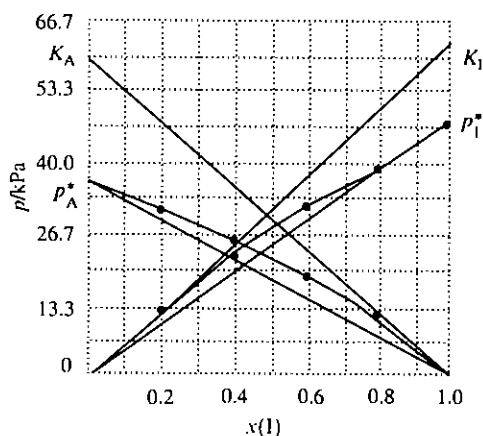


Figure 5.3

Then draw up the following table based on the values of the partial pressures obtained from the plots at the values of x_I given in the figure.

x_I	0	0.2	0.4	0.6	0.8	1.0
p_I/kPa	0	12.3	22.0	30.7	38.7	47.12^\ddagger
p_A/kPa	37.38^\ddagger	30.7	24.7	18.0	10.7	0
$\gamma_I(\text{R})$	—	1.30	1.17	1.09	1.03	$1.000[p_I/x_I p_I^*]$
$\gamma_A(\text{R})$	1.000	1.03	1.10	1.20	1.43	$— [p_A/x_A p_A^*]$
$\gamma_I(\text{H})$	1.000	0.990	0.887	0.824	0.780	$0.760[p_I/x_I K_I^*]$

‡ The value of p_A^* ; ‡ the value of p_I^* .

Question. In this problem both I and A were treated as solvents, but only I as a solute. Extend the table by including a row for $\gamma_A(\text{H})$.

P5.10 The partial molar volume of cyclohexane is

$$V_c = \left(\frac{\partial V}{\partial n_c} \right)_{p, T, n_2}$$

A similar expression holds for V_p . V_c can be evaluated graphically by plotting V against n_c and finding the slope at the desired point. In a similar manner, V_p can be evaluated by plotting V against n_p . To find V_c , V is needed at a variety of n_c while holding n_p constant, say at 1.0000 mol; likewise to find V_p , V is needed at a variety of n_p while holding n_c constant. The mole fraction in this system is

$$x_c = \frac{n_c}{n_c + n_p} \quad \text{so } n_c = \frac{x_c n_p}{1 - x_c}$$

From n_c and n_p , the mass of the sample can be calculated, and the volume can be calculated from

$$V = \frac{m}{\rho} = \frac{n_c M_c + n_p M_p}{\rho}$$

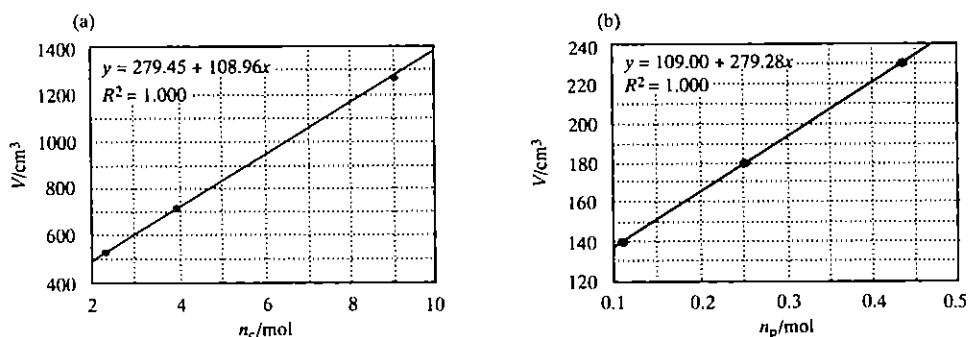


Figure 5.4

The following table is drawn up

$n_c/\text{mol}(n_p = 1)$	V/cm^3	x_c	$\rho/\text{g cm}^{-3}$	$n_p/\text{mol}(n_c = 1)$	V/cm^3
2.295	529.4	0.6965	0.7661	0.4358	230.7
3.970	712.2	0.7988	0.7674	0.2519	179.4
9.040	1264	0.9004	0.7697	0.1106	139.9

These values are plotted in Figures 5.4(a) and (b).

These plots show no curvature, so in this case, perhaps due to the limited number of data points, the molar volumes are independent of the mole numbers and are

$$V_c = 109.0 \text{ cm}^3 \text{ mol}^{-1} \quad \text{and} \quad V_p = 279.3 \text{ cm}^3 \text{ mol}^{-1}$$

P5.12 The activity of a solvent is

$$a_A = \frac{p_A}{p_A^*} = x_A \gamma_A$$

so the activity coefficient is

$$\gamma_A = \frac{p_A}{x_A p_A^*} = \frac{y_A p}{x_A p_A^*}$$

where the last equality applies Dalton's law of partial pressures to the vapor phase.

Substituting the data, the following table of results is obtained.

p/kPa	x_T	y_T	γ_T	γ_E
23.40	0.000	0.000		
21.75	0.129	0.065	0.418	0.998
20.25	0.228	0.145	0.490	1.031
18.75	0.353	0.285	0.576	1.023
18.15	0.511	0.535	0.723	0.920
20.25	0.700	0.805	0.885	0.725
22.50	0.810	0.915	0.966	0.497
26.30	1.000	1.000		

- P5.14** $S = S_0 e^{\tau/T}$ may be written in the form $\ln S = \ln S_0 + (\tau/T)$, which indicates that a plot of $\ln S$ against $1/T$ should be linear with slope τ and intercept $\ln S_0$. Linear regression analysis gives $\tau = 165 \text{ K}$, standard deviation = 2 K

$$\ln(S_0/\text{mol dm}^{-3}) = 2.990, \text{ standard deviation} = 0.007; S_0 = e^{2.990} \text{ mol dm}^{-3} = 19.89 \text{ mol dm}^{-3}$$

$$R = 0.99978$$

The linear regression explains 99.98 percent of the variation.

Equation 5.39 is

$$x_B = e^{-\left(\frac{\Delta_{\text{fus}}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right)} = e^{-\Delta_{\text{fus}}H/RT} e^{\Delta_{\text{fus}}H/RT^*}$$

Comparing to $S = S_0 e^{\tau/T}$, we see that

$$S_0 = e^{-\Delta_{\text{fus}}H/RT^*}$$

where T^* is the normal melting point of the solute and $\Delta_{\text{fus}}H$ is its heat of fusion $\tau = \Delta_{\text{fus}}H/R$

- P5.16** According to the Debye-Hückel limiting law

$$\log \gamma_{\pm} = -0.509 |z_+ z_-| I^{1/2} = -0.509 \left(\frac{b}{b^{\ominus}}\right)^{1/2} \quad [5.71]$$

We draw up the following table

$b/(\text{mmol kg}^{-1})$	1.0	2.0	5.0	10.0	20.0
$I^{1/2}$	0.032	0.045	0.071	0.100	0.141
$\gamma_{\pm}(\text{calc})$	0.964	0.949	0.920	0.889	0.847
$\gamma_{\pm}(\text{exp})$	0.9649	0.9519	0.9275	0.9024	0.8712
$\log \gamma_{\pm}(\text{calc})$	-0.0161	-0.0228	-0.0360	-0.0509	-0.0720
$\log \gamma_{\pm}(\text{exp})$	-0.0155	-0.0214	-0.0327	-0.0446	-0.0599

The points are plotted against $I^{1/2}$ in Figure 5.5. Note that the limiting slopes of the calculated and experimental curves coincide. A sufficiently good value of B in the extended Debye-Hückel law may be obtained by assuming that the constant A in the extended law is the same as A in the limiting law. Using the data at $20.0 \text{ mmol kg}^{-1}$ we may solve for B .

$$B = -\frac{A}{\log \gamma_{\pm}} - \frac{1}{I^{1/2}} = -\frac{0.509}{(-0.0599)} - \frac{1}{0.141} = 1.405$$

Thus,

$$\log \gamma_{\pm} = -\frac{0.509 I^{1/2}}{1 + 1.405 I^{1/2}}$$

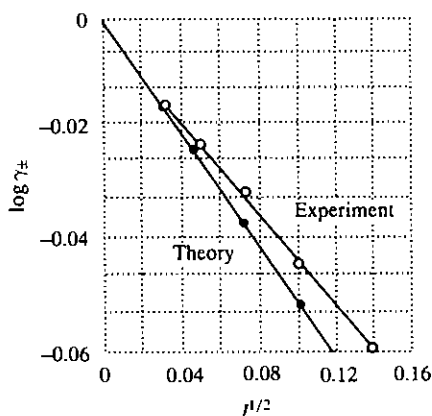


Figure 5.5

In order to determine whether or not the fit is improved, we use the data at $10.0 \text{ mmol kg}^{-1}$

$$\log \gamma_{\pm} = \frac{-(0.509) \times (0.100)}{(1) + (1.405) \times (0.100)} = -0.0446$$

which fits the data almost exactly. The fits to the other data points will also be almost exact.

Solutions to theoretical problems

P5.18 $x_A d\mu_A + x_B d\mu_B = 0$ [5.12, Gibbs–Duhem equation]

Therefore, after dividing through by dx_A

$$x_A \left(\frac{\partial \mu_A}{\partial x_A} \right)_{p,T} + x_B \left(\frac{\partial \mu_B}{\partial x_A} \right)_{p,T} = 0$$

or, since $dx_B = -dx_A$, as $x_A + x_B = 1$

$$x_A \left(\frac{\partial \mu_A}{\partial x_A} \right)_{p,T} - x_B \left(\frac{\partial \mu_B}{\partial x_B} \right)_{p,T} = 0$$

$$\text{or, } \left(\frac{\partial \mu_A}{\partial \ln x_A} \right)_{p,T} = \left(\frac{\partial \mu_B}{\partial \ln x_B} \right)_{p,T} \left[d \ln x = \frac{dx}{x} \right]$$

$$\text{Then, since } \mu = \mu^\ominus + RT \ln \frac{f}{p^\ominus}, \left(\frac{\partial \ln f_A}{\partial \ln x_A} \right)_{p,T} = \left(\frac{\partial \ln f_B}{\partial \ln x_B} \right)_{p,T}$$

$$\text{On replacing } f \text{ by } p, \left(\frac{\partial \ln p_A}{\partial \ln x_A} \right)_{p,T} = \left(\frac{\partial \ln p_B}{\partial \ln x_B} \right)_{p,T}$$

If A satisfies Raoult's law, we can write $p_A = x_A p_A^*$, which implies that

$$\left(\frac{\partial \ln p_A}{\partial \ln x_A} \right)_{p,T} = \frac{\partial \ln x_A}{\partial \ln x_A} + \frac{\partial \ln p_A^*}{\partial \ln x_A} = 1 + 0$$

Therefore, $\left(\frac{\partial \ln p_B}{\partial \ln x_B}\right)_{p,T} = 1$

which is satisfied if $p_B = x_B p_B$ (by integration, or inspection). Hence, if A satisfies Raoult's law, so does B.

P5.20 $\ln x_A = -\Delta_{\text{fus}}G/RT$ (Section 5.5 analogous to equation for $\ln x_B$ used in derivation of eqn 5.39)

$$\frac{d \ln x_A}{dT} = -\frac{1}{R} \times \frac{d}{dT} \left(\frac{\Delta_{\text{fus}}G}{T} \right) \quad [\text{Gibbs-Helmholtz equation}]$$

$$\int_1^{x_A} d \ln x_A = \int_{T^*}^T \frac{\Delta_{\text{fus}}H}{RT^2} dT \approx \frac{\Delta_{\text{fus}}H}{R} \int_{T^*}^T \frac{dT}{T^2}$$

$$\boxed{\ln x_A = \frac{-\Delta_{\text{fus}}H}{R} \times \left(\frac{1}{T} - \frac{1}{T^*} \right)}$$

The approximations $\ln x_A \approx -x_B$ and $T \approx T^*$ then lead to eqns 5.33 and 5.37, as in the text.

P5.22 Retrace the argument leading to eqn 5.40 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,

$$\mu_A^*(p) = \mu_A^*(p + \Pi) + RT \ln a_A = \mu_A^*(p) + \int_p^{p+\Pi} V_m dp + RT \ln a_A$$

and hence that $\int_p^{p+\Pi} V_m dp = -RT \ln a_A$

For an incompressible solution, the integral evaluates to V_m , so $V_m = -RT \ln a_A$

In terms of the osmotic coefficient ϕ (Problem 5.21)

$$\Pi V_m = r\phi RT \quad r = \frac{x_B}{x_A} = \frac{n_B}{n_A} \quad \phi = -\frac{x_A}{x_B} \ln a_A = -\frac{1}{r} \ln a_A$$

For a dilute solution, $n_A V_m \approx V$

Hence, $V = n_B \phi RT$

and therefore, with $[B] = \frac{n_B}{V}$ $\boxed{\Pi = \phi[B]RT}$

Solutions to applications

P5.24 The 97% saturated haemoglobin in the lungs releases oxygen in the capillary until the haemoglobin is 75% saturated.

100 cm³ of blood in the lung containing 15 g of Hb at 97% saturated with O₂ binds

$$1.34 \text{ cm}^3 \text{ g}^{-1} \times 15 \text{ g} = 20 \text{ cm}^3 \text{ O}_2$$

The same 100 cm^3 of blood in the arteries would contain

$$20 \text{ cm}^3 \text{ O}_2 \times \frac{75\%}{97\%} = 15.5 \text{ cm}^3$$

Therefore, about $(20 - 15.5) \text{ cm}^3$ or 4.5 cm^3 of O_2 is given up in the capillaries to body tissue.

P5.26

$$\nu = \frac{[\text{EB}]_{\text{bound}}}{[\text{M}]} \quad \text{and} \quad [\text{EB}]_{\text{bound}} = [\text{EB}]_{\text{in}} - [\text{EB}]_{\text{out}}$$

Draw up the following table:

$[\text{EB}]_{\text{out}}/(\mu\text{mol dm}^{-3})$	0.042	0.092	0.204	0.526	1.150
$[\text{EB}]_{\text{bound}}/(\mu\text{mol dm}^{-3})$	0.250	0.498	1.000	2.005	3.000
ν	0.250	0.498	1.000	2.005	3.000
$\nu/[\text{EB}]_{\text{out}}$ $2 \mu\text{mol}^{-1}$	5.95	5.41	4.90	3.81	2.61

A plot of $\nu/[\text{EB}]_{\text{out}}$ is shown in Figure 5.6.

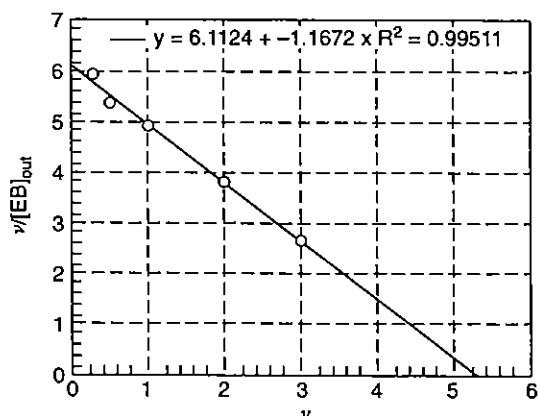
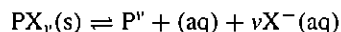


Figure 5.6

The slope is $-1.167 \text{ dm}^3 \mu\text{mol}^{-1}$, hence $K = 1.167 \text{ dm}^3 \mu\text{mol}^{-1}$. The intercept at $\nu = 0$ is $N = 5.24$ and this is the average number of binding sites per oligonucleotide. The close fit of the data to a straight line indicates that the identical and independent sites model is applicable.

P5.28



This process is a solubility equilibrium described by a solubility constant K_s

$$K_s = a_{\text{P}^\nu} + a_{\text{X}^-}^\nu$$

Introducing activity coefficients and concentrations, b , we obtain

$$K_s = b_{\text{P}^\nu} + b_{\text{X}^-}^\nu \gamma_\pm^{\nu+1}$$

At low to moderate ionic strengths we can use the Debye-Hückel limiting law as a good approximation for γ_{\pm}

$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2}$$

Addition of a salt, such as $(\text{NH}_4)_2\text{SO}_4$ causes I to increase and $\log \gamma_{\pm}$ to become more negative and γ_{\pm} will decrease. However, K_s is a true equilibrium constant and remains unchanged. Therefore, the concentration of P^{v+} increases and the protein solubility increases proportionately.

We may also explain this effect with the use of Le Chatelier's principle. As the ionic strength increases by the addition of an inert electrolyte such as $(\text{NH}_4)_2\text{SO}_4$, the ions of the protein that are in solution attract one another less strongly, so that the equilibrium is shifted in the direction of increased solubility.

The explanation of the salting out effect is somewhat more complicated and can be related to the failure of the Debye-Hückel limiting law at higher ionic strengths. At high ionic strengths we may write

$$\log \gamma_{\pm} = -|z_+| A I^{1/2} + K I$$

where K is the salting out constant. At low concentrations of inert salt, $I^{1/2} > I$, and salting in occurs, but at high concentrations, $I > I^{1/2}$, and salting out occurs. The Le Chatelier's principle explanation is that the water molecules are tied up by ion-dipole interactions and become unavailable for solvating the protein, thereby leading to decreased solubility.

P5.30 We use eqn 5.41 in the form given in Example 5.4 with $\Pi = \rho g h$, then

$$\frac{\Pi}{c} = \frac{RT}{M} \left(1 + \frac{B}{M} c \right) = \frac{RT}{M} + \frac{RTB}{M^2} c$$

where c is the mass concentration of the polymer. Therefore plot Π/c against c . The intercept gives RT/M and the slope gives RT/M^2 .

The transformed data to plot are given in the table

$c/(\text{mg cm}^{-3})$	1.33	2.10	4.52	7.18	9.87
$(\Pi/c)/(\text{N m}^{-2} \text{ mg}^{-1} \text{ cm}^3)$	22.56	24.29	29.20	34.26	39.51

The plot is shown in Figure 5.7. The intercept is $29.09 \text{ N m}^{-2}/(\text{mg cm}^{-3})$. The slope is $1.974 \text{ N m}^{-2}/(\text{mg cm}^{-3})^2$. Therefore

$$\begin{aligned}
 M &= \frac{RT}{29.09 \text{ N m}^{-2}/(\text{mg cm}^{-3})} \\
 &= \frac{8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 303.15 \text{ K}}{20.09 \text{ N m}^{-2}/(\text{mg cm}^{-3})} \times \left(\frac{1 \text{ g}}{10^3 \text{ mg}} \right) \times \left(\frac{10^6 \text{ cm}^3}{1 \text{ m}^3} \right) \\
 &= 1.255 \times 10^5 \text{ g mol}^{-1} = \boxed{1.26 \times 10^5 \text{ g mol}^{-1}}
 \end{aligned}$$

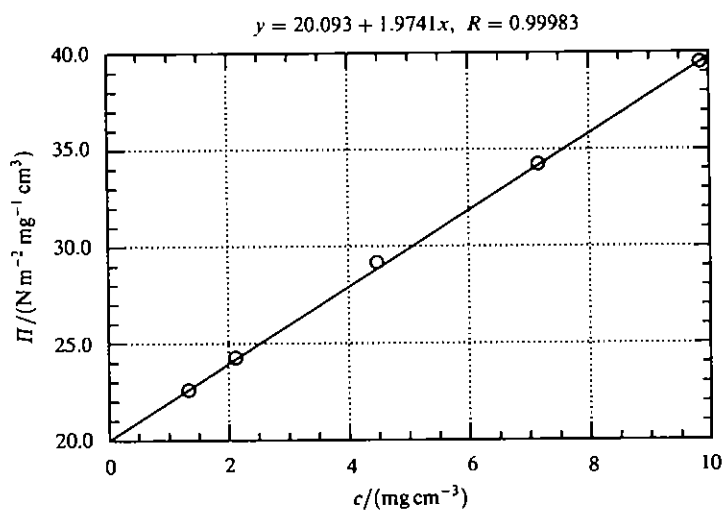


Figure 5.7

$$\begin{aligned}
 B &= \frac{M}{RT} \times 1.974 \text{ N m}^{-2} / (\text{mg cm}^{-3})^2 \\
 &= \frac{M}{\left(\frac{RT}{M}\right)} \times 1.974 \text{ N m}^{-2} / (\text{mg cm}^{-3})^2 \\
 &= \frac{1.255 \times 10^5 \text{ g mol}^{-1} \times 1.974 \text{ N m}^{-2} / (\text{mg cm}^{-3})^2}{20.09 \text{ N m}^{-2} / (\text{mg cm}^{-3})} \\
 &= 1.23 \times 10^4 \text{ g mol}^{-1} / (\text{mg cm}^{-3}) \\
 &= 1.23 \times 10^7 \text{ g mol}^{-1} / (\text{g cm}^{-3}) \\
 &= \boxed{1.23 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}}
 \end{aligned}$$

6 Phase diagrams

Answers to discussion questions

- D6.2** 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 vapor lines are to each other, the more theoretical plates needed. See Figure 6.15 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
- D6.4** See Figures 6.1(a) and 6.1(b).

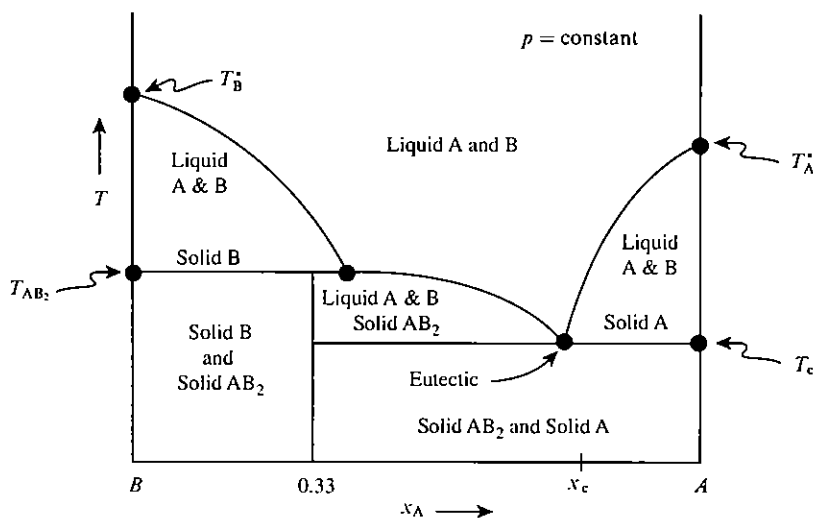


Figure 6.1(a)

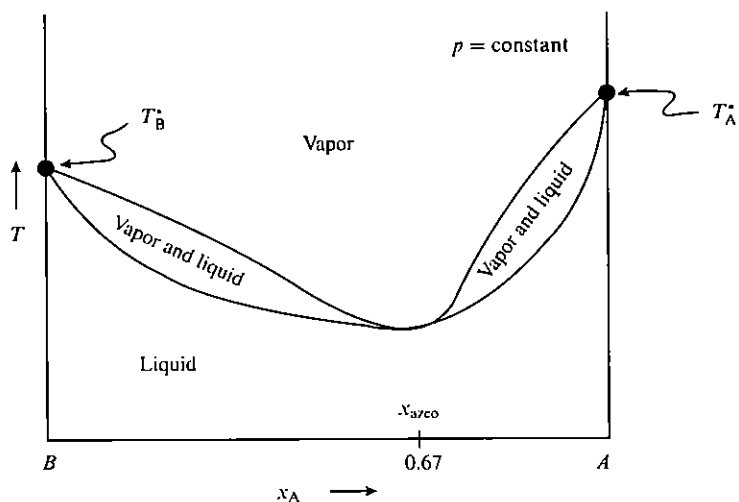


Figure 6.1(b)

D6.6 See Figure 6.2.

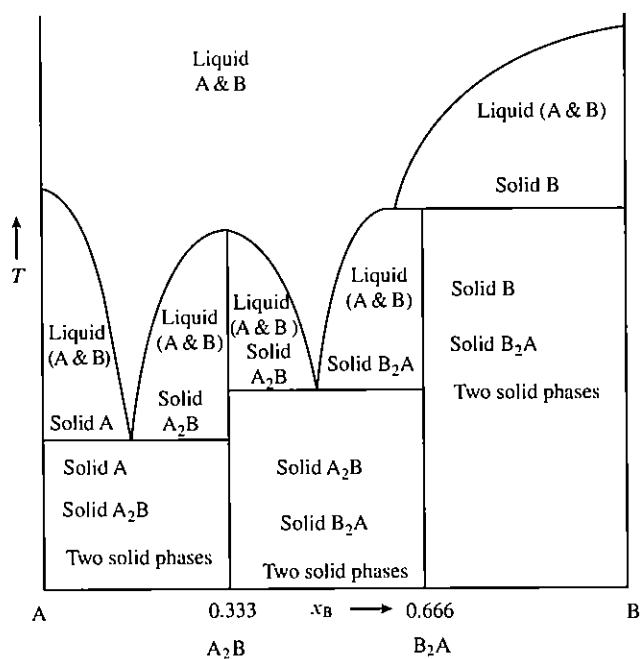


Figure 6.2

Solutions to exercises

E6.1(b) $p = p_A + p_B = x_A p_A^* + (1 - x_A) p_B^*$

$$x_A = \frac{p - p_B^*}{p_A^* - p_B^*}$$

$$x_A = \frac{19 \text{ kPa} - 18 \text{ kPa}}{20 \text{ kPa} - 18 \text{ kPa}} = \boxed{(0.5)} \quad \text{A is 1, 2-dimethylbenzene}$$

$$y_A = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*) x_A} = \frac{(0.5) \times (20 \text{ kPa})}{18 \text{ kPa} + (20 \text{ kPa} - 18 \text{ kPa}) 0.5} = 0.526 \approx \boxed{0.5}$$

$$y_B = 1 - 0.526 = 0.474 \approx 0.5$$

E6.2(b)

$$p_A = y_A p = 0.612 p = x_A p_A^* = x_A (68.8 \text{ kPa})$$

$$p_B = y_B p = (1 - y_A) p = 0.388 p = x_B p_B^* = (1 - x_A) \times 82.1 \text{ kPa}$$

$$\frac{y_A p}{y_B p} = \frac{x_A p_A^*}{x_B p_B^*} \quad \text{and} \quad \frac{0.612}{0.388} = \frac{68.8 x_A}{82.1 (1 - x_A)}$$

$$(0.388) \times (68.8) x_A = (0.612) \times (82.1) - (0.612)(82.1) x_A$$

$$26.694 x_A = 50.245 - 50.245 x_A$$

$$x_A = \frac{50.245}{26.694 + 50.245} = \boxed{0.653} \quad x_B = 1 - 0.653 = \boxed{0.347}$$

$$p = x_A p_A^* + x_B p_B^* = (0.653) \times (68.8 \text{ kPa}) + (0.347) \times (82.1 \text{ kPa}) = \boxed{73.4 \text{ kPa}}$$

E6.3(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 the solution is ideal.

(b)

$$y_A = \frac{p_A}{p} = \frac{46.43 \text{ kPa}}{101.33 \text{ kPa}} = \boxed{0.4582}$$

$$y_B = 1 - y_A = 1.000 - 0.4582 = \boxed{0.5418}$$

E6.4(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

$$p = x_B p_B^* + x_T p_T^* \quad [6.3] = (0.500) \times (9.9 \text{ kPa}) + (0.500) \times (2.9 \text{ kPa})$$

$$= 4.95 \text{ kPa} + 1.45 \text{ kPa} = \boxed{6.4 \text{ kPa}}$$

(b)

$$y_B = \frac{p_B}{p} \quad [6.4] = \frac{4.95 \text{ kPa}}{6.4 \text{ kPa}} = \boxed{0.77} \quad y_T = 1 - 0.77 = \boxed{0.23}$$

(c) Near the end of the distillation

$$y_B = z_B = 0.500 \quad \text{and} \quad y_T = z_T = 0.500$$

Equation 6.5 may be solved for x_A [A = benzene = B here]

$$x_B = \frac{y_B p_T^*}{p_B^* + (p_T^* - p_B^*) y_B} = \frac{(0.500) \times (2.9 \text{ kPa})}{(9.9 \text{ kPa}) + (2.9 - 9.9) \text{ kPa} \times (0.500)} = 0.23$$

$$x_T = 1 - 0.23 = 0.77$$

This result for the special case of $z_B = z_T = 0.500$ could have been obtained directly by realizing that

$$y_B (\text{initial}) = x_T (\text{final}); y_T (\text{initial}) = x_B (\text{final})$$

$$p(\text{final}) = x_B p_B^* + x_T p_T^* = (0.23) \times (9.9 \text{ kPa}) + (0.77) \times (2.9 \text{ kPa}) = \boxed{4.5 \text{ kPa}}$$

Thus in the course of the distillation the vapor pressure fell from 6.4 kPa to 4.5 kPa

E6.5(b) See the phase diagram in Figure 6.3.

(a) $y_A = \boxed{0.81}$

(b) $x_A = \boxed{0.67}$ $y_A = \boxed{0.925}$

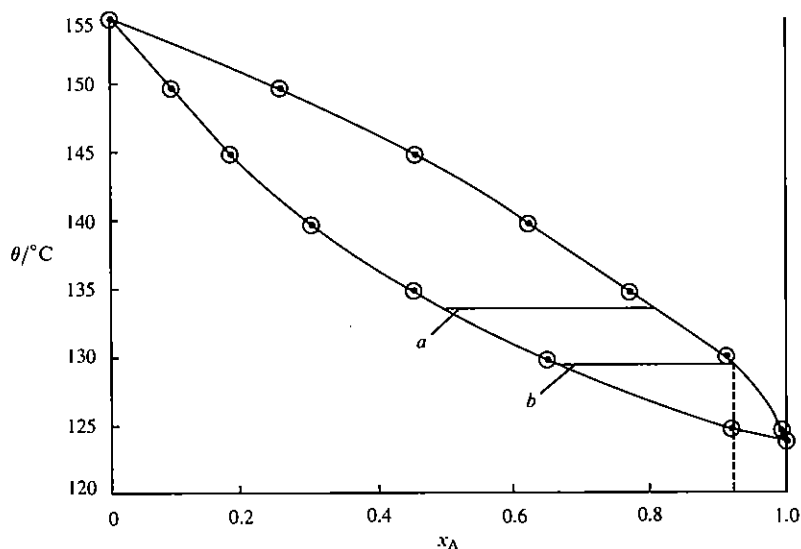
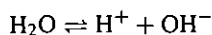
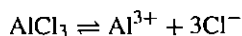
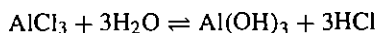


Figure 6.3

E6.6(b) Al^{3+} , H^+ , AlCl_3 , $\text{Al}(\text{OH})_3$, OH^- , Cl^- , H_2O giving seven species. There are also three equilibria

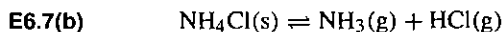


and one condition of electrical neutrality

$$[\text{H}^+] + 3[\text{Al}^{3+}] = [\text{OH}^-] + [\text{Cl}^-]$$

Hence, the number of independent components is

$$C = 7 - (3 + 1) = \boxed{3}$$



(a) For this system $C = 1$ [Example 6.1] and $P = 2$ (s and g).

(b) If ammonia is added before heating, $C = 2$ (because NH_4Cl , NH_3 are now independent) and $P = 2$ (s and g).

E6.8(b) (a) Still $C = 2$ (Na_2SO_4 , H_2O), but now there is no solid phase present, so $P = 2$ (liquid solution, vapor).

(b) The variance is $F = 2 - 2 + 2 = 2$. 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.

E6.9(b) See Figure 6.4.

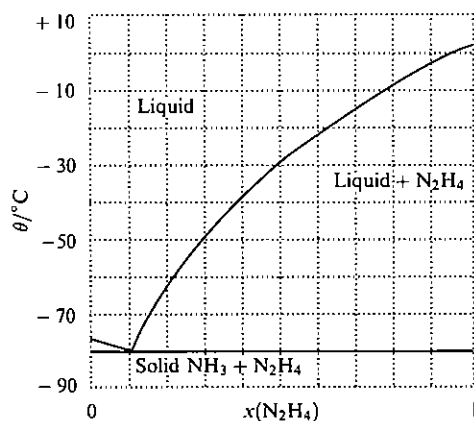


Figure 6.4

E6.10(b) See Figure 6.5. The phase diagram should be labeled as in figure 6.5. (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

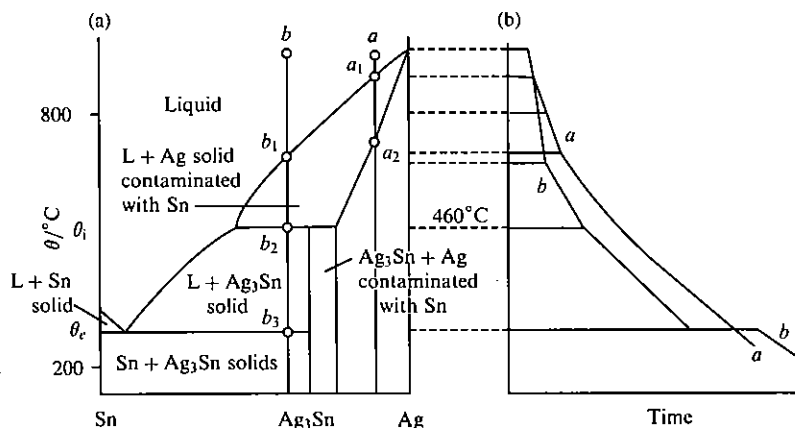


Figure 6.5

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.

- E6.11(b)** See Figure 6.6. The feature denoting incongruent melting is circled. Arrows on the tie line indicate the decomposition products. There are two eutectics: one at $x_B = 0.53$, $T = T_2$; another at $x_B = 0.82$, $T = T_3$.

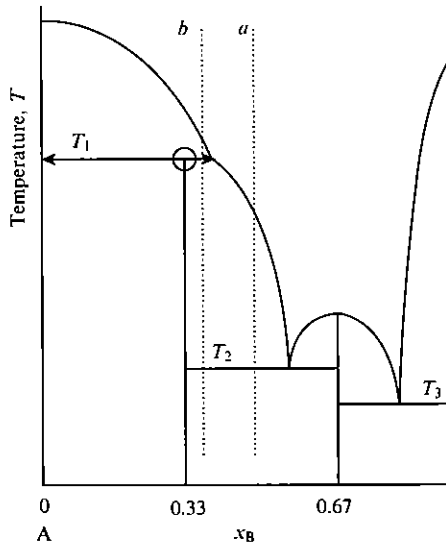


Figure 6.6

- E6.12(b)** The cooling curves corresponding to the phase diagram in Figure 6.7(a) are shown in Figure 6.7(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 .

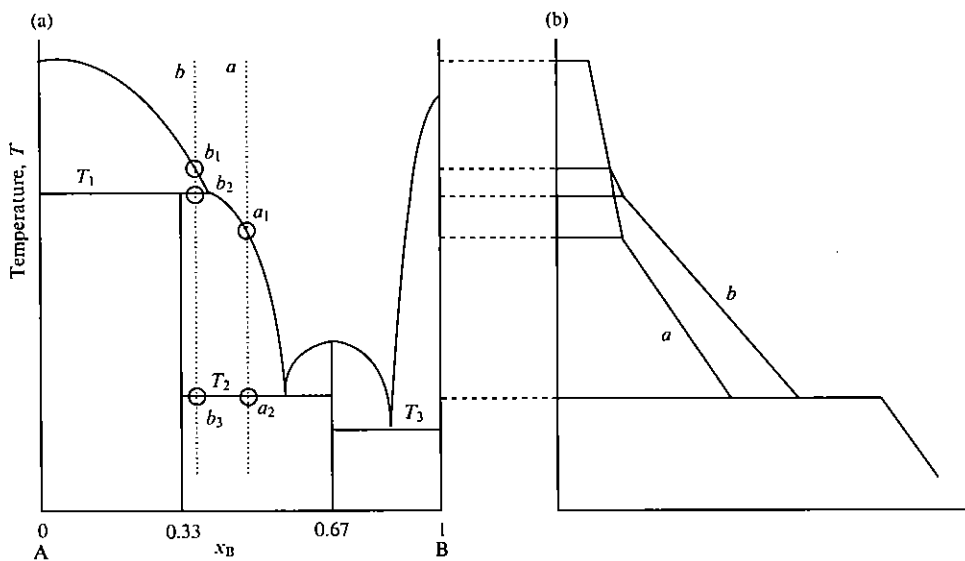


Figure 6.7

E6.13(b) Rough estimates based on Figure 6.37 of the text are

(a) $x_B \approx 0.75$ (b) $x_{AB_2} \approx 0.8$ (c) $x_{AB_2} \approx 0.6$

E6.14(b) The phase diagram is shown in Figure 6.8. The given data points are circled. The lines are schematic at best.

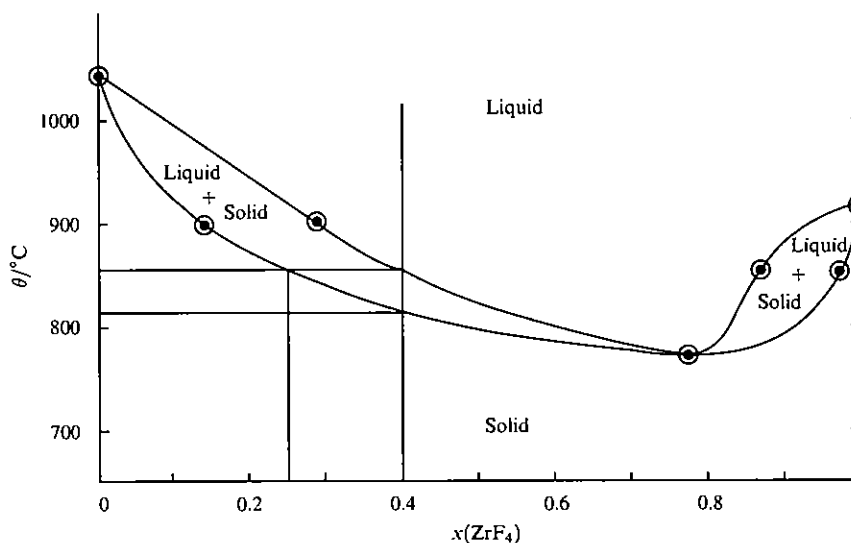


Figure 6.8

A solid solution with $x(\text{ZrF}_4) = 0.24$ appears at 855 °C. The solid solution continues to form, and its ZrF_4 content increases until it reaches $x(\text{ZrF}_4) = 0.40$ and 820 °C. At that temperature, the entire sample is solid.

E6.15(b) The phase diagram for this system (Figure 6.9) is very similar to that for the system methyl ethyl ether and diborane of Exercise 6.9(a). 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.

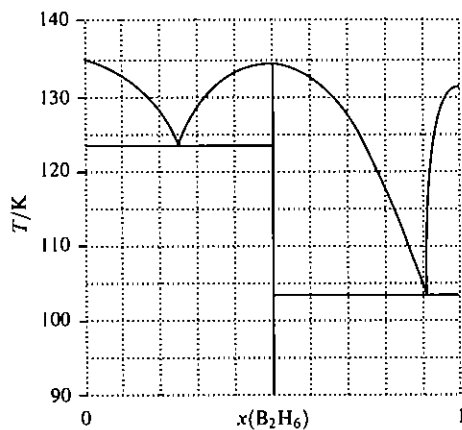
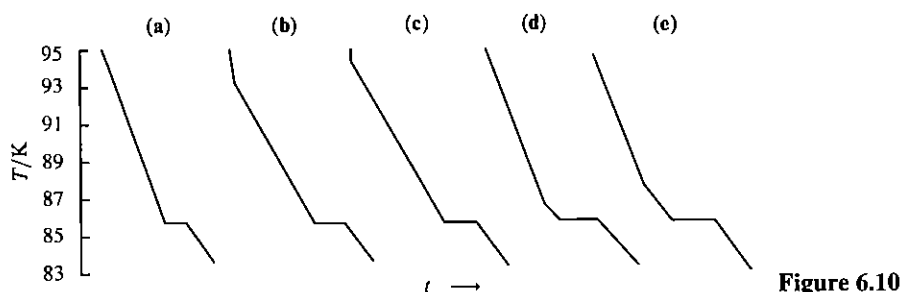


Figure 6.9

E6.16(b) Refer to the phase diagram in the solution to Exercise 6.14(a). The cooling curves are sketched in Figure 6.10.



- E6.17(b)** (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 Figure 6.11.

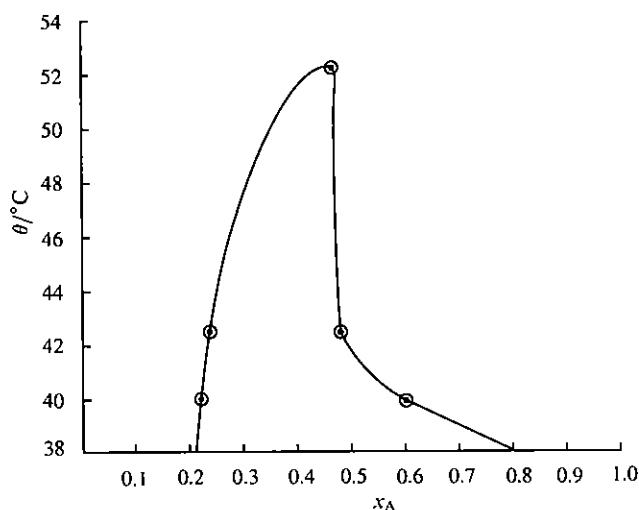


Figure 6.11

Solutions to problems

Solutions to numerical problems

- P6.2** (a) The phase diagram is shown in Figure 6.12.
- (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 phases are in an inverse ratio of the distance their mole fractions are from the composition point in

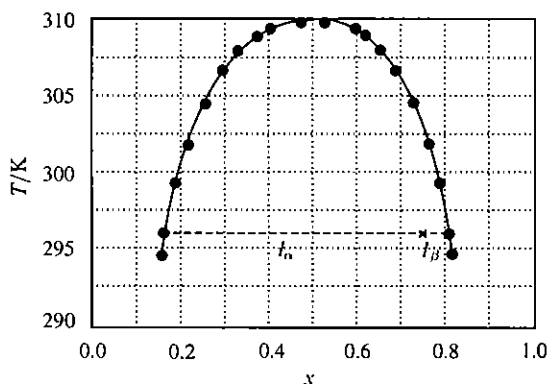


Figure 6.12

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.

P6.4

The phase diagram is shown in Figure 6.13(a). The values of x_S corresponding to the three compounds are: (1) P_4S_3 , 0.43; (2) P_4S_7 , 0.64; (3) P_4S_{10} , 0.71.

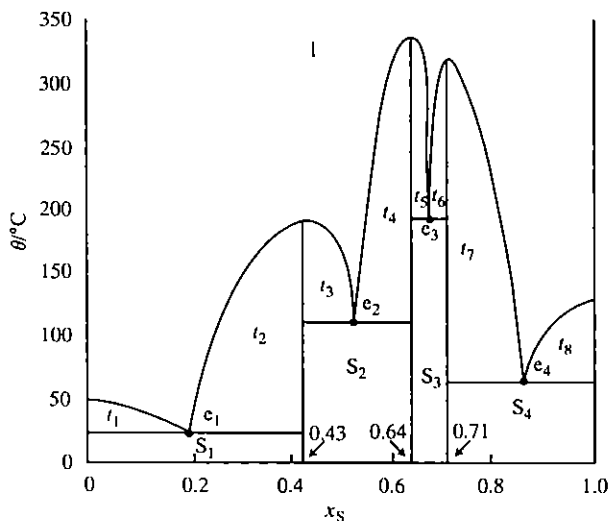


Figure 6.13(a)

The diagram has four eutectics labelled e_1 , e_2 , e_3 , and e_4 ; eight two-phase liquid–solid regions, t_1 through t_8 ; and four two-phase solid regions, S_1 , S_2 , S_3 , and S_4 . The composition and physical state of the regions are as follows:

l : liquid S and P;

S_1 : solid P and solid P_4S_3 ; S_2 : solid P_4S_3 and solid P_4S_7 ;

S_3 : solid P_4S_7 and P_4S_{10} ; S_4 : solid P_4S_{10} and solid S

t_1 : liquid P and S and solid P

t_2 : liquid P and S and solid P_4S_3

t_3 : liquid P and S and solid P_4S_3

t_4 : liquid P and S and solid P_4S_7

t_5 : liquid P and S and solid P_4S_7

t_6 : liquid P and S and solid P_4S_{10}

t_7 : liquid P and S and solid P_4S_{10}

t_8 : liquid P and S and solid S

A break in the cooling curve (Figure 6.13(b)) occurs at point $b_1 \approx 125^\circ\text{C}$ as a result of solid P_4S_3 forming; a eutectic halt occurs at point $e_1 \approx 20^\circ\text{C}$.

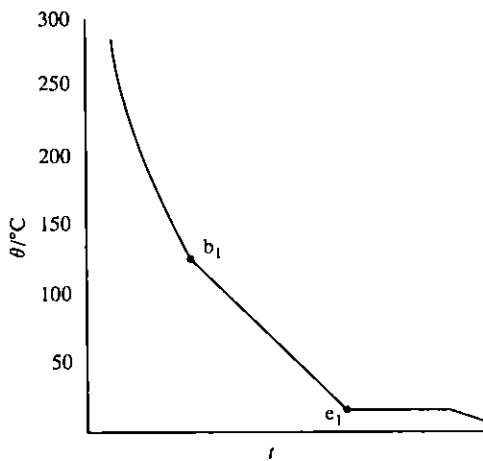


Figure 6.13(b)

P6.6

See Figure 6.14(a). The number of distinct chemical species (as opposed to components) and phases present at the indicated points are, respectively

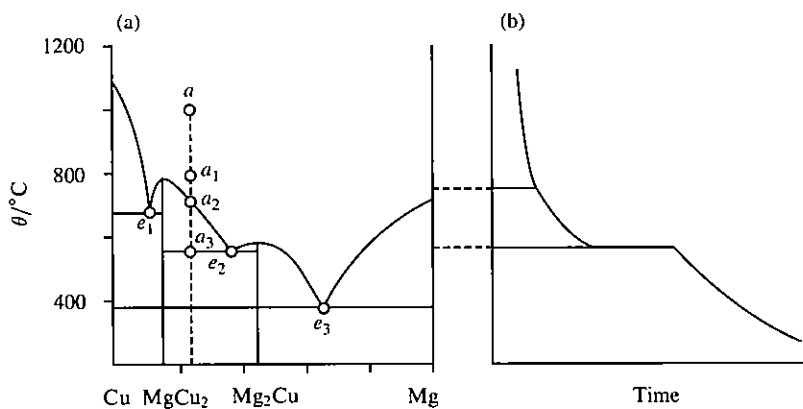


Figure 6.14(a)

$b(3, 2)$, $d(2, 2)$, $e(4, 3)$, $f(4, 3)$, $g(4, 3)$, $k(2, 2)$

[Liquid A and solid A are here considered distinct species.]

The cooling curves are shown in Figure 6.14(b).

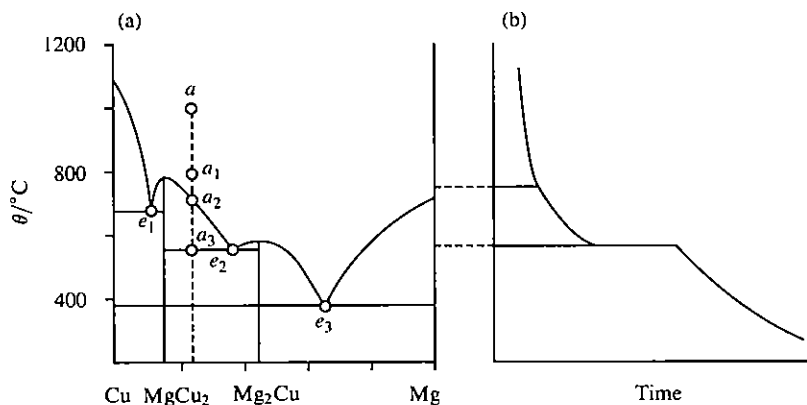


Figure 6.14(b)

P6.8

- (a) The $\Delta_{\text{mix}}G(x_{\text{Pb}})$ curves show that at 1500 K lead and copper are totally miscible. They mix to form a homogeneous solution no matter what the relative amounts may be. However, the curve at 1300 K appears to have a small double minimum, which indicates two partially miscible phases (Sections 5.4b and 6.5b) at temperatures lower than 1300 K (1100 K curve of the figure) there are two very distinct minimum and we expect two partially miscible phases. The upper critical temperature is about 1300 K at 1500 K,

$$F = C - P + 2 = 2 - 1 + 2 = \boxed{3} \text{ at 1100 K}$$

$$F = C - P + 2 = 2 - 2 + 2 = \boxed{2}$$

- (b) When a homogeneous, equilibrium mixture with $x_{\text{Pb}} = 0.1$ is cooled from 1500 K to 1100 K, no phase separation occurs. The solution composition does not change.

If an $x_{\text{Pb}} = 0.7$ homogeneous, equilibrium mixture is cooled slowly, two partially miscible phases appear at about 1300 K. The separation occurs because the composition lies between two minimum on the $\Delta_{\text{mix}}G$ curve at 1300 K and phase separation lowers the total Gibbs energy.

The composition of the two phases is determined by the equilibrium criterion $\mu_i(\alpha) = \mu_i(\beta)$ between the α and β phase. Since the chemical potential is the tangent of the $\Delta_{\text{mix}}G$ curve, we conclude that the straight line that is tangent to $\Delta_{\text{mix}}G(x)$ at two volumes of x (a double tangent) determine the composition of the two partially miscible phases. The 1100 K data is expanded (this can be done on a photocopy machine) so that the numerical values may be extracted more easily. The double tangent is drawn and the tangent points give the composition $x_{\text{Pb}}(\alpha) = 0.19$ and $x_{\text{Pb}}(\beta) = 0.86$. See Figure 6.15. (Notice that the tangent points and the minimum do not normally coincide.) The relative amounts of the two phases is determined by the lever rule (eqn 6.7).

$$\frac{n_{\alpha}}{n_{\beta}} = \frac{l_{\beta}}{l_{\alpha}} = \frac{0.86 - 0.70}{0.70 - 0.19} = \boxed{0.36}$$

- (c) Solubility at 1100 K is determined by the positions of the two minimum in the $\Delta_{\text{mix}}G$ curve. The maximum amount of lead that can be dissolved in copper yields a mixture that has $x_{\text{Pb}} = 0.17$, any

more lead produces a second phase.

$$\text{solubility of Pb in Cu} = \left(\frac{0.17 \text{ mol Pb}}{0.83 \text{ mol Cu}} \right) \times \left(\frac{207.19 \text{ g Pb}}{1 \text{ mol Pb}} \right) \times \left(\frac{1 \text{ mol Cu}}{63.54 \text{ g Cu}} \right) = \boxed{0.67 \text{ g Pb/g Cu}}$$

The second minimum in the $\Delta_{\text{mix}}G$ curve at 1100 K is at $x_{\text{Pb}} = 0.86$.

$$\begin{aligned} \text{solubility of Cu in Pb} &= \left(\frac{0.14 \text{ mol Cu}}{0.86 \text{ mol Pb}} \right) \times \left(\frac{63.54 \text{ g Cu}}{1 \text{ mol Cu}} \right) \times \left(\frac{1 \text{ mol Pb}}{207.19 \text{ g Pb}} \right) \\ &= \boxed{0.050 \text{ g Cu/g Pb}} \end{aligned}$$

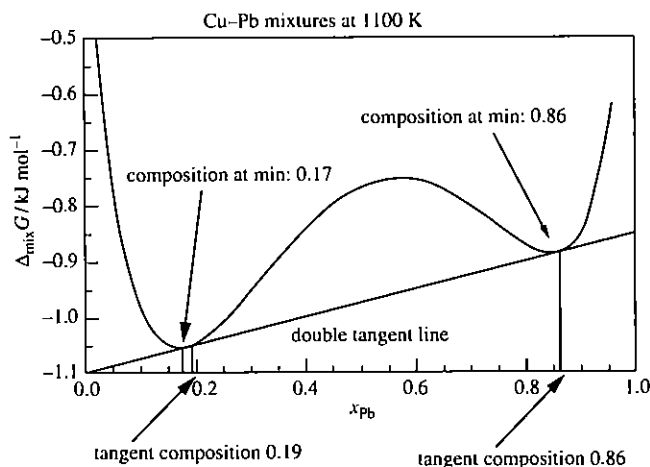


Figure 6.15

P6.10

The data are plotted in Figure 6.16. At 360 °C, $\text{K}_2\text{FeCl}_4(\text{s})$ appears. The solution becomes richer in FeCl_2 until the temperature reaches 351 °C, at which point $\text{KFeCl}_3(\text{s})$ also appears. Below 351 °C the system is a mixture of $\text{K}_2\text{FeCl}_4(\text{s})$ and $\text{KFeCl}_3(\text{s})$.

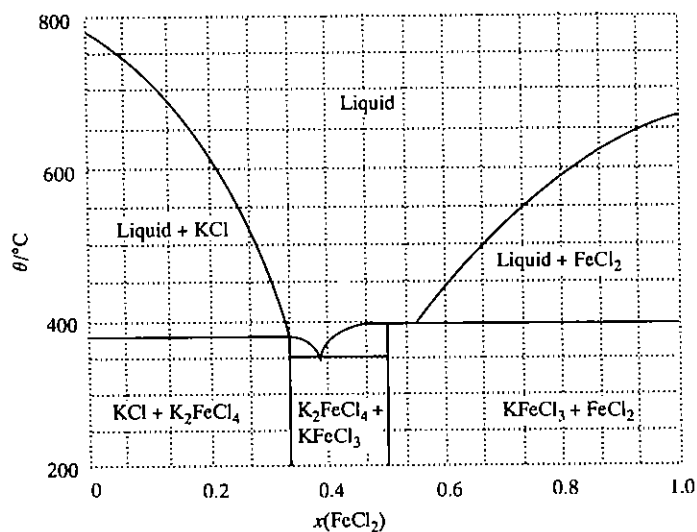


Figure 6.16

Solutions to theoretical problems

- P6.12** The implication of this problem is that energy in the form of heat may be transferred between phases and that the volumes of the phases may also change. However, $U_\alpha + U_\beta = \text{constant}$ and $V_\alpha + V_\beta = \text{constant}$. Hence,

$$dU_\beta = -dU_\alpha \text{ (b) and } dV_\beta = -dV_\alpha \text{ (c)}$$

The general condition of equilibrium in an isolated system is $dS = 0$; hence

$$dS = dS_\alpha + dS_\beta = 0 \text{ (a)}$$

$$S = S(U, V)$$

$$dS = \left(\frac{\partial S_\alpha}{\partial U_\alpha} \right)_{V_\alpha} dU_\alpha + \left(\frac{\partial S_\alpha}{\partial V_\alpha} \right)_{U_\alpha} dV_\alpha + \left(\frac{\partial S_\beta}{\partial U_\beta} \right)_{V_\beta} dU_\beta + \left(\frac{\partial S_\beta}{\partial V_\beta} \right)_{U_\beta} dV_\beta$$

Using conditions (b) and (c), and eqn 3.45

$$dS = \left(\frac{1}{T_\alpha} - \frac{1}{T_\beta} \right) dU_\alpha + \left(\frac{p_\alpha}{T_\alpha} - \frac{p_\beta}{T_\beta} \right) dV_\alpha = 0$$

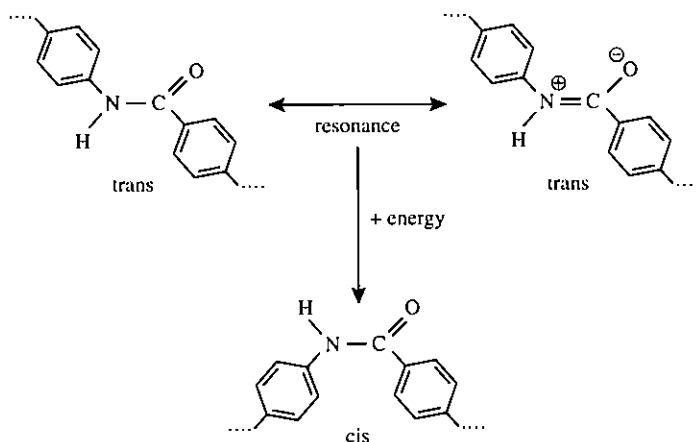
The only way in which this expression may, in general, equal zero is for

$$\frac{1}{T_\alpha} - \frac{1}{T_\beta} = 0 \quad \text{and} \quad \frac{p_\alpha}{T_\alpha} - \frac{p_\beta}{T_\beta} = 0$$

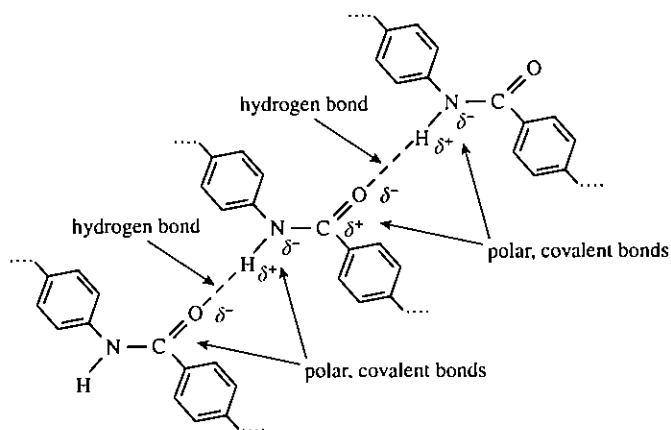
Therefore, $T_\alpha = T_\beta$ and $p_\alpha = p_\beta$

Solutions to applications

- P6.14** Above about 33 °C the membrane has the highly mobile liquid crystal form. At 33 °C the membrane consists of liquid crystal in equilibrium with a relatively small amount of the gel form. Cooling from 33 °C to about 20 °C, the equilibrium persists but shifts to a greater relative abundance of the gel form. Below 20 °C the gel form alone is stable.
- P6.16** Kevlar is a polyaromatic amide. Phenyl groups provide aromaticity and a planar, rigid structure. The amide group is expected to be like the peptide bond that connects amino acid residues within protein molecules. This group is also planar because resonance produces partial double bond character between the carbon and nitrogen atoms. There is a substantial energy barrier preventing free rotation about the C—N bond. The two bulky phenyl groups on the ends of an amide group are *trans* because steric hindrance makes the *cis* conformation unfavorable.



The flatness of the Kevlar polymeric molecule makes it possible to process the material so that many molecules with parallel alignment form highly ordered, untangled crystal bundles. The alignment makes possible both considerable van der Waals attractions between adjacent molecules and for strong hydrogen bonding between the polar amide groups on adjacent molecules. These bonding forces create the high thermal stability and mechanical strength observed in Kevlar.



Kevlar is able to absorb great quantities of energy, such as the kinetic energy of a spreading bullet, through hydrogen bond breakage and the transition to the cis conformation.

P6.18 In the float zoning (FZ) method of silicon purification, a polycrystalline silicon rod is positioned atop a seed crystal and lowered through an electromagnetic coil. The magnetic field generated by the coil creates electric currents, heating, and local melting in the rod. By slowly moving the coil upward impurities move with the melt zone. The lower surface of the melt zone solidifies to an ultrapure, single crystal as it slowly cools. See Figure 6.17. Search www.nrel.gov

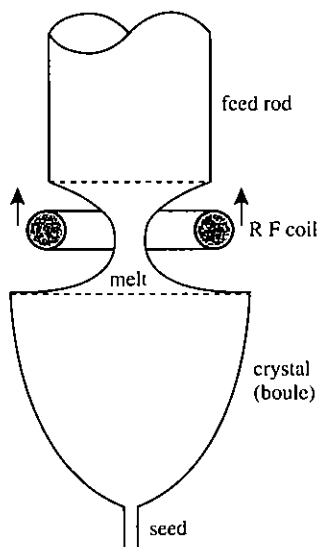


Figure 6.17

Advantages	Disadvantages
Produces ultrapure silicon for high efficiency photovoltaic cells and infrared detectors for space, defense, and environmental applications	Requires a smooth, uniform diameter, and crack-free feed rod
No crucible contamination	High cost of heating
Produces large boules (10 cm diameter)	Process must be conducted under helium or argon and 10^{-5} Torr vacuum
	Boron impurity is not removed from silicon
	Boule must be sliced with a diamond saw into thin wafers for microelectronic devices. This reduces the useful volume of the boule

P6.20 The temperature–composition lines can be calculated from the formula for the depression of freezing point [5.36].

$$\Delta T \approx \frac{RT^*{}^2 x_B}{\Delta_{\text{fus}} H}$$

For bismuth

$$\frac{RT^*{}^2}{\Delta_{\text{fus}} H} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (544.5 \text{ K})^2}{10.88 \times 10^3 \text{ J mol}^{-1}} = 227 \text{ K}$$

For cadmium

$$\frac{RT^*{}^2}{\Delta_{\text{fus}} H} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (594.5 \text{ K})^2}{6.07 \times 10^3 \text{ J mol}^{-1}} = 483 \text{ K}$$

We can use these constants to construct the following tables

$x(\text{Cd})$	0.1	0.2	0.3	0.4	
$\Delta T/\text{K}$	22.7	45.4	68.1	90.8	$(\Delta T = x(\text{Cd}) \times 227 \text{ K})$
T_f/K	522	499	476	454	$(T_f = T_f^* - \Delta T)$

$x(\text{Bi})$	0.1	0.2	0.3	0.4	
$\Delta T/\text{K}$	48.3	96.6	145	193	$(\Delta T = x(\text{Bi}) \times 483 \text{ K})$
T_f/K	546	497	449	401	$(T_f = T_f^* - \Delta T)$

These points are plotted in Figure 6.18(a).

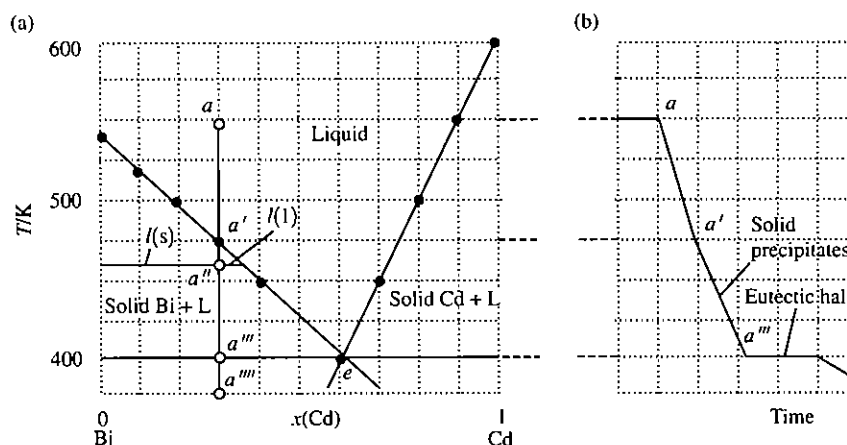


Figure 6.18

The eutectic temperature and concentration are located by extrapolation of the plotted freezing point lines until they intersect at e , which corresponds to $T_E \approx 400 \text{ K}$ and $x_E(\text{Cd}) \approx 0.60$

Liquid at a cools without separation of a solid until a' is reached (at 476 K). Solid Bi then separates, and the liquid becomes richer in Cd. At a''' (400 K) the composition is pure solid Bi + liquid of composition $x_{\text{Bi}} = 0.4$. The whole mass then solidifies to solid Bi + solid Cd.

(a) At 460 K (point a'), $\frac{n(l)}{n(s)} = \frac{l(s)}{l(l)} \approx 5$ by the lever rule.

(b) At 375 K (point a''') there is no liquid. The cooling curve is shown in Figure 6.18(b).

COMMENT. The experimental values of T_E and $x_E(\text{Cd})$ 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.

7

Chemical equilibrium

Answers to discussion questions

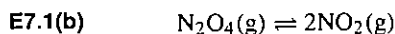
- D7.2** The thermodynamic equilibrium constant involves activities rather than pressures. See eqn 7.16 and Example 7.1. For systems involving gases, the activities are the dimensionless fugacities. At low pressures, the fugacity may be replaced with pressures with little error, but at high pressures 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 7.25.
- D7.4** 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 their reacting system resulting in a more positive $\ln K$, favoring products.
- D7.6** 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. Infinitesimally small changes from this equilibrium are reversible with constant concentration and, consequently, it is possible to relate emf to thermodynamic properties.
- D7.8** Construct a cell using a standard hydrogen electrode and an electrode designed around the redox couple of interest. The cell potential E is measured with a high impedance voltmeter under zero current conditions. When using SHE as a reference electrode, E is the desired half-reaction potential [7.13]. Should the redox couple have one or more electroactive species (i) that are solvated with concentration b_i , E must be measured over a range of b_i values.

The Nernst equation [7.29], with Q being the cell reaction quotient, is the starting point for analysis of the $E(b_i)$ data.

$$E = E^\ominus - \frac{RT}{\nu F} \ln Q$$

It would seem that substitution of E and Q values would allow the computation of the standard redox potential E^\ominus for the couple. However, a problem arises because the calculation of Q requires not only knowledge of the concentrations of the species involved in the cell reaction but also of their activity coefficients. These coefficients are not usually available, so the calculation cannot be directly completed. However, at very low concentrations, the Debye–Hückel limiting law for the coefficients holds. The procedure then is to substitute the Debye–Hückel law for the activity coefficients into the specific form of the Nernst equation for the cell under investigation and carefully examine the equation to determine what kind of plot to make of the $E(b_i)$ data so that extrapolation of the plot to zero concentration, where the Debye–Hückel law is valid, gives a plot intercept that equals E^\ominus . See Section 7.8 for the details of this procedure and an example for which the relevant graph involves a plot of $E + (2RT/F) \ln b$ against $b^{1/2}$.

Solutions to exercises



Amount at equilibrium $(1 - \alpha)n$ $2\alpha n$

Mole fraction $\frac{1 - \alpha}{1 + \alpha}$ $\frac{2\alpha}{1 + \alpha}$

Partial pressure $\frac{(1 - \alpha)P}{1 + \alpha}$ $\frac{2\alpha P}{1 + \alpha}$

Assuming that the gases are perfect, $a_J = \frac{p_J}{p^\ominus}$

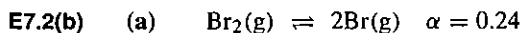
$$K = \frac{(p_{\text{NO}_2}/p^\ominus)^2}{(p_{\text{N}_2\text{O}_4}/p^\ominus)} = \frac{4\alpha^2 p}{(1 - \alpha^2)p^\ominus}$$

For $p = p^\ominus$, $K = \frac{4\alpha^2}{1 - \alpha^2}$

(a) $\boxed{\Delta_r G = 0}$ at equilibrium

(b) $\alpha = 0.201$ $K = \frac{4(0.201)^2}{1 - 0.201^2} = \boxed{0.16841}$

(c) $\Delta_r G^\ominus = -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(0.16841)$
 $= \boxed{4.41 \text{ kJ mol}^{-1}}$



Amount at equilibrium	$(1 - \alpha)n$	$2\alpha n$
Mole fraction	$\frac{1 - \alpha}{1 + \alpha}$	$\frac{2\alpha}{1 + \alpha}$
Partial pressure	$\frac{(1 - \alpha)P}{1 + \alpha}$	$\frac{2\alpha P}{1 + \alpha}$

Assuming both gases are perfect $a_i = \frac{p_i}{p^\ominus}$

$$K = \frac{(p_{\text{Br}}/p^\ominus)^2}{p_{\text{Br}_2}/p^\ominus} = \frac{4\alpha^2 p}{(1 - \alpha^2)p^\ominus} = \frac{4\alpha}{1 - \alpha} [p = p^\ominus]$$

$$= \frac{4(0.24)^2}{1 - (0.24)^2} = 0.2445 = \boxed{0.24}$$

(b) $\Delta_r G^\ominus = -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1600 \text{ K}) \times \ln(0.2445)$

$$= \boxed{19 \text{ kJ mol}^{-1}}$$

(c) $\ln K(2273 \text{ K}) = \ln K(1600 \text{ K}) - \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{2273 \text{ K}} - \frac{1}{1600 \text{ K}} \right)$

$$= \ln(0.2445) - \left(\frac{112 \times 10^3 \text{ mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times (-1.851 \times 10^{-4})$$

$$= 1.084$$

$$K(2273 \text{ K}) = e^{1.084} = \boxed{2.96}$$



(a) $\Delta_r G^\ominus = \Delta_f G^\ominus(\text{CHCl}_3, \text{l}) + 3\Delta_f G^\ominus(\text{HCl}, \text{g}) - \Delta_f G^\ominus(\text{CH}_4, \text{g})$

$$= (-73.66 \text{ kJ mol}^{-1}) + (3) \times (-95.30 \text{ kJ mol}^{-1}) - (-50.72 \text{ kJ mol}^{-1})$$

$$= \boxed{-308.84 \text{ kJ mol}^{-1}}$$

$$\ln K = -\frac{\Delta_r G^\ominus}{RT} [7.8] = \frac{-(-308.84 \times 10^3 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})} = 124.584$$

$$K = \boxed{1.3 \times 10^{54}}$$

(b) $\Delta_r H^\ominus = \Delta_f H^\ominus(\text{CHCl}_3, \text{l}) + 3\Delta_f H^\ominus(\text{HCl}, \text{g}) - \Delta_f H^\ominus(\text{CH}_4, \text{g})$

$$= (-134.47 \text{ kJ mol}^{-1}) + (3) \times (-92.31 \text{ kJ mol}^{-1}) - (-74.81 \text{ kJ mol}^{-1})$$

$$= -336.59 \text{ kJ mol}^{-1}$$

$$\ln K(50^\circ\text{C}) = \ln K(25^\circ\text{C}) - \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{323.2\text{ K}} - \frac{1}{298.2\text{ K}} \right) \quad [7.25]$$

$$= 124.584 - \left(\frac{-336.59 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times (-2.594 \times 10^{-4} \text{ K}^{-1}) = 114.08\bar{3}$$

$$K(50^\circ\text{C}) = \boxed{3.5 \times 10^{49}}$$

$$\Delta_r G^\ominus(50^\circ\text{C}) = -RT \ln K(50^\circ\text{C}) \quad [7.17] = -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (323.15 \text{ K}) \times (114.08\bar{3})$$

$$= \boxed{306.52 \text{ kJ mol}^{-1}}$$

E7.4(b) Draw up the following table.

	A	+	B	\rightleftharpoons	C	+	2D	Total
Initial amounts/mol	2.00		1.00		0		3.00	6.00
Stated change/mol					+0.79			
Implied change/mol	-7.09		-7.09		+7.09		+1.58	
Equilibrium amounts/mol	1.21		0.21		0.79		4.58	6.79
Mole fractions	0.1782		0.0302		0.1162		0.6742	0.9999

(a) Mole fractions are given in the table.

(b) $K_x = \prod_j x_j^{\nu_j}$,

$$K_x = \frac{(0.1162) \times (0.6742)^2}{(0.1782) \times (0.0302)} = \boxed{9.6}$$

(c) $p_j = x_j p$. Assuming the gases are perfect, $a_j = p_j/p^\ominus$, so

$$K = \frac{(p_C/p^\ominus) \times (p_D/p^\ominus)^2}{(p_A/p^\ominus) \times (p_B/p^\ominus)} = K_x \left(\frac{p}{p^\ominus} \right) = K_x \quad \text{when } p = 1.00 \text{ bar}$$

$$K = K_x = \boxed{9.6}$$

(d) $\Delta_r G^\ominus = -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(9.609)$

$$= \boxed{-5.6 \text{ kJ mol}^{-1}}$$

E7.5(b) At 1120 K, $\Delta_r G^\ominus = +22 \times 10^3 \text{ J mol}^{-1}$

$$\ln K(1120 \text{ K}) = \frac{\Delta_r G^\ominus}{RT} = -\frac{(22 \times 10^3 \text{ J mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1120 \text{ K})} = -2.36\bar{3}$$

$$K = e^{-2.36\bar{3}} = 9.41 \times 10^{-2}$$

$$\ln K_2 = \ln K_1 - \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Solve for T_2 at $\ln K_2 = 0$ ($K_2 = 1$)

$$\frac{1}{T_2} = \frac{R \ln K_1}{\Delta_r H^\circ} + \frac{1}{T_1} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (-2.363)}{(125 \times 10^3 \text{ J mol}^{-1})} + \frac{1}{1120 \text{ K}} = 7.36 \times 10^{-4}$$

$$T_2 = \boxed{1.4 \times 10^3 \text{ K}}$$

E7.6(b) Use $\frac{d(\ln K)}{d(1/T)} = \frac{-\Delta_r H^\circ}{R}$

We have $\ln K = -2.04 - 1176 \text{ K} \left(\frac{1}{T}\right) + 2.1 \times 10^7 \text{ K}^3 \left(\frac{1}{T}\right)^3$

$$-\frac{\Delta_r H^\circ}{R} = -1176 \text{ K} + (2.1 \times 10^7 \text{ K}^3) \times 3 \left(\frac{1}{T}\right)^2$$

 $T = 450 \text{ K}$ so

$$-\frac{\Delta_r H^\circ}{R} = -1176 \text{ K} + (2.1 \times 10^7 \text{ K}^3) \times 3 \left(\frac{1}{450 \text{ K}}\right)^2 = -865 \text{ K}$$

$$\Delta_r H^\circ = +(865 \text{ K}) \times (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) = \boxed{7.191 \text{ kJ mol}^{-1}}$$

Find $\Delta_r S^\circ$ from $\Delta_r G^\circ$

$$\Delta_r G^\circ = -RT \ln K$$

$$\begin{aligned} &= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (450 \text{ K}) \times \left\{ -2.04 - \frac{1176 \text{ K}}{450 \text{ K}} + \frac{2.1 \times 10^7 \text{ K}^3}{(450 \text{ K})^3} \right\} \\ &= 16.55 \text{ kJ mol}^{-1} \end{aligned}$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$$

$$\begin{aligned} \Delta_r S^\circ &= \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \frac{7.191 \text{ kJ mol}^{-1} - 16.55 \text{ kJ mol}^{-1}}{450 \text{ K}} = -20.79 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= \boxed{-21 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

E7.7(b) $\text{U(s)} + \frac{3}{2} \text{H}_2(\text{g}) \rightleftharpoons \text{UH}_3(\text{s}), \quad \Delta_r G^\circ = -RT \ln K$

At this low pressure, hydrogen is nearly a perfect gas, $a(\text{H}_2) = (p/p^\circ)$. The activities of the solids are 1.

Hence, $\ln K = \ln \left(\frac{p}{p^\circ} \right)^{-3/2} = -\frac{3}{2} \ln \frac{p}{p^\circ}$

$$\begin{aligned} \Delta_r G^\circ &= \frac{3}{2} RT \ln \frac{p}{p^\circ} \\ &= \left(\frac{3}{2} \right) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (500 \text{ K}) \times \ln \left(\frac{139 \text{ Pa}}{1.00 \times 10^5 \text{ Pa}} \right) \\ &= \boxed{-41.0 \text{ kJ mol}^{-1}} \end{aligned}$$

E7.8(b) $K_x = \prod_j x_j^{\nu_j}$ [analogous to 7.16]

The relation of K_x to K is established in *Illustration 7.5*

$$\begin{aligned} K_x &= \prod_j \left(\frac{p_j}{p^\ominus} \right)^{\nu_j} \left[7.16 \text{ with } a_j = \frac{p_j}{p^\ominus} \right] \\ &= \prod_j x_j^{\nu_j} \left(\frac{p_j}{p^\ominus} \right)^{\sum_j \nu_j} [p_j = x_j p] = K_x \times \left(\frac{p}{p^\ominus} \right)^\nu \left[\nu \equiv \sum_j \nu_j \right] \end{aligned}$$

Therefore, $K_x = K (p/p^\ominus)^{-\nu}$, $K_x \propto p^{-\nu}$ [K and p^\ominus are constants]

$\nu = 1 + 1 - 1 - 1 = 0$, thus $K_x(2 \text{ bar}) = K_x(1 \text{ bar})$

E7.9(b) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ $K = 1.69 \times 10^{-3}$ at 2300 K

Initial moles $\text{N}_2 = \frac{5.0 \text{ g}}{28.01 \text{ g mol}^{-1}} = 0.2380 \text{ mol N}_2$

Initial moles $\text{O}_2 = \frac{2.0 \text{ g}}{32.00 \text{ g mol}^{-1}} = 6.250 \times 10^{-2} \text{ mol O}_2$

	N_2	O_2	NO	Total
Initial amount/mol	0.2380	0.0625	0	0.300
Change/mol	$-z$	$-z$	$+2z$	0
Equilibrium amount/mol	$0.2380 - z$	$0.0625 - z$	$2z$	0.300
Mole fractions	$\frac{0.2380 - z}{0.300}$	$\frac{0.0625 - z}{0.300}$	$\frac{2z}{0.300}$	(1)

$K = K_x \left(\frac{p}{p^\ominus} \right)^\nu \left[\nu = \sum_j \nu_j = 0 \right]$, then

$$\begin{aligned} K &= K_x = \frac{(2z/0.300)^2}{\left(\frac{0.2380 - z}{0.300} \right) \times \left(\frac{0.0625 - z}{0.300} \right)} \\ &= \frac{4z^2}{(0.2380 - z)(0.0625 - z)} = 1.69 \times 10^{-3} \end{aligned}$$

$$\begin{aligned} 4z^2 &= 1.69 \times 10^{-3} \{0.01488 - 0.3005z + z^2\} \\ &= 2.514 \times 10^{-5} - (5.078 \times 10^{-4})z + (1.69 \times 10^{-3})z^2 \end{aligned}$$

$4.00 - 1.69 \times 10^{-3} = 4.00$ so

$4z^2 + (5.078 \times 10^{-4})z - 2.514 \times 10^{-5} = 0$

$$z = \frac{-5.078 \times 10^{-4} \pm \{(5.078 \times 10^{-4})^2 - 4 \times (4) \times (-2.514 \times 10^{-5})\}^{1/2}}{8}$$

$$= \frac{1}{8}(-5.078 \times 10^{-4} \pm 2.006 \times 10^{-2})$$

$z > 0$ [$z < 0$ is physically impossible] so

$$z = 2.444 \times 10^{-3}$$

$$x_{\text{NO}} = \frac{2z}{0.300} = \frac{2(2.444 \times 10^{-3})}{0.300} = \boxed{1.6 \times 10^{-2}}$$

E7.10(b) $\ln \frac{K'}{K} = \frac{\Delta_f H^\ominus}{R} \left(\frac{1}{T} - \frac{1}{T'} \right)$ so $\Delta_f H^\ominus = \frac{R \ln \left(\frac{K'}{K} \right)}{\left(\frac{1}{T} - \frac{1}{T'} \right)}$

$$T = 310 \text{ K}, \quad T' = 325 \text{ K}; \quad \text{let } \frac{K'}{K} = \kappa$$

$$\text{Now } \Delta_f H^\ominus = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})}{((1/310 \text{ K}) - (1/325 \text{ K}))} \times \ln \kappa = 55.84 \text{ kJ mol}^{-1} \ln \kappa$$

(a) $\kappa = 2$ $\Delta_f H^\ominus = (55.84 \text{ kJ mol}^{-1}) \times (\ln 2) = \boxed{39 \text{ kJ mol}^{-1}}$

(b) $\kappa = \frac{1}{2}$ $\Delta_f H^\ominus = (55.84 \text{ kJ mol}^{-1}) \times (\ln \frac{1}{2}) = \boxed{-39 \text{ kJ mol}^{-1}}$

E7.11(b) $\text{NH}_4\text{Cl}(s) \rightleftharpoons \text{NH}_3(g) + \text{HCl}(g)$

$$p = p(\text{NH}_3) + p(\text{HCl}) = 2p(\text{NH}_3) \quad [p(\text{NH}_3) = p(\text{HCl})]$$

(a) $K = \prod_j a_j^{v_j}$ [7.16]; $a(\text{gases}) = \frac{p_j}{p^\ominus}$; $a(\text{NH}_4\text{Cl}, s) = 1$

$$K = \left(\frac{p(\text{NH}_3)}{p^\ominus} \right) \times \left(\frac{p(\text{HCl})}{p^\ominus} \right) = \frac{p(\text{NH}_3)^2}{p^{\ominus 2}} = \frac{1}{4} \times \left(\frac{p}{p^\ominus} \right)^2$$

$$\text{At } 427^\circ \text{C} (700 \text{ K}), \quad K = \frac{1}{4} \times \left(\frac{608 \text{ kPa}}{100 \text{ kPa}} \right)^2 = \boxed{9.24}$$

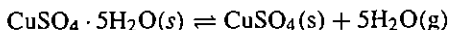
$$\text{At } 459^\circ \text{C} (732 \text{ K}), \quad K = \frac{1}{4} \times \left(\frac{1115 \text{ kPa}}{100 \text{ kPa}} \right)^2 = \boxed{31.08}$$

(b) $\Delta_r G^\ominus = -RT \ln K$ [7.8] $= (-8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (700 \text{ K}) \times (\ln 9.24)$
 $= \boxed{-12.9 \text{ kJ mol}^{-1}} \quad (\text{at } 427^\circ \text{C})$

(c) $\Delta_r H^\ominus \approx \frac{R \ln(K'/K)}{(1/T - 1/T')} [7.25]$
 $\approx \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln(31.08/9.24)}{(1/700 \text{ K}) - (1/732 \text{ K})} = \boxed{+161 \text{ kJ mol}^{-1}}$

(d) $\Delta_r S^\ominus = \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T} = \frac{(161 \text{ kJ mol}^{-1}) - (-12.9 \text{ kJ mol}^{-1})}{700 \text{ K}} = \boxed{+248 \text{ J K}^{-1} \text{ mol}^{-1}}$

E7.12(b) The reaction is

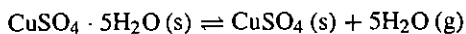


For the purposes of this exercise we may assume that the required temperature is that temperature at which $K=1$, which corresponds to a pressure of 1 bar for the gaseous products. For $K = 1$, $\ln K = 0$, and $\Delta_r G^\ominus = 0$.

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus = 0 \quad \text{when } \Delta_r H^\ominus = T \Delta_r S^\ominus$$

Therefore, the decomposition temperature (when $K = 1$) is

$$T = \frac{\Delta_r H^\ominus}{\Delta_r S^\ominus}$$

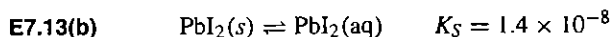


$$\Delta_r H^\ominus = [(-771.36) + (5) \times (-241.82) - (-2279.7)] \text{ kJ mol}^{-1} = +299.2 \text{ kJ mol}^{-1}$$

$$\Delta_r S^\ominus = [(109) + (5) \times (188.83) - (300.4)] \text{ J K}^{-1} \text{ mol}^{-1} = 752.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{Therefore, } T = \frac{299.2 \times 10^3 \text{ J mol}^{-1}}{752.8 \text{ J K}^{-1} \text{ mol}^{-1}} = \boxed{397 \text{ K}}$$

Question. What would the decomposition temperature be for decomposition defined as the state at which $K = 1/2$?



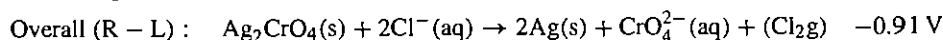
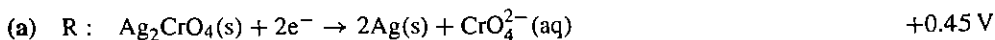
$$\begin{aligned} \Delta_r G^\ominus &= -RT \ln K_S = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K}) \times \ln(1.4 \times 10^{-8}) \\ &= 44.83 \text{ kJ mol}^{-1} \end{aligned}$$

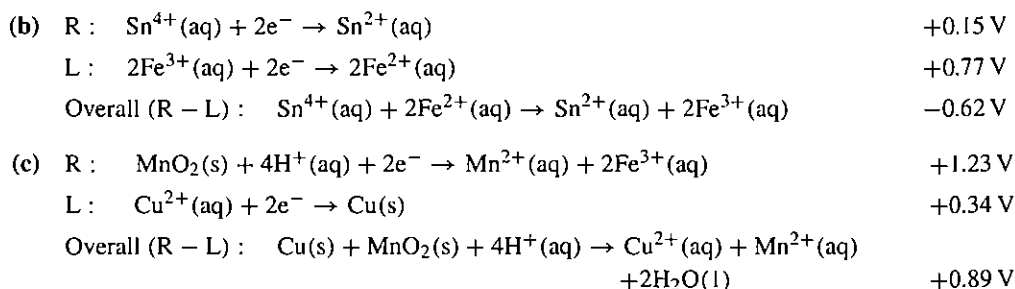
$$\Delta_r G^\ominus = \Delta_f G^\ominus(\text{PbI}_2, aq) - \Delta_f G^\ominus(\text{PbI}_2, s)$$

$$\begin{aligned} \Delta_f G^\ominus(\text{PbI}_2, aq) &= \Delta_r G^\ominus + \Delta_f G^\ominus(\text{PbI}_2, s) \\ &= 44.83 \text{ kJ mol}^{-1} - 173.64 \text{ kJ mol}^{-1} \\ &= \boxed{-128.8 \text{ kJ mol}^{-1}} \end{aligned}$$

E7.14(b) The cell notation specifies the right and left electrodes. Note that for proper cancellation we must equalize the number of electrons in half-reactions being combined.

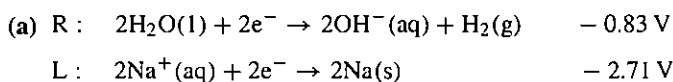
For the calculation of the standard emfs of the cells we have used $E^\ominus = E_R^\ominus - E_L^\ominus$, with standard electrode potentials from Table 7.2.



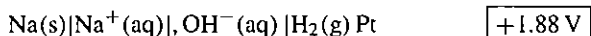


COMMENT. Those cells for which $E^{\ominus} > 0$ may operate as spontaneous galvanic cells under standard conditions. Those for which $E^{\ominus} < 0$ may operate as nonspontaneous electrolytic cells. Recall that E^{\ominus} informs us of the spontaneity of a cell under standard conditions only. For other conditions we require E .

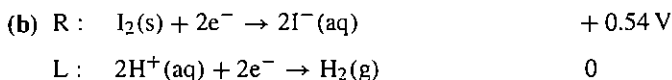
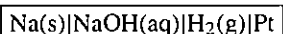
E7.15(b) The conditions (concentrations, etc.) under which these reactions occur are not given. For the purposes of this exercise we assume standard conditions. The specification of the right and left electrodes is determined by the direction of the reaction as written. As always, in combining half-reactions 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.



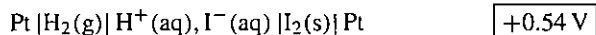
and the cell is



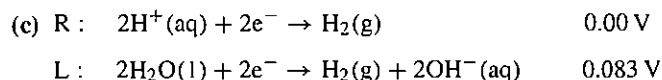
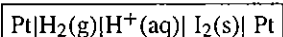
or more simply



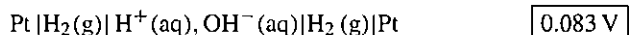
and the cell is



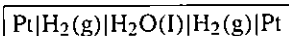
or more simply



and the cell is



or more simply



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.

E7.16(b) (a) $E = E^\ominus - \frac{RT}{\nu F} \ln Q \quad \nu = 2$

$$\begin{aligned} Q &= \prod_j a_j^{\nu_j} = a_{\text{H}^+}^2 a_{\text{Cl}^-}^2 \quad [\text{all other activities} = 1] \\ &= a_+^2 a_-^2 = (\gamma_+ b_+)^2 \times (\gamma_- b_-)^2 \quad \left[b \equiv \frac{b}{b^\ominus} \text{ here and below} \right] \\ &= (\gamma_+ \gamma_-)^2 \times (b_+ b_-)^2 = \gamma_\pm^4 b^4 \quad [5.66, b_+ = b, b_- = b] \end{aligned}$$

Hence, $E = E^\ominus - \frac{RT}{2F} \ln(\gamma_\pm^4 b^4) = \boxed{E^\ominus - \frac{2RT}{F} \ln(\gamma_\pm b)}$

(b) $\Delta_r G = -\nu F E [7.27] = -(2) \times (9.6485 \times 10^4 \text{ C mol}^{-1}) \times (0.4658 \text{ V}) = \boxed{-89.89 \text{ kJ mol}^{-1}}$

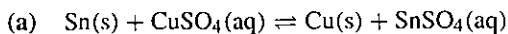
(c) $\log \gamma_\pm = -|z_+ z_-| A I^{1/2} [5.69] = -(0.509) \times (0.010)^{1/2} [I = b \text{ for HCl(aq)}] = -0.0509$

$$\gamma_\pm = 0.889$$

$$\begin{aligned} E^\ominus &= E + \frac{2RT}{F} \ln(\gamma_\pm b) = (0.4658 \text{ V}) + (2) \times (25.693 \times 10^{-3} \text{ V}) \times \ln(0.889 \times 0.010) \\ &= \boxed{+0.223 \text{ V}} \end{aligned}$$

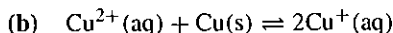
The value compares favorably to that given in Table 7.2.

E7.17(b) In each case $\ln K = \frac{\nu F E^\ominus}{RT} [7.30]$



$$\begin{array}{l} \text{R: } \text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)} \quad +0.34 \text{ V} \\ \text{L: } \text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn(s)} \quad -0.14 \text{ V} \end{array} \quad \left. \vphantom{\begin{array}{l} \text{R: } \\ \text{L: } \end{array}} \right\} +0.48 \text{ V}$$

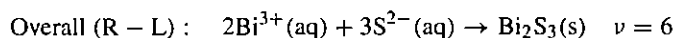
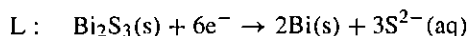
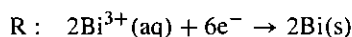
$$\ln K = \frac{(2) \times (0.48 \text{ V})}{25.693 \text{ mV}} = +37.4, \quad K = \boxed{1.7 \times 10^{16}}$$



$$\begin{array}{l} \text{R: } \text{Cu}^{2+}(\text{aq}) + \text{e}^- \rightarrow \text{Cu(aq)} \quad +0.16 \text{ V} \\ \text{L: } \text{Cu}^+(\text{aq}) + \text{e}^- \rightarrow \text{Cu(s)} \quad +0.52 \text{ V} \end{array} \quad \left. \vphantom{\begin{array}{l} \text{R: } \\ \text{L: } \end{array}} \right\} -0.36 \text{ V}$$

$$\ln K = \frac{-0.36 \text{ V}}{25.693 \text{ mV}} = -14.0, \quad K = \boxed{8.2 \times 10^{-7}}$$

E7.18(b)



$$\ln K = \frac{\nu FE^{\circ}}{RT} = \frac{6(0.96 \text{ V})}{(25.693 \times 10^{-3} \text{ V})} = 224$$

$$K = e^{224}$$

$$(a) \quad K = \frac{a_{\text{Bi}_2\text{S}_3(\text{s})}}{a_{\text{Bi}^{3+}(\text{aq})}^2 a_{\text{S}^{2-}(\text{aq})}^3} = \frac{M^5}{[\text{Bi}^{3+}]^2 [\text{S}^{2-}]^3} = e^{224}$$

In the above equation the activity of the solid equals 1 and, since the solution is extremely dilute, the activity coefficients of dissolved ions also equals 1. Substituting $[\text{S}^{2-}] = 1.5[\text{Bi}^{3+}]$ and solving for $[\text{Bi}^{3+}]$ gives $[\text{Bi}^{3+}] = 2.7 \times 10^{-20} \text{ M}$. Bi_2S_3 has a solubility equal to $1.4 \times 10^{-20} \text{ M}$.

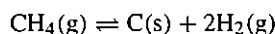
(b) The solubility equilibrium is written as the reverse of the cell reaction. Therefore,

$$K_S = K^{-1} = 1/e^{224} = 5.2 \times 10^{-98}$$

Solutions to problems

Solutions to numerical problems

P7.2



This reaction is the reverse of the formation reaction.

$$(a) \quad \Delta_r G^{\circ} = -\Delta_f G^{\circ}$$

$$\begin{aligned} \Delta_f G^{\circ} &= \Delta_f H^{\circ} - T \Delta_f S^{\circ} \\ &= -74850 \text{ J mol}^{-1} - 298 \text{ K} \times (-80.67 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= -5.08 \times 10^4 \text{ J mol}^{-1} \end{aligned}$$

$$\ln K = \frac{\Delta_r G^{\circ}}{-RT} [7.8] = \frac{5.08 \times 10^4 \text{ J mol}^{-1}}{-8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = -20.508$$

$$K = 1.24 \times 10^{-9}$$

$$(b) \quad \Delta_r H^{\circ} = -\Delta_f H^{\circ} = 74.85 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \ln K(50^{\circ}\text{C}) &= \ln K(298 \text{ K}) - \frac{\Delta_r H^{\circ}}{R} \left(\frac{1}{323 \text{ K}} - \frac{1}{298 \text{ K}} \right) [7.25] \\ &= -20.508 - \left(\frac{74850 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times (-2.597 \times 10^{-4}) = -18.170 \end{aligned}$$

$$K(50^{\circ}\text{C}) = 1.29 \times 10^{-8}$$

(c) Draw up the equilibrium table

	CH ₄ (g)	H ₂ (g)
Amounts	$(1 - \alpha)n$	$2\alpha n$
Mole fractions	$\frac{1 - \alpha}{1 + \alpha}$	$\frac{2\alpha}{1 + \alpha}$
Partial pressures	$\left(\frac{1 - \alpha}{1 + \alpha}\right)p$	$\frac{2\alpha}{1 + \alpha}$

$$K = \prod_j a_j^{v_j} [7.16] = \frac{(p_{H_2}/p^\ominus)^2}{(p_{CH_4}/p^\ominus)}$$

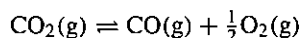
$$1.24 \times 10^{-9} = \frac{(2\alpha)^2}{1 - \alpha^2} \left(\frac{p}{p^\ominus}\right) \approx 4\alpha^2 p \quad [\alpha \ll 1]$$

$$\alpha = \frac{1.24 \times 10^{-9}}{4 \times 0.010} = \boxed{1.8 \times 10^{-4}}$$

(d) Le Chatelier's principle provides the answers.

As pressure increases, α decreases, since the more compact state (less moles of gas) is favored at high pressures. As temperature increases the side of the reaction which can absorb heat is favored. 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.

P7.4



Draw up the following equilibrium table

	CO ₂	CO	O ₂
Amounts	$(1 - \alpha)n$	αn	$\frac{1}{2}\alpha n$
Mole fractions	$\frac{(1 - \alpha)}{(1 + (\alpha/2))}$	$\frac{\alpha}{(1 + (\alpha/2))}$	$\frac{(1/2)\alpha}{(1 + (\alpha/2))}$
Partial pressures	$\frac{(1 - \alpha)p}{(1 + (\alpha/2))}$	$\frac{\alpha p}{(1 + (\alpha/2))}$	$\frac{\alpha p}{2(1 + (\alpha/2))}$

$$K = \left(\prod_j a_j^{v_j} \right)_{\text{equilibrium}} [7.16] = \frac{(p_{\text{CO}}/p^\ominus) \times (p_{\text{O}_2}/p^\ominus)^{1/2}}{(p_{\text{CO}_2}/p^\ominus)}$$

$$= \frac{(\alpha)/((1 + (\alpha/2)) \times ((\alpha/2))/(1 + (\alpha/2))^{1/2} \times (p/p^\ominus)^{1/2}}{(1 - \alpha)/(1 + (\alpha/2))}$$

$$K \approx \frac{\alpha^{3/2}}{\sqrt{2}} \quad [\alpha \ll 1 \text{ at all the specified temperatures}]$$

$$\Delta_r G^\ominus = -RT \ln K [7.8]$$

The calculated values of K and $\Delta_r G^\ominus$ are given in the table below. From any two pairs of K and T , $\Delta_r H^\ominus$ may be calculated.

$$\ln K_2 = \ln K_1 - \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) [7.25]$$

Solving for $\Delta_r H^\ominus$

$$\begin{aligned} \Delta_r H^\ominus &= \frac{R \ln \left(\frac{K_2}{K_1} \right)}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} [\text{Exercise 7.10}] = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left(\frac{7.23 \times 10^{-6}}{1.22 \times 10^{-6}} \right)}{\left(\frac{1}{1395 \text{ K}} - \frac{1}{1498 \text{ K}} \right)} \\ &= \boxed{3.00 \times 10^5 \text{ J mol}^{-1}} \end{aligned}$$

$$\Delta_r S^\ominus = \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T}$$

The calculated values of $\Delta_r S^\ominus$ are also given in the table.

T/K	1395	1443	1498
$\alpha/10^{-4}$	1.44	2.50	4.71
$K/10^{-6}$	1.22	2.80	7.23
$\Delta_r G^\ominus/(\text{kJ mol}^{-1})$	158	153	147
$\Delta_r S^\ominus/(\text{J K}^{-1} \text{ mol}^{-1})$	102	102	102

COMMENT. $\Delta_r S^\ominus$ is essentially constant over this temperature range but it is much different from its value at 25 °C. $\Delta_r H^\ominus$, however, is only slightly different.

Question. What are the values of $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ at 25 °C for this reaction?

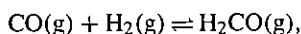
P7.6

$$\Delta_r G^\ominus(\text{H}_2\text{CO}, \text{g}) = \Delta_r G^\ominus(\text{H}_2\text{CO}, \text{l}) + \Delta_{\text{vap}} G^\ominus(\text{H}_2\text{CO}, \text{l})$$

$$\text{For } \text{H}_2\text{CO}(\text{l}) \rightleftharpoons \text{H}_2\text{CO}(\text{g}), \quad K(\text{vap}) = \frac{p}{p^\ominus}$$

$$\begin{aligned} \Delta_{\text{vap}} G^\ominus &= -RT \ln K(\text{vap}) = -RT \ln \frac{p}{p^\ominus} \quad p^\ominus = 750 \text{ Torr} \\ &= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln \left(\frac{1500 \text{ Torr}}{750 \text{ Torr}} \right) = -1.72 \text{ kJ mol}^{-1} \end{aligned}$$

Therefore, for the reaction



$$\Delta_r G^\ominus = (+28.95) + (-1.72) \text{ kJ mol}^{-1} = +27.23 \text{ kJ mol}^{-1}$$

$$\text{Hence, } K = e^{-(27.23 \times 10^3 \text{ J mol}^{-1})/(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} = e^{-10.99} = \boxed{1.69 \times 10^{-5}}$$

P7.8 Draw up the following table using $\text{H}_2(\text{g}) + \text{I}_2 \rightleftharpoons 2\text{HI}(\text{g})$

	H_2	I_2	HI	Total
Initial amounts/mol	0.300	0.400	0.200	0.900
Change/mol	$-x$	$-x$	$+2x$	
Equilibrium amounts/mol	$0.300 - x$	$0.400 - x$	$0.200 + 2x$	0.900
Mole fraction	$(0.300 - x)/0.900$	$(0.400 - x)/0.900$	$(0.200 + 2x)/0.900$	1

$$K = \frac{\left(\frac{p(\text{HI})}{p^\ominus}\right)^2}{\left(\frac{p(\text{H}_2)}{p^\ominus}\right)\left(\frac{p(\text{I}_2)}{p^\ominus}\right)} = \frac{x(\text{HI})^2}{x(\text{H}_2)x(\text{I}_2)} [p(\text{J}) = x_{\text{J}}p] = \frac{(0.200 + 2x)^2}{(0.300 - x)(0.400 - x)} = 870 \text{ [given]}$$

Therefore,

$$(0.0400) + (0.800x) + 4x^2 = (870) \times (0.120 - 0.700x + x^2) \quad \text{or}$$

$$866x^2 - 609.80x + 104.36 = 0$$

which solves to $x = 0.293$ [$x = 0.411$ is excluded because x cannot exceed 0.300]. The final composition is therefore $\boxed{0.007 \text{ mol H}_2}$, 0.107 mol I_2 , and $\boxed{0.786 \text{ mol HI}}$.

P7.10 If we knew $\Delta_r H^\ominus$ for this reaction, we could calculate $\Delta_f H^\ominus(\text{HClO})$ from

$$\Delta_r H^\ominus = 2\Delta_f H^\ominus(\text{HClO}) - \Delta_f H^\ominus(\text{Cl}_2\text{O}) - \Delta_f H^\ominus(\text{H}_2\text{O})$$

We can find $\Delta_r H^\ominus$ if we know $\Delta_r G^\ominus$ and $\Delta_r S^\ominus$, since

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$$

And we can find $\Delta_r G^\ominus$ from the equilibrium constant.

$$K = \exp(-\Delta_r G^\ominus/RT) \quad \text{so} \quad \Delta_r G^\ominus = -RT \ln K,$$

$$\Delta_r G^\ominus = -(8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \ln 8.2 \times 10^{-2}$$

$$= 6.2 \text{ kJ mol}^{-1}$$

$$\Delta_r H^\ominus = \Delta_r G^\ominus + T\Delta_r S^\ominus$$

$$= 6.2 \text{ kJ mol}^{-1} + (298 \text{ K}) \times (16.38 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}),$$

$$\Delta_r H^\ominus = 11.1 \text{ kJ mol}^{-1}$$

Finally,

$$\Delta_f H^\ominus(\text{HClO}) = \frac{1}{2} [\Delta_r H^\ominus + \Delta_f H^\ominus(\text{Cl}_2\text{O}) + \Delta_f H^\ominus(\text{H}_2\text{O})],$$

$$\Delta_f H^\ominus(\text{HClO}) = \frac{1}{2} [11.1 + 77.2 + (-241.82)] \text{ kJ mol}^{-1}$$

$$= \boxed{76.8 \text{ kJ mol}^{-1}}$$

P7.12 The equilibrium to be considered is (A = gas)

$$A(g, 1 \text{ bar}) \rightleftharpoons A(\text{sol'n}) \quad K = \frac{(c/c^\ominus)}{(p/p^\ominus)} = \frac{s}{s^\ominus}$$

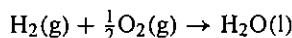
$$\Delta_r H^\ominus = -R \times \frac{d \ln K}{d(1/T)} \quad [7.23]$$

$$\ln K = \ln \left(\frac{s}{s^\ominus} \right) = 2.303 \log \left(\frac{s}{s^\ominus} \right)$$

$$\begin{aligned} \Delta_r H^\ominus(\text{H}_2) &= -(2.303) \times (R) \times \frac{d}{d(1/T)} \left(-5.39 - \frac{768 \text{ K}}{T} \right) \\ &= 2.303R \times 768 \text{ K} = \boxed{+14.7 \text{ kJ mol}^{-1}} \end{aligned}$$

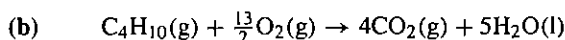
$$\begin{aligned} \Delta_r H^\ominus(\text{CO}) &= -(2.303) \times (R) \times \frac{d}{d(1/T)} \left(-5.98 - \frac{980 \text{ K}}{T} \right) \\ &= 2.303R \times 980 \text{ K} = \boxed{+18.8 \text{ kJ mol}^{-1}} \end{aligned}$$

P7.14 (a) The cell reaction is



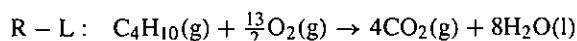
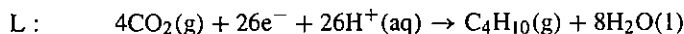
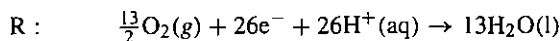
$$\Delta_r G^\ominus = \Delta_f G^\ominus(\text{H}_2\text{O}, \text{l}) = -237.13 \text{ kJ mol}^{-1} \quad [\text{Table 2.7}]$$

$$E^\ominus = \frac{\Delta_r G^\ominus}{\nu F} \quad [7.28] = \frac{+237.13 \text{ kJ mol}^{-1}}{(2) \times (96.485 \text{ kC mol}^{-1})} = \boxed{+1.23 \text{ V}}$$



$$\begin{aligned} \Delta_r G^\ominus &= 4\Delta_f G^\ominus(\text{CO}_2, \text{g}) + 5\Delta_f G^\ominus(\text{H}_2\text{O}, \text{l}) - \Delta_f G^\ominus(\text{C}_4\text{H}_{10}, \text{g}) \\ &= (4) \times (-394.36) + (5) \times (-237.13) - (-17.03) \text{ kJ mol}^{-1} \quad [\text{Table 2.7}] \\ &= -2746.06 \text{ kJ mol}^{-1} \end{aligned}$$

In this reaction the number of electrons transferred, ν is not immediately apparent as in part (a). To find ν we break the cell reaction down into half-reactions as follows



Hence, $\nu = 26$.

$$\text{Therefore, } E = \frac{-\Delta_r G^\ominus}{\nu F} = \frac{+2746.06 \text{ kJ mol}^{-1}}{(26) \times (96.485 \text{ kC mol}^{-1})} = \boxed{+1.09 \text{ V}}$$

P7.16 (a) $E = E^\ominus - \frac{25.693 \text{ mV}}{\nu} \ln Q$ [Illustration 7.10, 25 °C]
 $Q = a(\text{Zn}^{2+})a^2(\text{Cl}^-)$
 $= \gamma_+ \left(\frac{b}{b^\ominus} \right) (\text{Zn}^{2+}) \gamma_-^2 \left(\frac{b}{b^\ominus} \right)^2 (\text{Cl}^-); b(\text{Zn}^{2+}) = b; b(\text{Cl}^-) = 2b; \gamma_+ \gamma_-^2 = \gamma_\pm^3$
 Therefore, $Q = \gamma_\pm^3 \times 4b^3 \left[b \equiv \frac{b}{b^\ominus} \text{ here and below} \right]$
 and $E = E^\ominus - \frac{25.693 \text{ mV}}{2} \ln(4b^3 \gamma_\pm^3) = E^\ominus - \left(\frac{3}{2} \right) \times (25.693 \text{ mV}) \times \ln(4^{1/3} b \gamma_\pm)$

$$= \boxed{E^\ominus - (38.54 \text{ mV}) \times \ln(4^{1/3} b) - (38.54 \text{ mV}) \ln(\gamma_\pm)}$$

(b) $E^\ominus(\text{Cell}) = E_R^\ominus - E_L^\ominus = E^\ominus(\text{Hg}_2\text{Cl}_2, \text{Hg}) - E^\ominus(\text{Zn}^{2+}, \text{Zn})$
 $= (0.2676 \text{ V}) - (-0.7628 \text{ V}) = \boxed{+1.0304 \text{ V}}$

(c) $\Delta_r G = -\nu F E = -(2) \times (9.6485 \times 10^4 \text{ C mol}^{-1}) \times (1.2272 \text{ V}) = -236.81 \text{ kJ mol}^{-1}$
 $\Delta_r G^\ominus = -\nu F E^\ominus = -(2) \times (9.6485 \times 10^4 \text{ C mol}^{-1}) \times (1.0304 \text{ V}) = \boxed{-198.84 \text{ kJ mol}^{-1}}$
 $\ln K = -\frac{\Delta_r G^\ominus}{RT} = \frac{1.9884 \times 10^5 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})} = 80.211 \quad K = \boxed{6.84 \times 10^{34}}$

(d) From part (a)

$$1.2272 \text{ V} = 1.0304 \text{ V} - (38.54 \text{ mV}) \times \ln(4^{1/3} \times 0.0050) - (38.54 \text{ mV}) \times \ln \gamma_\pm$$

$$\ln \gamma_\pm = -\frac{(1.2272 \text{ V}) - (1.0304 \text{ V}) - (0.1864 \text{ V})}{0.03854 \text{ V}} = -0.2698; \quad \gamma_\pm = \boxed{0.763}$$

(e) $\log \gamma_\pm = -|z_- z_+| A I^{1/2}$ [5.69]

$$I = \frac{1}{2} \sum_i z_i^2 \left(\frac{b_i}{b^\ominus} \right) \text{ [5.70]}$$

$$b(\text{Zn}^{2+}) = b = 0.0050 \text{ mol kg}^{-1} \quad b(\text{Cl}^-) = 2b = 0.010 \text{ mol kg}^{-1}$$

$$I = \frac{1}{2} [(4) \times (0.0050) + (0.010)] = 0.015$$

$$\log \gamma_\pm = -(2) \times (0.509) \times (0.015)^{1/2} = -0.125; \quad \gamma_\pm = \boxed{0.75}$$

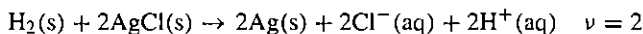
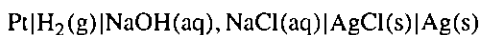
This compares remarkably well to the value obtained from experimental data in part (d).

(f) $\Delta_r S = - \left(\frac{\partial \Delta_r G}{\partial T} \right)_p$
 $= \nu F \left(\frac{\partial E}{\partial T} \right)_p$ [7.39] $= (2) \times (9.6485 \times 10^4 \text{ C mol}^{-1}) \times (-4.52 \times 10^{-4} \text{ V K}^{-1})$
 $= \boxed{-87.2 \text{ J K}^{-1} \text{ mol}^{-1}}$

$$\Delta_r H = \Delta_r G + T \Delta_r S = (-236.81 \text{ kJ mol}^{-1}) + (298.15 \text{ K}) \times (-87.2 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$= \boxed{-262.4 \text{ kJ mol}^{-1}}$$

P7.18



$$\begin{aligned} E &= E^\ominus - \frac{RT}{2F} \ln Q, \quad Q = a(\text{H}^+)^2 a(\text{Cl}^-)^2 \quad [f/p^\ominus = 1] \\ &= E^\ominus - \frac{RT}{F} \ln a(\text{H}^+) a(\text{Cl}) = E^\ominus - \frac{RT}{F} \ln \frac{K_w a(\text{Cl}^-)}{a(\text{OH}^-)} = E^\ominus - \frac{RT}{F} \ln \frac{K_w \gamma_{\pm} b(\text{Cl}^-)}{\gamma_{\pm} b(\text{OH}^-)} \\ &= E^\ominus - \frac{RT}{F} \ln \frac{K_w b(\text{Cl}^-)}{b(\text{OH}^-)} = E^\ominus - \frac{RT}{F} \ln K_w - \frac{RT}{F} \ln \frac{b(\text{Cl}^-)}{b(\text{OH}^-)} \\ &= E^\ominus + (2.303) \frac{RT}{F} \times \text{p}K_w - \frac{RT}{F} \ln \frac{b(\text{Cl}^-)}{b(\text{OH}^-)} \quad \left(\text{p}K_w = -\log K_w = \frac{-\ln K_w}{2.303} \right) \end{aligned}$$

$$\text{Hence, } \text{p}K_w = \frac{E - E^\ominus}{2.303RT/F} + \frac{\ln \left(\frac{b(\text{Cl}^-)}{b(\text{OH}^-)} \right)}{2.303} = \frac{E - E^\ominus}{2.303RT/F} + 0.05114$$

$$E^\ominus = E_R^\ominus - E_L^\ominus = E^\ominus(\text{AgCl}, \text{Ag}) - E^\ominus(\text{H}^+/\text{H}_2) = +0.22 \text{ V} - 0 \text{ [Table 7.2]}$$

We then draw up the following table with the more precise value for $E^\ominus = +0.2223 \text{ V}$ [See the solution to Problem 10.8, 7th edition]

$\theta/^\circ\text{C}$	20.0	25.0	30.0
E/V	1.04774	1.04864	1.04942
$\frac{(2.303RT/F)}{\text{V}}$	0.05819	0.05918	0.06018
$\text{p}K_w$	14.23	14.01	13.79

$$\frac{d \ln K_w}{dT} = \frac{\Delta_r H^\ominus}{RT^2} \quad [7.23]$$

$$\text{Hence, } \Delta_r H^\ominus = -(2.303)RT^2 \frac{d}{dT}(\text{p}K_w)$$

$$\text{then with } \frac{d \text{p}K_w}{dT} \approx \frac{\Delta \text{p}K_w}{\Delta T}$$

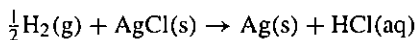
$$\begin{aligned} \Delta_r H^\ominus &\approx -(2.303) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})^2 \times \frac{13.79 - 14.23}{10 \text{ K}} \\ &= \text{+74.9 kJ mol}^{-1} \end{aligned}$$

$$\Delta_r G^\ominus = -RT \ln K_w = 2.303 RT \times \text{p}K_w = \text{+80.0 kJ mol}^{-1}$$

$$\Delta_r S^\ominus = \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T} = \text{-17.1 J K}^{-1} \text{ mol}^{-1}$$

See the original reference for a careful analysis of the precise data.

P7.20 The method of the solution is first to determine $\Delta_r G^\ominus$, $\Delta_r H^\ominus$, and $\Delta_r S^\ominus$ for the cell reaction



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)

$$\begin{aligned} E^\ominus/\text{V} &= (0.23659) - (4.8564 \times 10^{-4}) \times (25.00) - (3.4205 \times 10^{-6}) \times (25.00)^2 \\ &\quad + (5.869 \times 10^{-9}) \times (25.00)^3 = +0.22240 \text{ V} \end{aligned}$$

Therefore, $\Delta_r G^\ominus = -(96.485 \text{ kC mol}^{-1}) \times (0.22240 \text{ V}) = -21.46 \text{ kJ mol}^{-1}$

$$\Delta_r S^\ominus = -\left(\frac{\partial \Delta_r G^\ominus}{\partial T}\right)_p = \left(\frac{\partial E^\ominus}{\partial T}\right)_p \times \nu F = \nu F \left(\frac{\partial E^\ominus}{\partial \theta}\right)_p \frac{^\circ\text{C}}{\text{K}} \quad [\text{d}\theta/^\circ\text{C} = \text{d}T/\text{K}] \quad (\text{a})$$

$$\begin{aligned} \frac{(\partial E^\ominus/\partial \theta)_p}{\text{V}} &= (-4.8564 \times 10^{-4}/^\circ\text{C}) - (2) \times (3.4205 \times 10^{-6}\theta/^\circ\text{C}^2) \\ &\quad + (3) \times (5.869 \times 10^{-9}\theta^2/^\circ\text{C}^3) \end{aligned}$$

$$\frac{(\partial E^\ominus/\partial \theta)_p}{\text{V}/^\circ\text{C}} = (-4.8564 \times 10^{-4}) - (6.8410 \times 10^{-6}(\theta/^\circ\text{C})) + (1.7607 \times 10^{-8}(\theta/^\circ\text{C})^2)$$

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

$$\left(\frac{\partial E^\ominus}{\partial T}\right)_p = (-6.4566 \times 10^{-4} \text{ V}/^\circ\text{C}) \times (^\circ\text{C}/\text{K}) = -6.4566 \times 10^{-4} \text{ V K}^{-1}$$

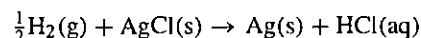
Hence, from equation (a)

$$\Delta_r S^\ominus = (-96.485 \text{ kC mol}^{-1}) \times (6.4566 \times 10^{-4} \text{ V K}^{-1}) = -62.30 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{and } \Delta_r H^\ominus = \Delta_r G^\ominus + T \Delta_r S^\ominus$$

$$= -(21.46 \text{ kJ mol}^{-1}) + (298.15 \text{ K}) \times (-62.30 \text{ J K}^{-1} \text{ mol}^{-1}) = -40.03 \text{ kJ mol}^{-1}$$

For the cell reaction



$$\begin{aligned} \Delta_r G^\ominus &= \Delta_f G^\ominus(\text{H}^+) + \Delta_f G^\ominus(\text{Cl}^-) - \Delta_f G^\ominus(\text{AgCl}) \\ &= \Delta_f G^\ominus(\text{Cl}^-) - \Delta_f G^\ominus(\text{AgCl}) \quad [\Delta_f G^\ominus(\text{H}^+) = 0] \end{aligned}$$

$$\begin{aligned}\text{Hence, } \Delta_f G^\ominus(\text{Cl}^-) &= \Delta_r G^\ominus + \Delta_f G^\ominus(\text{AgCl}) = [(-21.46) - (109.79) \text{ kJ mol}^{-1}] \\ &= \boxed{-131.25 \text{ kJ mol}^{-1}}\end{aligned}$$

$$\begin{aligned}\text{Similarly, } \Delta_f H^\ominus(\text{Cl}^-) &= \Delta_r H^\ominus + \Delta_f H^\ominus(\text{AgCl}) = (-40.03) - (127.07 \text{ kJ mol}^{-1}) \\ &= \boxed{-167.10 \text{ kJ mol}^{-1}}\end{aligned}$$

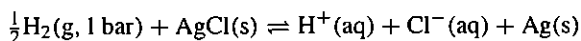
For the entropy of Cl^- in solution we use

$$\Delta_r S^\ominus = S^\ominus(\text{Ag}) + S^\ominus(\text{H}^+) + S^\ominus(\text{Cl}^-) - \frac{1}{2}S^\ominus(\text{H}_2) - S^\ominus(\text{AgCl})$$

with $S^\ominus(\text{H}^+) = 0$. Then,

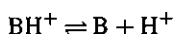
$$\begin{aligned}S^\ominus(\text{Cl}^-) &= \Delta_r S^\ominus - S^\ominus(\text{Ag}) + \frac{1}{2}S^\ominus(\text{H}_2) + S^\ominus(\text{AgCl}) \\ &= (-62.30) - (42.55) + \left(\frac{1}{2}\right) \times (130.68) + (96.2) = \boxed{+56.7 \text{ J K}^{-1} \text{ mol}^{-1}}\end{aligned}$$

P7.22 Electrochemical cell equation:



$$\text{where } f(\text{H}_2) = 1 \text{ bar} = p^\ominus a_{\text{Cl}^-} = \gamma_{\text{Cl}^-} b$$

Weak acid equilibrium:



$$\text{where } b_{\text{BH}} = b_{\text{B}} = b$$

$$\text{and } K_a = a_{\text{B}} a_{\text{H}^+} / a_{\text{BH}} = \gamma_{\text{B}} b a_{\text{H}^+} / \gamma_{\text{BH}} b = \gamma_{\text{B}} a_{\text{H}^+} / \gamma_{\text{BH}}$$

$$\text{or } a_{\text{H}} = \gamma_{\text{BH}} K_a / \gamma_{\text{B}}$$

Ionic strength (neglect b_{H^+} because $b_{\text{H}^+} \ll b$):

$$I = \frac{1}{2} \{z_{\text{BH}}^2 b_{\text{BH}} + z_{\text{Cl}^-}^2 b_{\text{Cl}^-}\} = b$$

according to the Nernst equation [7.29]

$$E = E^\ominus - \frac{RT}{F} \ln \left(\frac{a_{\text{H}} + a_{\text{Cl}^-}}{f(\text{H}_2)/p^\ominus} \right) = E^\ominus - \frac{RT \ln(10)}{F} \log(a_{\text{H}} + a_{\text{Cl}^-})$$

$$\begin{aligned}\frac{F}{RT \ln(10)} (E - E^\ominus) &= -\log(a_{\text{H}} + \gamma_{\text{Cl}^-} b) = -\log \left(\frac{K_a \gamma_{\text{BH}} \gamma_{\text{Cl}^-} b}{\gamma_{\text{B}}} \right) \\ &= pK_a - \log(b) - 2 \log(\gamma_{\pm})\end{aligned}$$

$$\frac{F}{RT \ln(10)} (E - E^\ominus) = pK_a - \log(b) + \frac{2A\sqrt{b}}{1 + B\sqrt{b}} - 2kb$$

where $A = 0.5091$.

The expression to the left of the above equality is experimental data that is a function of b . The parameters pK_a , B , and k on the right side are systematically varied with a mathematical regression software until the right side fits the left side in a least squares sense.

$$\begin{aligned} pK_a &= 6.736, & B &= 1.997 \text{ kg}^{0.5} \text{ mol}^{-0.5} \\ k &= -0.121 \text{ kg mol}^{-1} \end{aligned}$$

$$\gamma_{\pm} = 10^{\left(\frac{-A_f I^{1/2}}{1+B_f I^{1/2}} + kb\right)}$$

P7.24 (a) The Nernst equation appropriate to the fluoride selective electrode is

$$E = E_{ap} + \beta \frac{RT}{F} \ln(a_{F^-} + k_{F^-, OH^-} a_{OH^-})$$

at 298 K, this may be written, after setting $\beta \approx 1$,

$$E = E_{ap} + 0.05916 \text{ V} \log(a_{F^-} + k_{F^-, OH^-} a_{OH^-})$$

(b) At high pH, a_{OH^-} is large, and the second term inside the parentheses may be a significant fraction of a_{F^-} . At low pH, F^- is converted to HF, to which the electrode is insensitive. The activities of the species involved are related to each other through K_a .

$$K_a = \frac{a_{H^+} a_{F^-}}{a_{HF}}, \quad a_{F^-} = \frac{K_a a_{HF}}{a_{H^+}} = \frac{3.5 \times 10^{-4} a_{HF}}{a_{H^+}}$$

a_{H^+} and a_{OH^-} are related through $K_w = a_{H^+} a_{OH^-}$.

$$E = E_{ap} + 0.05916 \text{ V} \log \left[a_{F^-} + k_{F^-, OH^-} \left(\frac{K_w}{a_{H^+}} \right) \right]$$

In the following analysis, let us set all activity coefficients equal to 1. Let us draw up the following table for $E - E_{ap}$

$[F^-] \backslash \text{pH}$	4	5	6	7	8	9
10^{-7}	-0.414	-0.414	-0.414	-0.412	-0.396	-0.353
10^{-6}	-0.355	-0.355	-0.355	-0.355	-0.353	-0.337
10^{-5}	-0.296	-0.296	-0.296	-0.296	-0.296	-0.293
10^{-4}	-0.237	-0.237	-0.237	-0.237	-0.237	-0.236
10^{-3}	-0.177	-0.177	-0.177	-0.177	-0.177	-0.177
10^{-2}	-0.118	-0.118	-0.118	-0.118	-0.118	-0.118
10^{-1}	-0.059	-0.059	-0.059	-0.059	-0.059	-0.059
1	0	0	0	0	0	0

We see that at $\text{pH} \leq 8$ the emf responds linearly to $\log a_{F^-}$. At $\text{pH} = 5$ and below, the ratio

$$\frac{a_{HF}}{a_{F^-}} = \frac{a_{H^+}}{K_a} = \frac{a_{H^+}}{3.5 \times 10^{-4}} = \frac{10^{-5}}{3.5 \times 10^{-4}} = 0.029$$

indicates that a significant fraction (>0.03) of F^- has been removed from the test solution. Therefore, the acceptable pH range for the use of this electrode is $5 < \text{pH} < 8$.

Solutions to theoretical problems

P7.26

$$\Delta_r G = \Delta_r H - T \Delta_r S$$

$$\Delta_r H' = \Delta_r H + \int_T^{T'} \Delta_r C_p dT \quad [2.36]$$

$$\Delta_r S' = \Delta_r S + \int_T^{T'} \frac{\Delta_r C_p}{T} dT \quad [3.19, \text{with } \Delta_r S \text{ in place of } S]$$

$$\Delta_r G' = \Delta_r G + \int_T^{T'} \Delta_r C_p dT + (T - T') \Delta_r S - T' \int_T^{T'} \frac{\Delta_r C_p}{T} dT$$

$$= \Delta_r G + (T - T') \Delta_r S + \int_T^{T'} \left(1 - \frac{T'}{T}\right) \Delta_r C_p dT$$

$$\Delta_r C_p = \Delta a + T \Delta b + \frac{\Delta c}{T^2}$$

$$\left(1 - \frac{T'}{T}\right) \Delta_r C_p = \Delta a + T \Delta b + \frac{\Delta c}{T^2} - \frac{T' \Delta a}{T} - T' \Delta b - \frac{T' \Delta c}{T^3}$$

$$= \Delta a - T' \Delta b + T \Delta b - \frac{T' \Delta a}{T} + \frac{\Delta c}{T^2} - \frac{T' \Delta c}{T^3}$$

$$\int_T^{T'} \left(1 - \frac{T'}{T}\right) \Delta_r C_p dT = (\Delta a - T' \Delta b)(T' - T) + \frac{1}{2}(T'^2 - T^2) \Delta b - T' \Delta a \ln \frac{T'}{T}$$

$$+ \Delta c \left(\frac{1}{T} - \frac{1}{T'}\right) - \frac{1}{2} T' \Delta c \left(\frac{1}{T^2} - \frac{1}{T'^2}\right)$$

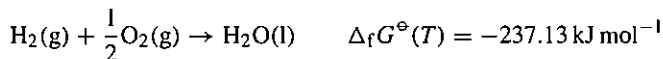
Therefore, $\boxed{\Delta_r G' = \Delta_r G + (T - T') \Delta_r S + \alpha \Delta a + \beta \Delta b + \gamma \Delta c}$

where $\alpha = T' - T - T' \ln \frac{T'}{T}$

$$\beta = \frac{1}{2}(T'^2 - T^2) - T'(T' - T)$$

$$\gamma = \frac{1}{T} - \frac{1}{T'} + \frac{1}{2} T' \left(\frac{1}{T^2} - \frac{1}{T'^2}\right)$$

For water,



$$\Delta_r S^\ominus(T) = -163.34 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned}\Delta a &= a(\text{H}_2\text{O}) - a(\text{H}_2) - \frac{1}{2}a(\text{O}_2) = (75.29 - 27.88 - 14.98) \text{ J K}^{-1} \text{ mol}^{-1} \\ &= +33.03 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$\Delta b = [(0) - (3.26 \times 10^{-3}) - (2.09 \times 10^{-3})] \text{ J K}^{-2} \text{ mol}^{-1} = -5.35 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1}$$

$$\Delta c = [(0) - (0.50 \times 10^5) + (0.83 \times 10^5)] \text{ J K mol}^{-1} = +0.33 \times 10^5 \text{ J K mol}^{-1}$$

$$T = 298 \text{ K}, \quad T' = 372 \text{ K}, \text{ so}$$

$$\alpha = -8.5 \text{ K}, \quad \beta = -2738 \text{ K}^2, \quad \gamma = -8.288 \times 10^{-5} \text{ K}^{-1}$$

and so

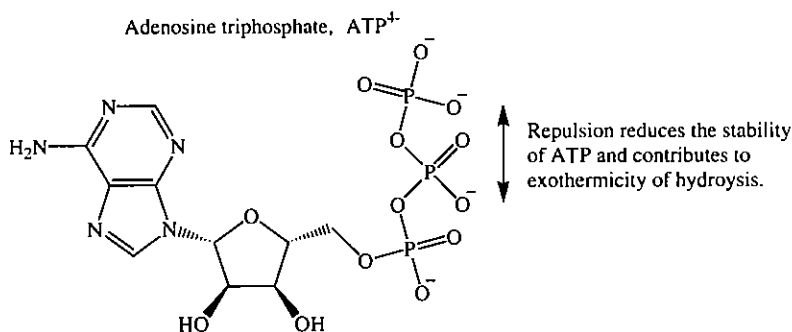
$$\begin{aligned}\Delta_r G^\ominus(372 \text{ K}) &= (-237.13 \text{ kJ mol}^{-1}) + (-74 \text{ K}) \times (-163.34 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &\quad + (-8.5 \text{ K}) \times (33.03 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \\ &\quad + (-2738 \text{ K}^2) \times (-5.35 \times 10^{-6} \text{ kJ K}^{-2} \text{ mol}^{-1}) \\ &\quad + (-8.288 \times 10^{-5} \text{ K}^{-1}) \times (0.33 \times 10^2 \text{ kJ K mol}^{-1}) \\ &= [(-237.13) + (12.09) - (0.28) + (0.015) - (0.003)] \text{ kJ mol}^{-1} \\ &= \boxed{-225.31 \text{ kJ mol}^{-1}}\end{aligned}$$

Note that the β and γ terms are not significant (for this reaction and temperature range).

Solutions to applications

- P7.28** (a) ATP hydrolysis at physiological pH, $\text{ATP}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{ADP}(\text{aq}) + \text{P}_i^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$, converts two reactant moles in three product moles. The increased number of chemical species present in solution increases the disorder of the system by increasing the number of molecular rotational, vibrational, and translational degrees of freedom. This is an effective increase in the number of available molecular states and an increase in entropy.
- (b) At physiological pH the oxygen atoms of ATP are deprotonated, negatively charged, and the molecule is best represented as ATP^{4-} . The electrostatic repulsions between the highly charged oxygen atoms of ATP^{4-} is expected to give it an exergonic hydrolysis free energy by making the hydrolysis enthalpy negative. Also, the deprotonated phosphate species, $\text{P}_i(\text{aq})$, produced in the hydrolysis ATP has more resonance structures than ATP^{4-} . Resonance lowers the energy of the dissociated phosphate making the hydrolysis enthalpy more negative and contributing to the exergonicity of the hydrolysis.

The electrostatic repulsion between the highly charged oxygen atoms of ATP^{4-} is a hypothesis that is consistent with the observation that protonated ATP, H_4ATP , has an exergonic hydrolysis free energy of smaller magnitude because the negative repulsions of oxygen atoms are not present. Likewise for MgATP^{2-} because the Mg^{2+} ion lies between negatively charged oxygen atoms, thereby, reducing repulsions and stabilizing the ATP molecule.



P7.30 Refer to *Impact* 17.2 for information necessary to the solution of this problem. The biological standard value of the Gibbs energy for ATP hydrolysis is $\approx -30 \text{ kJ mol}^{-1}$. The standard Gibbs energy of combustion of glucose is $-2880 \text{ kJ mol}^{-1}$.

- (a) If we assume that each mole of ATP formed during the aerobic breakdown of glucose produces about -30 kJ mol^{-1} , then

$$\text{efficiency} = \frac{38 \times (-30 \text{ kJ mol}^{-1})}{-2880 \text{ kJ mol}^{-1}} \times 100\% \approx \boxed{40\%}$$

- (b) For the oxidation of glucose under the biological conditions of $p_{\text{CO}_2} = 5.3 \times 10^{-2} \text{ atm}$, $p_{\text{O}_2} = 0.132 \text{ atm}$, and $[\text{glucose}] = 5.6 \times 10^{-2} \text{ mol dm}^{-3}$ we have

$$\Delta_r G' = \Delta_r G^\ominus + RT \ln Q$$

$$\text{where } Q = \frac{(p_{\text{CO}_2}/p^\ominus)^6}{[\text{glucose}] \times (p_{\text{O}_2}/p^\ominus)^9} = \frac{(5.3 \times 10^{-2})^6}{5.6 \times 10^{-2} \times (0.132)^9} = 32.5$$

Then

$$\begin{aligned} \Delta_r G' &= -2880 \text{ kJ mol}^{-1} + 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 310 \text{ K} \times \ln(32.5) \\ &= \boxed{-2871 \text{ kJ mol}^{-1}} \end{aligned}$$

which is not much different from the standard value.

For the $\text{ATP} \rightarrow \text{ADP}$ conversion under the given conditions

$$\Delta_r G' = \Delta_r G^\ominus + RT \ln \frac{Q'}{Q^\ominus}$$

$$\text{where } Q^\ominus = \frac{[\text{ADP}][\text{Pi}][\text{H}_3\text{O}^+]}{[\text{ATP}]} = \frac{1 \times 1 \times 10^{-7}}{1} = 10^{-7}$$

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

$$\begin{aligned}\Delta_r G' &= -30 \text{ kJ mol}^{-1} + RT \ln(10^{-4.4}) \\ &= -30 \text{ kJ mol}^{-1} + 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 310 \text{ K} \times (-10.1) \\ &= \boxed{-56 \text{ kJ mol}^{-1}}\end{aligned}$$

With this value for $\Delta_r G'$ the efficiency becomes

$$\text{efficiency} = \frac{38 \times (-56 \text{ kJ mol}^{-1})}{-2871 \text{ kJ mol}^{-1}} = \boxed{74\%}$$

(c) The theoretical limit of the diesel engine is

$$\varepsilon = 1 - \frac{T_c}{T_h} = 1 - \frac{873 \text{ K}}{1923 \text{ K}} = 55\%$$

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.

P7.32 Refer to *Impact* I7.2. $\Delta \text{pH} = -1.4$

The contribution to ΔG_m from the potential difference is now

$$\Delta G_m = F \Delta \phi = 9.6485 \times 10^4 \text{ C mol}^{-1} \times 0.070 \text{ V} = +6.8 \text{ kJ mol}^{-1}$$

The total ΔG_m is then $+8.0 \text{ kJ mol}^{-1} + 6.8 \text{ kJ mol}^{-1}$ or 14.8 kJ mol^{-1} .

For 4 mol H^+ , $\Delta G = 4 \times 14.8 \text{ kJ mol}^{-1} = +59.2 \text{ kJ}$

Therefore, the amount of ATP that could be synthesized is

$$\frac{59.2 \text{ kJ}}{31 \text{ kJ mol}^{-1}} = 1.9 \text{ mol} \approx \boxed{2 \text{ mol}}$$

P7.34 (a) The equilibrium constant is given by

$$K = \exp\left(\frac{-\Delta_r G^\ominus}{RT}\right) = \exp\left(\frac{-\Delta_r H^\ominus}{RT}\right) \exp\left(\frac{\Delta_r S^\ominus}{R}\right)$$

$$\text{so } \ln K = -\frac{\Delta_r H^\ominus}{RT} + \frac{\Delta_r S^\ominus}{R}$$

A plot of $\ln K$ against $1/T$ should be a straight line with a slope of $-\Delta_r H^\ominus/R$ and a y-intercept of $\Delta_r S^\ominus/R$ (Figure 7.1).

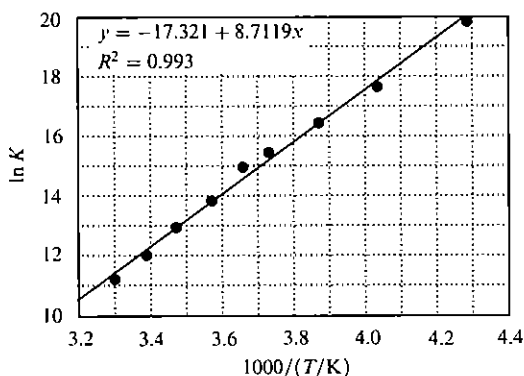
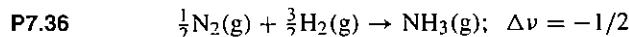


Figure 7.1

$$\begin{aligned}\text{So } \Delta_r H^\ominus &= -R \times \text{slope} = -\left(8.3145 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}\right) \times \left(8.71 \times 10^3 \text{ K}\right) \\ &= \boxed{-72.4 \text{ kJ mol}^{-1}}\end{aligned}$$

$$\text{and } \Delta_r S^\ominus = R \times \text{intercept} = \left(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}\right) \times (-17.3) = \boxed{-144 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\begin{aligned}\text{(b) } \Delta_r H^\ominus &= \Delta_r H^\ominus ((\text{ClO})_2) - 2\Delta_r H^\ominus (\text{ClO}) \quad \text{so} \quad \Delta_r H^\ominus ((\text{ClO})_2) = \Delta_r H^\ominus + 2\Delta_r H^\ominus (\text{ClO}), \\ \Delta_r H^\ominus ((\text{ClO})_2) &= [-72.4 + 2(101.8)] \text{ kJ mol}^{-1} = \boxed{+131.2 \text{ kJ mol}^{-1}} \\ S^\ominus ((\text{ClO})_2) &= [-144 + 2(226.6)] \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{+309.2 \text{ J K}^{-1} \text{ mol}^{-1}}\end{aligned}$$



First, calculate the standard reaction thermodynamic functions with formation thermodynamic properties found in the appendix (Table 2.7).

$$\Delta_r H^\ominus(298) = -46.11 \text{ kJ} \quad \text{and} \quad \Delta_r S^\ominus(298) = -99.38 \text{ J K}^{-1}$$

Use appendix information to define functions for the constant pressure heat capacity of reactants and products (Table 2.2). Define a function $\Delta_r C_p^\ominus(T)$ that makes it possible to calculate $\Delta_r C_p$ at 1 bar and any temperature (eqn 2.37). Define functions that make it possible to calculate the reaction enthalpy and entropy at 1 bar and any temperature (eqns 2.36 and 3.19).

$$\begin{aligned}\Delta_r H^\ominus(T) &= \Delta_r H^\ominus(298) + \int_{298.15 \text{ K}}^T \Delta_r C_p^\ominus(T) dT \\ \Delta_r S^\ominus(T) &= \Delta_r S^\ominus(298) + \int_{298.15 \text{ K}}^T \frac{\Delta_r C_p^\ominus(T)}{T} dT\end{aligned}$$

For a perfect gas reaction mixture $\Delta_r H$ is independent of pressure at constant temperature. Consequently, $\Delta_r H(T, p) = \Delta_r H^\ominus(T)$. The pressure dependence of the reaction entropy may be evaluated with the

expression:

$$\begin{aligned}
 \Delta_r S(T_p) &= \Delta_r S^\ominus(T) + \sum_{\text{Products}-\text{Reactants}} \nu \int_{1 \text{ bar}}^p \left(\frac{\partial S_m}{\partial p} \right)_T dp \\
 &= \Delta_r S^\ominus(T) - \sum_{\text{Products}-\text{Reactants}} \nu \int_{1 \text{ bar}}^p \left(\frac{\partial V_m}{\partial T} \right)_p dp \quad [\text{Table 3.5}] \\
 &= \Delta_r S^\ominus(T) - \sum_{\text{Products}-\text{Reactants}} \nu \int_{1 \text{ bar}}^p \frac{R}{p} dp \\
 &= \Delta_r S^\ominus(T) - \left[\sum_{\text{Products}-\text{Reactants}} \nu \right] R \ln \left(\frac{p}{1 \text{ bar}} \right) \\
 &= \Delta_r S^\ominus(T) - 1/2 R \ln \left(\frac{p}{1 \text{ bar}} \right)
 \end{aligned}$$

The above two eqns make it possible to calculate $\Delta_r G(T, p)$.

$$\Delta_r G(T, p) = \Delta_r H(T, p) - T \Delta_r S(T, p)$$

Once the above functions have been defined on a scientific calculator or with mathematical software on a computer, the root function may be used to evaluate pressure where $\Delta_r G(T, p) = -500 \text{ J}$ at a given temperature.

(i) (a) and (b) perfect gas mixture:

$$\text{For } T = (450 + 273.15) \text{ K} = 723.15 \text{ K, root}(\Delta_r G(723.15 \text{ K}, p) + 500 \text{ J}) = \boxed{156.5 \text{ bar}}$$

$$\text{For } T = (400 + 273.15) \text{ K} = 673.15 \text{ K, root}(\Delta_r G(673.15 \text{ K}, p) + 500 \text{ J}) = \boxed{81.8 \text{ bar}}$$

For a van der Waals gas mixture $\Delta_r H$ does depend upon pressure. The calculational equation is:

$$\begin{aligned}
 \Delta_r H(T, P) &= \Delta_r H^\ominus(T) + \sum_{\text{Products}-\text{Reactants}} \nu \int_{1 \text{ bar}}^p \left(\frac{\partial H_m}{\partial p} \right)_T dp \\
 &= \Delta_r H^\ominus(T) + \sum_{\text{Products}-\text{Reactants}} \nu \int_{1 \text{ bar}}^p \left[V_m - T \left(\frac{\partial H_m}{\partial p} \right)_p \right] dp \\
 &\quad [\text{Theoretical Problem 3.28}]
 \end{aligned}$$

$$\text{where } (\partial V_m / \partial T)_p = R(V_m - b)^{-1} (RT(V_m - b)^{-2} - 2aV_m^{-3})^{-1}$$

$$\text{and } V_m(T, p) = \text{root} \left(P - \frac{RT}{V_m - b} + \frac{a}{V_m^2} \right)$$

The functional equation for $\Delta_r S$ calculations is:

$$\Delta_r S(T, P) = \Delta_r S^\ominus(T) - \sum_{\text{Products}-\text{Reactants}} \nu \int_{1 \text{ bar}}^p \left(\frac{\partial V_m}{\partial T} \right)_p dp$$

where $(\partial V_m / \partial T)_p$ and $V_m(T, p)$ are calculated as described above. As usual, $\Delta_r G(T, p) = \Delta_r H(T, p) - T \Delta_r S(T, p)$.

(a) and (b) van der Waals gas mixture:

$$\text{For } T = 723.15 \text{ K, } \text{root}(\Delta_r G(723.15 \text{ K}, p) + 500 \text{ J}) = \boxed{132.5 \text{ bar}}$$

$$\text{For } T = 673.15 \text{ K, } \text{root}(\Delta_r G(673.15 \text{ K}, p) + 500 \text{ J}) = \boxed{73.7 \text{ bar}}$$

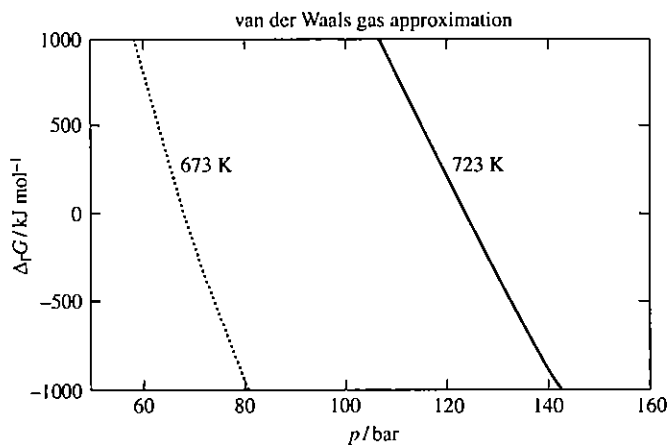


Figure 7.2

(c) $\Delta_r G(T, p)$ isotherms Le Chatelier's principle. Along an isotherm, $\Delta_r G$ decreases as pressure increases. This corresponds to a shift to the right in the reaction equation and reduces the stress by shifting to the side that has fewer total moles of gas. Additionally the reaction is exothermic, so Chatelier's principle predicts a shift to the left with an increase in temperature. The isotherms confirm this as an increase in $\Delta_r G$ as temperature is increased at constant pressure. See Figure 7.2.

PART 2 Structure

8

Quantum theory: introduction and principles

Answers to discussion questions

D8.2 A successful theory of black-body radiation must be able to explain the energy density distribution of the radiation as a function of wavelength, in particular, the observed drop to zero as $\lambda \rightarrow 0$. 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.

D8.4 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 8.25b)

$$\Omega\Psi = \omega\Psi$$

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 8.34.

$$\langle\Omega\rangle = \int \Psi^* \Omega \Psi d\tau.$$

D8.6 See Figs. 8.16, 8.26–8.30 of the text.

Solutions to exercises

E8.1(b) The de Broglie relation is

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad \text{so} \quad v = \frac{h}{m\lambda} = \frac{6.626 \times 10^{-34} \text{ J s}}{(1.675 \times 10^{-27} \text{ kg}) \times (3.0 \times 10^{-2} \text{ m})}$$

$$v = \boxed{1.3 \times 10^{-5} \text{ m s}^{-1}} \quad \text{extremely slow!}$$

E8.2(b) The moment 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

$$p = mv \quad \text{so} \quad v = \frac{p}{m} = \frac{1.89 \times 10^{-27} \text{ kg m s}^{-1}}{2(1.0078 \times 10^{-3} \text{ kg mol}^{-1}) / (6.022 \times 10^{23} \text{ mol}^{-1})}$$

$$v = \boxed{0.565 \text{ m s}^{-1}}$$

E8.3(b) The uncertainty principle is

$$\Delta p \Delta x \geq \frac{1}{2} \hbar$$

so the minimum uncertainty in position is

$$\Delta x = \frac{\hbar}{2\Delta p} = \frac{\hbar}{2m\Delta v} = \frac{1.0546 \times 10^{-34} \text{ J s}}{2(9.11 \times 10^{-31} \text{ kg}) \times (0.000010) \times (995 \times 10^3 \text{ m s}^{-1})}$$

$$= \boxed{5.8 \times 10^{-6} \text{ m}}$$

E8.4(b) $E = h\nu = \frac{hc}{\lambda}$; $E(\text{per mole}) = N_A E = \frac{N_A hc}{\lambda}$

$$hc = (6.62608 \times 10^{-34} \text{ J s}) \times (2.99792 \times 10^8 \text{ m s}^{-1}) = 1.986 \times 10^{-25} \text{ J m}$$

$$N_A hc = (6.02214 \times 10^{23} \text{ mol}^{-1}) \times (1.986 \times 10^{-25} \text{ J m}) = 0.1196 \text{ J m mol}^{-1}$$

$$\text{Thus, } E = \frac{1.986 \times 10^{-25} \text{ J m}}{\lambda}; \quad E(\text{per mole}) = \frac{0.1196 \text{ J m mol}^{-1}}{\lambda}$$

We can therefore draw up the following table

λ	E/J	$E/(\text{kJ mol}^{-1})$
(a) 200 nm	0.93×10^{-19}	598
(b) 150 pm	1.32×10^{-15}	7.98×10^5
(c) 1.00 cm	1.99×10^{-23}	0.012

- E8.5(b)** Assuming that the ^4He atom is free and stationary, if a photon is absorbed, the atom acquires its momentum p achieving a speed v such that $p = mv$.

$$v = \frac{p}{m} \quad m = 4.00 \times 1.6605 \times 10^{-27} \text{ kg} = 6.642 \times 10^{-27} \text{ kg}$$

$$p = \frac{h}{\lambda}$$

$$(a) \quad p = \frac{6.626 \times 10^{-34} \text{ J s}}{200 \times 10^{-9} \text{ m}} = 3.313 \times 10^{-27} \text{ kg m s}^{-1}$$

$$v = \frac{p}{m} = \frac{3.313 \times 10^{-27} \text{ kg m s}^{-1}}{6.642 \times 10^{-27} \text{ kg}} = \boxed{0.499 \text{ m s}^{-1}}$$

$$(b) \quad p = \frac{6.626 \times 10^{-34} \text{ J s}}{150 \times 10^{-12} \text{ m}} = 4.417 \times 10^{-24} \text{ kg m s}^{-1}$$

$$v = \frac{p}{m} = \frac{4.417 \times 10^{-24} \text{ kg m s}^{-1}}{6.642 \times 10^{-27} \text{ kg}} = \boxed{665 \text{ m s}^{-1}}$$

$$(c) \quad p = \frac{6.626 \times 10^{-34} \text{ J s}}{1.00 \times 10^{-2} \text{ m}} = 6.626 \times 10^{-32} \text{ kg m s}^{-1}$$

$$v = \frac{p}{m} = \frac{6.626 \times 10^{-32} \text{ kg m s}^{-1}}{6.642 \times 10^{-27} \text{ kg}} = \boxed{9.98 \times 10^{-6} \text{ m s}^{-1}}$$

- E8.6(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 $Nh/\lambda m_{\text{rocket}}$. The rate of photon emission is the power (rate of energy emission) divided by the energy per photon (hc/λ), so

$$N = \frac{tP\lambda}{hc} \quad \text{and} \quad v = \left(\frac{tP\lambda}{hc} \right) \times \left(\frac{h}{\lambda m_{\text{rocket}}} \right) = \frac{tP}{cm_{\text{rocket}}}$$

$$v = \frac{(10.0 \text{ yr}) \times (365 \text{ day yr}^{-1}) \times (24 \text{ h day}^{-1}) \times (3600 \text{ s h}^{-1}) \times (1.50 \times 10^{-3} \text{ W})}{(2.998 \times 10^8 \text{ m s}^{-1}) \times (10.0 \text{ kg})}$$

$$= \boxed{158 \text{ m s}^{-1}}$$

- E8.7(b)** Rate of photon emission is rate of energy emission (power) divided by energy per photon (hc/λ)

$$(a) \quad \text{rate} = \frac{P\lambda}{hc} = \frac{(0.10 \text{ W}) \times (700 \times 10^{-9} \text{ m})}{(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1})} = \boxed{3.52 \times 10^{17} \text{ s}^{-1}}$$

$$(b) \quad \text{rate} = \frac{(1.0 \text{ W}) \times (700 \times 10^{-9} \text{ J s})}{(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1})} = \boxed{3.52 \times 10^{18} \text{ s}^{-1}}$$

- E8.8(b)** Conservation of energy requires

$$E_{\text{photon}} = \Phi + E_K = h\nu = hc/\lambda \quad \text{so} \quad E_K = hc/\lambda - \Phi$$

$$\text{and } E_K = \frac{1}{2}m_e v^2 \quad \text{so} \quad v = \left(\frac{2E_K}{m_e} \right)^{1/2}$$

$$(a) \quad E_K = \frac{(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1})}{650 \times 10^{-9} \text{ m}} - (2.09 \text{ eV}) \times (1.60 \times 10^{-19} \text{ J eV}^{-1})$$

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.

$$(b) \quad E_K = \frac{(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1})}{195 \times 10^{-9} \text{ m}} - (2.09 \text{ eV}) \times (1.60 \times 10^{-19} \text{ J eV}^{-1})$$

$$= \boxed{6.84 \times 10^{-19} \text{ J}}$$

$$\text{and } v = \left(\frac{2(6.84 \times 10^{-19} \text{ J})}{9.11 \times 10^{-31} \text{ kg}} \right)^{1/2} = \boxed{1.23 \times 10^6 \text{ m s}^{-1}}$$

E8.9(b) $E = h\nu = h/\tau$, so

$$(a) \quad E = 6.626 \times 10^{-34} \text{ J s} / 2.50 \times 10^{-15} \text{ s} = \boxed{2.65 \times 10^{-19} \text{ J} = 160 \text{ kJ mol}^{-1}}$$

$$(b) \quad E = 6.626 \times 10^{-34} \text{ J s} / 2.21 \times 10^{-15} \text{ s} = \boxed{3.00 \times 10^{-19} \text{ J} = 181 \text{ kJ mol}^{-1}}$$

$$(c) \quad E = 6.626 \times 10^{-34} \text{ J s} / 1.0 \times 10^{-13} \text{ s} = \boxed{6.62 \times 10^{-21} \text{ J} = 4.0 \times 10^{-10} \text{ kJ mol}^{-1}}$$

E8.10(b) The de Broglie wavelength is

$$\lambda = \frac{h}{p}$$

The momentum is related to the kinetic energy by

$$E_K = \frac{p^2}{2m} \quad \text{so} \quad p = (2mE_K)^{1/2}$$

The kinetic energy of an electron accelerated through 1 V is 1 eV = 1.60×10^{-19} J, so

$$\lambda = \frac{h}{(2mE_K)^{1/2}}$$

$$(a) \quad \lambda = \frac{6.626 \times 10^{-34} \text{ J s}}{(2(9.11 \times 10^{-31} \text{ kg}) \times (100 \text{ eV}) \times (1.60 \times 10^{-19} \text{ J eV}^{-1}))^{1/2}} \\ = \boxed{1.23 \times 10^{-10} \text{ m}}$$

$$(b) \quad \lambda = \frac{6.626 \times 10^{-34} \text{ J s}}{(2(9.11 \times 10^{-31} \text{ kg}) \times (1.0 \times 10^3 \text{ eV}) \times (1.60 \times 10^{-19} \text{ J eV}^{-1}))^{1/2}} \\ = \boxed{3.9 \times 10^{-11} \text{ m}}$$

$$(c) \quad \lambda = \frac{6.626 \times 10^{-34} \text{ J s}}{(2(9.11 \times 10^{-31} \text{ kg}) \times (100 \times 10^3 \text{ eV}) \times (1.60 \times 10^{-19} \text{ J eV}^{-1}))^{1/2}} \\ = \boxed{3.88 \times 10^{-12} \text{ m}}$$

- E8.11(b)** The upper sign in the following equations represents the math using the $\hat{A} + i\hat{B}$ operator. The lower sign is for the $\hat{A} - i\hat{B}$ operator. τ is a generalized coordinate.

$$\begin{aligned}\int \psi_i^* |\hat{A} \pm i\hat{B}| \psi_j d\tau &= \int \psi_i^* \hat{A} |\psi_j d\tau \pm i \int \psi_i^* \hat{B} |\psi_j d\tau \\ &= \left\{ \int \psi_j^* \hat{A} |\psi_i d\tau \right\}^* \pm i \left\{ \int \psi_j^* \hat{B} |\psi_i d\tau \right\}^* \quad \hat{A} \text{ and } \hat{B} \text{ are hermitian [8.30]} \\ &= \left\{ \int \psi_j^* \hat{A} |\psi_i d\tau \mp i \int \psi_j^* \hat{B} |\psi_i d\tau \right\}^* \\ &= \left\{ \int \psi_j^* |\hat{A} \mp i\hat{B} |\psi_i d\tau \right\}^*\end{aligned}$$

This shows that the $\hat{A} \pm i\hat{B}$ operators are not hermitian. If they were hermitian, the result would be $\left\{ \int \psi_j^* |\hat{A} \pm i\hat{B} |\psi_i d\tau \right\}^*$.

- E8.12(b)** The minimum uncertainty in position is 100 pm. Therefore, since $\Delta x \Delta p \geq \frac{1}{2} \hbar$

$$\begin{aligned}\Delta p &\geq \frac{\hbar}{2\Delta x} = \frac{1.0546 \times 10^{-34} \text{ J s}}{2(100 \times 10^{-12} \text{ m})} = 5.3 \times 10^{-25} \text{ kg m s}^{-1} \\ \Delta v &= \frac{\Delta p}{m} = \frac{5.3 \times 10^{-25} \text{ kg m s}^{-1}}{9.11 \times 10^{-31} \text{ kg}} = \boxed{5.8 \times 10^5 \text{ m s}^{-1}}\end{aligned}$$

- E8.13(b)** Conservation of energy requires

$$\begin{aligned}E_{\text{photon}} &= E_{\text{binding}} + \frac{1}{2} m_e v^2 = h\nu = hc/\lambda \quad \text{so} \quad E_{\text{binding}} = hc/\lambda - \frac{1}{2} m_e v^2 \\ \text{and } E_{\text{binding}} &= \frac{(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1})}{121 \times 10^{-12} \text{ m}} \\ &\quad - \frac{1}{2} (9.11 \times 10^{-31} \text{ kg}) \times (5.69 \times 10^7 \text{ m s}^{-1})^2 \\ &= \boxed{1.67 \times 10^{-16} \text{ J}}\end{aligned}$$

COMMENT. This calculation uses the non-relativistic kinetic energy, which is only about 3 percent less than the accurate (relativistic) value of $1.52 \times 10^{-15} \text{ J}$. 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 $E_{\text{binding}} = 1.26 \times 10^{-16} \text{ J}$.

- E8.14(b)** The quantity $\hat{\mathcal{S}}_1 \hat{\mathcal{S}}_2 - \hat{\mathcal{S}}_2 \hat{\mathcal{S}}_1$ [Illustration 8.3] is referred to as the commutator of the operators $\hat{\mathcal{S}}_1$ and $\hat{\mathcal{S}}_2$. In obtaining the commutator it is necessary to realize that the operators operate on functions; thus, we form

$$\hat{\mathcal{S}}_1 \hat{\mathcal{S}}_2 f(x) - \hat{\mathcal{S}}_2 \hat{\mathcal{S}}_1 f(x)$$

$$p_x = \frac{\hbar}{i} \frac{d}{dx}$$

$$\text{Therefore } a = \left(\hat{x} + \hbar \frac{d}{dx} \right) \text{ and } a^\dagger = \left(\hat{x} - \hbar \frac{d}{dx} \right)$$

$$\text{Then } aa^\dagger f(x) = \frac{1}{2} \left(\hat{x} + \hbar \frac{d}{dx} \right) \times \left(\hat{x} - \hbar \frac{d}{dx} \right) f(x)$$

$$\text{and } a^\dagger a f(x) = \frac{1}{2} \left(\hat{x} - \hbar \frac{d}{dx} \right) \times \left(\hat{x} + \hbar \frac{d}{dx} \right) f(x)$$

The terms in \hat{x}^2 and $(d/dx)^2$ obviously drop out when the difference is taken and are ignored in what follows; thus

$$aa^\dagger f(x) = \frac{1}{2} \left(-\hat{x}\hbar \frac{d}{dx} + \hbar \frac{d}{dx} \hat{x} \right) f(x)$$

$$a^\dagger a f(x) = \frac{1}{2} \left(\hat{x}\hbar \frac{d}{dx} - \hbar \frac{d}{dx} \hat{x} \right) f(x)$$

These expressions are the negative of each other, therefore

$$\begin{aligned} (aa^\dagger - a^\dagger a)f(x) &= \hbar \frac{d}{dx} \hat{x} f(x) - \hbar \hat{x} \frac{d}{dx} f(x) \\ &= \hbar \left(\frac{d}{dx} \hat{x} - \hat{x} \frac{d}{dx} \right) f(x) = \hbar f(x) \end{aligned}$$

Therefore, $(aa^\dagger - a^\dagger a) = \boxed{\hbar}$

Solutions to problems

Solutions to numerical problems

P8.2

$$\lambda_{\max} T = \frac{c_2}{5} \text{ where } c_2 = \frac{hc}{k}$$

Therefore, $\lambda_{\max} T = hc/5k$ and, if we find the mean of the $\lambda_{\max} T$ values, we can obtain h from the equation $h = 5k/c (\lambda_{\max} T)_{\text{mean}}$. We draw up the following table.

$\theta/^\circ\text{C}$	1000	1500	2000	2500	3000	3500
T/K	1273	1773	2273	2773	3273	3773
λ_{\max}/nm	2181	1600	1240	1035	878	763
$\lambda_{\max} T / (10^6 \text{ nm K})$	2.776	2.837	2.819	2.870	2.874	2.879

The mean is $2.84 \times 10^6 \text{ nm K}$ with a standard deviation of $0.04 \times 10^6 \text{ nm K}$

$$\text{and } h = \frac{(5) \times (1.38066 \times 10^{-23} \text{ J K}^{-1}) \times (2.84 \times 10^{-3} \text{ m K})}{2.99792 \times 10^8 \text{ m s}^{-1}} = \boxed{6.54 \times 10^{-34} \text{ J s}}$$

COMMENT. Planck's estimate of the constant h in his first paper of 1900 on black body radiation was $6.55 \times 10^{-27} \text{ erg sec}$ (1 erg = 10^{-7} J) which is remarkably close to the current value of $6.626 \times 10^{-34} \text{ J s}$ and is essentially the same as the value obtained above. Also from his analysis of the experimental data he

obtained values of k (the Boltzmann constant), N_A (the Avogadro constant), and e (the fundamental charge). His values of these constants remained the most accurate for almost 20 years.

- P8.4** The full solution of the Schrödinger equation for the problem of a particle in a one-dimensional box is given in Chapter 9. Here we need only the wavefunction which is provided. It is the square of the wavefunction that is related to the probability. Here $\psi^2 = \frac{2}{L} \sin^2 \frac{\pi x}{L}$ and the probability that the particle will be found between a and b is

$$\begin{aligned} P(a, b) &= \int_a^b \psi^2 dx \quad [\text{Section 8.4}] \\ &= \frac{2}{L} \int_a^b \sin^2 \frac{\pi x}{L} dx = \left(\frac{x}{L} - \frac{1}{2\pi} \sin \frac{2\pi x}{L} \right) \Big|_a^b \\ &= \frac{b-a}{L} - \frac{1}{2\pi} \left(\sin \frac{2\pi b}{L} - \sin \frac{2\pi a}{L} \right) \end{aligned}$$

$$L = 10.0 \text{ nm}$$

- (a) $P(4.95, 5.05) = \frac{0.10}{10.0} - \frac{1}{2\pi} \left(\sin \frac{(2\pi) \times (5.05)}{10.0} - \sin \frac{(2\pi) \times (4.95)}{10.0} \right)$
 $= 0.010 + 0.010 = \boxed{0.020}$
- (b) $P(1.95, 2.05) = \frac{0.10}{10.0} - \frac{1}{2\pi} \left(\sin \frac{(2\pi) \times (2.05)}{10.0} - \sin \frac{(2\pi) \times (1.95)}{10.0} \right)$
 $= 0.010 - 0.0031 = \boxed{0.007}$
- (c) $P(9.90, 10.0) = \frac{0.10}{10.0} - \frac{1}{2\pi} \left(\sin \frac{(2\pi) \times (10.0)}{10.0} - \sin \frac{(2\pi) \times (9.90)}{10.0} \right)$
 $= 0.010 - 0.009993 = \boxed{7 \times 10^{-6}}$
- (d) $P(5.0, 10.0) = \boxed{0.5}$ [by symmetry]
- (e) $P\left(\frac{1}{3}L, \frac{2}{3}L\right) = \frac{1}{3} - \frac{1}{2\pi} \left(\sin \frac{4\pi}{3} - \sin \frac{2\pi}{3} \right) = \boxed{0.61}$

- P8.6** The average position (angle) is given by:

$$\langle \phi \rangle = \int \psi^* \phi \psi d\tau = \int_0^{2\pi} \frac{e^{im\phi}}{(2\pi)^{1/2}} \phi \frac{e^{-im\phi}}{(2\pi)^{1/2}} d\phi = \frac{1}{2\pi} \int_0^{2\pi} \phi d\phi = \frac{1}{2\pi} \frac{\phi^2}{2} \Big|_0^{2\pi} = \boxed{\pi}.$$

Note: this result applies to all values of the quantum number m , for it drops out of the calculation.

- P8.8** The expectation value of the commutator is:

$$\langle [\hat{x}, \hat{p}] \rangle = \int \psi^* [\hat{x}, \hat{p}] \psi d\tau.$$

First evaluate the commutator acting on the wavefunction. The commutator of the position and momentum operators is defined as

$$[\hat{x}, \hat{p}] = \hat{x}\hat{p} - \hat{p}\hat{x} = x \times \frac{\hbar}{i} \frac{d}{dx} - \frac{\hbar}{i} \frac{d}{dx} x,$$

so the commutator acting on the wavefunction is

$$[\hat{x}, \hat{p}]\psi = x \times \frac{\hbar}{i} \frac{d\psi}{dx} - \frac{\hbar}{i} \frac{d}{dx}(x\psi),$$

where $\psi = (2a)^{1/2}e^{-ax}$.

Evaluating this expression yields

$$[\hat{x}, \hat{p}]\psi = \frac{x\hbar}{i}(2a)^{1/2}ae^{-ax} - \frac{\hbar}{i}[(2a)^{1/2}e^{-ax} + xa(2a)^{1/2}e^{-ax}],$$

$$[\hat{x}, \hat{p}]\psi = \frac{\hbar(2a)^{1/2}e^{-ax}}{i}(xa - 1 - xa) = i\hbar(2a)^{1/2}e^{-ax},$$

which is just $i\hbar$ times the original wavefunction. Putting this result into the expectation value yields:

$$\langle [\hat{x}, \hat{p}] \rangle = \int_0^\infty (2a)^{1/2}e^{-ax}(i\hbar)(2a)^{1/2}e^{-ax}dx = 2ia\hbar \int_0^\infty e^{-2ax}dx$$

$$\langle [\hat{x}, \hat{p}] \rangle = 2ia\hbar \times \frac{e^{-2ax}}{-2a} \Big|_0^\infty = \boxed{i\hbar}.$$

Note: Although the commutator is a well defined and useful operator in quantum mechanics, it does not correspond to an observable quantity. Thus one need not be concerned about obtaining an imaginary expectation value.

Solutions to theoretical problems

P8.10 We look for the value of λ at which ρ is a maximum, using (as appropriate) the short-wavelength (high-frequency) approximation

$$\rho = \frac{8\pi hc}{\lambda^5} \left(\frac{1}{e^{hc/\lambda kT} - 1} \right) \quad [8.5]$$

$$\frac{d\rho}{d\lambda} = -\frac{5}{\lambda}\rho + \frac{hc}{\lambda^2 kT} \left(\frac{e^{hc/\lambda kT}}{e^{hc/\lambda kT} - 1} \right) \rho = 0 \quad \text{at } \lambda = \lambda_{\max}$$

$$\text{Then, } -5 + \frac{hc}{\lambda kT} \times \frac{e^{hc/\lambda kT}}{e^{hc/\lambda kT} - 1} = 0$$

$$\text{Hence, } 5 - 5e^{hc/\lambda kT} + \frac{hc}{\lambda kT} e^{hc/\lambda kT} = 0$$

If $hc/\lambda kT \gg 1$ [short wavelengths, high frequencies], this expression simplifies. We neglect the initial 5, cancel the two exponents, and obtain

$$hc = 5\lambda kT \quad \text{for } \lambda = \lambda_{\max} \quad \text{and} \quad \frac{hc}{\lambda kT} \gg 1$$

$$\text{or } \boxed{\lambda_{\max} T = \frac{hc}{5k} = \frac{c_2}{5}}, \text{ in accord with observation.}$$

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 $\lambda_{\max} \approx 0.2 \text{ cm}$?

- P8.12** (a) With a little manipulation, a small-wavelength approximation of the Planck distribution can be derived that has the same form as Wien's formula. First examine the Planck distribution,

$$\rho_{\text{Planck}} = \frac{8\pi hc}{\lambda^5 (e^{hc/\lambda kT} - 1)},$$

for small-wavelength behavior. The factor λ^{-5} gets large as λ itself gets small, but the other factor, namely $1/(e^{hc/\lambda kT} - 1)$ gets small even faster. Focus on that factor, and try to express it in terms of a single decaying exponential (as in Wien's formula), at least in the small- λ limit. Multiplying it by one in the form of $e^{-hc/\lambda kT}/e^{-hc/\lambda kT}$, yields $e^{-hc/\lambda kT}/(1 - e^{-hc/\lambda kT})$, where $e^{-hc/\lambda kT}$ is small, so let us call it ϵ . The factor, then, becomes $\epsilon/(1 - \epsilon)$, which can be expressed as a power series in ϵ as $\epsilon(1 + \epsilon + \dots)$. For sufficiently small wavelengths, then, the Planck distribution may be approximated as:

$$\rho_{\text{Planck}} \approx \frac{8\pi hc \epsilon}{\lambda^5} = \frac{8\pi hc e^{-hc/\lambda kT}}{\lambda^5}.$$

This has the same form as Wien's formula:

$$\rho_{\text{Wien}} = \frac{a}{\lambda^5} e^{-b/\lambda kT}.$$

Comparing the two formulas gives the values of the Wien constants:

$$a = \boxed{8\pi hc} \quad \text{and} \quad b = \boxed{hc}.$$

- (b) The wavelength at which the Wien distribution is a maximum is found by setting the derivative of the distribution function to zero:

$$\frac{d\rho_{\text{Wien}}}{d\lambda} = 0 = \frac{a}{\lambda^5} e^{-b/\lambda kT} \left(\frac{b}{\lambda^2 kT} \right) - \frac{5a}{\lambda^6} e^{-b/\lambda kT} = \frac{a}{\lambda^6} e^{-b/\lambda kT} \left(\frac{b}{\lambda kT} - 5 \right),$$

$$\text{so } \frac{b}{\lambda kT} - 5 = 0 \text{ and } \lambda_{\max} = \frac{b}{5kT} = \frac{hc}{5kT}.$$

Putting this in the same form as the Wien displacement law, we get:

$$T\lambda_{\max} = \frac{1}{5} c_2, \quad \text{where } c_2 = \frac{hc}{k},$$

as was demonstrated in Problem 8.10.

The Stefan-Boltzmann law gives the energy density as a function of temperature. The energy density is related to the distribution function by:

$$dE = \rho d\lambda \quad \text{so} \quad E = \int_0^\infty \rho d\lambda.$$

The energy density implied by the Wien distribution is:

$$E = \int_0^\infty \frac{a}{\lambda^5} e^{-b/\lambda kT} d\lambda.$$

Integration by parts several times yields:

$$E = e^{-b/\lambda kT} \left(\left(\frac{b}{k\lambda} \right)^3 + 3 \left(\frac{b}{k\lambda} \right)^2 T + \frac{6bT^2}{k\lambda} + 6T^3 \right) \frac{aTk^4}{b^4} \Big|_0^\infty = \frac{6aT^4 k^4}{b^4},$$

$$E = \frac{48\pi k^4 T^4}{h^3 c^3},$$

in other words, a constant times T^4 , consistent with the Stefan–Boltzmann law.

P8.14 In each case form $N\psi$; integrate

$$\int (N\psi)^* (N\psi) \, d\tau$$

set the integral equal to 1 and solve for N .

$$(a) \quad \psi = N \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0}$$

$$\psi^2 = N^2 \left(2 - \frac{r}{a_0} \right)^2 e^{-r/a_0}$$

$$\begin{aligned} \int \psi^2 \, d\tau &= N^2 \int_0^\infty \left(4r^2 - \frac{4r^3}{a_0} + \frac{r^4}{a_0^2} \right) e^{-r/a_0} \, dr \int_0^\pi \sin \theta \, d\theta \int_0^{2\pi} d\phi \\ &= N^2 \left(4 \times 2a_0^3 - 4 \times \frac{6a_0^4}{a_0} + \frac{24a_0^5}{a_0^2} \right) \times (2) \times (2\pi) = 32\pi a_0^3 N^2; \end{aligned}$$

$$\text{hence } N = \left(\frac{1}{32\pi a_0^3} \right)^{1/2}$$

where we have used

$$\int_0^\infty x^n e^{-ax} \, dx = \frac{n!}{a^{n+1}} \quad [\text{Problem 8.13 and inside front cover}]$$

$$\psi = Nr \sin \theta \cos \phi e^{-r/(2a_0)}$$

$$\begin{aligned} \int \psi^2 \, d\tau &= N^2 \int_0^\infty r^4 e^{-r/a_0} \, dr \int_0^\pi \sin^2 \theta \sin \theta \, d\theta \int_0^{2\pi} \cos^2 \phi \, d\phi \\ &= N^2 4! a_0^5 \int_{-1}^1 (1 - \cos^2 \theta) \, d \cos \theta \times \pi \\ &= N^2 4! a_0^5 \left(2 - \frac{2}{3} \right) \pi = 32\pi a_0^5 N^2; \quad \text{hence } N = \left(\frac{1}{32\pi a_0^5} \right)^{1/2} \end{aligned}$$

where we have used $\int_0^\pi \cos^n \theta \sin \theta d\theta = -\int_1^{-1} \cos^n \theta d \cos \theta = \int_{-1}^1 x^n dx$ and the relations at the end of the solution to Problem 8.13.

- (b) The functions will be orthogonal if the following integral, which uses the unnormalized functions, proves to equal zero.

$$\begin{aligned} \int \psi_1 \psi_2 d\tau &= \int \left\{ \left(2 - \frac{r}{a_0} \right) e^{\frac{r}{2a_0}} \right\} \left\{ r \sin \theta \cos \phi e^{\frac{r}{2a_0}} \right\} d\tau \\ &= \int_0^\infty \left\{ \left(2r - \frac{r^2}{a_0} \right) e^{\frac{r}{a_0}} \right\} dr \int_0^\pi \sin^2 \theta d\theta \int_0^{2\pi} \cos \phi d\phi \end{aligned}$$

The integral on the far right equals zero.

$$\int_0^{2\pi} \cos \phi d\phi = \sin \phi \Big|_0^{2\pi} = \sin(2\pi) - \sin(0) = 0 - 0 = 0$$

Consequently, the functions are orthogonal.

- P8.16** Operate on each function with \hat{t} ; if the function is regenerated multiplied by a constant, it is an eigenfunction of \hat{t} and the constant is the eigenvalue.

(a) $f = x^3 - kx$
 $\hat{t}(x^3 - kx) = -x^3 + kx = -f$

Therefore, f is an eigenfunction with eigenvalue, $\boxed{-1}$

(b) $f = \cos kx$
 $\hat{t} \cos kx = \cos(-kx) = \cos kx = f$

Therefore, f is an eigenfunction with eigenvalue, $\boxed{+1}$

(c) $f = x^2 + 3x - 1$
 $\hat{t}(x^2 + 3x - 1) = x^2 - 3x - 1 \neq \text{constant} \times f$

Therefore, f is not an eigenfunction of \hat{t} .

- P8.18** $\psi = (\cos \chi)e^{ikx} + (\sin \chi)e^{-ikx} = c_1 e^{ikx} + c_2 e^{-ikx}$. The linear momentum operator is $\hat{p}_x = \frac{\hbar}{i} \frac{d}{dx}$ [8.26]

As demonstrated in the text (Example 8.6), e^{-ikx} is an eigenfunction of \hat{p}_x with eigenvalue $+k\hbar$; likewise e^{-ikx} is an eigenfunction of \hat{p}_x with eigenvalue $-k\hbar$. Therefore, by the principle of linear superposition (Section 8.5(d), *Justification* 8.4),

(a) $P = c_1^2 = \boxed{\cos^2 \chi}$

(b) $P = c_2^2 = \boxed{\sin^2 \chi}$

$$(c) \quad c_1^2 = 0.90 = \cos^2 \chi, \text{ so } \cos \chi = 0.95$$

$$c_2^2 = 0.10 = \sin^2 \chi, \text{ so } \sin \chi = \pm 0.32; \text{ hence}$$

$$\boxed{\psi = 0.95e^{ikx} \pm 0.32e^{-ikx}}$$

P8.20

$$p_x = \frac{\hbar}{i} \frac{d}{dx} \quad [8.26]$$

$$\langle p_x \rangle = N^2 \int \psi^* \hat{p}_x \psi dx; \quad N^2 = \frac{1}{\int \psi^* \psi d\tau}$$

$$= \frac{\int \psi^* \hat{p}_x \psi dx}{\int \psi^* \psi dx} = \frac{\frac{\hbar}{i} \int \psi^* \left(\frac{d\psi}{dx} \right) dx}{\int \psi^* \psi dx}$$

$$(a) \quad \psi = e^{ikx}, \quad \frac{d\psi}{dx} = ik\psi$$

Hence,

$$\langle p_x \rangle = \frac{\hbar}{i} \times \frac{ik \int \psi^* \psi dx}{\int \psi^* \psi dx} = \boxed{k\hbar}$$

$$(b) \quad \psi = \cos kx, \quad \frac{d\psi}{dx} = -k \sin kx$$

$$\int_{-\infty}^{\infty} \psi^* \frac{d\psi}{dx} dx = -k \int_{-\infty}^{\infty} \cos kx \sin kx dx = 0$$

$$\text{Therefore, } \langle p_x \rangle = \boxed{0}$$

$$(c) \quad \psi = e^{-\alpha x^2}, \quad \frac{d\psi}{dx} = -2\alpha x e^{-\alpha x^2}$$

$$\int_{-\infty}^{\infty} \psi^* \frac{d\psi}{dx} dx = -2\alpha \int_{-\infty}^{\infty} x e^{-2\alpha x^2} dx = 0 \quad [\text{by symmetry, since } x \text{ is an odd function}]$$

$$\text{Therefore, } \langle p_x \rangle = \boxed{0}$$

P8.22

$$\psi = \left(\frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0} \quad [\text{Example 8.4}]$$

$$(a) \quad \langle V \rangle = \int \psi^* \hat{V} \psi d\tau \left[\hat{V} = -\frac{e^2}{4\pi\epsilon_0 r}, \text{ Section 10.1} \right]$$

$$\langle V \rangle = \int \psi^* \left(\frac{-e^2}{4\pi\epsilon_0} \cdot \frac{1}{r} \right) \psi d\tau = \frac{1}{\pi a_0^3} \left(\frac{-e^2}{4\pi\epsilon_0} \right) \int_0^\infty r e^{-2r/a_0} dr \times 4\pi$$

$$= \frac{1}{\pi a_0^3} \left(\frac{-e^2}{4\pi\epsilon_0} \right) \times \left(\frac{a_0}{2} \right)^2 \times 4\pi = \boxed{\frac{-e^2}{4\pi\epsilon_0 a_0}}$$

(b) For three-dimensional systems such as the hydrogen atom the kinetic energy operator is

$$\hat{T} = -\frac{\hbar^2}{2m_e} \nabla^2 \quad [\text{Table 8.1, } m_e \approx \mu \text{ for the hydrogen atom}]$$

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \Lambda^2 = \left(\frac{1}{r}\right) \times \left(\frac{\partial^2}{\partial r^2}\right) r + \frac{1}{r^2} \Lambda^2$$

$$\Lambda^2 \psi = 0 \quad [\psi \text{ has no angular coordinates}]$$

$$\begin{aligned} \nabla^2 \psi &= \left(\frac{1}{\pi a_0^3}\right)^{1/2} \times \left(\frac{1}{r}\right) \times \left(\frac{d^2}{dr^2}\right) r e^{-r/a_0} \\ &= \left(\frac{1}{\pi a_0^3}\right)^{1/2} \times \left[-\left(\frac{2}{a_0 r}\right) + \frac{1}{a_0^2}\right] e^{-r/a_0} \end{aligned}$$

$$\begin{aligned} \text{Then, } \langle T \rangle &= -\left(\frac{\hbar^2}{2m_e}\right) \times \left(\frac{1}{\pi a_0^3}\right) \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty \left[-\left(\frac{2}{a_0 r}\right) + \left(\frac{1}{a_0^2}\right)\right] e^{-2r/a_0} r^2 dr \\ &= -\left(\frac{2\hbar^2}{m_e a_0^3}\right) \int_0^\infty \left[-\left(\frac{2r}{a_0}\right) + \left(\frac{r^2}{a_0^2}\right)\right] e^{-2r/a_0} dr \\ &= -\left(\frac{2\hbar^2}{m_e a_0^3}\right) \times \left(-\frac{a_0}{4}\right) \left[\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}\right] = \boxed{\frac{\hbar^2}{2m_e a_0^2}} \end{aligned}$$

$$\text{Inserting } a_0 = \frac{4\pi \epsilon_0 \hbar^2}{m_e e^2} \quad [\text{Chapter 10}]$$

$$\langle T \rangle = \frac{e^2}{8\pi \epsilon_0 a_0} = -\frac{1}{2} \langle V \rangle$$

P8.24 $\langle \Omega^2 \rangle = \int \psi^* \hat{\Omega}^2 \psi d\tau = \int \psi^* \hat{\Omega} \hat{\Omega} \psi d\tau = \left\{ \int (\hat{\Omega} \psi)^* \hat{\Omega} \psi d\tau \right\}^*$ because $\hat{\Omega}$ is an hermitian operator

The integrand on the far right is a function times its complex conjugate, which must always be a real, positive number. When this type of integrand is integrated over real space, the result is always real, positive number. Thus, the expectation value of the square of an hermitian operator is always positive.

Solutions to applications

P8.26 $\lambda_{\max} = \frac{1.44 \text{ cm K}}{5T} \quad [\text{See problems 8.2 and 8.10}]$

$$= \frac{1.44 \text{ cm K}}{5(5800 \text{ K})} = 5.0 \times 10^{-5} \text{ cm} \left(\frac{10^9 \text{ nm}}{10^2 \text{ cm}} \right)$$

$\lambda_{\max} = \boxed{500 \text{ nm, blue-green}} \quad [\text{see Figure 10.1 in the text}]$

P8.28 $I = al + M = al + \sigma T^4 \text{ so } T = \left(\frac{I(1-a)}{\sigma} \right)^{1/4} = \left(\frac{(343 \text{ W m}^{-2}) \times (1-0.30)}{5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}} \right)^{1/4}$
 $= \boxed{255 \text{ K}}$

where I is the incoming energy flux, a the albedo (fraction of incoming radiation absorbed), M the excitation and σ the Stefan–Boltzmann constant. (See the solution to Problem 8.11.) Wien's displacement law relates the temperature to the wavelength of the most intense radiation

$$\begin{aligned} T\lambda_{\max} &= c_2/5, \text{ so } \lambda_{\max} = \frac{c_2}{5T} = \frac{1.44 \text{ cm K}}{5(255 \text{ K})} \\ &= 1.13 \times 10^{-3} \text{ cm} = \boxed{11.3 \mu\text{m}} \text{ in the infrared.} \end{aligned}$$



9

Quantum theory: techniques and applications

Answers to discussion questions

- D9.2** 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 9.7 to eqn 9.4a) 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 9.1(c).
- The harmonic oscillator provides another example of the correspondence principle. The same effects mentioned above are observed. We see from Figure 9.26 of the text that probability distributions for large values on n approach the classical picture of the motion. (Look at the graph for $v = 20$.)
- D9.4** The physical origin of tunnelling is related to the probability density of the particle, which according to the Born interpretation is the square of the wavefunction that represents the particle. This interpretation requires that the wavefunction of the system be everywhere continuous, even at barriers. Therefore, if the wavefunction is non-zero on one side of a barrier it must be non-zero on the other side of the barrier and this implies that the particle has tunnellled through the barrier. The transmission probability depends upon the mass of the particle (specifically $m^{1/2}$, through eqns 9.16 and 9.20): 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.
- D9.6** Macroscopic synthesis and material development always contains elements of molecular randomness. Crystal structures are never perfect. A product of organic synthesis is never absolutely free of impurities, although impurities may be at a level that is lower than measurement techniques make possible. Alloys are grainy and slightly non-homogeneous within any particular grain. Furthermore, the random distribution of atomic/molecular positions and orientations within, and between, macroscopic objects causes the conversion of energy to non-useful heat during manufacturing processes. Production efficiencies are difficult to improve. Nanometer technology on the 1 nm to 100 nm scale may resolve many of these problems. Self-organization and production processes by nanoparticles and nanomachines may be able

to exclude impurities and greatly improve homogeneity by effective examination and selection of each atom/molecule during nanosynthesis and nanoproduction processes. Higher efficiencies of energy usage may be achievable as nanomachines produce idealized materials at the smaller sizes and pass their products to larger nanomachines for production of larger scale materials.

The directed, non-random, use of atoms and molecules by nanotechniques holds the promise for the production of smaller transistors and wires for the electronics and computer industries. Unusual material strengths, optical properties, magnetic properties, and catalytic properties may be achievable. Higher efficiencies of photo-electronic conversion would be a boon to mankind. There is hope that science will devise nanoparticles that destroy pathogens and repair tissues. See Impact 9.1 for discussion of SPM examination of atom positions on a macroscopic surface and for the current nanotechnological method for positioning atoms on a surface. See Impact 9.2 for discussion of nano-quantum dots that have unusual optical and magnetic properties.

Solutions to exercises

E9.1(b)
$$E = \frac{n^2 h^2}{8m_e L^2} \quad [9.4a]$$
$$\frac{h^2}{8m_e L^2} = \frac{(6.626 \times 10^{-34} \text{ J s})^2}{8(9.109 \times 10^{-31} \text{ kg}) \times (1.50 \times 10^{-9} \text{ m})^2} = 2.678 \times 10^{-20} \text{ J}$$

The conversion factors required are

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}; \quad 1 \text{ cm}^{-1} = 1.986 \times 10^{-23} \text{ J}; \quad 1 \text{ eV} = 96.485 \text{ kJ mol}^{-1}$$

(a) $E_3 - E_1 = (9 - 1) \frac{h^2}{8m_e L^2} = 8(2.678 \times 10^{-20} \text{ J})$

$$= \boxed{2.14 \times 10^{-19} \text{ J}} = \boxed{1.34 \text{ eV}} = \boxed{1.08 \times 10^4 \text{ cm}^{-1}} = \boxed{129 \text{ kJ mol}^{-1}}$$

(b) $E_7 - E_6 = (49 - 36) \frac{h^2}{8m_e L^2} = 13(2.678 \times 10^{-20} \text{ J})$

$$= \boxed{3.48 \times 10^{-19} \text{ J}} = \boxed{2.17 \text{ eV}} = \boxed{1.75 \times 10^4 \text{ cm}^{-1}} = \boxed{210 \text{ kJ mol}^{-1}}$$

E9.2(b) The probability is

$$P = \int \psi^* \psi \, dx = \frac{2}{L} \int \sin^2\left(\frac{n\pi x}{L}\right) dx \approx \frac{2\Delta x}{L} \sin^2\left(\frac{n\pi x}{L}\right)$$

where $\Delta x = 0.02L$ and the function is evaluated at $x = 0.66L$.

(a) For $n = 1$
$$P = \frac{2(0.02L)}{L} \sin^2(0.66\pi) = \boxed{0.031}$$

(b) For $n = 2$
$$P = \frac{2(0.02L)}{L} \sin^2[2(0.66\pi)] = \boxed{0.029}$$

E9.3(b) The expectation value is

$$\langle \hat{p} \rangle = \int \psi^* \hat{p} \psi \, dx$$

but first we need $\hat{p}\psi$

$$\hat{p}\psi = -i\hbar \frac{d}{dx} \left(\frac{2}{L} \right)^{1/2} \sin \left(\frac{n\pi x}{L} \right) = -i\hbar \left(\frac{2}{L} \right)^{1/2} \frac{n\pi}{L} \cos \left(\frac{n\pi x}{L} \right)$$

$$\text{so } \langle \hat{p} \rangle = \frac{-2i\hbar n\pi}{L^2} \int_0^L \sin \left(\frac{n\pi x}{L} \right) \cos \left(\frac{n\pi x}{L} \right) dx = \boxed{0}$$

$$\text{and } \langle \hat{p}^2 \rangle = 2m \langle \hat{H} \rangle = 2mE_n = \frac{\hbar^2 n^2}{4L^2}$$

for all n . So for $n = 2$

$$\langle \hat{p}^2 \rangle = \boxed{\frac{\hbar^2}{L^2}}$$

E9.4(b) The zero-point energy is the ground-state energy, that is, with $n_x = n_y = n_z = 1$:

$$E = \frac{(n_x^2 + n_y^2 + n_z^2)\hbar^2}{8mL^2} \text{ [9.12b with equal lengths]} = \frac{3\hbar^2}{8mL^2}$$

Set this equal to the rest energy mc^2 and solve for L :

$$mc^2 = \frac{3\hbar^2}{8mL^2} \quad \text{so } L = \boxed{\left(\frac{3}{8} \right)^{1/2} \frac{\hbar}{mc} = \left(\frac{3}{8} \right)^{1/2} \lambda_C}$$

where λ_C is the Compton wavelength of a particle of mass m .

E9.5(b)
$$\psi_5 = \left(\frac{2}{L} \right)^{1/2} \sin \left(\frac{5\pi x}{L} \right)$$

$$P(x) \propto \psi_5^2 \propto \sin^2 \left(\frac{5\pi x}{L} \right)$$

Maxima and minima in $P(x)$ correspond to $\frac{dP(x)}{dx} = 0$

$$\frac{d}{dx} P(x) \propto \frac{d\psi^2}{dx} \propto \sin \left(\frac{5\pi x}{L} \right) \cos \left(\frac{5\pi x}{L} \right) \propto \sin \left(\frac{10\pi x}{L} \right) \quad [2 \sin \alpha \cos \alpha = \sin 2\alpha]$$

$\sin \theta = 0$ when $\theta = 0, \pi, 2\pi, \dots, n'\pi$ ($n' = 0, 1, 2, \dots$)

$$\frac{10\pi x}{L} = n'\pi \quad \text{for } n' \leq 10 \quad \text{so } x = \frac{n'L}{10}$$

$x = 0, x = L$ are minima. Maxima and minima alternate, so maxima correspond to

$$n' = 1, 3, 5, 7, 9 \quad x = \boxed{\frac{L}{10}}, \boxed{\frac{3L}{10}}, \boxed{\frac{L}{2}}, \boxed{\frac{7L}{10}}, \boxed{\frac{9L}{10}}$$

E9.6(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 $(n_1, n_2, n_3) = (1, 2, 3), (1, 3, 2), (2, 1, 3), (2, 3, 1), (3, 1, 2),$ or $(3, 2, 1)$.

E9.7(b) $E = \frac{3}{2}kT$ is the average translational energy of a gaseous molecule (see Chapter 17).

$$E = \frac{3}{2}kT = \frac{(n_1^2 + n_2^2 + n_3^2)h^2}{8mL^2} = \frac{n^2 h^2}{8mL^2}$$

$$E = \left(\frac{3}{2}\right) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (300 \text{ K}) = 6.214 \times 10^{-21} \text{ J}$$

$$n^2 = \frac{8mL^2}{h^2} E$$

If $L^3 = 1.00 \text{ m}^3$, then $L^2 = 1.00 \text{ m}^2$.

$$\frac{h^2}{8mL^2} = \frac{(6.626 \times 10^{-34} \text{ J s})^2}{(8) \times \left(\frac{0.02802 \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}}\right) \times 100 \text{ m}^2} = 1.180 \times 10^{-42} \text{ J}$$

$$n^2 = \frac{6.214 \times 10^{-21} \text{ J}}{1.180 \times 10^{-42} \text{ J}} = 5.265 \times 10^{21}; \quad n = \boxed{7.26 \times 10^{10}}$$

$$\Delta E = E_{n+1} - E_n = E_{7.26 \times 10^{10} + 1} - E_{7.26 \times 10^{10}}$$

$$\begin{aligned} \Delta E &= (2n + 1) \times \left(\frac{h^2}{8mL^2}\right) = [(2) \times (7.26 \times 10^{10}) + 1] \times \left(\frac{h^2}{8mL^2}\right) = \frac{14.52 \times 10^{10} h^2}{8mL^2} \\ &= (14.52 \times 10^{10}) \times (1.180 \times 10^{-42} \text{ J}) = \boxed{1.71 \times 10^{-31} \text{ J}} \end{aligned}$$

The de Broglie wavelength is obtained from

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad [8.12]$$

The velocity is obtained from

$$E_K = \frac{1}{2}mv^2 = \frac{3}{2}kT = 6.214 \times 10^{-21} \text{ J}$$

$$v^2 = \frac{6.214 \times 10^{-21} \text{ J}}{\left(\frac{1}{2}\right) \times \left(\frac{0.02802 \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}}\right)} = 2.671 \times 10^5 \text{ m}^2 \text{ s}^{-2}; \quad v = 517 \text{ m s}^{-1}$$

$$\lambda = \frac{6.626 \times 10^{-34} \text{ J s}}{(4.65 \times 10^{-26} \text{ kg}) \times (517 \text{ m s}^{-1})} = 2.75 \times 10^{-11} \text{ m} = \boxed{27.5 \text{ pm}}$$

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,

$$\frac{\Delta E}{E} \ll 1.$$

E9.8(b) The zero-point energy is

$$E_0 = \frac{1}{2}\hbar\omega = \frac{1}{2}\hbar\left(\frac{k}{m}\right)^{1/2} = \frac{1}{2}(1.0546 \times 10^{-34} \text{ J s}) \times \left(\frac{285 \text{ N m}^{-1}}{5.16 \times 10^{-26} \text{ kg}}\right)^{1/2}$$

$$= \boxed{3.92 \times 10^{-21} \text{ J}}$$

E9.9(b) The difference in adjacent energy levels is

$$\Delta E = E_{v+1} - E_v = \hbar\omega \quad [9.26] = \hbar\left(\frac{k}{m}\right)^{1/2} \quad [9.25]$$

$$\text{so } k = \frac{m(\Delta E)^2}{\hbar^2} = \frac{(2.88 \times 10^{-25} \text{ kg}) \times (3.17 \times 10^{-21} \text{ J})^2}{(1.0546 \times 10^{-34} \text{ J s})^2} = \boxed{260 \text{ N m}^{-1}}$$

E9.10(b) The difference in adjacent energy levels, which is equal to the energy of the photon, is

$$\Delta E = \hbar\omega = h\nu \quad \text{so } \hbar\left(\frac{k}{m}\right)^{1/2} = \frac{hc}{\lambda}$$

and

$$\lambda = \frac{hc}{\hbar\left(\frac{k}{m}\right)^{1/2}} = 2\pi c\left(\frac{m}{k}\right)^{1/2}$$

$$= 2\pi(2.998 \times 10^8 \text{ m s}^{-1}) \times \left(\frac{(15.9949 \text{ u}) \times (1.66 \times 10^{-27} \text{ kg u}^{-1})}{544 \text{ N m}^{-1}}\right)^{1/2}$$

$$\lambda = 1.32 \times 10^{-5} \text{ m} = \boxed{13.2 \text{ }\mu\text{m}}$$

E9.11(b) The difference in adjacent energy levels, which is equal to the energy of the photon, is

$$\Delta E = \hbar\omega = \hbar\nu \text{ so } \hbar\left(\frac{k}{m}\right)^{1/2} = \frac{\hbar c}{\lambda}$$

$$\text{and } \lambda = \frac{\hbar c}{\hbar\left(\frac{k}{m}\right)^{1/2}} = 2\pi c\left(\frac{m}{k}\right)^{1/2}$$

Doubling the mass, then, increases the wavelength by a factor of $2^{1/2}$. So taking the result from Exercise 9.10(b), the new wavelength is

$$\lambda = 2^{1/2}(13.2 \mu\text{m}) = \boxed{18.7 \mu\text{m}}$$

E9.12(b) $\Delta E = \hbar\omega = \hbar\nu$

$$\text{(a)} \quad \Delta E = \hbar\nu = (6.626 \times 10^{-34} \text{ J Hz}^{-1}) \times (33 \times 10^3 \text{ Hz}) = \boxed{2.2 \times 10^{-29} \text{ J}}$$

$$\text{(b)} \quad \Delta E = \hbar\omega = \hbar\left(\frac{k}{m_{\text{eff}}}\right)^{1/2} \left[\frac{1}{m_{\text{eff}}} = \frac{1}{m_1} + \frac{1}{m_2} \text{ with } m_1 = m_2 \right]$$

For a two-particle oscillator m_{eff} replaces m in the expression for ω . (See Chapter 13 for a more complete discussion of the vibration of a diatomic molecule.)

$$\begin{aligned} \Delta E &= \hbar\left(\frac{2k}{m}\right)^{1/2} = (1.055 \times 10^{-34} \text{ J s}) \times \left(\frac{(2) \times (1177 \text{ N m}^{-1})}{(16.00) \times (1.6605 \times 10^{-27} \text{ kg})}\right)^{1/2} \\ &= \boxed{3.14 \times 10^{-20} \text{ J}} \end{aligned}$$

E9.13(b) The first excited-state wavefunction has the form

$$\psi = 2N_1 y \exp\left(-\frac{1}{2}y^2\right)$$

where N_1 is a collection of constants and $y \equiv x(m\omega/\hbar)^{1/2}$. To see if it satisfies Schrödinger's equation, we see what happens when we apply the energy operator to this function

$$\hat{H}\psi = -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2 \psi$$

We need derivatives of ψ

$$\frac{d\psi}{dx} = \frac{d\psi}{dy} \frac{dy}{dx} = \left(\frac{m\omega}{\hbar}\right)^{1/2} (2N_1) \times (1 - y^2) \times \exp\left(-\frac{1}{2}y^2\right)$$

$$\text{and } \frac{d^2\psi}{dx^2} = \frac{d^2\psi}{dy^2} \left(\frac{dy}{dx}\right)^2 = \left(\frac{m\omega}{\hbar}\right) \times (2N_1) \times (-3y + y^3) \times \exp\left(-\frac{1}{2}y^2\right) = \left(\frac{m\omega}{\hbar}\right) \times (y^2 - 3) \psi$$

$$\begin{aligned} \text{So } \hat{H}\psi &= -\frac{\hbar^2}{2m} \times \left(\frac{m\omega}{\hbar}\right) \times (y^2 - 3) \psi + \frac{1}{2}m\omega^2 x^2 \psi \\ &= -\frac{1}{2}\hbar\omega \times (y^2 - 3) \times \psi + \frac{1}{2}\hbar\omega y^2 \psi = \frac{3}{2}\hbar\omega \psi \end{aligned}$$

Thus, ψ is a solution of the Schrödinger equation with energy eigenvalue

$$E = \boxed{\frac{3}{2}\hbar\omega}$$

E9.14(b) The harmonic oscillator wavefunctions have the form

$$\psi_v(x) = N_v H_v(y) \exp\left(-\frac{1}{2}y^2\right) \quad \text{with } y = \frac{x}{\alpha} \quad \text{and } \alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4} \quad [9.28]$$

The exponential function approaches zero only as x approaches $\pm\infty$, so the nodes of the wavefunction are the nodes of the Hermite polynomials.

$$H_5(y) = 32y^5 - 160y^3 + 120y = 0 \quad [\text{Table 9.1}] = 8y(4y^4 - 20y^2 + 15)$$

So one solution is $y = 0$, which leads to $x = 0$. The other factor can be made into a quadratic equation by letting $z = y^2$

$$4z^2 - 20z + 15 = 0$$

$$\text{so } z = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{20 \pm \sqrt{20^2 - 4 \times 4 \times 15}}{2 \times 4} = \frac{5 \pm \sqrt{10}}{2}$$

Evaluating the result numerically yields $z = 0.92$ or 4.08 , so $y = \pm 0.96$ or ± 2.02 . Therefore $x = \boxed{0, \pm 0.96\alpha, \text{ or } \pm 2.02\alpha}$.

COMMENT. Numerical values could also be obtained graphically by plotting $H_5(y)$.

E9.15(b) The zero-point energy is

$$E_0 = \frac{1}{2}\hbar\omega = \frac{1}{2}\hbar\left(\frac{k}{m_{\text{eff}}}\right)^{1/2}$$

For a homonuclear diatomic molecule, the effective mass is half the mass of an atom, so

$$E_0 = \frac{1}{2}(1.0546 \times 10^{-34} \text{ J s}) \times \left(\frac{2293.8 \text{ N m}^{-1}}{\frac{1}{2}(14.0031 \text{ u}) \times (1.66054 \times 10^{-27} \text{ kg u}^{-1})}\right)^{1/2}$$

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

E9.16(b) Orthogonality requires that

$$\int \psi_m^* \psi_n \, d\tau = 0$$

if $m \neq n$.

Performing the integration

$$\int \psi_m^* \psi_n \, d\tau = \int_0^{2\pi} N e^{-im\phi} N e^{in\phi} \, d\phi = N^2 \int_0^{2\pi} e^{i(n-m)\phi} \, d\phi$$

If $m \neq n$, then

$$\int \psi_m^* \psi_n d\tau = \frac{N^2}{i(n-m)} e^{i(n-m)\phi} \Big|_0^{2\pi} = \frac{N^2}{i(n-m)} (1 - 1) = 0$$

Therefore, they are orthogonal.

E9.17(b) The magnitude of angular momentum is

$$\langle \hat{L}^2 \rangle^{1/2} = \{l(l+1)\}^{1/2} \hbar [9.54a] = \{2(3)\}^{1/2} (1.0546 \times 10^{-34} \text{ J s}) = \boxed{2.58 \times 10^{-34} \text{ J s}}$$

Possible projections onto an arbitrary axis are

$$\langle \hat{L}_z \rangle = m_l \hbar [9.54b]$$

where $m_l = 0$ or ± 1 or ± 2 . So possible projections include

$$\boxed{0, \pm 1.0546 \times 10^{-34} \text{ J s and } \pm 2.1109 \times 10^{-34} \text{ J s}}$$

E9.18(b) The cones are constructed as described in Section 9.7(d) and Figure 9.40(b) of the text; their edges are of length $\{6(6+1)\}^{1/2} = 6.48$ and their projections are $m_j = +6, +5, \dots, -6$. See Figure 9.1(a).

The vectors follow, in units of \hbar . From the highest-pointing to the lowest-pointing vectors (Figure 9.1(b)), the values of m_l are 6, 5, 4, 3, 2, 1, 0, -1, -2, -3, -4, -5, and -6.

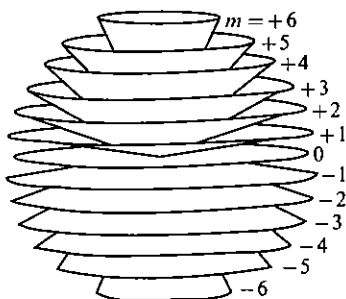


Figure 9.1(a)

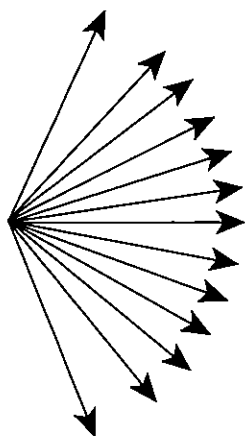


Figure 9.1(b)

Solutions to problems

Solutions to numerical problems

P9.2 $\omega = \left(\frac{k}{\mu}\right)^{1/2}$ [9.25 with μ in place of m]

Also, $\omega = 2\pi\nu = \frac{2\pi c}{\lambda} = 2\pi c\tilde{\nu}$

Therefore $k = \omega^2 \mu = 4\pi^2 c^2 \tilde{\nu}^2 \mu = \frac{4\pi^2 c^2 \tilde{\nu}^2 m_1 m_2}{m_1 + m_2}$.

We draw up the following table using information from the Data Section, p. 991.

	$^1\text{H}^{35}\text{Cl}$	$^1\text{H}^{81}\text{Br}$	$^1\text{H}^{127}\text{I}$	$^{12}\text{C}^{16}\text{O}$	$^{14}\text{N}^{16}\text{O}$
$\tilde{\nu}/\text{m}^{-1}$	299 000	265 000	231 000	217 000	190 400
$10^{27} m_1/\text{kg}$	1.6735	1.6735	1.6735	19.926	23.253
$10^{27} m_2/\text{kg}$	58.066	134.36	210.72	26.560	26.560
$k/(\text{N m}^{-1})$	516	412	314	1902	1595

Therefore, the order of stiffness, is $\boxed{\text{HI} < \text{HBr} < \text{HCl} < \text{NO} < \text{CO}}$.

P9.4 $E = \frac{l(l+1)\hbar^2}{2I}$ [9.53] $= \frac{l(l+1)\hbar^2}{2m_{\text{eff}}R^2}$ [$I = m_{\text{eff}}R^2$, m_{eff} in place of m]

$$E = \left(\frac{l(l+1) \times (1.055 \times 10^{-34} \text{ Js})^2}{(2) \times (1.6605 \times 10^{-27} \text{ kg}) \times (160 \times 10^{-12} \text{ m})^2} \right) \times \left(\frac{1}{1.008} + \frac{1}{126.90} \right)$$

$$\left[\frac{1}{m_{\text{eff}}} = \frac{1}{m_1} + \frac{1}{m_2} \right]$$

Therefore,

$$E = l(l+1) \times (1.31 \times 10^{-22} \text{ J})$$

The energies may be expressed in terms of equivalent frequencies with

$$\nu = \frac{E}{h} = (1.509 \times 10^{33} \text{ J}^{-1} \text{ s}^{-1}) E.$$

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

P9.6 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:

$$E_1^{(1)} = \int_0^L \psi_1^{(0)*} H^{(1)} \psi_1^{(0)} dx = \int_0^L \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right) mgx \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right) dx,$$

$$E_1^{(1)} = \frac{2mg}{L} \int_0^L x \sin^2\left(\frac{\pi x}{L}\right) dx,$$

$$E_1^{(1)} = \frac{2mg}{L} \left[\frac{x^2}{4} - \frac{xL}{2\pi} \cos\left(\frac{\pi x}{L}\right) \sin\left(\frac{\pi x}{L}\right) - \frac{L^2}{4\pi^2} \cos^2\left(\frac{\pi x}{L}\right) \right]_0^L,$$

$$E_1^{(1)} = \boxed{\frac{1}{2}mgL}$$

Not surprisingly, this amounts to the energy perturbation evaluated at the midpoint of the box. For $m = m_e$, $E_1^{(1)}/L = 4.47 \times 10^{-30} \text{ J m}^{-1}$.

Solutions to theoretical problems

P9.8 The energy of any given molecule is

$$E = \frac{n^2 h^2}{8mL^2} \text{ [9.12b with } n^2 = n_x^2 + n_y^2 + n_z^2 \text{ and equal lengths]}$$

(The lowest energy level is $n_x = n_y = n_z = 1$, so $n^2 = 3$; however, what follows applies to any allowed energy level.) So the internal energy of a sample of N molecules is

$$U = NE = \frac{Nn^2 h^2}{8mL^2} = \frac{Nn^2 h^2}{8mV^{2/3}}$$

In the last step we used $V = L^3$, because we are interested in how the energy changes with volume. Consider an adiabatic change of volume, that is, a change in which no heat enters or leaves the sample. In that case, the change in energy is entirely work (First Law with $q = 0$). Differentiate the expression for U :

$$dw = \left(\frac{\partial U}{\partial V} \right)_{\text{adiabatic}} dV = -\frac{Nn^2 h^2}{12mV^{5/3}} dV \quad (\text{a})$$

In Chapter 2, we learned that expansion work has the form $dw = -p_{\text{ex}} dV$. Can these expressions be reconciled, and if so, under what conditions? First, note that the expression that multiplies dV in equation (a) refers to the sample, so if it is some sort of pressure, it must be the sample pressure, and not an arbitrary external pressure, so if the expressions can be reconciled, it must be for *reversible* adiabatic expansion or compression. The expression that multiplies dV can be expressed as

$$\frac{Nn^2 h^2}{12mV^{5/3}} = \frac{2}{3} \frac{N}{V} E.$$

In fact, the kinetic model of gases (Chapter 21) says that the pressure of a gas is equal to $\frac{2}{3} \frac{N}{V} E$ where E is the average kinetic energy of the gas molecules—completely consistent with interpreting it as the

average particle-in-a-box energy. To summarize, reversible adiabatic work for a gas of particle-in-a-box molecules is $dw = -pdV$, where the pressure is

$$p = \frac{Nn^2h^2}{12mL^5} = \frac{2}{3} \frac{N}{V} E$$

In expansion, the volume increases, meaning that the box gets bigger. Equation 9.12b tells us that the kinetic energy decreases, even as the quantum numbers remain constant. This is also consistent with what we know of adiabatic expansion and the kinetic model of gases: the temperature of the sample drops on expansion, and temperature is related to the kinetic energy ($T^2 \propto E$).

In isothermal expansion, energy must enter the system as heat to maintain the temperature. We can interpret this influx of heat as an increase in quantum numbers (an excitation of the molecules) that offsets the falling energy levels.

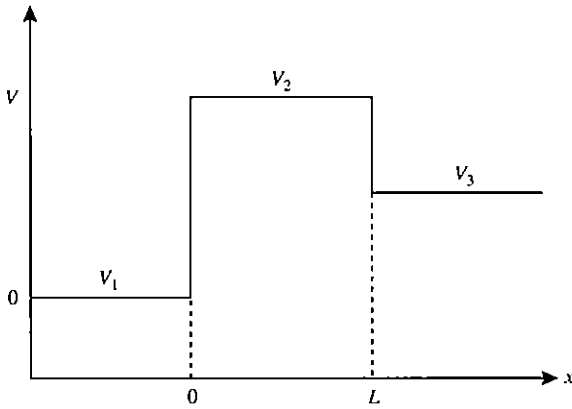


Figure 9.2a

P9.10 (a) The wavefunctions in each region (see Figure 9.2(a)) are (eqns 9.14, 9.16, and 9.17):

$$\psi_1(x) = e^{ik_1x} + B_1e^{-ik_2x}$$

$$\psi_2(x) = A_2e^{k_2x} + B_2e^{-k_2x}$$

$$\psi_3(x) = A_3e^{ik_3x}$$

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 with respect to 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:

$$1 + B_1 - A_2 - B_2 = 0$$

$$(-ik_1 - k_2)A_2 + (-ik_1 + k_2)B_2 + 2ik_1 = 0$$

$$A_2e^{k_2L} + B_2e^{-k_2L} - A_3e^{ik_3L} = 0$$

$$A_2k_2e^{k_2L} - B_2k_2e^{-k_2L} - iA_3k_3e^{ik_3L} = 0$$

Solving the simultaneous equations for A_3 gives

$$A_3 = \frac{4k_1k_2e^{ik_3L}}{(ia+b)e^{k_2L} - (ia-b)e^{-k_2L}}$$

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:

$$A_3 = \frac{2k_1k_2e^{ik_3L}}{(ia+b)\sinh(k_2L) + be^{-k_2L}}$$

$$T = |A_3|^2 = A_3 \times A_3^* = \frac{4k_1^2k_2^2}{(a^2 + b^2)\sinh^2(k_2L) + b^2}$$

where $a^2 + b^2 = (k_1^2 + k_2^2)(k_2^2 + k_3^2)$ and $b^2 = k_2^2(k_1 + k_3)^2$

(b) In the special case for which $V_1 = V_3 = 0$, eqns 9.14 and 9.17 require that $k_1 = k_3$. Additionally,

$$\left(\frac{k_1}{k_2}\right)^2 = \frac{E}{V_2 - E} = \frac{\varepsilon}{1 - \varepsilon} \quad \text{where } \varepsilon = E/V_2.$$

$$a^2 + b^2 = (k_1^2 + k_2^2)^2 = k_2^4 \left\{ 1 + \left(\frac{k_1}{k_2}\right)^2 \right\}^2$$

$$b^2 = 4k_1^2k_2^2$$

$$\frac{a^2 + b^2}{b^2} = \frac{k_2^2 \left\{ 1 + \left(\frac{k_1}{k_2}\right)^2 \right\}^2}{4k_1^2} = \frac{1}{4\varepsilon(1 - \varepsilon)}$$

$$T = \frac{b^2}{b^2 + (a^2 + b^2)\sinh^2(k_2L)} = \frac{1}{1 + \left(\frac{a^2 + b^2}{b^2}\right)\sinh^2(k_2L)}$$

$$T = \left\{ 1 + \frac{\sinh^2(k_2L)}{4\varepsilon(1 - \varepsilon)} \right\}^{-1} = \left\{ 1 + \frac{(e^{k_2L} - e^{-k_2L})^2}{16\varepsilon(1 - \varepsilon)} \right\}^{-1}$$

This proves eqn 9.20a 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 $e^{2k_2L}/\{16\varepsilon(1 - \varepsilon)\}$. The previous equation simplifies to

$$T = 16\varepsilon(1 - \varepsilon)e^{-2k_2L} \quad [9.20b]$$

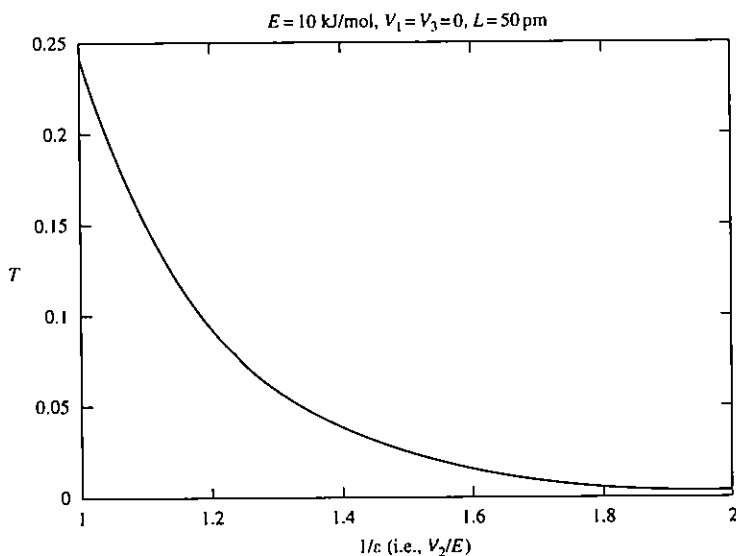


Figure 9.2(b)

P9.12 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 $\frac{d\psi}{dx} = -2gxe^{-gx^2}$

$$\frac{d^2\psi}{dx^2} = -2ge^{-gx^2} + 4g^2x^2e^{-gx^2} = -2g\psi + 4g^2x^2\psi$$

$$\left(\frac{\hbar^2g}{m}\right)\psi - \left(\frac{2\hbar^2g^2}{m}\right)x^2\psi + \frac{1}{2}kx^2\psi = E\psi$$

$$\left[\left(\frac{\hbar^2g}{m}\right) - E\right]\psi + \left(\frac{1}{2}k - \frac{2\hbar^2g^2}{m}\right)x^2\psi = 0$$

This equation is satisfied if

$$E = \frac{\hbar^2g}{m} \quad \text{and} \quad 2\hbar^2g^2 = \frac{1}{2}mk, \quad \text{or} \quad \boxed{g = \frac{1}{2} \left(\frac{mk}{\hbar^2}\right)^{1/2}}$$

Therefore,

$$E = \frac{1}{2}\hbar \left(\frac{k}{m}\right)^{1/2} = \frac{1}{2}\hbar\omega \quad \text{if } \omega = \left(\frac{k}{m}\right)^{1/2}$$

P9.14

$$\langle x^n \rangle = \alpha^n \langle y^n \rangle = \alpha^n \int_{-\infty}^{+\infty} \psi y^n \psi dx = \alpha^{n+1} \int_{-\infty}^{+\infty} \psi^2 y^n dy \quad [x = \alpha y]$$

$$\langle x^3 \rangle \propto \int_{-\infty}^{+\infty} \psi^2 y^3 dy = \boxed{0} \quad \text{by symmetry} \quad [y^3 \text{ is an odd function of } y]$$

$$\langle x^4 \rangle = \alpha^5 \int_{-\infty}^{+\infty} \psi y^4 \psi dy$$

$$y^4 \psi = y^4 N H_\nu e^{-y^2/2}$$

$$\begin{aligned}
y^4 H_\nu &= y^3 \left(\frac{1}{2} H_{\nu+1} + \nu H_{\nu-1} \right) = y^2 \left[\frac{1}{2} \left(\frac{1}{2} H_{\nu+2} + (\nu+1) H_\nu \right) + \nu \left(\frac{1}{2} H_\nu + (\nu-1) H_{\nu-2} \right) \right] \\
&= y^2 \left[\frac{1}{4} H_{\nu+2} + \left(\nu + \frac{1}{2} \right) H_\nu + \nu(\nu-1) H_{\nu-2} \right] \\
&= y \left[\frac{1}{4} \left(\frac{1}{2} H_{\nu+3} + (\nu+2) H_{\nu+1} \right) + \left(\nu + \frac{1}{2} \right) \times \left(\frac{1}{2} H_{\nu+1} + \nu H_{\nu-1} \right) \right. \\
&\quad \left. + \nu(\nu-1) \times \left(\frac{1}{2} H_{\nu-1} + (\nu-2) H_{\nu-3} \right) \right] \\
&= y \left(\frac{1}{8} H_{\nu+3} + \frac{3}{4} (\nu+1) H_{\nu+1} + \frac{3}{2} \nu^2 H_{\nu-1} + \nu(\nu-1) \times (\nu-2) H_{\nu-3} \right)
\end{aligned}$$

Only $yH_{\nu+1}$ and $yH_{\nu-1}$ lead to H_ν and contribute to the expectation value (since H_ν is orthogonal to all except H_ν) [Table 9.1]; hence

$$\begin{aligned}
y^4 H_\nu &= \frac{3}{4} y \{ (\nu+1) H_{\nu+1} + 2\nu^2 H_{\nu-1} \} + \dots \\
&= \frac{3}{4} \left[(\nu+1) \left(\frac{1}{2} H_{\nu+2} + (\nu+1) H_\nu \right) + 2\nu^2 \left(\frac{1}{2} H_\nu + (\nu-1) H_{\nu-2} \right) \right] + \dots \\
&= \frac{3}{4} \{ (\nu+1)^2 H_\nu + \nu^2 H_\nu \} + \dots \\
&= \frac{3}{4} (2\nu^2 + 2\nu + 1) H_\nu + \dots
\end{aligned}$$

Therefore

$$\int_{-\infty}^{+\infty} \psi y^4 \psi \, dy = \frac{3}{4} (2\nu^2 + 2\nu + 1) N^2 \int_{-\infty}^{+\infty} H_\nu^2 e^{-y^2} \, dy = \frac{3}{4\alpha} (2\nu^2 + 2\nu + 1)$$

and so

$$\langle x^4 \rangle = \langle \alpha^5 \rangle \times \left(\frac{3}{4\alpha} \right) \times (2\nu^2 + 2\nu + 1) = \boxed{\frac{3}{4} (2\nu^2 + 2\nu + 1) \alpha^4}$$

P9.16

$$\mu \equiv \int \psi_{\nu'} x \psi_\nu \, dx = \alpha^2 \int \psi_{\nu'} y \psi_\nu \, dy \quad [x = \alpha y]$$

$$y \psi_\nu = N_\nu \left(\frac{1}{2} H_{\nu+1} + \nu H_{\nu-1} \right) e^{-y^2/2} \text{ [Table 9.1]}$$

$$\text{Hence } \mu = \alpha^2 N_\nu N_{\nu'} \int \left(\frac{1}{2} H_{\nu'} H_{\nu+1} + \nu H_{\nu'} H_{\nu-1} \right) e^{-y^2} \, dy = 0 \quad \text{unless } \nu' = \nu \pm 1 \text{ [Table 9.1]}$$

For $\nu' = \nu + 1$

$$\mu = \frac{1}{2} \alpha^2 N_\nu N_{\nu+1} \int H_{\nu+1}^2 e^{-y^2} \, dy = \frac{1}{2} \alpha^2 N_\nu N_{\nu+1} \pi^{1/2} 2^{\nu+1} (\nu+1)! = \boxed{\alpha \left(\frac{\nu+1}{2} \right)^{1/2}}$$

For $\nu' = \nu - 1$

$$\mu = \nu \alpha^2 N_\nu N_{\nu-1} \int H_{\nu-1}^2 e^{-y^2} \, dy = \nu \alpha^2 N_\nu N_{\nu-1} \pi^{1/2} 2^{\nu-1} (\nu-1)! = \boxed{\alpha \left(\frac{\nu}{2} \right)^{1/2}}$$

No other values of ν' result in a non-zero value for μ ; hence, no other transitions are allowed.

P9.18 To address this time-dependent problem, we need a time-dependent wavefunction, made up from solutions of the time-dependent Schrödinger equation

$$\hat{H}\Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t} \quad [\text{Table 8.1}]$$

If $\psi(x)$ is an eigenfunction of the energy operator with energy eigenvalue E , then

$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar}$$

is a solution of the time-dependent Schrödinger equation (provided the energy operator is not itself time dependent). To verify this, evaluate both sides of the time-dependent Schrödinger equation. On the left we have

$$\hat{H}\Psi(x, t) = \hat{H}\psi(x)e^{-iEt/\hbar} = E\psi(x)e^{-iEt/\hbar} = E\Psi(x, t)$$

On the right we have

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = i\hbar \psi(x) \frac{\partial}{\partial t} e^{-iEt/\hbar} = -i^2 E \psi(x) e^{-iEt/\hbar} = E\Psi(x, t),$$

the same as on the left. Our wavepacket is an arbitrary superposition of time-evolving harmonic oscillator states,

$$\Psi(x, t) = \sum_{v=0} c_v \psi_v(x) e^{-iE_v t/\hbar}$$

where $\psi_v(x)$ are time-independent harmonic-oscillator wavefunctions and

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega \quad [9.25]$$

Hence, the wavepacket is

$$\Psi(x, t) = e^{-i\omega t/2} \sum_{v=0} c_v \psi_v(x) e^{-i v \omega t}$$

The angular frequency ω is related to the period T by $T = 2\pi/\omega$, so we can evaluate the wavepacket at any whole number of periods after t , that is at a time $t + nT$, where n is any integer. (Note: n is not a quantum number.) Note that

$$t + nT = t + 2\pi n/\omega,$$

so

$$\begin{aligned} \Psi(x, t + nT) &= e^{-i\omega t/2} e^{-i\omega nT/2} \sum_{v=0} c_v \psi_v(x) e^{-i v \omega t} e^{-i v \omega nT} \\ &= e^{-i\omega t/2} e^{-i\pi n} \sum_{v=0} c_v \psi_v(x) e^{-i v \omega t} e^{-2\pi i v n} \end{aligned}$$

Noting that the exponential of $(2\pi i \times \text{any integer}) = 1$, we note that the last factor inside the sum is 1 for every state. Also, since $e^{-i\pi n} = (-1)^n$, we have

$$\Psi(x, t + nT) = (-1)^n \Psi(x, t)$$

At any whole number of periods after time t , the wavefunction is either the same at time t or -1 times its value at time t . In any event, $|\Psi|^2$ returns to its original value each period, so the wavepacket returns to the same spatial distribution each period.

P9.20 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

$$\langle \Omega \rangle = \int \psi^* \hat{\Omega} \psi \, d\tau \quad [8.34]$$

$$(a) \quad \hat{l}_z e^{i\phi} = \frac{\hbar}{i} \frac{d}{d\phi} e^{i\phi} = \hbar e^{i\phi}; \text{ hence } l_z = \boxed{+\hbar}$$

$$(b) \quad \hat{l}_z e^{-2i\phi} = \frac{\hbar}{i} \frac{d}{d\phi} e^{-2i\phi} = -2\hbar e^{-2i\phi}; \text{ hence } l_z = \boxed{-2\hbar}$$

$$(c) \quad \langle l_z \rangle \propto \int_0^{2\pi} \cos \phi \left(\frac{\hbar}{i} \frac{d}{d\phi} \cos \phi \right) d\phi \propto -\frac{\hbar}{i} \int_0^{2\pi} \cos \phi \sin \phi \, d\phi = \boxed{0}$$

$$\begin{aligned} (d) \quad \langle l_z \rangle &= N^2 \int_0^{2\pi} (\cos \chi e^{i\phi} + \sin \chi e^{-i\phi})^* \left(\frac{\hbar}{i} \frac{d}{d\phi} \right) \times (\cos \chi e^{i\phi} + \sin \chi e^{-i\phi}) \, d\phi \\ &= \frac{\hbar}{i} N^2 \int_0^{2\pi} (\cos \chi e^{-i\phi} + \sin \chi e^{i\phi}) \times (i \cos \chi e^{i\phi} - \sin \chi e^{-i\phi}) \, d\phi \\ &= \hbar N^2 \int_0^{2\pi} (\cos^2 \chi - \sin^2 \chi + \cos \chi \sin \chi [e^{2i\phi} - e^{-2i\phi}]) \, d\phi \\ &= \hbar N^2 (\cos^2 \chi - \sin^2 \chi) \times (2\pi) = 2\pi \hbar N^2 \cos 2\chi \end{aligned}$$

We must evaluate the normalization constant:

$$\begin{aligned} N^2 \int_0^{2\pi} (\cos \chi e^{i\phi} + \sin \chi e^{-i\phi})^* (\cos \chi e^{i\phi} + \sin \chi e^{-i\phi}) \, d\phi &= 1 \\ 1 &= N^2 \int_0^{2\pi} (\cos^2 \chi + \sin^2 \chi + \cos \chi \sin \chi [e^{2i\phi} + e^{-2i\phi}]) \, d\phi \\ &= 2\pi N^2 (\cos^2 \chi + \sin^2 \chi) = 2\pi N^2 \quad \text{so } N^2 = \frac{1}{2\pi} \end{aligned}$$

Therefore

$$\langle l_z \rangle = \boxed{\hbar \cos 2\chi} \quad [\chi \text{ is a parameter}]$$

$$\text{For the kinetic energy we use } \hat{T} \equiv \hat{E}_K = \frac{\hat{J}_z^2}{2I} \quad [9.36] = -\frac{\hbar^2}{2I} \frac{d^2}{d\phi^2} \quad [9.40]$$

$$(a) \quad \hat{T} e^{i\phi} = -\frac{\hbar^2}{2I} (i^2 e^{i\phi}) = \frac{\hbar^2}{2I} e^{i\phi}; \text{ hence } \langle T \rangle = \boxed{\frac{\hbar^2}{2I}}$$

$$(b) \quad \hat{T} e^{-2i\phi} = -\frac{\hbar^2}{2I} (2i)^2 e^{-2i\phi} = \frac{4\hbar^2}{2I} e^{-2i\phi}; \text{ hence } \langle T \rangle = \boxed{\frac{2\hbar^2}{I}}$$

$$(c) \quad \hat{T} \cos \phi = -\frac{\hbar^2}{2I} (-\cos \phi) = \frac{\hbar^2}{2I} \cos \phi; \text{ hence } \langle T \rangle = \boxed{\frac{\hbar^2}{2I}}$$

$$(d) \quad \hat{T} (\cos \chi e^{i\phi} + \sin \chi e^{-i\phi}) = -\frac{\hbar^2}{2I} (-\cos \chi e^{i\phi} - \sin \chi e^{-i\phi}) = \frac{\hbar^2}{2I} (\cos \chi e^{i\phi} + \sin \chi e^{-i\phi})$$

$$\text{and hence } \langle T \rangle = \boxed{\frac{\hbar^2}{2I}}$$

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.

P9.22 Mathematical software can animate the real part or the imaginary part of $\Psi(\phi, t)$, or you may wish to have it display $|\Psi^2(\phi, t)|$. Try a “pure” state, that is, let $c = 1$ for one value of m_l and 0 for all others. This “packet” does not spread, but only circulates. Also try making all the coefficients in the sum equal (all 1, for example). Whatever your choice of coefficients, the pattern will repeat with a period T that makes all the time-dependent factors equal to the exponential of $(2\pi i \times \text{an integer})$:

$$T = \frac{4\pi I}{\hbar}$$

making the exponent $iE_{m_l}t/\hbar$ equal to $2\pi i m_l^2$ when $t = T$ and at intervals of T thereafter. (See Problem 9.18.) An example of this approach using Mathcad is illustrated below:

Wavepacket on a Ring as a MathCad Document. Let $\tau = \frac{\hbar \cdot t}{4 \cdot \pi \cdot I}$ and let each function in the superposition of $m + 1$ functions contribute with equal probability. The normalized angular functions are:

$$\psi(m, \phi) := \left(\frac{1}{2 \cdot \pi}\right)^{\frac{1}{2}} \cdot e^{i \cdot m \cdot \phi} \quad ([9.38b] \text{ where } m \text{ is an integer.})$$

The normalized superposition is:

$$\Psi(m_{\max}, \phi, \tau) := \left(\frac{1}{m+1}\right)^{\frac{1}{2}} \cdot \sum_{m=0}^{m_{\max}} \psi(m, \phi) \cdot e^{-i \cdot m^2 \cdot \tau}$$

$$N := 500 \quad j := 0..N \quad \phi_j := \frac{2 \cdot \pi \cdot j}{N} \quad m_{\max} := 8 \quad \Delta\tau := .03$$

The probability density of the superposition is: $P(\phi, \tau) := \Psi(m_{\max}, \phi, \tau) \cdot \overline{\Psi(m_{\max}, \phi, \tau)}$

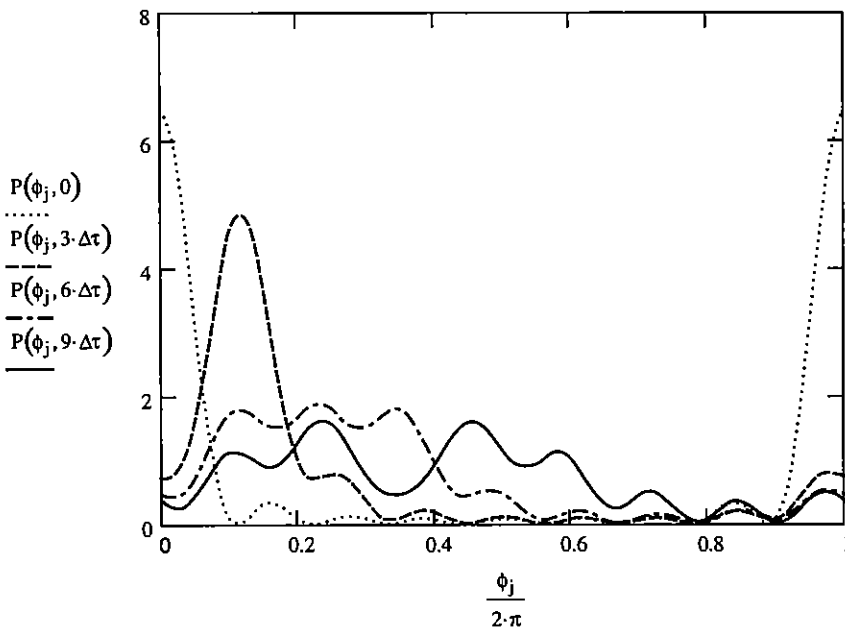


Figure 9.3

The above plot (Figure 9.3) shows that as the initially localized wave propagates around the ring it spreads with time and the uncertainty in knowing particle position increases. The effect of increasing or decreasing the energies accessible to the particle may be explored by increasing or decreasing the value of m_{\max} in the MathCad document.

$$\begin{aligned}
 \text{P9.24} \quad \int_0^\pi \int_0^{2\pi} Y_{3,3}^* Y_{3,3} \sin \theta \, d\theta \, d\phi &= \left(\frac{1}{64}\right) \times \left(\frac{35}{\pi}\right) \int_0^\pi \sin^6 \theta \sin \theta \, d\theta \int_0^{2\pi} d\phi \quad [\text{Table 9.3}] \\
 &= \left(\frac{1}{64}\right) \times \left(\frac{35}{\pi}\right) \times (2\pi) \int_{-1}^1 (1 - \cos^2 \theta)^3 \, d \cos \theta \\
 &\quad [\sin \theta \, d\theta = d \cos \theta, \sin^2 \theta = 1 - \cos^2 \theta] \\
 &= \frac{35}{32} \int_{-1}^1 (1 - 3x^2 + 3x^4 - x^6) \, dx \quad [x = \cos \theta] \\
 &= \frac{35}{32} \left(x - x^3 + \frac{3}{5}x^5 - \frac{1}{7}x^7\right) \Big|_{-1}^1 = \frac{35}{32} \times \frac{32}{35} = \boxed{1}
 \end{aligned}$$

$$\begin{aligned}
 \text{P9.26} \quad \nabla^2 &= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \\
 \frac{\partial^2}{\partial x^2} f &= -a^2 f \quad \frac{\partial^2}{\partial y^2} f = -b^2 f \quad \frac{\partial^2}{\partial z^2} f = -c^2 f
 \end{aligned}$$

and f is an eigenfunction with eigenvalue $\boxed{-(a^2 + b^2 + c^2)}$

P9.28 Upon making the operator substitutions

$$p_x = \frac{\hbar}{i} \frac{\partial}{\partial x} \quad \text{and} \quad p_y = \frac{\hbar}{i} \frac{\partial}{\partial y}$$

into \hat{l}_z we find

$$\hat{l}_z = \frac{\hbar}{i} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

But $\frac{\partial}{\partial \phi} = \frac{\partial x}{\partial \phi} \frac{\partial}{\partial x} + \frac{\partial y}{\partial \phi} \frac{\partial}{\partial y} + \frac{\partial z}{\partial \phi} \frac{\partial}{\partial z}$ which is the chain rule of partial differentiation.

$$\frac{\partial x}{\partial \phi} = \frac{\partial}{\partial \phi} (r \sin \theta \cos \phi) = -r \sin \theta \sin \phi = -y$$

$$\frac{\partial y}{\partial \phi} = \frac{\partial}{\partial \phi} (r \sin \theta \sin \phi) = r \sin \theta \cos \phi = x$$

$$\frac{\partial z}{\partial \phi} = 0$$

$$\text{Thus, } \frac{\partial}{\partial \phi} = -y \frac{\partial}{\partial x} + x \frac{\partial}{\partial y}$$

Upon substitution,

$$\hat{l}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi} = -i\hbar \frac{\partial}{\partial \phi}$$

P9.30

- (a) Suppose that a particle moves classically at the constant speed v . It starts at $x = 0$ at $t = 0$ and at $t = \tau$ is at position $x = L$. $v = L/\tau$ and $x = vt$.

$$\begin{aligned}\langle x \rangle &= \frac{1}{\tau} \int_0^\tau x \, dt = \frac{1}{\tau} \int_0^\tau vt \, dt \\ &= \frac{v}{\tau} \int_0^\tau t \, dt = \frac{v}{2\tau} t^2 \Big|_0^\tau \\ &= \frac{v\tau^2}{2\tau} = \frac{v\tau}{2} = \boxed{\frac{L}{2} = \langle x \rangle}\end{aligned}$$

$$\begin{aligned}\langle x^2 \rangle &= \frac{1}{\tau} \int_0^\tau x^2 \, dt = \frac{v^2}{\tau} \int_0^\tau t^2 \, dt \\ &= \frac{v^2}{3\tau} t^3 \Big|_0^\tau = \frac{(v\tau)^2}{3} = \frac{L^2}{3}\end{aligned}$$

$$\boxed{\langle x^2 \rangle^{1/2} = \frac{L}{3^{1/2}}}$$

(b) $\psi_n = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)$ for $0 \leq x \leq L$ [9.4b]

$$\begin{aligned}\langle x \rangle_n &= \int_{x=0}^L \psi_n^* x \psi_n \, dx = \frac{2}{L} \int_0^L x \sin^2\left(\frac{n\pi x}{L}\right) \, dx \\ &= \frac{2}{L} \left[\frac{x^2}{4} - \frac{x \sin\left(\frac{2n\pi x}{L}\right)}{4(n\pi/L)} - \frac{\cos\left(\frac{2n\pi x}{L}\right)}{8(n\pi/L)^2} \right]_{x=0}^{x=L} \\ &= \frac{2}{L} \left[\frac{L^2}{4} \right] = \boxed{\frac{L}{2} = \langle x \rangle_n}\end{aligned}$$

This agrees with the classical result.

$$\begin{aligned}\langle x^2 \rangle_n &= \int_{x=0}^L \psi_n^* x^2 \psi_n \, dx = \frac{2}{L} \int_0^L x^2 \sin^2\left(\frac{n\pi x}{L}\right) \, dx \\ &= \frac{2}{L} \left[\frac{x^3}{6} - \left(\frac{x^2}{4(n\pi/L)} - \frac{1}{8(n\pi/L)^3} \right) \sin\left(\frac{2n\pi x}{L}\right) - \frac{x \cos\left(\frac{2n\pi x}{L}\right)}{8(n\pi/L)^2} \right]_{x=0}^{x=L} \\ &= \frac{2}{L} \left[\frac{L^3}{6} - \frac{L}{8(n\pi/L)^2} \right] \\ &= \frac{L^2}{3} - \frac{1}{4(n\pi/L)^2}\end{aligned}$$

$$\boxed{\langle x^2 \rangle_n^{1/2} = \left(\frac{L^2}{3} - \frac{1}{4(n\pi/L)^2} \right)^{1/2}}$$

This agrees with the classical result in the limit of large quantum numbers:

$$\lim_{n \rightarrow \infty} \langle x^2 \rangle_n^{1/2} = \frac{L}{3^{1/2}}$$

Solutions to applications

- P9.32** The rate of tunnelling is proportional to the transmission probability, so a ratio of tunnelling rates is equal to the corresponding ratio of transmission probabilities (given in eqn 9.20a). The desired factor is T_1/T_2 , where the subscripts denote the tunnelling distances in nanometers:

$$\frac{T_1}{T_2} = \frac{1 + \frac{(e^{\kappa L_2} - e^{-\kappa L_2})^2}{16\varepsilon(1-\varepsilon)}}{1 + \frac{(e^{\kappa L_1} - e^{-\kappa L_1})^2}{16\varepsilon(1-\varepsilon)}}$$

If $\frac{(e^{\kappa L_2} - e^{-\kappa L_2})^2}{16\varepsilon(1-\varepsilon)} \gg 1$,

then $\frac{T_1}{T_2} \approx \frac{(e^{\kappa L_2} - e^{-\kappa L_2})^2}{(e^{\kappa L_1} - e^{-\kappa L_1})^2} \approx e^{2\kappa(L_2 - L_1)} = e^{2(7/\text{nm})(2.0 - 1.0)\text{nm}} = \boxed{1.2 \times 10^6}$.

This is, the tunnelling rate increases about a million-fold. Note: if the first approximation does not hold, we need more information, namely $\varepsilon = E/V$. If the first approximation is valid, then the second is also likely to be valid, namely that the negative exponential is negligible compared to the positive one.

- P9.34** Assuming that one can identify the CO peak in the infrared spectrum of the CO-myoglobin complex, taking infrared spectra of each of the isotopic variants of CO-myoglobin complexes can show which atom binds to the haem group and determine the $\text{C}\equiv\text{O}$ force constant. Compare isotopic variants to $^{12}\text{C}^{16}\text{O}$ as the standard; when an isotope changes but the vibrational frequency does not, then the atom whose isotope was varied is the atom that binds to the haem. See table below, which includes predictions of the wavenumber of all isotopic variants compared to that of $\tilde{\nu}(^{12}\text{C}^{16}\text{O})$. (As usual, the better the experimental results agree with the whole set of predictions, the more confidence one would have with the conclusion.)

Wavenumber for isotopic variant	If O binds	If C binds
$\tilde{\nu}(^{12}\text{C}^{18}\text{O}) =$	$\tilde{\nu}(^{12}\text{C}^{16}\text{O})^\dagger$	$(16/18)^{1/2}\tilde{\nu}(^{12}\text{C}^{16}\text{O})$
$\tilde{\nu}(^{13}\text{C}^{16}\text{O}) =$	$(12/13)^{1/2}\tilde{\nu}(^{12}\text{C}^{16}\text{O})$	$\tilde{\nu}(^{12}\text{C}^{16}\text{O})^\dagger$
$\tilde{\nu}(^{13}\text{C}^{18}\text{O}) =$	$(12/13)^{1/2}\tilde{\nu}(^{12}\text{C}^{16}\text{O})$	$(16/18)^{1/2}\tilde{\nu}(^{12}\text{C}^{16}\text{O})$

† That is, no change compared to the standard.

The wavenumber is related to the force constant as follows:

$$\omega = 2\pi c\tilde{\nu} = \left(\frac{k}{m}\right)^{1/2} \quad \text{so} \quad k = m(2\pi c\tilde{\nu})^2,$$

$$k = m(1.66 \times 10^{-27} \text{ kg u}^{-1})[(2\pi)(2.998 \times 10^{10} \text{ cm s}^{-1})\tilde{\nu}(^{12}\text{C}^{16}\text{O})]^2,$$

and $k/(\text{kg s}^{-1}) = (5.89 \times 10^{-5})(m/\text{u})[\tilde{\nu}(^{12}\text{C}^{16}\text{O})/\text{cm}^{-1}]^2$.

Here m is the mass of the atom that is not bound, i.e. 12 u if O is bound and 16 u if C is bound. (Of course, one can compute k from any of the isotopic variants, and take k to be a mean derived from all the relevant data.)

P9.36 See solution to P2.38, parts (c) and (d). First, let $f = n/N$; therefore, f is the fraction of the totally stretched chain represented by the end-to-end distance.

$$\begin{aligned} F &= -\frac{kT}{2l} \ln \left(\frac{N+n}{N-n} \right) = -\frac{kT}{2l} \ln \left(\frac{N(1+f)}{N(1-f)} \right) = -\frac{kT}{2l} \ln \left(\frac{1+f}{1-f} \right) \\ &= -\frac{kT}{2l} [\ln(1+f) - \ln(1-f)] \end{aligned}$$

When $n \ll N$, then $f \ll 1$, and the natural log can be expanded: $\ln(1+f) \approx f$ and $\ln(1-f) \approx -f$. Therefore

$$F \approx -\frac{kT}{2l} [f - (-f)] = -\frac{fkT}{l} = -\frac{nkT}{Nl} = -\frac{kT}{Nl^2} x.$$

In the last step, we note that the distance x between ends is equal to nl , so $n = x/l$. This is a Hooke's law force with force constant kT/Nl^2 .

The root mean square displacement is $\langle x^2 \rangle^{1/2}$. In part (b) of P9.15, $\langle x^2 \rangle$ for a harmonic oscillator was evaluated and was found to be

$$\langle x^2 \rangle = \left(\nu + \frac{1}{2} \right) \times \left(\frac{\hbar^2}{mk_{\text{force}}} \right)^{1/2}$$

Therefore, putting in the appropriate values for the ground state ($\nu = 0$) of this model

$$\langle x^2 \rangle = \frac{1}{2} \times \left(\frac{\hbar^2}{Nm} \times \frac{Nl^2}{kT} \right)^{1/2} = \frac{\hbar l}{2} \times \left(\frac{1}{mkT} \right)^{1/2}$$

$$\text{and } \langle x^2 \rangle^{1/2} = \left[\left(\frac{\hbar l}{2} \right)^{1/2} \times \left(\frac{1}{mkT} \right)^{1/4} \right]$$

P9.38 (a) In the box, the Schrödinger equation is

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi = E\psi$$

Assume that the solution is a product of three functions of a single variable; that is, let

$$\psi(x, y, z) = X(x)Y(y)Z(z).$$

Substituting into the Schrödinger equation gives

$$-\frac{\hbar^2}{2m} \left(YZ \frac{\partial^2 X}{\partial x^2} + XZ \frac{\partial^2 Y}{\partial y^2} + XY \frac{\partial^2 Z}{\partial z^2} \right) = EXYZ$$

Divide both sides by XYZ :

$$-\frac{\hbar^2}{2m} \left(\frac{1}{X} \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} \right) = E$$

For the purposes of illustration, isolate the terms that depend on x on the left side of the equation:

$$-\frac{\hbar^2}{2m} \left(\frac{1}{X} \frac{\partial^2 X}{\partial x^2} \right) = E + \frac{\hbar^2}{2m} \left(\frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} + \frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} \right)$$

Note that the left side depends only on one variable, x , while the right side depends on two different and independent variables, y and z . The only way that the two sides can be equal to each other for all x , y , and z is if they are both equal to a constant. Call that constant E_x , and we have, from the left side of the equation:

$$-\frac{\hbar^2}{2m} \left(\frac{1}{X} \frac{\partial^2 X}{\partial x^2} \right) = E_x \quad \text{so} \quad -\frac{\hbar^2}{2m} \frac{\partial^2 X}{\partial x^2} = E_x X.$$

Note that this is just the Schrödinger equation for a particle in a one-dimensional box. Note also that we could just as easily have isolated y terms or z terms, leading to similar equations.

$$-\frac{\hbar^2}{2m} \frac{\partial^2 Y}{\partial y^2} = E_y Y \quad \text{and} \quad -\frac{\hbar^2}{2m} \frac{\partial^2 Z}{\partial z^2} = E_z Z$$

The assumption that the wavefunction can be written as a product of single-variable functions is a valid one, for we can find ordinary differential equations for the assumed factors. That is what it means for a partial differential equation to be separable.

- (b) Since X , Y , and Z are particle-in-a-box wavefunctions of independent variables x , y , and z respectively, each of them has its own quantum number. The three-dimensional wavefunction is a product of the three, and therefore depends on all three quantum numbers:

$$\psi(x, y, z) = X(x)Y(y)Z(z) = \left(\frac{2}{L_1} \right)^{1/2} \sin \frac{n_x \pi x}{L_1} \times \left(\frac{2}{L_2} \right)^{1/2} \sin \frac{n_y \pi y}{L_2} \times \left(\frac{2}{L_3} \right)^{1/2} \sin \frac{n_z \pi z}{L_3}$$

Each constant of separation (E_x , E_y , and E_z) depends on its own quantum number. The three constants of separation add up to the total energy, which therefore depends on all three quantum numbers:

$$E = E_x + E_y + E_z = \frac{\hbar^2}{8m} \left(\frac{n_x^2}{L_1^2} + \frac{n_y^2}{L_2^2} + \frac{n_z^2}{L_3^2} \right)$$

- (c) For a cubic box, $L_1 = L_2 = L_3 = L$, so

$$E = \frac{\hbar^2(n_x^2 + n_y^2 + n_z^2)}{8mL^2}$$

The energy levels are shown in Figure 9.4.

- (d) Compare this energy-level diagram to Figure 9.2 of the textbook. The energy levels here are much more closely spaced. In a one-dimensional box, the 15th energy level is not reached until

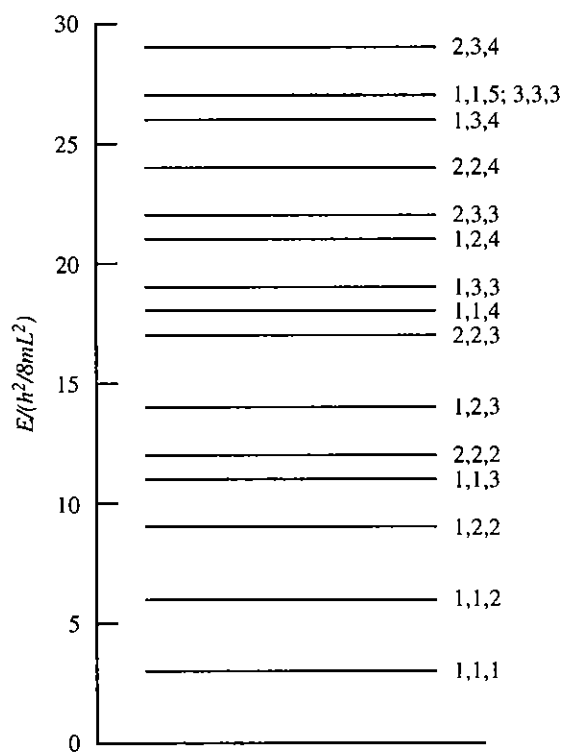


Figure 9.4

$\frac{E}{h^2/8mL^2} = 225$, and the previous level is 29 units below that. In the three-dimensional box, the first 15 energy levels fit within the range of 29 units. The energy levels in a one-dimensional box are sparse compared to those in a three-dimensional box.



10

Atomic structure and atomic spectra

Answers to discussion questions

- D10.2** (1) The principal quantum number, n , determines the energy of a hydrogenic atomic orbital through eqn 10.11.
- (2) The azimuthal quantum number, l , determines the magnitude of the angular momentum of a hydrogenic atomic orbital through the formula $\{l(l+1)\}^{1/2}\hbar$.
- (3) The magnetic quantum number, m_l , determines the z-component of the angular momentum of a hydrogenic orbital through the formula $m_l\hbar$.
- (4) The spin quantum number, s , determines the magnitude of the spin angular momentum through the formula $\{s(s+1)\}^{1/2}\hbar$. For hydrogenic atomic orbitals, s can only be $1/2$.
- (5) The spin quantum number, m_s , determines the z-component of the spin angular momentum through the formula $m_s\hbar$. For hydrogenic atomic orbitals, m_s can only be $\pm 1/2$.
- D10.4** (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.
- D10.6** 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.
- D10.8** 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 Figure 10.27. The total angular momentum of an electron in an atom is the vector sum of the orbital and spin angular momenta as illustrated in Figure 10.28 and expressed in eqn 10.46. The spin-orbit coupling results in a splitting of the energy levels associated with atomic terms as shown in Figures 10.29 and 10.30. This splitting shows up in atomic spectra as a fine structure as illustrated in Figure 10.30.

Solutions to exercises

E10.1(b) The energy of the photon that struck the Xe atom goes into liberating the bound electron and giving it any kinetic energy it now possesses

$$E_{\text{photon}} = I + E_{\text{kinetic}} \quad I = \text{ionization energy}$$

The energy of a photon is related to its frequency and wavelength

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

and the kinetic energy of an electron is related to its mass and speed, s

$$E_{\text{kinetic}} = \frac{1}{2}m_e s^2$$

$$\text{So } \frac{hc}{\lambda} = I + \frac{1}{2}m_e s^2 \Rightarrow I = \frac{hc}{\lambda} - \frac{1}{2}m_e s^2$$

$$\begin{aligned} I &= \frac{(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1})}{58.4 \times 10^{-9} \text{ m}} - \frac{1}{2} (9.11 \times 10^{-31} \text{ kg}) \\ &\quad \times (1.79 \times 10^6 \text{ m s}^{-1})^2 \\ &= \boxed{1.94 \times 10^{-18} \text{ J}} = 12.1 \text{ eV} \end{aligned}$$

E10.2(b) The radial wavefunction is [Table 10.1]

$$R_{3,0} = A \left(6 - 2\rho + \frac{1}{9}\rho^2 \right) e^{-\rho/6} \text{ where } \rho \equiv \frac{2Zr}{a_0}, \text{ and } A \text{ is a collection of constants.}$$

[Note: ρ defined here is $3 \times \rho$ as defined in Table 10.1]

Differentiating with respect to ρ yields

$$\begin{aligned} \frac{dR_{3,0}}{d\rho} &= 0 = A \left(6 - 2\rho + \frac{1}{9}\rho^2 \right) \times \left(-\frac{1}{6} \right) e^{-\rho/6} + \left(-2 + \frac{2}{9}\rho \right) A e^{-\rho/6} \\ &= A e^{-\rho/6} \left(-\frac{\rho^2}{54} + \frac{5}{9}\rho - 3 \right) \end{aligned}$$

This is a quadratic equation

$$0 = a\rho^2 + b\rho + c \quad \text{where } a = -\frac{1}{54}, \quad b = \frac{5}{9}, \quad \text{and } c = -3.$$

The solution is

$$\rho = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a} = 15 \pm 3\sqrt{7}$$

$$\text{so } r = \left(\frac{15}{2} \pm \frac{3(7^{1/2})}{2} \right) \frac{a_0}{Z}$$

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 $a_0 = 5.292 \times 10^{-11} \text{ m}$, $r = \boxed{607 \text{ pm}}$ and $\boxed{187 \text{ pm}}$.

The other maximum in the wavefunction is at $\boxed{r = 0}$. It is a physical maximum, but not a calculus maximum: the first derivative of the wavefunction does not vanish there, so it cannot be found by differentiation.

E10.3(b) The complete radial wavefunction, $R_{4,1}$ is not given in Table 10.1; however in the statement of the exercise we are told that it is proportional to

$$(20 - 10\rho + \rho^2)\rho \quad \text{where } \rho = \frac{2Zr}{a_0} \quad [\text{Note: } \rho \text{ defined here is } n \times \rho \text{ as defined in Table 10.1}]$$

The radial nodes occur where the radial wavefunction vanishes, namely where

$$(20 - 10\rho + \rho^2)\rho = 0.$$

The zeros of this function occur at

$$\rho = 0, \quad \boxed{r = 0}$$

and when

$$(20 - 10\rho + \rho^2) = 0, \quad \text{with roots } \rho = 2.764, \quad \text{and } \rho = 7.236$$

$$\text{then } r = \frac{\rho a_0}{2Z} = \frac{\rho a_0}{2} = \frac{2.764a_0}{2} = \boxed{1.382a_0} \quad \text{and} \quad \frac{7.236a_0}{2} = \boxed{3.618a_0}$$

$$\text{or } r = \boxed{7.31 \times 10^{-11} \text{ m}} \quad \text{and} \quad \boxed{1.917 \times 10^{-10} \text{ m}}$$

E10.4(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

$$\int_0^\infty e^{-r/k} r^2 dr = 2k^3, \quad \int_0^\infty e^{-r/k} r^3 dr = 6k^4, \quad \text{and} \quad \int_0^\infty e^{-r/k} r^4 dr = 24k^5.$$

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

E10.5(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 $N = \frac{1}{4} \left(\frac{Z^3}{2\pi a_0^3} \right)^{1/2}$ and $\rho \equiv \frac{Zr}{a_0}$ here

$$\hat{E}_K = -\frac{\hbar^2}{2m} \nabla^2 \quad d\tau = r^2 \sin \theta dr d\theta d\phi = \frac{a_0^3 \rho^2 \sin \theta d\rho d\theta d\phi}{Z^3}$$

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

$$\nabla^2 \psi = \frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r} \frac{\partial \psi}{\partial r} = \frac{\partial^2 \psi}{\partial \rho^2} \left(\frac{\partial \rho}{\partial r} \right)^2 + \frac{2Z}{\rho a_0} \left(\frac{\partial \psi}{\partial \rho} \right) \frac{\partial \rho}{\partial r} = \left(\frac{Z}{a_0} \right)^2 \times \left(\frac{\partial^2 \psi}{\partial \rho^2} + \frac{2}{\rho} \frac{\partial \psi}{\partial \rho} \right)$$

$$\frac{\partial \rho}{\partial r} = N(2 - \rho) \times \left(-\frac{1}{2} \right) e^{-\rho/2} - N e^{-\rho/2} = N \left(\frac{1}{2} \rho - 2 \right) e^{-\rho/2}$$

$$\frac{\partial^2 \psi}{\partial \rho^2} = N \left(\frac{1}{2} \rho - 2 \right) \times \left(-\frac{1}{2} \right) e^{-\rho/2} + \frac{1}{2} N e^{-\rho/2} = N \left(\frac{3}{2} - \frac{1}{4} \rho \right) e^{-\rho/2}$$

$$\nabla^2 \psi = \left(\frac{Z}{a_0} \right)^2 N e^{-\rho/2} (-4/\rho + 5/2 - \rho/4)$$

and

$$\begin{aligned} \langle \hat{E}_K \rangle &= \int_0^\infty \int_0^\pi \int_0^{2\pi} N(2 - \rho) e^{-\rho/2} \left(\frac{Z}{a_0} \right)^2 \times \left(\frac{-\hbar^2}{2m} \right) \\ &\quad \times N e^{-\rho/2} (-4/\rho + 5/2 - \rho/4) \frac{a_0^3 d\phi \sin \theta d\theta \rho^2 d\rho}{Z^3} \end{aligned}$$

The integrals over angles give a factor of 4π , so

$$\langle \hat{E}_K \rangle = 4\pi N^2 \left(\frac{a_0}{Z} \right) \times \left(-\frac{\hbar^2}{2m} \right) \int_0^\infty (2 - \rho) \times \left(-4 + \frac{5}{2} \rho - \frac{1}{4} \rho^2 \right) \rho e^{-\rho} d\rho$$

The integral in this last expression works out to -2 , using $\int_0^\infty e^{-\rho} \rho^n d\rho = n!$ for $n = 1, 2$, and 3 . So

$$\langle \hat{E}_K \rangle = 4\pi \left(\frac{Z^3}{32\pi a_0^3} \right) \times \left(\frac{a_0}{Z} \right) \times \left(\frac{\hbar^2}{m} \right) = \boxed{\frac{\hbar^2 Z^2}{8ma_0^2}}$$

The average potential energy is

$$\langle V \rangle = \int \psi^* V \psi \, d\tau \quad \text{where} \quad V = -\frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{Z^2 e^2}{4\pi\epsilon_0 a_0 \rho}$$

$$\text{and } \langle V \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} N(2-\rho)e^{-\rho/2} \left(-\frac{Z^2 e^2}{4\pi\epsilon_0 a_0 \rho} \right) N(2-\rho)e^{-\rho/2} \frac{a_0^3 \rho^2 \sin\theta \, d\rho \, d\theta \, d\phi}{Z^3}$$

The integrals over angles give a factor of 4π , so

$$\langle V \rangle = 4\pi N^2 \left(\frac{Z^2 e^2}{4\pi\epsilon_0 a_0} \right) \times \left(\frac{a_0^3}{Z^3} \right) \int_0^\infty (2-\rho)^2 \rho e^{-\rho} \, d\rho$$

The integral in this last expression works out to 2, using $\int_0^\infty e^{-\rho} \rho^n \, d\rho = n!$ for $n = 1, 2, 3$, and 4. So

$$\langle V \rangle = 4\pi \left(\frac{Z^3}{32\pi a_0^3} \right) \times \left(-\frac{Z^2 e^2}{4\pi\epsilon_0 a_0} \right) \times \left(\frac{a_0^3}{Z^3} \right) \times (2) = \boxed{-\frac{Z^2 e^2}{16\pi\epsilon_0 a_0}}$$

E10.6(b) The radial distribution function is defined as

$$P = 4\pi r^2 \psi^2 \quad \text{so} \quad P_{3s} = 4\pi r^2 (Y_{0,0} R_{3,0})^2,$$

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

where $\rho \equiv \frac{2Zr}{na_0} = \frac{2Zr}{3a_0}$ 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

$$P_{3s} = C \rho^2 (6 - 6\rho + \rho^2)^2 e^{-\rho}$$

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 $(P_{3s})^{1/2}$

$$\begin{aligned} \frac{d(P_{3s})^{1/2}}{d\rho} = 0 &= \frac{d}{d\rho} C \rho (6 - 6\rho + \rho^2) e^{-\rho/2} \\ &= C [\rho(6 - 6\rho + \rho^2) \times \left(-\frac{1}{2}\right) + (6 - 12\rho + 3\rho^2)] e^{-\rho/2} \end{aligned}$$

$$0 = C \left(6 - 15\rho + 6\rho^2 - \frac{1}{2}\rho^3 \right) e^{-\rho/2} \quad \text{so} \quad 12 - 30\rho + 12\rho^2 - \rho^3 = 0$$

Numerical solution of this cubic equation yields

$$\rho = 0.49, \quad 2.79, \quad \text{and} \quad 8.72$$

corresponding to

$$r = \boxed{0.74a_0/Z, \quad 4.19a_0/Z, \quad \text{and} \quad 13.08a_0/Z}$$

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.

- E10.7(b)** The most probable radius occurs when the radial wavefunction is a maximum. At this point the derivative of the function wrt either r or ρ equals zero.

$$\left(\frac{dR_{31}}{d\rho}\right)_{\max} = 0 = \left(\frac{d((4-\rho)\rho e^{-\rho/2})}{d\rho}\right)_{\max} \quad [\text{Table 10.1}] = \left(4 - 4\rho + \frac{\rho^2}{2}\right) e^{-\rho/2}$$

The function is a maximum when the polynomial equals zero. The quadratic equation gives the roots $\rho = 4 + 2\sqrt{2} = 6.89$ and $\rho = 4 - 2\sqrt{2} = 1.17$. Since $\rho = (2Z/na_0)r$ and $n = 3$, these correspond to $r = 10.3 \times a_0/Z$ and $r = 1.76 \times a_0/Z$. However, $\left|\frac{R_{31}(\rho_1)}{R_{31}(\rho_2)}\right| = \left|\frac{R_{31}(1.17)}{R_{31}(10.3)}\right| = 4.90$. So, we conclude that the function is a maximum at $\rho = 1.17$ which corresponds to $r = 1.76a_0/Z$.

- E10.8(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 $\langle \hat{L}^2 \rangle^{1/2} = 6^{1/2}\hbar = 2.45 \times 10^{-34} \text{ J s}$ 2 angular nodes 1 radial node
- (b) $n = 2, l = 1$, so $\langle \hat{L}^2 \rangle^{1/2} = 2^{1/2}\hbar = 1.49 \times 10^{-34} \text{ J s}$ 1 angular nodes 0 radial nodes
- (c) $n = 3, l = 1$, so $\langle \hat{L}^2 \rangle^{1/2} = 2^{1/2}\hbar = 1.49 \times 10^{-34} \text{ J s}$ 1 angular node 1 radial node

- E10.9(b)** For $l > 0$, $j = l \pm 1/2$, so

- (a) $l = 1$, so $j = 1/2 \text{ or } 3/2$
- (b) $l = 5$, so $j = 9/2 \text{ or } 11/2$

- E10.10(b)** Use the Clebsch–Gordan series in the form

$$J = j_1 + j_2, j_1 + j_2 - 1, \dots, |j_1 - j_2|$$

Then, with $j_1 = 5$ and $j_2 = 3$

$$J = 8, 7, 6, 5, 4, 3, 2$$

- E10.11(b)** The degeneracy g of a hydrogenic atom with principal quantum number n is $g = n^2$. The energy E of hydrogenic atoms is

$$E = -\frac{hcZ^2R_H}{n^2} = -\frac{hcZ^2R_H}{g}$$

so the degeneracy is

$$g = -\frac{hcZ^2R_H}{E}$$

$$(a) \quad g = -\frac{hc(2)^2R_H}{-4hcR_H} = \boxed{1}$$

$$(b) \quad g = -\frac{hc(4)^2R_H}{-\frac{1}{4}hcR_H} = \boxed{64}$$

$$(c) \quad g = -\frac{hc(5)^2R_H}{-hcR_H} = \boxed{25}$$

E10.12(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 .

E10.13(b) The radial distribution function varies as

$$P = 4\pi r^2 \psi^2 = \frac{4}{a_0^3} r^2 e^{-2r/a_0}$$

The maximum value of P occurs at $r = a_0$ since

$$\frac{dP}{dr} \propto \left(2r - \frac{2r^2}{a_0}\right) e^{-2r/a_0} = 0 \quad \text{at } r = a_0 \quad \text{and } P_{\max} = \frac{4}{a_0} e^{-2}$$

P falls to a fraction f of its maximum given by

$$f = \frac{(4r^2/a_0^3)e^{-2r/a_0}}{(4/a_0)e^{-2}} = \frac{r^2}{a_0^2} e^{-2r/a_0}$$

and hence we must solve for r in

$$\frac{f^{1/2}}{e} = \frac{r}{a_0} e^{-r/a_0}$$

$$(a) \quad f = 0.50$$

$$0.260 = \frac{r}{a_0} e^{-r/a_0} \text{ solves to } r = 2.08a_0 = \boxed{110 \text{ pm}} \text{ and to } r = 0.380a_0 = \boxed{20.1 \text{ pm}}$$

$$(b) \quad f = 0.75$$

$$0.319 = \frac{r}{a_0} e^{-r/a_0} \text{ solves to } r = 1.63a_0 = \boxed{86 \text{ pm}} \text{ and to } r = 0.555a_0 = \boxed{29.4 \text{ pm}}$$

In each case the equation is solved numerically (or graphically) with readily available personal computer software. The solutions above are easily checked by substitution into the equation for f . The radial distribution function is readily plotted and is shown in Figure 10.1.

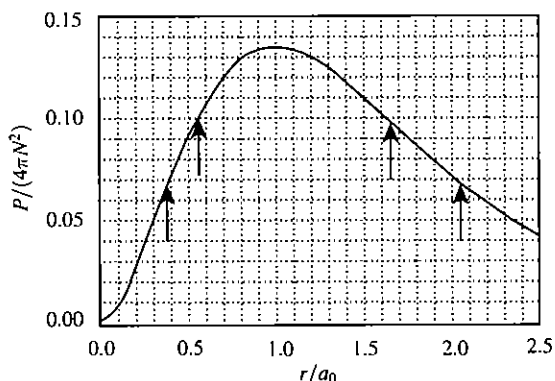


Figure 10.1

E10.14(b) (a) $5d \rightarrow 2s$ is **not** an allowed transition, for $\Delta l = -2$ (Δl must equal ± 1).

(b) $5p \rightarrow 3s$ is **allowed**, since $\Delta l = -1$.

(c) $5p \rightarrow 3f$ is **not** allowed, for $\Delta l = +2$ (Δl must equal ± 1).

(d) $6h : l = 5$; maximum occupancy = **22**

E10.15(b) $V^{2+} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 = [\text{Ar}]3d^3$

The only unpaired electrons are those in the $3d$ subshell. There are three.

$$S = \left[\frac{3}{2} \right] \text{ and } \frac{3}{2} - 1 = \left[\frac{1}{2} \right]$$

$$\text{For } S = \frac{3}{2}, M_S = \left[\pm \frac{1}{2} \text{ and } \pm \frac{3}{2} \right]$$

$$\text{for } S = \frac{1}{2}, M_S = \left[\pm \frac{1}{2} \right]$$

E10.16(b) (a) Possible values of S for four electrons in different orbitals are **2, 1, and 0**; the multiplicity is $2S + 1$, so multiplicities are **5, 3, and 1** respectively.

(b) Possible values of S for five electrons in different orbitals are **$5/2, 3/2$ and $1/2$** ; the multiplicity is $2S + 1$, so multiplicities are **6, 4, and 2** respectively.

E10.17(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

$$^1F_3; ^3F_4, ^3F_3, ^3F_2; ^1D_2; ^3D_3, ^3D_2, ^3D_1; ^1P_1, ^3P_2, ^3P_1, ^3P_0$$

Hund's rules state that the lowest energy level has maximum multiplicity. Consideration of spin–orbit coupling says the lowest energy level has the lowest value of $J(J + 1) - L(L + 1) - S(S + 1)$. So the lowest energy level is **3F_2** .

E10.18(b) (a) 3D has $S = 1$ and $L = 2$, so $J = \left[3, 2, \text{ and } 1 \right]$ are present. $J = 3$ has **7** states, with $M_J = 0, \pm 1, \pm 2$, or ± 3 ; $J = 2$ has **5** states, with $M_J = 0, \pm 1$, or ± 2 ; $J = 1$ has **3** states, with $M_J = 0$, or ± 1 .

- (b) 4D has $S = 3/2$ and $L = 2$, so $J = 7/2, 5/2, 3/2, \text{ and } 1/2$ are present. $J = 7/2$ has 8 possible states, with $M_J = \pm 7/2, \pm 5/2, \pm 3/2$ or $\pm 1/2$; $J = 5/2$ has 6 possible states, with $M_J = \pm 5/2, \pm 3/2$ or $\pm 1/2$; $J = 3/2$ has 4 possible states, with $M_J = \pm 3/2$ or $\pm 1/2$; $J = 1/2$ has 2 possible states, with $M_J = \pm 1/2$.
- (c) 2G has $S = 1/2$ and $L = 4$, so $J = 9/2$ and $7/2$ are present. $J = 9/2$ has 10 possible states, with $M_J = \pm 9/2, \pm 7/2, \pm 5/2, \pm 3/2$, or $\pm 1/2$; $J = 7/2$ has 8 possible states, with $M_J = \pm 7/2, \pm 5/2, \pm 3/2$, or $\pm 1/2$.

E10.19(b) Closed shells and subshells do not contribute to either L or S and thus are ignored in what follows.

(a) $\text{Sc}[\text{Ar}]3d^14s^2$: $S = \frac{1}{2}$, $L = 2$; $J = \frac{5}{2}, \frac{3}{2}$, so the terms are $^2D_{5/2}$ and $^2D_{3/2}$.

(b) $\text{Br}[\text{Ar}]3d^{10}4s^24p^5$. We treat the missing electron in the $4p$ subshell as equivalent to a single "electron" with $l = 1$, $s = \frac{1}{2}$. Hence $L = 1$, $S = \frac{1}{2}$, and $J = \frac{3}{2}, \frac{1}{2}$, so the terms are $^2P_{3/2}$ and $^2P_{1/2}$.

Solutions to problems

Solutions to numerical problems

P10.2 All lines in the hydrogen spectrum fit the Rydberg formula

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \left[10.1, \text{ with } \tilde{\nu} = \frac{1}{\lambda} \right] \quad R_H = 109\,677 \text{ cm}^{-1}$$

Find n_1 from the value of λ_{\max} , which arises from the transition $n_1 + 1 \rightarrow n_1$

$$\frac{1}{\lambda_{\max} R_H} = \frac{1}{n_1^2} - \frac{1}{(n_1 + 1)^2} = \frac{2n_1 + 1}{n_1^2(n_1 + 1)^2}$$

$$\lambda_{\max} R_H = \frac{n_1^2(n_1 + 1)^2}{2n_1 + 1} = (656.46 \times 10^{-9} \text{ m}) \times (109\,677 \times 10^2 \text{ m}^{-1}) = 7.20$$

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

$$\tilde{\nu} = \frac{1}{\lambda} = (109\,677 \text{ cm}^{-1}) \times \left(\frac{1}{4} - \frac{1}{49} \right) = 397.13 \text{ nm}$$

The energy required to ionize the atom is obtained by letting $n_2 \rightarrow \infty$. Then

$$\tilde{\nu} = \frac{1}{\lambda_{\infty}} = (109\,677 \text{ cm}^{-1}) \times \left(\frac{1}{4} - 0 \right) = 27\,419 \text{ cm}^{-1}, \quad \text{or } 3.40 \text{ eV}$$

(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.

P10.4

The lowest possible value of n in $1s^2nd^1$ is 3; thus the series of 2D terms correspond to $1s^23d$, $1s^24d$, etc. Figure 10.2 is a description consistent with the data in the problem statement.

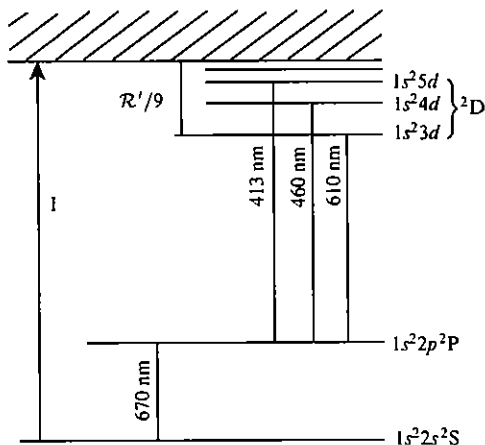


Figure 10.2

If we assume that the energies of the d orbitals are hydrogenic we may write

$$E(1s^2nd^1, ^2D) = -\frac{hcR'}{n^2} \quad [n = 3, 4, 5, \dots]$$

Then for the $^2D \rightarrow ^2P$ transitions

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{|E(1s^22p^1, ^2P)|}{hc} - \frac{R'}{n^2} \quad \left[\Delta E = h\nu = \frac{hc}{\lambda} = hc\tilde{\nu}, \quad \tilde{\nu} = \frac{\Delta E}{hc} \right]$$

from which we can write

$$\frac{|E(1s^22p^1, ^2P)|}{hc} = \frac{1}{\lambda} + \frac{R'}{n^2} = \begin{cases} \frac{1}{610.36 \times 10^{-7} \text{ cm}} + \frac{R'}{9} & \text{(a)} \\ \frac{1}{460.29 \times 10^{-7} \text{ cm}} + \frac{R'}{16} & \text{(b)} \\ \frac{1}{413.23 \times 10^{-7} \text{ cm}} + \frac{R'}{25} & \text{(c)} \end{cases}$$

$$\text{Then } \left. \begin{array}{l} \text{(b) - (a) solves to } R' = 109\,886 \text{ cm}^{-1} \\ \text{(a) - (c) solves to } R' = 109\,910 \text{ cm}^{-1} \\ \text{(b) - (c) solves to } R' = 109\,963 \text{ cm}^{-1} \end{array} \right\} \text{Mean} = 109\,920 \text{ cm}^{-1}$$

The binding energies are therefore

$$E(1s^23d^1, ^2D) = \frac{R'}{9} = -12\,213 \text{ cm}^{-1}$$

$$E(1s^22p^1, ^2P) = -\frac{1}{610.36 \times 10^{-7} \text{ cm}} - 12\,213 \text{ cm}^{-1} = -28\,597 \text{ cm}^{-1}$$

$$E(1s^22s^1, ^2S) = -\frac{1}{670.78 \times 10^{-7} \text{ cm}} - 28\,597 \text{ cm}^{-1} = -43\,505 \text{ cm}^{-1}$$

Therefore, the ionization energy is

$$I(1s^2 2s^1, ^2S) = 43\,505\text{ cm}^{-1}, \quad \text{or} \quad \boxed{5.39\text{ eV}}$$

- P10.6** The ground term is $[\text{Ar}]4s^1 2S_{1/2}$ and the first excited is $[\text{Ar}]4p^1 2P$. The latter has two levels with $J = 1 + \frac{1}{2} = \frac{3}{2}$ and $J = 1 - \frac{1}{2} = \frac{1}{2}$ which are split by spin-orbit coupling (Section 10.8). Therefore, ascribe the transitions to $\boxed{{}^2P_{3/2} \rightarrow {}^2S_{1/2}}$ and $\boxed{{}^2P_{1/2} \rightarrow {}^2S_{1/2}}$ (since both are allowed). For these values of J , the splitting is equal to $\frac{3}{2}A$ (Example 10.5). Hence, since

$$(766.70 \times 10^{-7}\text{ cm})^{-1} - (770.11 \times 10^{-7}\text{ cm})^{-1} = 57.75\text{ cm}^{-1}$$

we can conclude that $A = \boxed{38.50\text{ cm}^{-1}}$

- P10.8** The Rydberg constant for positronium (R_{Ps}) is given by

$$\begin{aligned} R_{\text{Ps}} &= \frac{R}{1 + \frac{m_e}{m_e}} = \frac{R}{1 + 1} = \frac{1}{2}R \quad [10.16; \text{also Problem 10.7; } m(\text{positron}) = m_e] \\ &= 54\,869\text{ cm}^{-1} \quad [R = 109\,737\text{ cm}^{-1}] \end{aligned}$$

Hence

$$\begin{aligned} \tilde{\nu} &= \frac{1}{\lambda} = (54\,869\text{ cm}^{-1}) \times \left(\frac{1}{4} - \frac{1}{n^2} \right), \quad n = 3, 4, \dots \\ &= \boxed{7621\text{ cm}^{-1}}, \boxed{10\,288\text{ cm}^{-1}}, \boxed{11\,522\text{ cm}^{-1}}, \dots \end{aligned}$$

The binding energy of Ps is

$$E = -hcR_{\text{Ps}}, \text{ corresponding to } (-)54\,869\text{ cm}^{-1}$$

The ionization energy is therefore $54\,869\text{ cm}^{-1}$, or $\boxed{6.80\text{ eV}}$.

- P10.10** If we assume that the innermost electron is a hydrogen-like $1s$ orbital we may write

$$r^* = \frac{a_0}{Z} [\text{Example 10.3}] = \frac{52.92\text{ pm}}{126} = \boxed{0.420\text{ pm}}$$

Solutions to theoretical problems

- P10.12** In each case we need to show that

$$\int_{\text{all space}} \psi_1^* \psi_2 \, d\tau = 0$$

$$(a) \quad \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{1s} \psi_{2s} r^2 \, dr \sin \theta \, d\theta \, d\phi = 0$$

$$\left. \begin{aligned} \psi_{1s} &= R_{1,0} Y_{0,0} \\ \psi_{2s} &= R_{2,0} Y_{0,0} \end{aligned} \right\} Y_{0,0} = \left(\frac{1}{4\pi} \right)^{1/2} \quad [\text{Table 9.3}]$$

Since $Y_{0,0}$ is a constant, the integral over the radial functions determines the orthogonality of the functions.

$$\begin{aligned}
 & \int_0^\infty R_{1,0} R_{2,0} r^2 dr \\
 R_{1,0} & \propto e^{-\rho/2} = e^{-Zr/a_0} \quad \left[\rho = \frac{2Zr}{a_0} \right] \\
 R_{2,0} & \propto (2 - \rho/2) e^{-\rho/4} = \left(2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0} \quad \left[\rho = \frac{2Zr}{a_0} \right] \\
 \int_0^\infty R_{1,0} R_{2,0} r^2 dr & \propto \int_0^\infty e^{-Zr/a_0} \left(2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0} r^2 dr \\
 & = \int_0^\infty 2e^{-(3/2)Zr/a_0} r^2 dr - \int_0^\infty \frac{Z}{a_0} e^{-(3/2)Zr/a_0} r^3 dr \\
 & = \frac{2 \times 2!}{\left(\frac{3}{2} \frac{Z}{a_0} \right)^3} - \left(\frac{Z}{a_0} \right) \times \frac{3!}{\left(\frac{3}{2} \frac{Z}{a_0} \right)^4} = \boxed{0}
 \end{aligned}$$

Hence, the functions are orthogonal.

(b) We use the p_x and p_y orbitals in the form given in Section 10.2(f), eqn 10.24

$$p_x \propto x, \quad p_y \propto y$$

Thus

$$\int_{\text{all space}} p_x p_y dx dy dz \propto \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} xy dx dy dz$$

This is an integral of an odd function of x and y over the entire range of variable from $-\infty$ to $+\infty$, therefore, the integral is zero. More explicitly we may perform the integration using the orbitals in the form (Section 10.2(f), eqn 10.24)

$$\begin{aligned}
 p_x &= f(r) \sin \theta \cos \phi & p_y &= f(r) \sin \theta \sin \phi \\
 \int_{\text{all space}} p_x p_y r^2 dr \sin \theta d\theta d\phi &= \int_0^\infty f(r)^2 r^2 dr \int_0^\pi \sin^2 \theta d\theta \int_0^{2\pi} \cos \phi \sin \phi d\phi
 \end{aligned}$$

The first factor is nonzero since the radial functions are normalized. The second factor is $\pi/2$. The third factor is zero. Therefore, the product of the integrals is zero and the functions are orthogonal.

P10.14 We use the p_x and p_y orbitals in the form (Section 10.2(f))

$$p_x = r f(r) \sin \theta \cos \phi \quad p_y = r f(r) \sin \theta \sin \phi$$

and use $\cos \phi = \frac{1}{2}(e^{i\phi} + e^{-i\phi})$ and $\sin \phi = \frac{1}{2i}(e^{i\phi} - e^{-i\phi})$ then

$$p_x = \frac{1}{2} r f(r) \sin \theta (e^{i\phi} + e^{-i\phi}) \quad p_y = \frac{1}{2i} r f(r) \sin \theta (e^{i\phi} - e^{-i\phi})$$

$$\hat{l}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \quad [\text{Problem 9.28 and Section 9.6 and eqn 9.46}]$$

$$\hat{l}_z p_x = \frac{\hbar}{2} r f(r) \sin \theta e^{i\phi} - \frac{\hbar}{2} r f(r) \sin \theta e^{-i\phi} = i\hbar p_y \neq \text{constant} \times p_x$$

$$\hat{l}_z p_y = \frac{\hbar}{2i} r f(r) \sin \theta e^{i\phi} + \frac{\hbar}{2i} r f(r) \sin \theta e^{-i\phi} = -i\hbar p_x \neq \text{constant} \times p_y$$

Therefore, neither p_x nor p_y are eigenfunctions of \hat{l}_z . However, $p_x + ip_y$ and $p_x - ip_y$ are eigenfunctions

$$p_x + ip_y = r f(r) \sin \theta e^{i\phi} \quad p_x - ip_y = r f(r) \sin \theta e^{-i\phi}$$

since both $e^{i\phi}$ and $e^{-i\phi}$ are eigenfunctions of \hat{l}_z with eigenvalues $+\hbar$ and $-\hbar$.

P10.16

$$\psi_{1s} = \left(\frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0} \quad [10.18]$$

The probability of the electron being within a sphere of radius r' is

$$\int_0^{r'} \int_0^\pi \int_0^{2\pi} \psi_{1s}^2 r^2 \, dr \sin \theta \, d\theta \, d\phi$$

We set this equal to 0.90 and solve for r' . The integral over θ and ϕ gives a factor of 4π ; thus

$$0.90 = \frac{4}{a_0^3} \int_0^{r'} r^2 e^{-2r/a_0} \, dr$$

$\int_0^{r'} r^2 e^{-2r/a_0} \, dr$ is integrated by parts to yield

$$\begin{aligned} & -\frac{a_0 r^2 e^{-2r/a_0}}{2} \Big|_0^{r'} + a_0 \left[-\frac{a_0 r e^{-2r/a_0}}{2} \Big|_0^{r'} + \frac{a_0}{2} \left(-\frac{a_0 e^{-2r/a_0}}{2} \right) \Big|_0^{r'} \right] \\ & = -\frac{a_0 (r')^2 e^{-2r'/a_0}}{2} - \frac{a_0^2 r'}{2} e^{-2r'/a_0} - \frac{a_0^3}{4} e^{-2r'/a_0} + \frac{a_0^3}{4} \end{aligned}$$

Multiplying by $4/a_0^3$ and factoring e^{-2r'/a_0}

$$0.90 = \left[-2 \left(\frac{r'}{a_0} \right)^2 - 2 \left(\frac{r'}{a_0} \right) - 1 \right] e^{-2r'/a_0} + 1 \quad \text{or} \quad 2 \left(\frac{r'}{a_0} \right)^2 + 2 \left(\frac{r'}{a_0} \right) + 1 = 0.10 e^{2r'/a_0}$$

It is easiest to solve this numerically. It is seen that $r' = 2.66a_0$ satisfies the above equation.

Mathematical software has powerful features for handling this type of problem. Plots are very convenient to both make and use. Solve blocks can be used as functions. Both features are demonstrated

below using Mathcad.

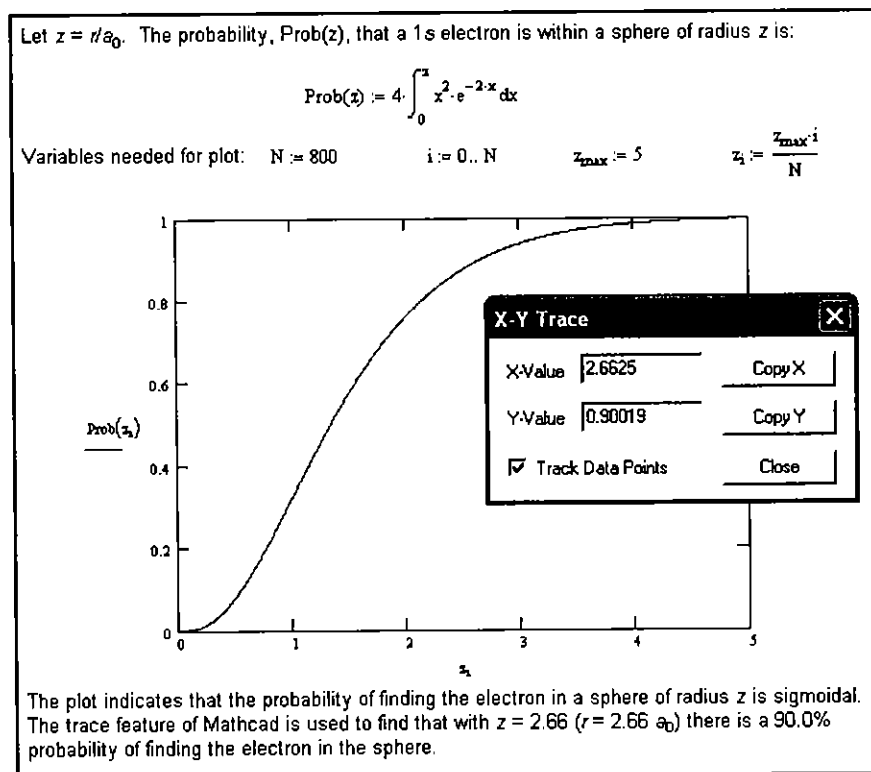


Figure 10.3(a)

The following Mathcad document develops a function for calculating the radius for any desired probability. The probability is presented to the function as an argument

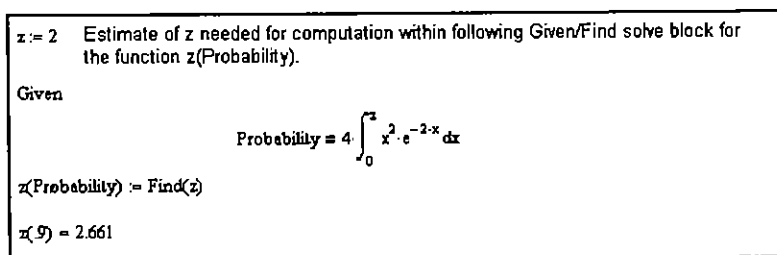


Figure 10.3(b)

P10.18 The attractive Coulomb force = $\frac{Ze^2}{4\pi\epsilon_0} \cdot \frac{1}{r^2}$

The repulsive centrifugal force = $\frac{(\text{angular momentum})^2}{m_e r^3} = \frac{(n\hbar)^2}{m_e r^3}$ [postulated]

The two forces balance when

$$\frac{Ze^2}{4\pi\epsilon_0} \times \frac{1}{r^2} = \frac{n^2 \hbar^2}{m_e r^3}, \text{ implying that } r = \frac{4\pi n^2 \hbar^2 \epsilon_0}{Ze^2 m_e}$$

The total energy is

$$\begin{aligned}
 E = E_K + V &= \frac{(\text{angular momentum})^2}{2I} - \frac{Ze^2}{4\pi\epsilon_0} \times \frac{1}{r} = \frac{n^2\hbar^2}{2m_e r^2} - \frac{Ze^2}{4\pi\epsilon_0 r} \text{ [postulated]} \\
 &= \left(\frac{n^2\hbar^2}{2m_e} \right) \times \left(\frac{Ze^2 m_e}{4\pi n^2 \hbar^2 \epsilon_0} \right)^2 - \left(\frac{Ze^2}{4\pi\epsilon_0} \right) \times \left(\frac{Ze^2 m_e}{4\pi n^2 \hbar^2 \epsilon_0} \right) = \boxed{\frac{Z^2 e^4 m_e}{32\pi^2 \epsilon_0^2 \hbar^2} \times \frac{1}{n^2}}
 \end{aligned}$$

P10.20 Refer to Problems 10.8 and 10.18 and their solutions.

$$\mu_H = \frac{m_e m_p}{m_e + m_p} \approx m_e \quad [m_p = \text{mass of proton}]$$

$$\mu_{Ps} = \frac{m_e m_{\text{pos}}}{m_e + m_{\text{pos}}} = \frac{m_e}{2} \quad [m_{\text{pos}} = \text{mass of proton} = m_e]$$

$$a_0 = r(n=1) = \frac{4\pi\hbar^2\epsilon_0}{e^2 m_e} \text{ [10.13 and Problem 10.18]}$$

To obtain a_{Ps} the radius of the first Bohr orbit of positronium, we replace m_e with $\mu_{Ps} = m_e/2$; hence,

$$\boxed{a_{Ps} = 2a_0} = \frac{\pi\hbar^2\epsilon_0}{e^2 m_e}$$

The energy of the first Bohr orbit of positronium is

$$E_{1,Ps} = -hcR_{Ps} = -\frac{hc}{2}R_\infty \text{ [Problem 10.8]}$$

$$\text{Thus, } \boxed{E_{1,Ps} = \frac{1}{2}E_{1,H}}$$

Question. What modifications are required in these relations when the finite mass of the hydrogen nucleus is recognized?

P10.22 (a) The speed distribution in the molecular beam is related to the speed distribution within the chamber by a factor of $v \cos \theta$ as shown in Figure 10.4. Since an integration over all possible θ must be performed, the $\cos \theta$ factor may be absorbed into the constant of proportionality.

$$f_{\text{beam}}(v) = C v f_{\text{chamber}}(v) \quad \text{where } C \text{ is to be determined}$$

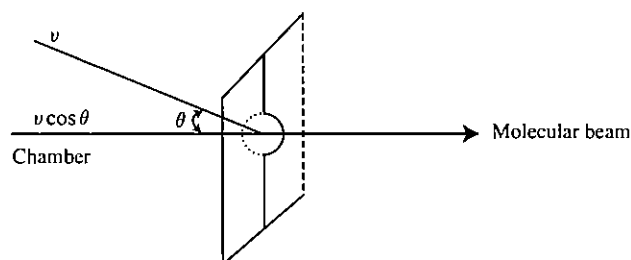


Figure 10.4

By normalization over the possible beam speeds ($0 < v_{\text{beam}} < \infty$)

$$\begin{aligned} f_{\text{beam}} &= C v \left(v^2 e^{-(mv^2/2kT)} \right) \\ &= C v^3 e^{-(mv^2/2kT)} \end{aligned}$$

$$\int_{v=0}^{\infty} f_{\text{beam}} dv = 1 = C \int_{v=0}^{\infty} v^3 e^{-(mv^2/2kT)} dv = C \left\{ \frac{1}{2(m/2kT)^2} \right\}$$

$$C = 2(m/2kT)^2$$

$$\langle v^2 \rangle = \int_{v=0}^{\infty} v^2 f_{\text{beam}}(v) dv = C \int_{v=0}^{\infty} v^5 e^{-(mv^2/2kT)} dv$$

$$= C \left\{ \frac{1}{(m/2kT)^3} \right\} = 2 \frac{(m/2kT)^2}{(m/2kT)^3}$$

$$= \frac{4kT}{m}$$

$$\langle E_K \rangle = \frac{m}{2} \langle v^2 \rangle = \frac{m}{2} \left(\frac{4kT}{m} \right) = \boxed{2kT}$$

$$\begin{aligned} \text{(b)} \quad \Delta x &= \left(\frac{2\mu_B L^2}{4E_K} \right) \frac{dB}{dz} \\ \frac{dB}{dz} &= \frac{4E_K \Delta x}{2\mu_B L^2} = \frac{4(2kT) \Delta x}{2\mu_B L^2} \\ \text{or} \quad &= \frac{4kT \Delta x}{\mu_B L^2} \\ &= \frac{4(1.3807 \times 10^{-23} \text{ J K}^{-1}) \times (1000 \text{ K}) \times (1.00 \times 10^{-3} \text{ m})}{(9.27402 \times 10^{-24} \text{ J T}^{-1}) \times (50 \times 10^{-2} \text{ m})^2} \\ \frac{dB}{dz} &= \boxed{23.8 \text{ T m}^{-1}} \end{aligned}$$

Solutions to applications

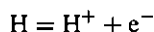
P10.24 A stellar surface temperature of 3000–4000 K (a “red star”) doesn’t have the energetic particles and photons that are required for either the collisional or radiation excitation of a neutral hydrogen atom. Atomic hydrogen affects neither the absorption nor the emission lines of red stars in the absence of excitation. “Blue stars” have surface temperature of 15 000–20 000 K. Both the kinetic energy and the blackbody emissions display energies great enough to completely ionize hydrogen. Lacking an electron, the remaining proton cannot affect absorption and emission lines either.

In contrast, a star with a surface temperature of 8000–10 000 K has a temperature low enough to avoid complete hydrogen ionization but high enough for blackbody radiation to cause electronic transitions of atomic hydrogen. Hydrogen spectral lines are intense for these stars.

Simple kinetic energy and radiation calculations confirm these assertions. For example, a plot of blackbody radiation against the radio photon energy and the ionization energy, I , is shown below. It is clearly

seen that at 25 000 K a large fraction of the radiation is able to ionize the hydrogen ($h\nu/I$). It is likely that at such high surface temperatures all hydrogen is ionized and, consequently, unable to affect spectra.

Alternatively, consider the equilibrium between hydrogen atoms and their component charged particles:

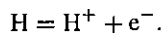


The equilibrium constant is:

$$K = \frac{p_+ p_-}{p_{\text{H}} p^\ominus} = \exp\left(\frac{-\Delta G^\ominus}{RT}\right) = \exp\left(\frac{-\Delta H^\ominus}{RT}\right) \times \exp\left(\frac{-\Delta S^\ominus}{R}\right).$$

Clearly ΔS^\ominus is positive for ionization, which makes two particles out of one, and ΔH^\ominus , which is close to the ionization energy, is also positive. At a sufficiently high temperature, ions will outnumber neutral molecules. Using concepts developed in Chapters 16 and 17, one can compute the equilibrium constant; it turns out to be 60. Hence, there are relatively few undissociated H atoms in the equilibrium mixture that is consistent with the weak spectrum of neutral hydrogen observed.

The details of the calculation of the equilibrium constant based on the methods of Chapter 17 follows. Consider the equilibrium between hydrogen atoms and their component charged particles:



The equilibrium constant is:

$$K = \frac{p_+ p_-}{p_{\text{H}} p^\ominus} = \exp\left(\frac{-\Delta G^\ominus}{RT}\right).$$

Jump ahead to Section 17.7(b) to use the statistical thermodynamic analysis of a dissociation equilibrium:

$$K = \frac{q_+^\ominus q_-^\ominus}{q_{\text{H}}^\ominus N_{\text{A}}} e^{-\Delta_r E_0/RT}.$$

$$\text{where } q^\ominus = \frac{RT}{gp^\ominus \Lambda^3} \text{ and } \Lambda = \left(\frac{h^2}{2\pi kTm}\right)^{1/2}$$

and where g is the degeneracy of the species. Note that $g_+ = 2$, $g_- = 2$, and $g_{\text{H}} = 4$. Consequently, these factors cancel in the expression for K .

$$\text{So } K = \frac{RT}{p^\ominus N_{\text{A}}} \left(\frac{2\pi kT}{h^2}\right)^{3/2} \left(\frac{m_- m_+}{m_{\text{H}}}\right)^{3/2} e^{-\Delta_r E_0/RT}$$

Note that the Boltzmann, Avogadro, and perfect gas constants are related ($R = N_{\text{A}} k$), and collect powers of kT ; note also that the product of masses is the reduced mass, which is approximately equal to the mass of the electron; note finally that the molar energy $\Delta_r E_0$ divided by R is the same as the atomic

ionization energy (2.179×10^{-18} J from Chapter 10.2(b)) divided by k :

$$K = \frac{(kT)^{5/2} (2\pi m_e)^{3/2}}{p^\ominus h^3} e^{-E/kT},$$

$$K = \frac{[(1.381 \times 10^{-23} \text{ J K}^{-1}) (25\,000 \text{ K})]^{5/2} [2\pi (9.11 \times 10^{-31} \text{ Kg})]^{3/2}}{(10^5 \text{ Pa}) (6.626 \times 10^{-34} \text{ Js})^3} \times \exp\left(\frac{-2.179 \times 10^{-18} \text{ J}}{(1.381 \times 10^{-23} \text{ J K}^{-1}) (25\,000 \text{ K})}\right).$$

$$K = 60.$$

Thus, the equilibrium favors the ionized species, even though the ionization energy is greater than kT .

P10.26

$$E_n = -\frac{hcR_H}{n^2} \text{ where } R_H = 109\,677 \text{ cm}^{-1} [10.11 \text{ with } 10.15]$$

For $n = 100$

$$\Delta E = E_{n+1} - E_n = -hcR_H \left(\frac{1}{101^2} - \frac{1}{100^2} \right) = 1.97 \times 10^{-6} hcR$$

$$\tilde{\nu} = \frac{\Delta E}{hc} = 1.97 \times 10^{-6} R = \boxed{0.216 \text{ cm}^{-1}}$$

$$\langle r \rangle_{n,l} = n^2 \left\{ 1 + \frac{1}{2} + \left(1 - \frac{l(l+1)}{n^2} \right) \right\} \frac{a_0}{Z} [10.19]$$

$$\langle r \rangle_{100} \approx \frac{n^2 a_0}{Z} = 100^2 a_0 = 10^4 a_0 = \boxed{529 \text{ nm}}$$

$$I = E_\infty - E_n = -E_n = \frac{hcR_H}{n^2}$$

$$I_{100} = 10^{-4} hcR_H \text{ so } \boxed{\frac{I_{100}}{hc} = 10.9677 \text{ cm}^{-1}}$$

At T

$$\frac{kT}{hc} = \frac{(1.38 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K}) \left(\frac{\text{m}}{10^2 \text{ cm}} \right)}{(6.63 \times 10^{-34} \text{ Js}) \times (3.00 \times 10^8 \text{ m s}^{-1})} = 207 \text{ cm}^{-1}$$

so the thermal energy is readily available to ionize the state $n = 100$. Let v_{\min} be the minimum speed required for collisional ionization. Then

$$\frac{1}{2} \frac{m_H v_{\min}^2}{hc} = \frac{I_{100}}{hc}$$

$$v_{\min} = \left[\frac{2hc}{m_H} \left(\frac{I_{100}}{hc} \right) \right]^{1/2}$$

$$= \sqrt{\frac{2(6.63 \times 10^{-34} \text{ Js}) \times (3.00 \times 10^8 \text{ m s}^{-1}) \times (10.97 \text{ cm}^{-1})}{(1.008 \times 10^{-3} \text{ kg mol}^{-1}) \times (6.022 \times 10^{23} \text{ mol}^{-1})^{-1} \times \left(\frac{\text{m}}{10^2 \text{ cm}} \right)}}$$

$$\boxed{v_{\min} = 511 \text{ m s}^{-1}} \quad [\text{very slow for an H atom}]$$

The radius of a Bohr orbit is $a_n \approx n^2 a_0$; hence the geometric cross-section $\pi a_n^2 \approx n^4 \pi a_0^2$. For $n = 1$ this is $8.8 \times 10^{-21} \text{ m}^2$; for $n = 100$, it is $8.8 \times 10^{-13} \text{ m}^2$. Thus a neutral H atom in its ground state is likely to pass right by the $n = 100$ Rydberg atom, leaving it undisturbed, since it is largely empty space.

The radial wavefunction for $n = 100$ will have 99 radial nodes and an extremely small amplitude above $r/a_0 \approx 20$. For large values of n we expect the radial wavefunction [10.14] to be governed largely by the product of ρ^{n-1} and $e^{-\rho/2n}$ and thus to approach a smoothly decreasing function of distance, as the exponential will predominate over the power term.

P10.28 Electronic configurations of neutral, fourth period transition atoms in the ground state are summarized in the following table along with observed, positive oxidation states. The most common, positive oxidation states are indicated with bright boxing.

Group	3	4	5	6	7	8	9	10	11	12
Oxidation State	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
0	$3d4s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s$	$3d^{10}4s^2$
+1										
+2										
+3										
+4										
+5										
+6										
+7										

Toward the middle of the first transition series (Cr, Mn, and Fe) elements exhibit the widest ranges of oxidation states. This phenomenon is related to the availability of both electrons and orbitals favorable for bonding. Elements to the left (Sc and Ti) of the series have few electrons and relatively low effective nuclear charge leaves d orbitals at high energies that are relatively unsuitable for bonding. To the far right (Cu and Zn) effective nuclear charge may be higher but there are few, if any, orbitals available for bonding. Consequently, it is more difficult to produce a range of compounds that promote a wide range of oxidation states for elements at either end of the series. At the middle and right of the series the +2 oxidation state is very commonly observed because normal reactions can provide the requisite ionization energies for the removal of $4s$ electrons. The readily available +2 and +3 oxidation states of Mn, Fe, and the +1 and +2 oxidation states of Cu make these cations useful in electron transfer processes occurring chains of specialized protein within biological cells. The special size and charge of the Zn^{2+} cation makes it useful for the function of some enzymes. The tendency of Fe^{2+} and Cu^+ to bind oxygen proves very useful in hemoglobin and electron transport (respiratory) chain, respectively.

11

Molecular structure

Answers to discussion questions

- D11.2** Consider the case of the carbon atom. Mentally we break the process of hybridization into two major steps. The first is promotion, in which we imagine that one of the electrons in the $2s$ orbital of carbon ($2s^2 2p^2$) is promoted to the empty $2p$ orbital giving the configuration $2s 2p^3$. In the second step we mathematically mix the four orbitals by way of the specific linear combinations in eqn 11.3 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 state function and therefore its value is determined only by the final state of the system, not by the path taken to achieve that state, and the path can even be imaginary.
- D11.4** 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 provides 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 an interpretation that we can perhaps visualize, but that is not essential. Examples of the mathematical steps involved are illustrated in Sections 11.5(c) and (d), *Justification* 11.3, and Section 11.6.
- D11.6** These are all terms originally associated with the Hückel approximation used in the treatment of conjugated π -electron molecules, in which the π -electrons are considered independent of the σ -electrons. π -electron binding energy is the sum of the energies of each π -electron in the molecule. The delocalization energy is the difference in energy between the conjugated molecule with n double bonds and the energy of n ethene molecules, each of which has one double bond. The π -bond formation energy is the energy released when a π -bond is formed. It is obtained from the total π -electron binding energy by subtracting the contribution from the Coulomb integrals, α .

- D11.8** 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. Density functional theory (DFT) is considered an *ab initio* method, but it is different from the Hartree-Fock (HF) or self-consistent field (SCF) approach in that DFT focuses on the electron density while HF/SCF methods focus on the wavefunction. They are both iterative self consistent methods in that the calculations are repeated until the energy and wavefunctions (HF) or energy and electron density (DFT) are unchanged to within some acceptable tolerance.

Solutions to exercises

- E11.1(b)** Use Figure 11.23 for H_2^- , 11.33 for N_2 , and 11.31 for O_2 .

- (a) H_2^- (3 electrons) : $1\sigma^2 2\sigma^{*1}$ $b = 0.5$
 (b) N_2 (10 electrons) : $1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2$ $b = 3$
 (c) O_2 (12 electrons) : $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*2}$ $b = 2$

- E11.2(b)** ClF is isoelectronic with F_2 , CS with N_2 .

- (a) ClF (14 electrons) : $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*4}$ $b = 1$
 (b) CS (10 electrons) : $1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2$ $b = 3$
 (c) O_2^- (13 electrons) : $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*3}$ $b = 1.5$

- E11.3(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, C_2 and CN are stabilized (have lower energy) by anion formation.
 (b) NO , O_2 and F_2 are stabilized by cation formation; in each of these cases the bond order increases.

- E11.4(b)** Figure 11.1 is based on Figure 11.31 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 1/2.

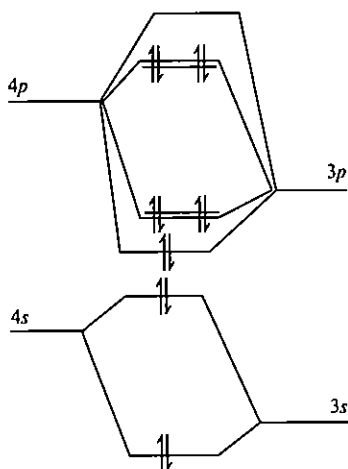


Figure 11.1

E11.5(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) : $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*4}$ $b = 1$

Each electron added to O_2^+ is added to an antibonding orbital, thus increasing the length. So the sequence

$\boxed{\text{O}_2^+, \text{O}_2, \text{O}_2^-, \text{O}_2^{2-}}$ has progressively longer bonds.

E11.6(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
$$N = \left(\frac{1}{1 + 2\lambda S + \lambda^2} \right)^{1/2}$$

E11.7(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

$$\int (aA + bB)N(0.145A + 0.844B) d\tau = 0$$

$$N \int [0.145aA^2 + (0.145b + 0.844a)AB + 0.844bB^2] d\tau = 0$$

The integrals of squares of orbitals are 1 and the integral $\int AB d\tau$ is the overlap integral S , 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

$$N(0.844A - 0.145B)$$

E11.8(b) The trial function $\psi = x^2(L - 2x)$ does not obey the boundary conditions of a particle in a box, so it is **not appropriate**. In particular, the function does not vanish at $x = L$.

E11.9(b) The variational principle says that the minimum energy is obtained by taking the derivative of the trial energy with respect to adjustable parameters, setting it equal to zero, and solving for the parameters:

$$E_{\text{trial}} = \frac{3a\hbar^2}{2\mu} - \frac{e^2}{\epsilon_0} \left(\frac{a}{2\pi^3} \right)^{1/2} \quad \text{so} \quad \frac{dE_{\text{trial}}}{da} = \frac{3\hbar^2}{2\mu} - \frac{e^2}{2\epsilon_0} \left(\frac{1}{2\pi^3 a} \right)^{1/2} = 0.$$

Solving for a yields:

$$\frac{3\hbar^2}{2\mu} = \frac{e^2}{2\epsilon_0} \left(\frac{1}{2\pi^3 a} \right)^{1/2} \quad \text{so} \quad a = \left(\frac{\mu e^2}{3\hbar^2 \epsilon_0} \right)^2 \left(\frac{1}{2\pi^3} \right) = \frac{\mu^2 e^4}{18\pi^3 \hbar^4 \epsilon_0^2}.$$

Substituting this back into the trial energy yields the minimum energy:

$$E_{\text{trial}} = \frac{3\hbar^2}{2\mu} \left(\frac{\mu^2 e^4}{18\pi^3 \hbar^4 \epsilon_0^2} \right) - \frac{e^2}{\epsilon_0} \left(\frac{\mu^2 e^4}{18\pi^3 \hbar^4 \epsilon_0^2 \cdot 2\pi^3} \right)^{1/2} = \boxed{\frac{-\mu e^4}{12\pi^3 \epsilon_0^2 \hbar^2}}.$$

E11.10(b) Energy is conserved, so when the photon is absorbed, its energy is transferred to the electron. Part of it overcomes the binding energy (ionization energy) and the remainder is manifest as the now freed electron's kinetic energy.

$$E_{\text{photon}} = I + E_{\text{kinetic}}$$

$$\begin{aligned} \text{so } E_{\text{kinetic}} &= E_{\text{photon}} - I = \frac{hc}{\lambda} - I = \frac{(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1})}{(584 \times 10^{-12} \text{ m}) \times (1.602 \times 10^{-19} \text{ J eV}^{-1})} - 4.69 \text{ eV} \\ &= \boxed{2119 \text{ eV}} = \boxed{3.39 \times 10^{-16} \text{ J}} \end{aligned}$$

E11.11(b) The molecular orbitals of the fragments and the molecular orbitals that they form are shown in Figure 11.2.

E11.12(b) We use the molecular orbital energy level diagram in Figure 11.41. 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) : $\boxed{a_{2u}^2 e_{1g}^4 e_{2u}^1}$

$$E = 2(\alpha + 2\beta) + 4(\alpha + \beta) + (\alpha - \beta) = \boxed{7\alpha + 7\beta}$$

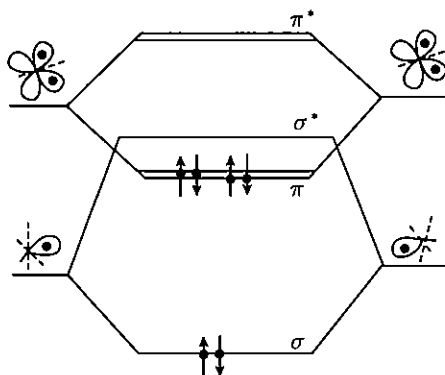


Figure 11.2

(b) C_6H_6^+ (5 electrons) : $a_{2u}^2 e_{1g}^3$

$$E = 2(\alpha + 2\beta) + 3(\alpha + \beta) = 5\alpha + 7\beta$$

E11.13(b) The secular determinants from E11.13(a) can be diagonalized with the assistance of general-purpose mathematical software. Alternatively, programs specifically designed for Hückel calculations (such as the one at Australia's Northern Territory University, <http://www.smeps.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 $\alpha + 2.414\,21\beta$, $\alpha + 2.000\,00\beta$, $\alpha + 1.414\,21\beta$ (doubly degenerate), $\alpha + 1.000\,00\beta$ (doubly degenerate), and $\alpha + 0.414\,21\beta$, so the total energy is $14\alpha + 19.313\,68\beta$ and the π energy is $19.313\,68\beta$.

(b) For phenanthrene, the energies of the filled orbitals are $\alpha + 2.434\,76\beta$, $\alpha + 1.950\,63\beta$, $\alpha + 1.516\,27\beta$, $\alpha + 1.305\,80\beta$, $\alpha + 1.142\,38\beta$, $\alpha + 0.769\,05\beta$, $\alpha + 0.605\,23\beta$, so the total energy is $14\alpha + 19.448\,24\beta$ and the π energy is $19.448\,24\beta$.

Solutions to problems

Solutions to numerical problems

P11.2 Draw up the following table

R/a_0	0	1	2	3	4	5	6	7	8	9	10
S	1.000	0.858	0.586	0.349	0.189	0.097	0.047	0.022	0.010	0.005	0.002

The points are plotted in Figure 11.3.

P11.4 Quantitatively correct values of the total amplitude require the properly normalized functions

$$\psi_{\pm} = \left(\frac{1}{2(1 \pm S)} \right)^{1/2} (A \pm B) \quad [11.7 \text{ and Example 11.1}]$$

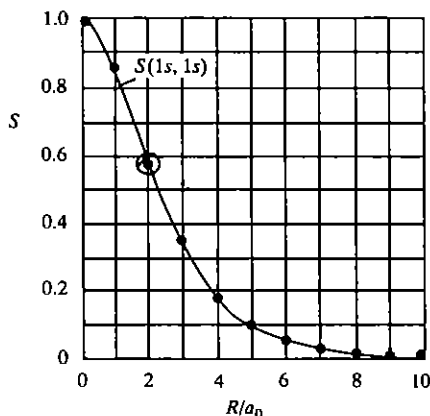


Figure 11.3

We first calculate the overlap integral at $R = 106 \text{ pm} = 2a_0$. (The expression for the overlap integral, S is given in Problem 11.2.)

$$S = \left(1 + 2 + \frac{1}{3}(2)^2\right) e^{-2} = 0.586$$

$$\text{Then } N_+ = \left(\frac{1}{2(1+S)}\right)^{1/2} = \left(\frac{1}{2(1+0.586)}\right)^{1/2} = 0.561$$

$$N_- = \left(\frac{1}{2(1-S)}\right)^{1/2} = \left(\frac{1}{2(1-0.586)}\right)^{1/2} = 1.099$$

We then calculate with $\psi = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r_A/a_0}$, $\psi_{\pm} = N_{\pm} \left(\frac{1}{\pi a_0^3}\right)^{1/2} \{e^{-r_A/a_0} \pm e^{-r_B/a_0}\}$ with r_A and r_B both measured from nucleus A, that is

$$\psi_{\pm} = N_{\pm} \left(\frac{1}{\pi a_0^3}\right)^{1/2} \{e^{-|z|/a_0} \pm e^{-|z-R|/a_0}\}$$

with z measured from A along the axis toward B. We draw up the following table with $R = 106 \text{ pm}$ and $a_0 = 52.9 \text{ pm}$.

z/pm	-100	-80	-60	-40	-20	0	20	40
$\frac{\psi_+}{(1/\pi a_0^3)^{1/2}}$	0.096	0.14	0.20	0.30	0.44	0.64	0.49	0.42
$\frac{\psi_-}{(1/\pi a_0^3)^{1/2}}$	0.14	0.21	0.31	0.45	0.65	0.95	0.54	0.20

z/pm	60	80	100	120	140	160	180	200
$\frac{\psi_+}{(1/\pi a_0^3)^{1/2}}$	0.42	0.47	0.59	0.49	0.33	0.23	0.16	0.11
$\frac{\psi_-}{(1/\pi a_0^3)^{1/2}}$	-0.11	-0.43	-0.81	-0.73	-0.50	-0.34	-0.23	-0.16

The points are plotted in Figure 11.4.

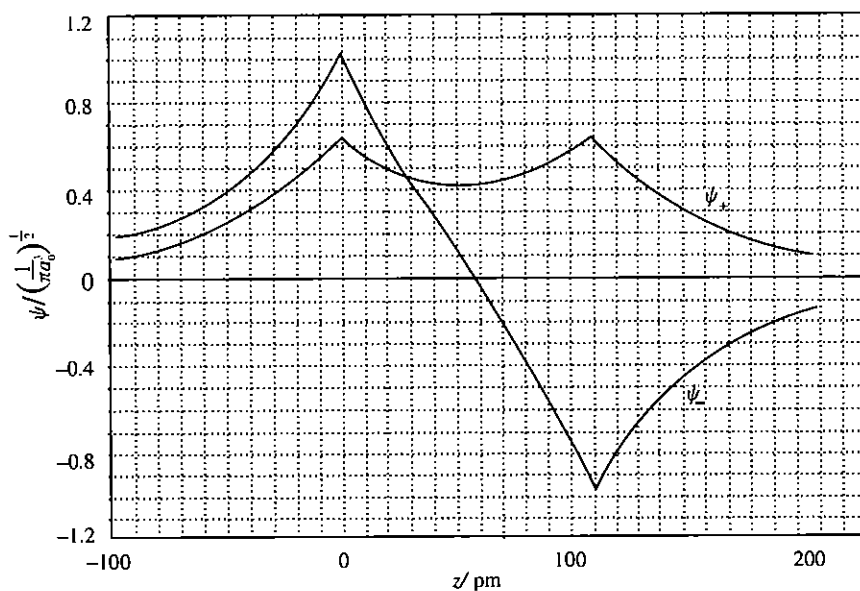
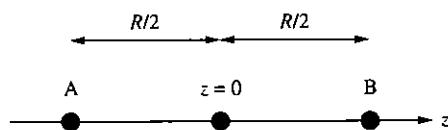


Figure 11.4

P11.6



- (a) With spatial dimensions in units (multiples) of a_0 , the atomic orbitals of atom A and atom B may be written in the form

$$p_{z,A} = \frac{1}{4(2\pi)^{1/2}} (z + R/2) e^{-[x^2 + y^2 + (z + R/2)^2]^{1/2}} / 2$$

and

$$p_{z,B} = \frac{1}{4(2\pi)^{1/2}} (z - R/2) e^{-[x^2 + y^2 + (z - R/2)^2]^{1/2}} / 2$$

Following eqn 11.7 and Example 11.1, we form LCAO-MOs of the form:

$$\psi_{\sigma_u} = \frac{p_{z,A} + p_{z,B}}{[2(1+S)]^{1/2}} \text{ [antibonding]} \quad \text{and} \quad \psi_{\sigma_g} = \frac{p_{z,A} - p_{z,B}}{[2(1-S)]^{1/2}} \text{ [bonding]}$$

$$\text{where } S = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p_{z,A} p_{z,B} \, dx \, dy \, dz \quad [11.17]$$

Computations and plots are readily prepared with mathematical software such as Mathcad.

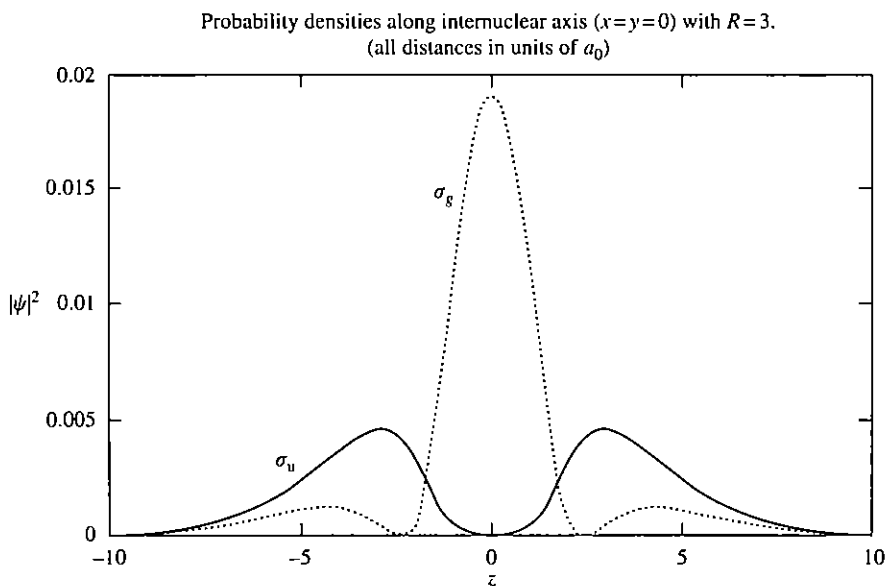


Figure 11.5(a)

- (b) With spatial dimensions in units of a_0 , the atomic orbitals for the construction of π molecular orbitals are:

$$p_{x,A} = \frac{1}{4(2\pi)^{1/2}} x e^{-[x^2+y^2+(z+R/2)^2]^{1/2}/2}$$

$$p_{x,B} = \frac{1}{4(2\pi)^{1/2}} x e^{-[x^2+y^2+(z-R/2)^2]^{1/2}/2}$$

The π -MOs are:

$$\psi_{\pi_u} = \frac{p_{x,A} + p_{x,B}}{[2(1+S)]^{1/2}} \text{ [bonding]} \quad \text{and} \quad \psi_{\pi_g} = \frac{p_{x,A} - p_{x,B}}{[2(1-S)]^{1/2}} \text{ [antibonding]}$$

$$\text{where } S = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p_{x,A} p_{x,B} \, dx \, dy \, dz$$

The plots clearly show the constructive interference that makes a bonding molecular orbital. Nodal planes created by destructive interference are clearly seen in the antibonding molecular orbitals.

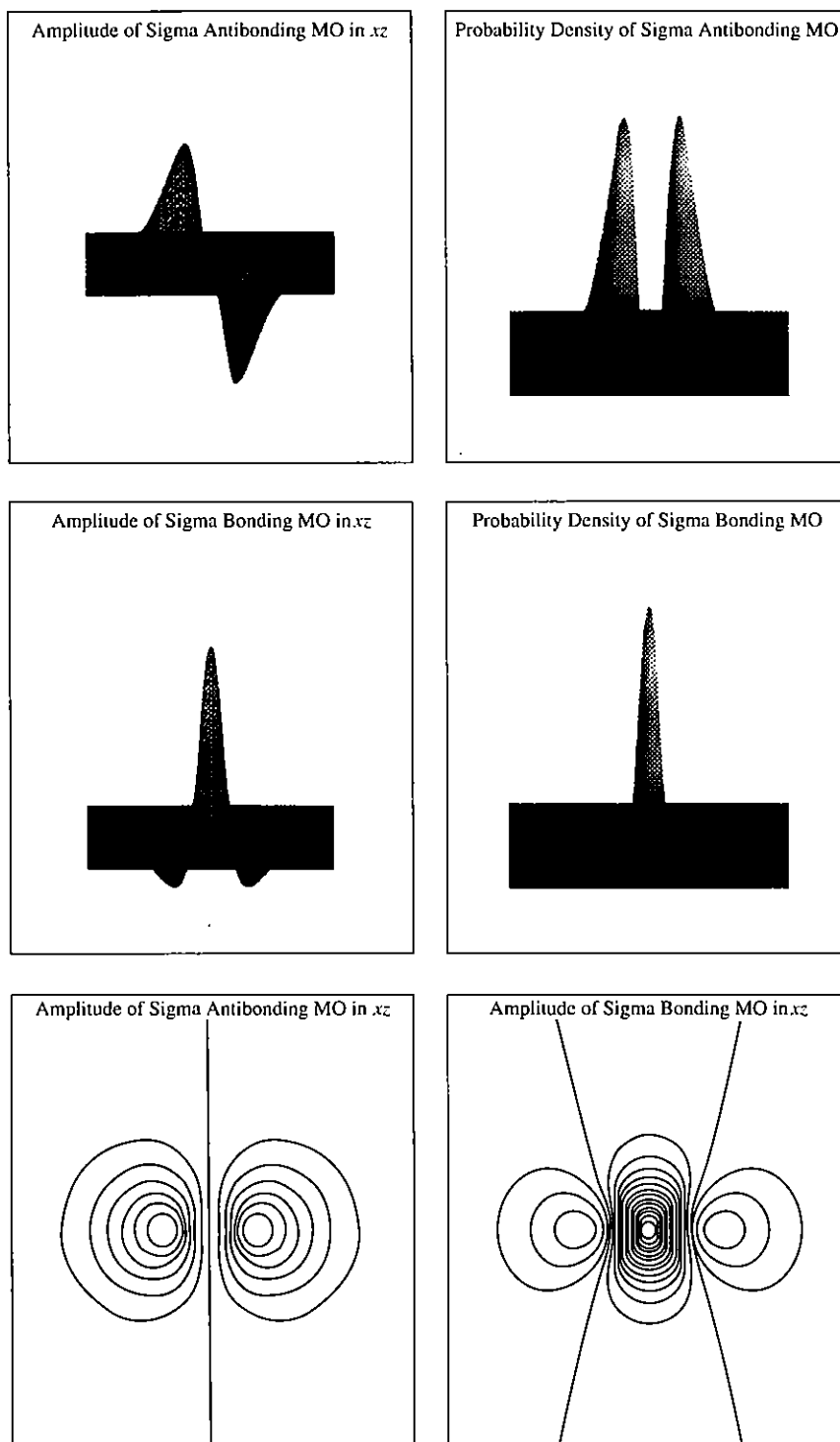
$R=3$ 

Figure 11.5(b)

$R=3$

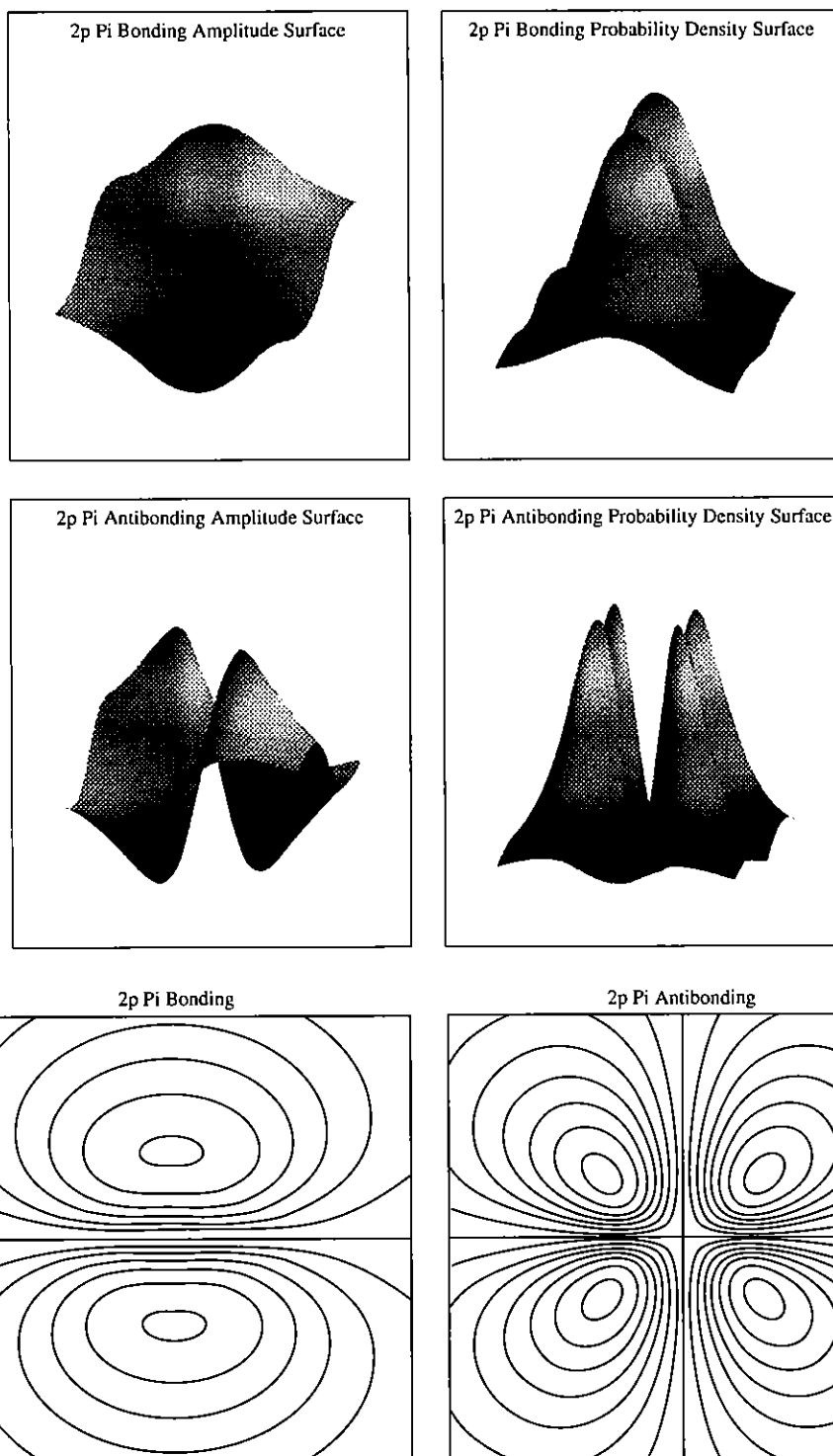


Figure 11.5(c)

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.

P11.8

$$E_H = E_I = -hcR_H \text{ [Section 10.2(b)]}$$

Draw up the following table using the data in question and using

$$\begin{aligned} \frac{e^2}{4\pi\epsilon_0 R} &= \frac{e^2}{4\pi\epsilon_0 a_0} \times \frac{a_0}{R} = \frac{e^2}{4\pi\epsilon_0 \times (4\pi\epsilon_0 \hbar^2 / m_e e^2)} \times \frac{a_0}{R} \\ &= \frac{m_e e^4}{16\pi^2 \epsilon_0^2 \hbar^2} \times \frac{a_0}{R} = E_h \times \frac{a_0}{R} \quad \left[E_h \equiv \frac{m_e e^4}{16\pi^2 \epsilon_0^2 \hbar^2} = 2hcR_H \right] \end{aligned}$$

so that $\frac{\left(\frac{e^2}{4\pi\epsilon_0 R}\right)}{E_h} = \frac{a_0}{R}$.

R/a_0	0	1	2	3	4	∞
$(e^2/4\pi\epsilon_0 R)/E_h$	∞	1	0.500	0.333	0.250	0
$(V_1 + V_2)/E_h$	2.000	1.465	0.843	0.529	0.342	0
$(E - E_H)/E_h$	∞	0.212	-0.031	-0.059	-0.038	0

The points are plotted in Figure 11.6.

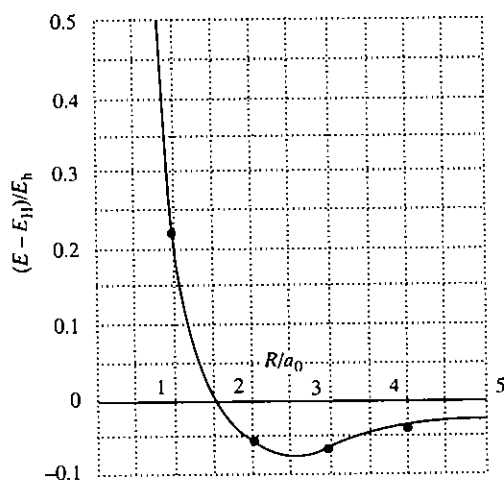


Figure 11.6

The minimum occurs at $R = 2.5a_0$, so $R = 130$ pm. At that bond length

$$E - E_H = -0.07E_h = -1.91 \text{ eV}$$

Hence, the dissociation energy is predicted to be about 1.9 eV and the equilibrium bond length about 130 pm.

P11.10 The electron configuration of F_2 is $1\sigma_g^2 2\sigma_u^{*2} 3\sigma_g^2 1\pi_u^4 2\pi_g^{*4}$; that of F_2^- is $1\sigma_g^2 2\sigma_u^{*2} 3\sigma_g^2 1\pi_u^4 2\pi_g^{*4} 4\sigma_u^{*1}$. So F_2^- has one more antibonding electron than does F_2 , suggesting a lower bond order (1/2 versus 1) and therefore a weaker bond. By definition a weaker bond has a smaller dissociation energy (hence the difference in D_e). Weaker bonds tend to be longer (hence the difference in R_e) and less stiff (hence the difference in $\tilde{\nu}$, reflecting a difference in the force constant k) than stronger bonds between similar atoms.

P11.12 Energy is conserved, so when the photon is absorbed, its energy is transferred to the electron. Part of it overcomes the binding energy (ionization energy) and the remainder is manifest as the now freed electron's kinetic energy.

$$E_{\text{photon}} = I + E_{\text{kinetic}} \quad \text{so} \quad I = E_{\text{photon}} - E_{\text{kinetic}}$$

so the first three ionization energies are:

$$I_1 = 21.21 \text{ eV} - 11.01 \text{ eV} = \boxed{10.20 \text{ eV}}$$

$$I_2 = 21.21 \text{ eV} - 8.23 \text{ eV} = \boxed{12.98 \text{ eV}}$$

$$\text{and } I_3 = 21.21 \text{ eV} - 5.22 \text{ eV} = \boxed{15.99 \text{ eV}}$$

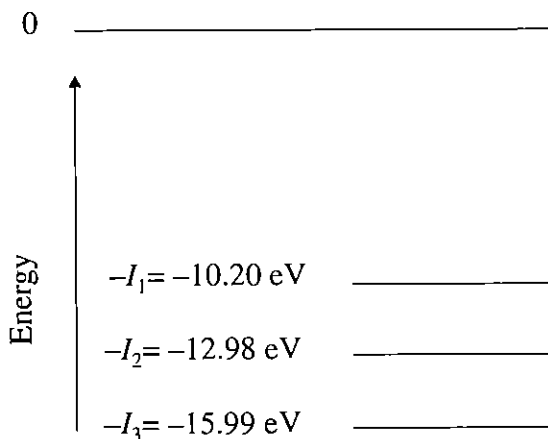


Figure 11.7

P11.14 $E_n = \frac{n^2 h^2}{8mL^2}$, $n = 1, 2, \dots$ and $\psi_n = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)$ [Section 9.1]

Two electrons occupy each level (by the Pauli principle), and so butadiene (in which there are four π electrons) has two electrons in ψ_1 and two electrons in ψ_2

$$\psi_1 = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right) \quad \text{and} \quad \psi_2 = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{2\pi x}{L}\right)$$

These orbitals are sketched in Figure 11.8(a).

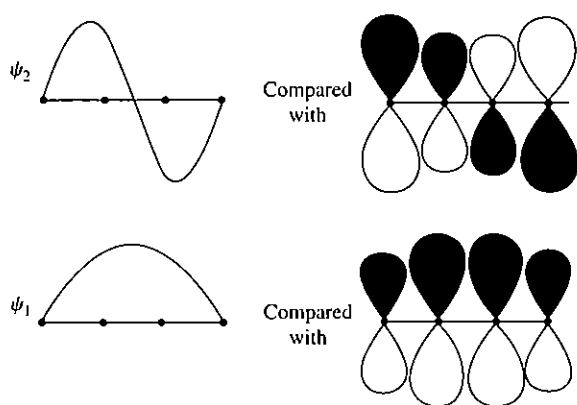


Figure 11.8(a)

The minimum excitation energy is

$$\Delta E = E_3 - E_2 = 5 \left(\frac{h^2}{8m_e L^2} \right)$$

In $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$ there are eight π electrons to accommodate, so the HOMO will be ψ_4 and the LUMO ψ_5 . From the particle-in-a-box solutions

$$\begin{aligned} \Delta E = E_5 - E_4 &= (25 - 16) \frac{h^2}{8m_e L^2} = \frac{9h^2}{8m_e L^2} \\ &= \frac{(9) \times (6.626 \times 10^{-34} \text{ J s})^2}{(8) \times (9.109 \times 10^{-31} \text{ kg}) \times (1.12 \times 10^{-9} \text{ m})^2} = 4.3 \times 10^{-19} \text{ J} \end{aligned}$$

which corresponds to $\boxed{2.7 \text{ eV}}$. The HOMO and LUMO are

$$\psi_n = \left(\frac{2}{L} \right)^{1/2} \sin \left(\frac{n\pi x}{L} \right)$$

with $n = 4, 5$ respectively; the two wavefunctions are sketched in Figure 11.8(b).

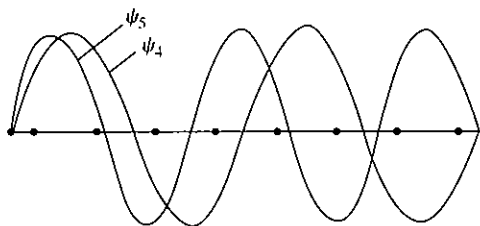


Figure 11.8(b)

COMMENT. It follows that

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1})}{4.3 \times 10^{-19} \text{ J}} = 4.6 \times 10^{-7} \text{ m, or } \boxed{460 \text{ nm.}}$$

The wavelength 460 nm corresponds to blue light; so the molecule is likely to appear orange in white light (since blue is subtracted).

- P11.16** (a) In the absence of numerical values for α and β , we express orbital energies as $(E_k - \alpha)/\beta$ for the purpose of comparison. Recall that β is negative (as is α for that matter), so the orbital with the greatest value of $(E_k - \alpha)/\beta$ has the lowest energy. Draw up the following table, evaluating

$$\frac{E_k - \alpha}{\beta} = 2 \cos \frac{2k\pi}{N}$$

	energy $(E_k - \alpha)/\beta$	
orbital, k	C_6H_6	C_8H_8
± 4		-2.000
± 3	-2.000	-1.414
± 2	-1.000	0
± 1	1.000	1.414
0	2.000	2.000

In each case, the lowest and highest energy levels are non-degenerate, while the other energy levels are doubly degenerate. The degeneracy is clear for all energy levels except, perhaps, the highest: each value of the quantum number k corresponds to a separate MO, and positive and negative values of k therefore give rise to a pair of MOs of the same energy. This is not the case for the highest energy level, though, because there are only as many MOs as there were AOs input to the calculation, which is the same as the number of carbon atoms; having a doubly-degenerate top energy level would yield one extra MO.

- (b) The total energy of the π electron system is the sum of the energies of occupied orbitals weighted by the number of electrons that occupy them. In C_6H_6 , each of the first three orbitals is doubly occupied, but the second level ($k = \pm 1$) is doubly degenerate, so

$$E_\pi = 2E_0 + 2 \times 2E_1 = 2(\alpha + 2\beta \cos 0) + 4 \left(\alpha + 2\beta \cos \frac{2\pi}{6} \right) = 6\alpha + 8\beta$$

The delocalization energy is the difference between this quantity and that of three isolated double bonds:

$$E_{\text{deloc}} = E_\pi - 6(\alpha + \beta) = 6\alpha + 8\beta - 6(\alpha + \beta) = \boxed{2\beta}$$

For linear hexatriene, $E_{\text{deloc}} = 0.988\beta$, so benzene has considerably more delocalization energy (assuming that β is similar in the two molecules). This extra stabilization is an example of the special stability of aromatic compounds.

- (c) In C_8H_8 , each of the first three orbitals is doubly occupied, but the second level ($k = \pm 1$) is doubly degenerate. The next level is also doubly degenerate, with a single electron occupying each orbital. So the energy is

$$\begin{aligned} E_\pi &= 2E_0 + 2 \times 2E_1 + 2 \times 1E_2 \\ &= 2(\alpha + 2\beta \cos 0) + 4 \left(\alpha + 2\beta \cos \frac{2\pi}{8} \right) + 2 \left(\alpha + 2\beta \cos \frac{4\pi}{8} \right) \\ &= 8\alpha + 9.657\beta \end{aligned}$$

The delocalization energy is the difference between this quantity and that of four isolated double bonds:

$$E_{\text{deloc}} = E_{\pi} - 8(\alpha + \beta) = 8\alpha + 9.657\beta - 8(\alpha + \beta) = \boxed{1.657\beta}$$

This delocalization energy is not much different from that of linear octatetraene (1.518β), so cyclooctatetraene does not have much additional stabilization over the linear structure. Once again, though, we do see that the delocalization energy stabilizes the π orbitals of the closed ring conjugated system to a greater extent than what is observed in the open chain conjugated system. However, the benzene/hexatriene comparison shows a much greater stabilization than does the cyclooctatetraene/octatetraene system. This is a demonstration of the Hückel $4n + 2$ rule, which states that any planar, cyclic, conjugated system exhibits unusual aromatic stabilization if it contains $4n + 2$ π electrons where “ n ” is an integer. Benzene with its six π electrons has this aromatic stabilization whereas cyclooctatetraene with eight π electrons doesn’t have this unusual stabilization. We can say that it is not aromatic, consistent with indicators of aromaticity such as the Hückel $4n + 2$ rule.

- P11.18** (a) The table displays computed orbital energies and experimental $\pi^* \leftarrow \pi$ wavenumbers of ethene and the first few conjugated linear polyenes.

Species	$E_{\text{LUMO}}/\text{eV}^*$	$E_{\text{HOMO}}/\text{eV}^*$	$\Delta E/\text{eV}^*$	$\tilde{\nu}/\text{cm}^{-1}$
C_2H_4	1.2282	-10.6411	11.8693	61500
C_4H_6	0.2634	-9.4671	9.7305	46080
C_6H_8	-0.2494	-8.8993	8.6499	39750
C_8H_{10}	-0.5568	-8.5767	8.0199	32900
$\text{C}_{10}\text{H}_{12}$	-0.7556	-8.3755	7.6199	

* Semi-empirical, PM3 level. PC Spartan Pro™

- (b) A plot of the computed energy difference vs. experimental wavenumbers appears in Figure 11.9. The computed points fall on a rather good straight line. Of course a better fit can be obtained to a quadratic and a perfect fit to a cubic polynomial; however, the improvement would be slight and the justification even more slight. The linear least-squares best fit is:

$$\boxed{\Delta E/\text{eV} = 3.3534 + 1.3791 \times 10^{-4} \tilde{\nu}/\text{cm}^{-1}} \quad (r^2 = 0.994)$$

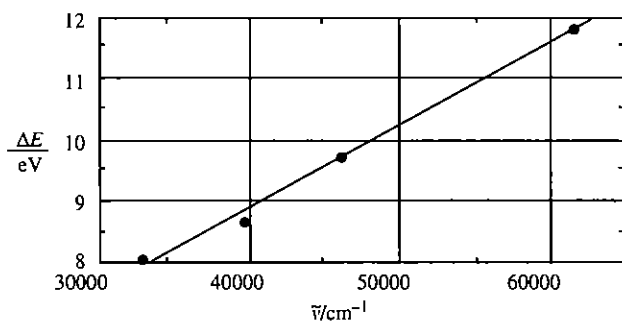


Figure 11.9

(c) Invert the fit equation obtained in (b) above:

$$\tilde{\nu}/\text{cm}^{-1} = \frac{\Delta E/\text{eV} - 3.3534}{1.3791 \times 10^{-4}}.$$

So for $\text{C}_{10}\text{H}_{12}$, we expect a transition at:

$$\tilde{\nu}/\text{cm}^{-1} = \frac{7.6199 - 3.3534}{1.3791 \times 10^{-4}} = \boxed{30937 \text{ cm}^{-1}}$$

(d) The fitting procedure is necessary because the orbital energies are only approximate. Remember that an orbital wavefunction is itself an approximation. A semi-empirical computation is a further approximation. If the orbitals were exact, then we would expect the energy difference to be directly proportional to the spectroscopic wavenumbers with the following proportionality:

$$\Delta E = hc\tilde{\nu} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^{10} \text{ cm s}^{-1})\tilde{\nu}}{1.602 \times 10^{-19} \text{ J/eV}},$$

$$\text{so } \Delta E/\text{eV} = 1.240 \times 10^{-4} \tilde{\nu}/\text{cm}^{-1}.$$

Clearly this is different than the fit reported above. A further illustration of why the fitting procedure is necessary can be discerned by comparing the table from part (a) to a corresponding table based on a different computational model, namely Hartree–Fock computations with an STO-3G basis set:

Species	$E_{\text{LUMO}}/\text{eV}^*$	$E_{\text{HOMO}}/\text{eV}^*$	$\Delta E/\text{eV}^*$
C_2H_4	8.9335	−9.1288	18.0623
C_4H_6	6.9667	−7.5167	14.4834
C_6H_8	6.0041	−6.6783	12.6824
C_8H_{10}	5.4488	−6.1811	11.6299
$\text{C}_{10}\text{H}_{12}$	5.0975	−5.8621	10.9596

* *Ab initio*, STO-3G, PC Spartan Pro™

Obviously these energy differences are not the same as the PM3 differences computed above. Nor are they energy differences that correspond to the experimental frequencies.

COMMENT. The STO-3G data also fit a straight line. That fit can also be used to estimate the transition in $C_{10}H_{12}$:

$$\bar{\nu}/\text{cm}^{-1} = \frac{\Delta E/\text{eV} - 3.8311}{2.3045 \times 10^{-4}},$$

so for $C_{10}H_{12}$ we expect a transition at

$$\bar{\nu}/\text{cm}^{-1} = \frac{10.9596 - 3.8311}{2.3045 \times 10^{-4}} = 30933.$$

Even though the computations differed considerably in detail, with the calibration procedure they result in nearly identical predictions.

- P11.20** (a) The standard enthalpy of formation ($\Delta_f H^\circ/\text{kJ mol}^{-1}$) of ethene and the first few linear polyenes is listed below.

Species	Computed*	Experimental†	% error
C_2H_4	69.580	52.46694	32.6
C_4H_6	129.834	108.8 ± 0.79	19.3
		111.9 ± 0.96	16.0
C_6H_8	188.523	$168. \pm 3$	12.2
C_8H_{10}	246.848	295.9^\ddagger	16.6

* Semi-empirical, PM3 level, PC Spartan Pro™

† <http://webbook.nist.gov/chemistry/>

‡ Pedley, Naylor, and Kirby, *Thermodynamic Data of Organic Compounds*.

- (b) The % error, shown in the table, is defined by:

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

- (c) For all of the molecules, the computed enthalpies of formation exceed the experimental values by much more than the uncertainty in the experimental value. This observation serves to illustrate that molecular modeling software is not a substitute for experimentation when it comes to quantitative measures. It is also worth noting, however, that the experimental uncertainty can vary a great deal. The NIST database reports $\Delta_f H^\circ$ for C_2H_4 to seven significant figures (with no explicit uncertainty). Even if the figure is not accurate to 1 part in 5000 000, it is clearly a very precisely known quantity—as one should expect in such a familiar and well studied substance. The database lists two different determinations for $\Delta_f H^\circ(C_4H_6)$, and the experimental values differ by more than the uncertainty claimed for each; a critical evaluation of the experimental data is called for. The uncertainty claimed

for $\Delta_f H^\circ(\text{C}_6\text{H}_8)$ is greater still (but still only about 2%). Finally, it should go without saying that not all of the figures reported by the molecular modeling software are physically significant.

Solutions to theoretical problems

P11.22 We need to determine whether $E_- + E_+ > 2E_H$

$$\begin{aligned} E_- + E_+ &= -\frac{V_1 - V_2}{1 - S} + \frac{e^2}{4\pi\epsilon_0 R} - \frac{V_1 + V_2}{1 + S} + \frac{e^2}{4\pi\epsilon_0 R} + 2E_H \\ &= -\frac{\{(V_1 - V_2) \times (1 + S) + (1 - S) \times (V_1 + V_2)\}}{(1 - S) \times (1 + S)} + \frac{2e^2}{4\pi\epsilon_0 R} + 2E_H \\ &= \frac{2(SV_2 - V_1)}{1 - S^2} + \frac{2e^2}{4\pi\epsilon_0 R} + 2E_H \end{aligned}$$

The nuclear repulsion term is always positive, and always tends to raise the mean energy of the orbitals above E_H . The contribution of the first term is difficult to assess. If $S \approx 0$, $SV_2 \approx 0$ and $V_1 \approx 0$, then the first term is small compared to the nuclear repulsion term. If $S \approx 1$ and $SV_2 \approx V_1$, then once again the nuclear repulsion term is dominant. At intermediate values of S , the first term is negative, but of smaller magnitude than the nuclear repulsion term. Thus in all cases $E_- + E_+ > 2E_H$.

P11.24 (a) $\psi = e^{-kr}$ $H = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$

$$\begin{aligned} \int \psi^2 d\tau &= \int_0^\infty r^2 e^{-2kr} dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi = \frac{\pi}{k^3} \\ \int \psi \frac{1}{r} \psi d\tau &= \int_0^\infty r e^{-2kr} dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi = \frac{\pi}{k^2} \\ \int \psi \nabla^2 \psi d\tau &= \int \psi \frac{1}{r} \frac{d^2}{dr^2} (r e^{-kr}) d\tau = \int \psi \left(k^2 - \frac{2k}{r} \right) \psi d\tau \\ &= \frac{\pi}{k} - \frac{2\pi}{k} = -\frac{\pi}{k} \end{aligned}$$

Therefore

$$\int \psi H \psi d\tau = \frac{\hbar^2}{2\mu} \times \frac{\pi}{k} - \frac{e^2}{4\pi\epsilon_0} \times \frac{\pi}{k^2}$$

and

$$E = \frac{\left(\frac{\hbar^2 \pi}{2\mu k} \right) - \left(\frac{e^2 \pi}{4\pi\epsilon_0 k^2} \right)}{\pi/k^3} = \frac{\hbar^2 k^2}{2\mu} - \frac{e^2 k}{4\pi\epsilon_0}$$

$$\frac{dE}{dk} = 2 \left(\frac{\hbar^2}{2\mu} \right) k - \frac{e^2}{4\pi\epsilon_0} = 0 \quad \text{when} \quad k = \frac{e^2 \mu}{4\pi\epsilon_0 \hbar^2}$$

The optimum energy is therefore

$$E = -\frac{e^4 \mu}{32\pi^2 \epsilon_0^2 \hbar^2} = \boxed{-hcR_H} \text{ the exact value.}$$

(b) $\psi = e^{-kr^2}$, H as before.

$$\int \psi^2 d\tau = \int_0^\infty e^{-2kr^2} r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi = \frac{\pi}{2} \left(\frac{\pi}{2k^3} \right)^{1/2}$$

$$\int \psi \frac{1}{r} \psi d\tau = \int_0^\infty r e^{-2kr^2} dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi = \frac{\pi}{k}$$

$$\begin{aligned} \int \psi \nabla^2 \psi d\tau &= -2 \int \psi (3k - 2k^2 r^2) \psi d\tau \\ &= -2 \int_0^\infty (3kr^2 - 2k^2 r^4) e^{-2kr^2} dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \\ &= -8\pi \left\{ \left(\frac{3k}{8} \right) \times \left(\frac{\pi}{2k^3} \right)^{1/2} - \frac{3k^2}{16} \left(\frac{\pi}{2k^5} \right)^{1/2} \right\} \end{aligned}$$

Therefore

$$\begin{aligned} E &= \frac{3\hbar^2 k}{2\mu} - \frac{e^2 k^{1/2}}{\epsilon_0 (2\pi)^{1/2}} \\ \frac{dE}{dk} &= 0 \quad \text{when} \quad k = \frac{e^4 \mu^2}{18\pi^3 \epsilon_0^2 \hbar^4} \end{aligned}$$

and the optimum energy is therefore

$$E = -\frac{e^4 \mu}{12\pi^3 \epsilon_0^2 \hbar^2} = \boxed{-\frac{8}{3\pi} \times hcR_H}$$

Since $8/3\pi < 1$, the energy in (a) is lower than in (b), and so the exponential wavefunction is better than the Gaussian.

Solutions to applications

P11.26 (a)
$$\begin{vmatrix} \alpha - E & \beta & \beta \\ \beta & \alpha - E & \beta \\ \beta & \beta & \alpha - E \end{vmatrix} = 0$$

$$(\alpha - E) \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} - \beta \begin{vmatrix} \beta & \beta \\ \beta & \alpha - E \end{vmatrix} + \beta \begin{vmatrix} \beta & \alpha - E \\ \beta & \beta \end{vmatrix} = 0$$

$$(\alpha - E) \times \{(\alpha - E)^2 - \beta^2\} - \beta\{\beta(\alpha - E) - \beta^2\} + \beta\{\beta^2 - (\alpha - E)\beta\} = 0$$

$$(\alpha - E) \times \{(\alpha - E)^2 - \beta^2\} - 2\beta^2\{\alpha - E - \beta\} = 0$$

$$(\alpha - E) \times (\alpha - E - \beta) \times (\alpha - E + \beta) - 2\beta^2(\alpha - E - \beta) = 0$$

$$(\alpha - E - \beta) \times \{(\alpha - E) \times (\alpha - E + \beta) - 2\beta^2\} = 0$$

$$(\alpha - E - \beta) \times \{(\alpha - E) \times (\alpha - E + 2\beta) - \beta(\alpha - E) - 2\beta^2\} = 0$$

$$(\alpha - E - \beta) \times \{(\alpha - E) \times (\alpha - E + 2\beta) - \beta(\alpha - E + 2\beta)\} = 0$$

$$(\alpha - E - \beta) \times (\alpha - E + 2\beta) \times (\alpha - E - \beta) = 0$$

Therefore, the desired roots are $E = \boxed{\alpha - \beta, \alpha - \beta, \text{ and } \alpha + 2\beta}$. The energy level diagram is shown in Figure 11.10.

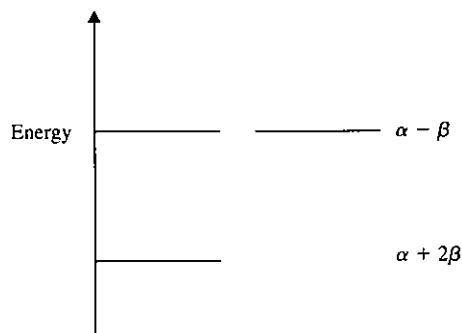
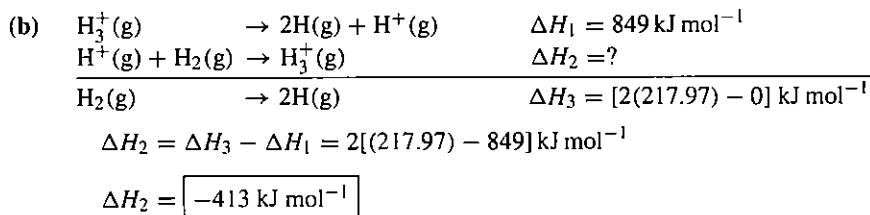


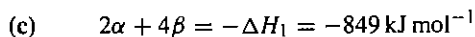
Figure 11.10

The binding energies are shown in the following table.

Species	Number of e^-	Binding energy
H_3^+	2	$2(\alpha + 2\beta) = 2\alpha + 4\beta$
H_3	3	$2(\alpha + 2\beta) + (\alpha - \beta) = 3\alpha + 3\beta$
H_3^-	4	$2(\alpha + 2\beta) + 2(\alpha - \beta) = 4\alpha + 2\beta$



This is only slightly less than the binding energy of H_2 ($435.94 \text{ kJ mol}^{-1}$)



$$\beta = \frac{-\Delta H_1 - 2\alpha}{4} \quad \text{where } \Delta H_1 = 849 \text{ kJ mol}^{-1}$$

Species	Binding energy
H_3^+	$2\alpha + 4\beta = -\Delta H_1 = \boxed{-849 \text{ kJ mol}^{-1}}$
H_3	$3\alpha + 3\beta = 3\left(\alpha - \frac{\Delta H_1 + 2\alpha}{4}\right) = 3\left(\frac{1}{2}\alpha - \frac{\Delta H_1}{4}\right) = \boxed{3(\alpha/2) - 212 \text{ kJ mol}^{-1}}$
H_3^-	$4\alpha + 2\beta = 4\alpha - \frac{\Delta H_1 + 2\alpha}{2} = 3\alpha - \frac{\Delta H_1}{2} = \boxed{3\alpha - 425 \text{ kJ mol}^{-1}}$

As α is a negative quantity, all three of these species are expected to be stable.

- P11.28** (a) The orbitals are sketched in Figure 11.11(a). ψ_1 is a bonding orbital, showing no nodes between adjacent atoms, and ψ_3 is antibonding with respect to all three atoms. ψ_2 is non-bonding, with neither constructive nor destructive interaction of the atomic orbitals of adjacent atoms.

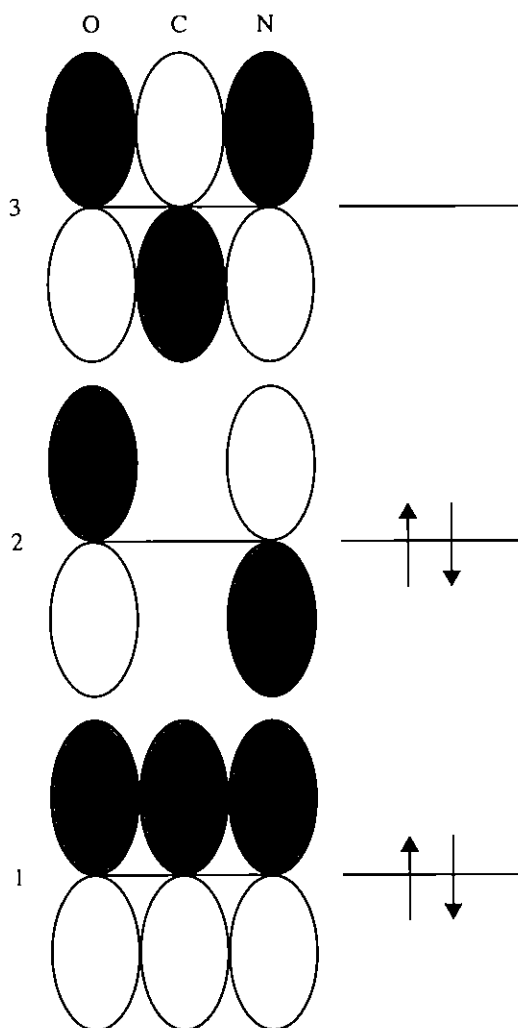


Figure 11.11(a)

- (b) This arrangement only works if the entire peptide link is coplanar. Let us call the plane defined by the O, C, and N atoms the xy plane; therefore, the p orbitals used to make the three MOs sketched above are p_z orbitals. If the p_z orbital of N is used in the π system, then the σ bonds it makes must be in the xy plane. Hence the H atom and the atom labeled $C_{\alpha 2}$ must also be in the xy plane. Likewise, if the p_z orbital of the C atom in the peptide link is used in the π system, then its σ bonds must also lie in the xy plane, putting the atom labeled $C_{\alpha 1}$ in that plane as well.
- (c) The relative energies of the orbitals and their occupancy are shown in Figure 11.11a. There are four electrons to be distributed. If we look at the conventional representation of the peptide link (**10** in the text), the two electrons represented by the $C=O \pi$ bond are obviously part of the π system, leaving the two lone pairs on O, the $C-O \sigma$ bond, and the two other σ bonds of C as part of the σ system. Turning now to the Lewis octet of electrons around the N atom, we must assign two electrons to

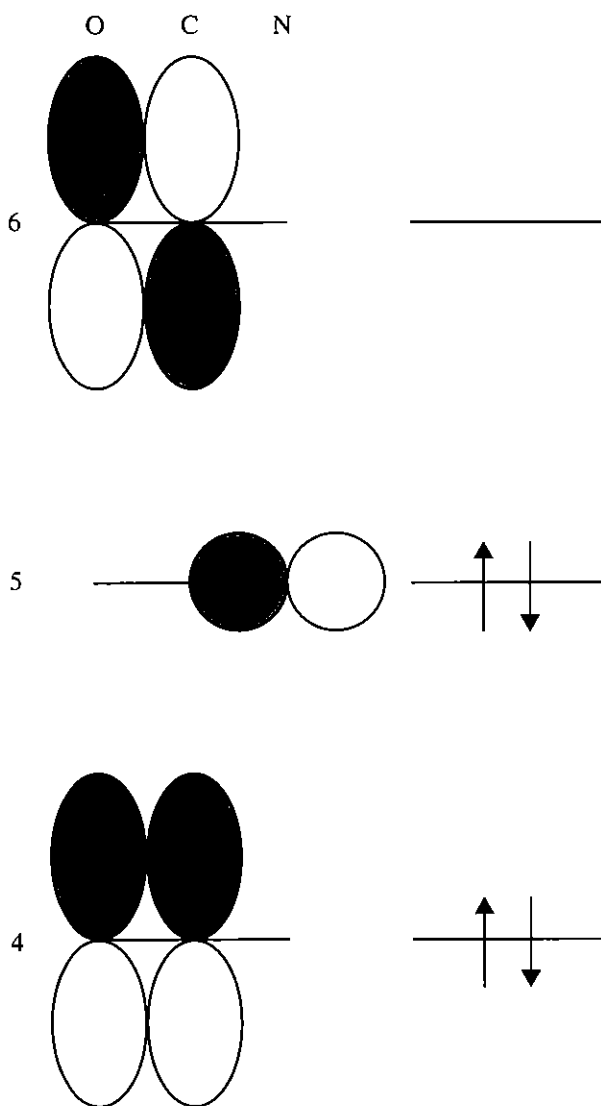


Figure 11.11(b)

each of the σ bonds involving N; clearly they cannot be part of the π system. That leaves the lone pair on N, which must occupy the other orbital that N contributes to the molecule, namely the p_z orbital that is part of the π system.

- (d) The orbitals are sketched in Figure 11.11(b). ψ_4 is a bonding orbital with respect to C and O, and ψ_6 is antibonding with respect to C and O. ψ_5 is non-bonding, involving only the N atom. There are four electrons to be placed in this system, as before, two each in a bonding and non-bonding orbital.
- (e) This system cannot be planar. As before, the atom labeled $C_{\alpha 1}$ must be in the xy plane. As before, the atoms bound to N must be in a plane perpendicular to the orbital that N contributes to this system, which is itself in the xy plane; the bonding partners of N are therefore forced out of the xy plane.
- (f) The bonding MO ψ_1 must have a lower energy than the bonding MO ψ_4 , for ψ_1 is bonding (stabilizing) with respect to all three atoms, while ψ_4 is bonding with respect to only two of them. Likewise, the antibonding MO ψ_3 must have a higher energy than the antibonding MO ψ_6 , for ψ_3 is antibonding (destabilizing) with respect to all three atoms pairwise, while ψ_6 is antibonding only with respect to two of them. The non-bonding MOs ψ_2 and ψ_5 must have similar energies, not much different than the parameter α , for there is no significant constructive or destructive interference between adjacent atoms in either one.
- (g) Because bonding orbital ψ_1 has a lower energy than ψ_4 , the planar arrangement has a lower energy than the non-planar one. The total energy of the planar arrangement is

$$E_{\text{planar}} = 2E_1 + 2E_2.$$

Compare this to the energy of the non-planar arrangement:

$$E_{\text{non-planar}} = 2E_4 + 2E_5 > 2E_1 + 2E_2 = E_{\text{planar}}.$$

The fact that $E_3 > E_6$ is immaterial, for neither of those orbitals is occupied.

12

Molecular symmetry

Answers to discussion questions

D12.2

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

D12.4

A molecule may be chiral, and therefore optically active, only if it does not possess an axis of improper rotation, S_n . An improper rotation is a rotation followed by a reflection and this combination of operations always converts a right-handed object into a left-handed object and *vice versa*; hence an S_n axis guarantees that a molecule cannot exist in chiral forms.

D12.6

See Sections 12.4(a) and (b).

D12.8

The direct sum is the decomposition of the direct product. The procedure for the decomposition is the set of steps outlined in Section 12.5(a) and demonstrated in *Illustration 12.1*.

Solutions to exercises

E12.1(b)

CCl_4 has $4 C_3$ axes (each C—Cl axis), $3 C_2$ axes (bisecting Cl—C—Cl angles), $3 S_4$ axes (the same as the C_2 axes), and 6 dihedral mirror planes (each Cl—C—Cl plane).

E12.2(b)

Only molecules belonging to C_s , C_n , and C_{nv} groups may be polar, so ...

(a) $\text{CH}_3\text{Cl}(C_{3v})$ may be polar along the C—Cl bond;

(b) $\text{HW}_2(\text{CO})_{10}(D_{4h})$ may not be polar

(c) $\text{SnCl}_4(T_d)$ may not be polar

E12.3(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 vanishes.

E12.4(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

$$c(A_{1g}) = (4) + 2(-1) + 2(1) + (-4) + 3(0) + 3(0) + (4) \\ + 2(-1) + 2(1) + (-4) + 3(0) + 3(0) = 0$$

Since the species A_{1g} is absent, the transition is forbidden for x - or y -polarized light. A similar analysis leads to the conclusion that A_{1g} is absent from the product $A_{1g}E_{2uz}$; therefore the transition is forbidden.

E12.5(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 A_1 .

E12.6(b) A molecule cannot be chiral if it has an axis of improper rotation. The point group T_d has S_4 axes and mirror planes ($= S_1$), which preclude chirality. The T_h group has, in addition, a center of inversion ($= S_2$).

E12.7(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^-	$\sigma_d(xy)$	$\sigma_d(-xy)$	$\sigma_v(y)$	$\sigma_v(x)$
C_4^-	C_4^-	E	C_2	C_4^+	$\sigma_d(-xy)$	$\sigma_d(xy)$	$\sigma_v(x)$	$\sigma_v(y)$
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

E12.8(b) See Figure 12.1.

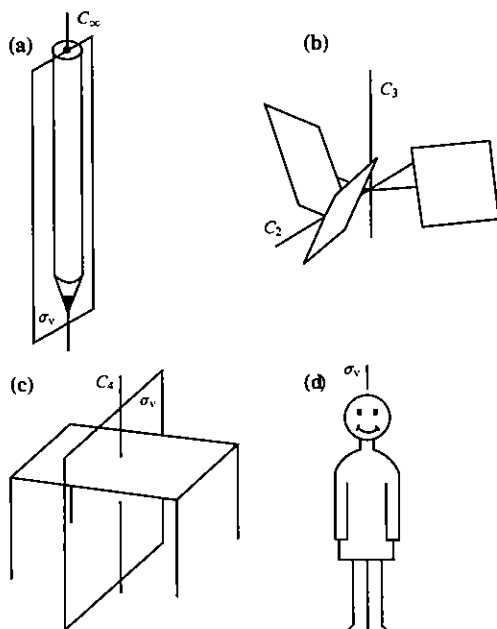


Figure 12.1

(a) Sharpened pencil: E, C_∞, σ_v ; therefore $C_{\infty v}$

(b) Propellor: $E, C_3, 3C_2$; therefore D_3

(c) Square table: $E, C_4, 4\sigma_v$; therefore C_{4v} ; Rectangular table: $E, C_2, 2\sigma_v$; therefore C_{2v}

(d) Person: E, σ_v (approximately); therefore C_s .

E12.9(b) We follow the flow chart in the text (Figure 12.7). The symmetry elements found in order as we proceed down the chart and the point groups are

(a) Naphthalene: $E, C_2, C_2', C_2'', 3\sigma_h, i$; D_{2h}

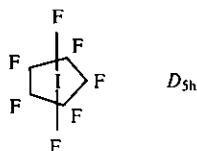
(b) Anthracene: $E, C_2, C_2', C_2'', 3\sigma_h, i$; D_{2h}

(c) Dichlorobenzenes:

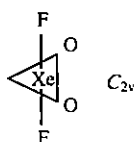
- (i) 1,2-dichlorobenzene: $E, C_2, \sigma_v, \sigma'_v$; C_{2v}
 (ii) 1,3-dichlorobenzene: $E, C_2, \sigma_v, \sigma'_v$; C_{2v}
 (iii) 1,4-dichlorobenzene: $E, C_2, C'_2, 3\sigma_h, i$; D_{2h} .

E12.10(b) (a) H-F $C_{\infty v}$

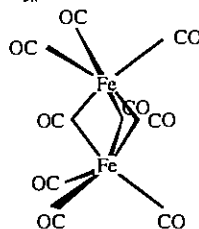
(b)



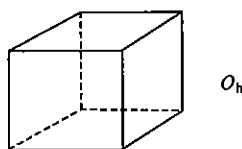
(c)



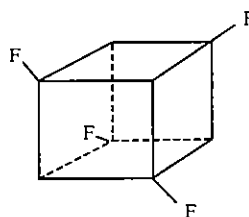
(d) D_{3h}



(e)



(f) T_d



The following responses refer to the text flow chart (Figure 12.7) for assigning point groups.

- (a) HF: linear, no i , so $C_{\infty v}$
 (b) IF₇: nonlinear, fewer than $2C_n$ with $n > 2$, $C_5, 5C'_2$ perpendicular to C_5, σ_h , so D_{5h}
 (c) XeO₂F₂: nonlinear, fewer than $2C_n$ with $n > 2$, C_2 , no C'_2 perpendicular to C_2 , no $\sigma_h, 2\sigma_v$, so C_{2v}
 (d) Fe₂(CO)₉: nonlinear, fewer than $2C_n$ with $n > 2$, $C_3, 3C_2$ perpendicular to C_3, σ_h , so D_{3h}
 (e) cubane (C₈H₈): nonlinear, more than $2C_n$ with $n > 2, i$, no C_5 , so O_h
 (f) tetrafluorocubane (23): nonlinear, more than $2C_n$ with $n > 2$, no i , so T_d .

E12.11(b) (a) Only molecules belonging to C_s, C_n , and C_{nv} groups may be polar. In Exercise 12.9(b) *ortho*-dichlorobenzene and *meta*-dichlorobenzene belong to C_{2v} and so may be polar; in Exercise 12.6(b), HF and XeO₂F₂ 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 12.5(b) and 12.6(b), all the molecules have mirror planes, so none can be chiral.

E12.12(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 p_x and p_y orbitals available to a bonding N atom have the proper symmetry. If d orbitals are available (as in SO₃), all d orbitals except d_{z^2} could have nonzero overlap.

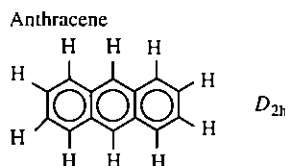
- E12.13(b)** The product $\Gamma_f \times \Gamma(\mu) \times \Gamma_i$ must contain A_1 (Example 12.7). Then, since $\Gamma_i = B_1$, $\Gamma(\mu) = \Gamma(y) = B_2$ (C_{2v} character table), we can draw up the following table of characters

	E	C_2	σ_v	σ'_v
B_2	1	-1	-1	1
B_1	1	-1	1	-1
$B_1 B_2$	1	1	-1	-1

$= A_2$

Hence, the upper state is A_2 , because $A_2 \times A_2 = A_1$.

- E12.14(b) (a)**



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 B_{3u} (x-polarized), B_{2u} (y-polarized), and 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 A_{2u} or E_{1u} symmetry.

- E12.15(b)**

	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
$\sin \theta$	1	Linear combinations of $\sin \theta$ and $\cos \theta$	1
$\cos \theta$	1		-1
Product	1	1	-1

The product does not contain A_1 , so **yes** the integral vanishes.

Solutions to problems

P12.2

The operations are illustrated in Figure 12.2. Note that $R^2 = E$ for all the operations of the groups, that $ER = RE = R$ always, and that $RR' = R'R$ for this group. Since $C_2\sigma_h = i$, $\sigma_h i = C_2$, and $iC_2 = \sigma_h$ we

can draw up the following group multiplication table

	E	C_2	σ_h	i
E	E	C_2	σ_h	i
C_2	C_2	E	i	σ_h
σ_h	σ_h	i	E	C_2
i	i	σ_h	C_2	E

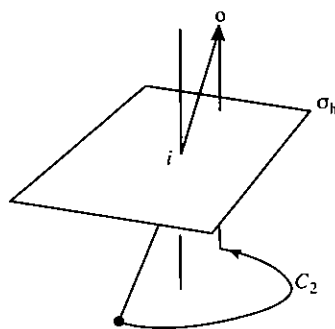


Figure 12.2

The $\boxed{\text{trans-CHCl=CHCl}}$ molecule belongs to the group C_{2h} .

COMMENT. Note that the multiplication table for C_{2h} can be put into a one-to-one correspondence with the multiplication table of D_2 obtained in Exercise 12.5. We say that they both belong to the same abstract group and are isomorphic.

Question. Can you find another abstract group of order 4 and obtain its multiplication table? There is only one other.

P12.4

Refer to Figure 12.3 of the text. Place orbitals h_1 and h_2 on the H atoms and s, p_x, p_y , and p_z on the O atom. The z -axis is the C_2 axis; x lies perpendicular to σ'_v , y lies perpendicular to σ_v . Then draw up the following table of the effect of the operations on the basis

	E	C_2	σ_v	σ'_v
h_1	h_1	h_2	h_2	h_1
h_2	h_2	h_1	h_1	h_2
s	s	s	s	s
p_x	p_x	$-p_x$	p_x	$-p_x$
p_y	p_y	$-p_y$	$-p_y$	p_y
p_z	p_z	p_z	p_z	p_z

Express the columns headed by each operation R in the form

$$(\text{new}) = D(R)(\text{original})$$

where $D(R)$ is the 6×6 representative of the operation R . We use the rules of matrix multiplication set out in Justification 12.1.

- (i) $E : (h_1, h_2, s, p_x, p_y, p_z) \leftarrow (h_1, h_2, s, p_x, p_y, p_z)$ is reproduced by the 6×6 unit matrix
 (ii) $C_2 : (h_2, h_1, s, -p_x, -p_y, p_z) \leftarrow (h_1, h_2, s, p_x, p_y, p_z)$ is reproduced by

$$D(C_2) = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

- (iii) $\sigma_v : (h_2, h_1, s, p_x, -p_y, p_z) \leftarrow (h_1, h_2, s, p_x, p_y, p_z)$ is reproduced by

$$D(\sigma_v) = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

- (iv) $\sigma'_v : (h_1, h_2, s, -p_x, p_y, p_z) \leftarrow (h_1, h_2, s, p_x, p_y, p_z)$ is reproduced by

$$D(\sigma'_v) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

- (a) To confirm the correct representation of $C_2\sigma_v = \sigma'_v$, we write

$$\begin{aligned} D(C_2)D(\sigma_v) &= \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \\ &= \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} = D(\sigma'_v) \end{aligned}$$

(b) Similarly, to confirm the correct representation of $\sigma_v\sigma'_v = C_2$, we write

$$\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} = D(C_2)$$

(a) The characters of the representatives are the sums of their diagonal elements:

E	C_2	σ_v	σ'_v
6	0	2	4

(b) The characters are not those of any one irreducible representation, so the representation is reducible.

(c) The sum of the characters of the specified sum is

	E	C_2	σ_v	σ'_v
$3A_1$	3	3	3	3
B_1	1	-1	1	-1
$2B_2$	2	-2	-2	2
$3A_1 + B_1 + 2B_2$	6	0	2	4

which is the same as the original. Therefore the representation is $3A_1 + B_1 + 2B_2$.

P12.6

Representation 1

$$D(C_3)D(C_2) = 1 \times 1 = 1 = D(C_6)$$

and from the character table is either A_1 or A_2 . Hence, either $D(\sigma_v) = D(\sigma_d) = \boxed{+1 \text{ or } -1}$ respectively.

Representation 2

$$D(C_3)D(C_2) = 1 \times (-1) = -1 = D(C_6)$$

and from the character table is either B_1 or B_2 . Hence, either $D(\sigma_v) = -D(\sigma_d) = \boxed{1}$ or $D(\sigma_v) = -D(\sigma_d) = \boxed{-1}$ respectively.

- P12.8** 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, $(\dots -f \dots) \leftarrow (\dots f \dots)$; 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 $A_1 + T_2$. 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 s and p orbitals of the C atom may form molecular orbitals with the four H 1s 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 (d_{xy}, d_{yz}, d_{zx}) may contribute to molecular orbital formation with the H orbitals.

- P12.10** The most distinctive symmetry operation is the S_4 axis through the central atom and aromatic nitrogens on both ligands. That axis is also a C_2 axis. The group is S_4 .

- P12.12**
- (a) Working through the flow diagram (Figure 12.7) in the text, we note that there are no C_n axes with $n > 2$ (for the C_3 axes present in a tetrahedron are not symmetry axes any longer), but it does have C_2 axes; in fact it has 2 C_2 axes perpendicular to whichever C_2 we call principal; it has no σ_h , but it has 2 σ_d . So the point group is D_{2d} .
 - (b) Within this point group, the distortion belongs to the fully symmetric species A_1 for its motion is unchanged by the S_4 operation, either class of C_2 , or σ_d .
 - (c) The resulting structure is a square bipyramid, but with one pyramid's apex farther from the base than the other's. Working through the flow diagram in Figure 12.7, we note that there is only one C_n axis with $n > 2$, namely a C_4 axis; it has no C_2 axes perpendicular to the C_4 , and it has no σ_h , but it has $4\sigma_v$. So the point group is C_{4v} .
 - (d) Within this point group, the distortion belongs to the fully symmetric species 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.

- P12.14**
- (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 must be zero
 - (b) xyz spans A_1 in T_d [Problem 12.13] and so its integral need not be zero
 - (c) $xyz \rightarrow -xyz$ under $z \rightarrow -z$ (the σ_h operation in D_{6h}), and so its integral must be zero

P12.16 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

$$a_1 = \frac{1}{\sqrt{6}}(\pi_1 + \pi_2 + \pi_3 + \pi_4 + \pi_5 + \pi_6)$$

$$b_1 = \frac{1}{\sqrt{6}}(\pi_1 - \pi_2 + \pi_3 - \pi_4 + \pi_5 - \pi_6)$$

$$e_2 = \begin{cases} \frac{1}{\sqrt{12}}(2\pi_1 - \pi_2 - \pi_3 + 2\pi_4 - \pi_5 - \pi_6) \\ \frac{1}{2}(\pi_2 - \pi_3 + \pi_5 - \pi_6) \end{cases}$$

$$e_1 = \begin{cases} \frac{1}{\sqrt{12}}(2\pi_1 + \pi_2 - \pi_3 - 2\pi_4 - \pi_5 + \pi_6) \\ \frac{1}{2}(\pi_2 + \pi_3 - \pi_5 - \pi_6) \end{cases}$$

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

$$A_1: \quad H_{a_1 a_1} = \frac{1}{6} \int (\pi_1 + \dots + \pi_6) H (\pi_1 + \dots + \pi_6) \, d\tau = \alpha + 2\beta$$

$$B_1: \quad H_{b_1 b_1} = \frac{1}{6} \int (\pi_1 - \pi_2 + \dots) H (\pi_1 - \pi_2 + \dots) \, d\tau = \alpha - 2\beta$$

$$E_1: \quad H_{e_1(a)e_1(a)} = \alpha - \beta, \quad H_{e_1(b)e_1(b)} = \alpha - \beta, \quad H_{e_1(a)e_1(b)} = 0$$

$$\text{Hence } \begin{vmatrix} \alpha - \beta - \varepsilon & 0 \\ 0 & \alpha - \beta - \varepsilon \end{vmatrix} = 0 \text{ solves to } \varepsilon = \alpha - \beta \text{ (twice)}$$

$$E_2: \quad H_{e_2(a)e_2(a)} = \alpha + \beta, \quad H_{e_2(b)e_2(b)} = \alpha + \beta, \quad H_{e_2(a)e_2(b)} = 0$$

$$\text{Hence } \begin{vmatrix} \alpha + \beta - \varepsilon & 0 \\ 0 & \alpha + \beta - \varepsilon \end{vmatrix} = 0 \text{ solves to } \varepsilon = \alpha + \beta \text{ (twice)}$$

- P12.18** (a) For a photon to induce a spectroscopic transition, the transition moment (μ) must be nonzero. The transition moment is the integral $\int \psi_f^* \mu \psi_i \, d\tau$, where the dipole moment operator has components proportional to the Cartesian coordinates. The integral vanishes unless the integrand, or at least some part of it, belongs to the totally symmetric representation of the molecule's point group. We can answer the first part of the question without reference to the character table, by considering the character of the integrand under inversion. Each component of μ has *u* character, but each state has *g* character; the integrand is $g \times g \times u = u$, so the integral vanishes and the transition is not allowed.
- (b) However, if a vibration breaks the inversion symmetry, a look at the *I* character table shows that the components of μ have T_1 character. To find the character of the integrand, we multiply together the characters of its factors. For the transition to T_1

	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$
A_1	1	1	1	1	1
$\mu(T_1)$	3	$\frac{1}{2}(1 + \sqrt{5})$	$\frac{1}{2}(1 - \sqrt{5})$	0	-1
T_1	3	$\frac{1}{2}(1 + \sqrt{5})$	$\frac{1}{2}(1 - \sqrt{5})$	0	-1
Integrand	9	$\frac{1}{2}(3 + \sqrt{5})$	$\frac{1}{2}(3 - \sqrt{5})$	0	1

The decomposition of the characters of the integrand into those of the irreducible representations is difficult to do by inspection, but when accomplished it is seen to contain A_1 . Therefore the transition to T_1 would become allowed. It is easier to use the formula below which is obtained from what is referred to as the "little orthogonality theorem" of group theory. (See the *Justification* in Section 15.5 of the 5th edition of this text.) The coefficient of A_1 in the integrand is given as

$$c_{A_1} = \frac{1}{h} \sum_C g(C) \chi(C) = \frac{\left\{ 9 + 12 \left[\frac{1}{2}(3 + \sqrt{5}) \right] + 12 \left[\frac{1}{2}(3 - \sqrt{5}) \right] + 20(0) + 15(1) \right\}}{60} = 1$$

So the integrand contains A_1 , and the transition to T_1 would become allowed. For the transition to G

	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$
A_1	1	1	1	1	1
$\mu(T_1)$	3	$\frac{1}{2}(1 + \sqrt{5})$	$\frac{1}{2}(1 - \sqrt{5})$	0	-1
G	4	-1	-1	1	0
Integrand	12	$-\frac{1}{2}(1 + \sqrt{5})$	$-\frac{1}{2}(1 - \sqrt{5})$	0	0

The little orthogonality theorem gives the coefficient of A_1 in the integrand as

$$c_{A_1} = \frac{1}{h} \sum_C g(C) \chi(C) = \frac{\left\{ 12 + 12 \left[-\frac{1}{2}(1 + \sqrt{5}) \right] + 12 \left[-\frac{1}{2}(1 - \sqrt{5}) \right] + 20(0) + 15(0) \right\}}{60} = 0$$

So the integrand does not contain A_1 , and the transition to G would still be forbidden.

Solutions to applications

- P12.20** The point group for the square H_4 molecule is D_{4h} with $h = 16$ symmetry species. To find the irreducible representations or symmetry species spanned by four s orbitals, we use the methodology of Section 12.5c.

D_{4h}	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Number of unchanged basis members	4	0	0	2	0	0	0	4	2	0

The basis representation is obviously a linear combination of the D_{4h} symmetry species; it is reducible. Only the E , $2C'_2$, σ_h and $2\sigma_v$ symmetry elements contribute (The others have factors of zero) to the number of times symmetry species Γ contributes ($a(\Gamma)$) to the representation of the basis.

	E	$2C'_2$	σ_h	$2\sigma_v$	
$a(A_{1g}) = \frac{1}{16}\{4 \cdot 1 \cdot 1 + 2 \cdot 2 \cdot 1 + 4 \cdot 1 \cdot 1 + 2 \cdot 2 \cdot 1\}$					$= 1$
$a(A_{2g}) = \frac{1}{16}\{4 \cdot 1 \cdot 1 + 2 \cdot 2 \cdot (-1) + 4 \cdot 1 \cdot 1 + 2 \cdot 2 \cdot (-1)\}$					$= 0$
$a(B_{1g}) = \frac{1}{16}\{4 \cdot 1 \cdot 1 + 2 \cdot 2 \cdot 1 + 4 \cdot 1 \cdot 1 + 2 \cdot 2 \cdot 1\}$					$= 1$
$a(B_{2g}) = \frac{1}{16}\{4 \cdot 1 \cdot 1 + 2 \cdot 2 \cdot (-1) + 4 \cdot 1 \cdot 1 + 2 \cdot 2 \cdot (-1)\}$					$= 0$
$a(E_g) = \frac{1}{16}\{4 \cdot 1 \cdot 2 + 2 \cdot 2 \cdot 0 + 4 \cdot 1 \cdot (-2) + 2 \cdot 2 \cdot 0\}$					$= 0$
$a(A_{1u}) = \frac{1}{16}\{4 \cdot 1 \cdot 1 + 2 \cdot 2 \cdot 1 + 4 \cdot 1 \cdot (-1) + 2 \cdot 2 \cdot (-1)\}$					$= 0$
$a(A_{2u}) = \frac{1}{16}\{4 \cdot 1 \cdot 1 + 2 \cdot 2 \cdot (-1) + 4 \cdot 1 \cdot (-1) + 2 \cdot 2 \cdot 1\}$					$= 0$
$a(B_{1u}) = \frac{1}{16}\{4 \cdot 1 \cdot 1 + 2 \cdot 2 \cdot 1 + 4 \cdot 1 \cdot (-1) + 2 \cdot 2 \cdot (-1)\}$					$= 0$
$a(B_{2u}) = \frac{1}{16}\{4 \cdot 1 \cdot 1 + 2 \cdot 2 \cdot (-1) + 4 \cdot 1 \cdot (-1) + 2 \cdot 2 \cdot 1\}$					$= 0$
$a(E_u) = \frac{1}{16}\{4 \cdot 1 \cdot 2 + 2 \cdot 2 \cdot 0 + 4 \cdot 1 \cdot 2 + 2 \cdot 2 \cdot 0\}$					$= 1$

The basis spans $A_{1g} + B_{1g} + E_u$.

P12.22 Can the E_u excited state be reached by a dipole transition from the A_{1g} ground state? Only if the representation of the product $\psi_f^* \mu \psi_i$ includes the totally symmetric species A_{1g} . The z component of the dipole operator belongs to symmetry species A_{2u} , and the x and y components belong to E_u . So

the products we must consider are $E_u A_{2u} A_{1g}$ and $E_u E_u A_{1g}$. For z -polarized transitions, the relevant characters are:

	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
E_u	2	0	-2	0	0	-2	0	2	0	0
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
A_{1g}	1	1	1	1	1	1	1	1	1	1
$E_u A_{2u} A_{1g}$	2	0	-2	0	0	2	0	-2	0	0

To see whether $E_u A_{2u} A_{1g}$ contains A_{1g} , we would multiply the characters of the $E_u A_{2u} A_{1g}$ by the characters of A_{1g} , sum those products, and divide the sum by the order h of the group; since the characters of A_{1g} are all 1, we can simply sum the characters of $E_u A_{2u} A_{1g}$. Since they sum to zero, the product $E_u A_{2u} A_{1g}$ does not contain A_{1g} , and the z -polarized transition is not allowed.

For x - or y -polarized transitions:

	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
E_u	2	0	-2	0	0	-2	0	2	0	0
E_u	2	0	-2	0	0	-2	0	2	0	0
A_{1g}	1	1	1	1	1	1	1	1	1	1
$E_u E_u A_{1g}$	4	0	4	0	0	4	0	4	0	0

Summing the characters of $E_u E_u A_{1g}$, yields 16, the order of the group. Therefore the product $E_u E_u A_{1g}$ does contain A_{1g} , and the transition is allowed.

13

Spectroscopy 1: rotational and vibrational spectroscopy

Answers to discussion questions

D13.2 The gross selection rules tell us which are the allowed spectroscopic transitions. For both microwave and infrared spectroscopy, the allowed transitions depend on the existence of an oscillating dipole moment which can stir the electromagnetic field into oscillation (and *vice versa* for absorption). For microwave rotational spectroscopy, this implies that the molecule must have a permanent dipole moment, which is equivalent to an oscillating dipole when the molecule is rotating. See Figure 13.17 of the text. In the case of infrared vibrational spectroscopy, the physical basis of the gross selection rule is that the molecule have a structure that allows for the existence of an oscillating dipole moment when the molecule vibrates. Polar molecules necessarily satisfy this requirement, but non-polar molecules may also have a fluctuating dipole moment upon vibration. See Figure 13.28.

D13.4 The answer to this question depends precisely on what is meant by equilibrium bond length. See the solution to Problem 13.22 where it is demonstrated that the centrifugally distorted bond length r_c is given by the relation

$$r_c = \frac{r_e}{1 - m_e r_e^2 \omega^2 / k}.$$

The angular velocity depends upon the quantum number J through the relation

$$\omega^2 = J(J+1)\hbar^2 / m_e r_e^4;$$

thus, the distortion is greater for higher rotational energy levels. But the equilibrium bond length r_e remains constant, if by that term one means the value of r corresponding to a vibrating non-rotating molecule with $J = 0$. However, if one describes the vibration of the molecule in a higher rotational state as having a new “equilibrium” distance r_c , the potential energy of vibration will also be different. It is lowered by the amount shown in eqn 13.33, that is, $-D_J J^2(J+1)^2$. A detailed analysis of the combined effects of rotation and vibration is quite complicated. The treatment in Section 13.12 ignores the effects of centrifugal distortion and anharmonicity. See the references under *Further Reading* for a more thorough discussion.

Solutions to exercises

E13.1(b) The ratio of coefficients A/B is

$$(a) \quad \frac{A}{B} = \frac{8\pi h\nu^3}{c^3} = \frac{8\pi(6.626 \times 10^{-34} \text{ J s}) \times (500 \times 10^6 \text{ s}^{-1})^3}{(2.998 \times 10^8 \text{ m s}^{-1})^3} = \boxed{7.73 \times 10^{-32} \text{ J m}^{-3} \text{ s}}$$

(b) The frequency is

$$\nu = \frac{c}{\lambda} \text{ so } \frac{A}{B} = \frac{8\pi h}{\lambda^3} = \frac{8\pi(6.626 \times 10^{-34} \text{ J s})}{(3.0 \times 10^{-2} \text{ m})^3} = \boxed{6.2 \times 10^{-28} \text{ J m}^{-3} \text{ s}}$$

E13.2(b) A source approaching an observer appears to be emitting light of frequency

$$\nu_{\text{approaching}} = \frac{\nu}{1 - \frac{s}{c}} \quad [13.15, \text{Section 13.3}]$$

$$\text{Since } \nu \propto \frac{1}{\lambda}, \lambda_{\text{obs}} = (1 - s/c) \lambda$$

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

$$\nu_{\text{obs}} = \left(\frac{1 + (s/c)}{1 - (s/c)}\right)^{1/2} \nu$$

should really be used. It gives $s = 7.02 \times 10^7 \text{ m s}^{-1}$.)**E13.3(b)** The linewidth is related to the lifetime τ by

$$\delta\bar{\nu} = \frac{5.31 \text{ cm}^{-1}}{\tau/\text{ps}} \quad [13.19] \text{ so } \tau = \frac{5.31 \text{ cm}^{-1}}{\delta\bar{\nu}} \text{ ps}$$

(a) We are given a frequency rather than a wavenumber

$$\bar{\nu} = \nu/c \text{ so } \tau = \frac{(5.31 \text{ cm}^{-1}) \times (2.998 \times 10^{10} \text{ cm s}^{-1})}{100 \times 10^6 \text{ s}^{-1}} \text{ ps} = 1.59 \times 10^3 \text{ ps}$$

$$\text{or } \boxed{1.59 \text{ ns}}$$

$$(b) \tau = \frac{5.31 \text{ cm}^{-1}}{2.14 \text{ cm}^{-1}} \text{ ps} = \boxed{2.48 \text{ ps}}$$

E13.4(b) The linewidth is related to the lifetime τ by

$$\delta\bar{\nu} = \frac{5.31 \text{ cm}^{-1}}{\tau/\text{ps}} \text{ so } \delta\nu = \frac{(5.31 \text{ cm}^{-1})c}{\tau/\text{ps}}$$

(a) If every collision is effective, then the lifetime is $1/(1.0 \times 10^9 \text{ s}^{-1}) = 1.0 \times 10^{-9} \text{ s} = 1.0 \times 10^3 \text{ ps}$

$$\delta\bar{\nu} = \frac{(5.31 \text{ cm}^{-1}) \times (2.998 \times 10^{10} \text{ cm s}^{-1})}{1.0 \times 10^3} = 1.6 \times 10^8 \text{ s}^{-1} = \boxed{160 \text{ MHz}}$$

(b) If only one collision in 10 is effective, then the lifetime is a factor of 10 greater, 1.0×10^4 ps

$$\delta\tilde{\nu} = \frac{(5.31 \text{ cm}^{-1}) \times (2.998 \times 10^{10} \text{ cm s}^{-1})}{1.0 \times 10^4} = 1.6 \times 10^7 \text{ s}^{-1} = \boxed{16 \text{ MHz}}$$

E13.5(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

$$B = \frac{h}{4\pi cI} = \frac{h}{4\pi m_{\text{eff}}R^2}$$

where I is moment of inertia, m_{eff} is effective mass, and R is the bond length. Putting these expressions together yields

$$\nu = 2cBJ = \frac{hJ}{2\pi m_{\text{eff}}R^2}$$

The reciprocal of the effective mass is

$$m_{\text{eff}}^{-1} = m_{\text{C}}^{-1} + m_{\text{O}}^{-1} = \frac{(12 \text{ u})^{-1} + (15.9949 \text{ u})^{-1}}{1.66054 \times 10^{-27} \text{ kg u}^{-1}} = 8.78348 \times 10^{25} \text{ kg}^{-1}$$

$$\text{So } \nu = \frac{(8.78348 \times 10^{25} \text{ kg}^{-1}) \times (1.0546 \times 10^{-34} \text{ J s}) \times (3)}{2\pi (112.81 \times 10^{-12} \text{ m})^2} = \boxed{3.4754 \times 10^{11} \text{ s}^{-1}}$$

E13.6(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

$$B = \frac{h}{4\pi cI}$$

where I is moment of inertia. Putting these expressions together yields

$$\tilde{\nu} = 2BJ = \frac{hJ}{2\pi cI} \text{ so } I = \frac{hJ}{c\tilde{\nu}} = \frac{(1.0546 \times 10^{-34} \text{ J s}) \times (1)}{2\pi (2.998 \times 10^{10} \text{ cm s}^{-1}) \times (16.93 \text{ cm}^{-1})}$$

$$I = \boxed{3.307 \times 10^{-47} \text{ kg m}^2}$$

(b) The moment of inertia is related to the bond length by

$$I = m_{\text{eff}}R^2 \text{ so } R = \left(\frac{I}{m_{\text{eff}}}\right)^{1/2}$$

$$m_{\text{eff}}^{-1} = m_{\text{H}}^{-1} + m_{\text{Br}}^{-1} = \frac{(1.0078 \text{ u})^{-1} + (80.9163 \text{ u})^{-1}}{1.66054 \times 10^{-27} \text{ kg u}^{-1}} = 6.0494 \times 10^{26} \text{ kg}^{-1}$$

$$\text{and } R = \{(6.0494 \times 10^{26} \text{ kg}^{-1}) \times (3.307 \times 10^{-47} \text{ kg m}^2)\}^{1/2}$$

$$= 1.414 \times 10^{-10} \text{ m} = \boxed{141.4 \text{ pm}}$$

E13.7(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

$$\Delta\tilde{\nu} = 2B = \frac{h}{2\pi cI} \text{ so } I = \frac{h}{2\pi c\Delta\tilde{\nu}}$$

where I is moment of inertia, m_{eff} is effective mass, and R is the bond length.

$$\text{So } I = \frac{(1.0546 \times 10^{-34} \text{ J s})}{2\pi(2.9979 \times 10^{10} \text{ cm s}^{-1}) \times (1.033 \text{ cm}^{-1})} = \boxed{5.420 \times 10^{-46} \text{ kg m}^2}$$

The moment of inertia is related to the bond length by

$$I = m_{\text{eff}}R^2 \text{ so } R = \left(\frac{I}{m_{\text{eff}}}\right)^{1/2}$$

$$m_{\text{eff}}^{-1} = m_{\text{F}}^{-1} + m_{\text{Cl}}^{-1} = \frac{(18.9984 \text{ u})^{-1} + (34.9688 \text{ u})^{-1}}{1.66054 \times 10^{-27} \text{ kg u}^{-1}} = 4.89196 \times 10^{25} \text{ kg}^{-1}$$

$$\text{and } R = \{(4.89196 \times 10^{25} \text{ kg}^{-1}) \times (5.420 \times 10^{-46} \text{ kg m}^2)\}^{1/2}$$

$$= 1.628 \times 10^{-10} \text{ m} = \boxed{162.8 \text{ pm}}$$

E13.8(b) The rotational constant is

$$B = \frac{h}{4\pi cI} = \frac{h}{4\pi c(2m_{\text{O}}R^2)} \text{ so } R = \left(\frac{h}{8\pi cm_{\text{O}}B}\right)^{1/2}$$

where I is moment of inertia, m_{eff} is effective mass, and R is the bond length.

$$R = \left(\frac{(1.0546 \times 10^{-34} \text{ J s})}{8\pi(2.9979 \times 10^{10} \text{ cm s}^{-1}) \times (15.9949 \text{ u}) \times (1.66054 \times 10^{-27} \text{ kg u}^{-1})(0.39021)}\right)^{1/2}$$

$$= 1.1621 \times 10^{-10} \text{ m} = \boxed{116.21 \text{ pm}}$$

E13.9(b) This exercise is analogous to Exercise 13.9(a), but here our solution will employ a slightly different algebraic technique. Let $R = R_{\text{OC}}$, $R' = R_{\text{CS}}$, $\text{O} = {}^{16}\text{O}$, $\text{C} = {}^{12}\text{C}$.

$$I = \frac{h}{4\pi B} \text{ [Comment 13.4]}$$

$$I(\text{OC}^{32}\text{S}) = \frac{1.05457 \times 10^{-34} \text{ J s}}{(4\pi) \times (6.0815 \times 10^9 \text{ s}^{-1})} = 1.3799 \times 10^{-45} \text{ kg m}^2 = 8.3101 \times 10^{-19} \text{ u m}^2$$

$$I(\text{OC}^{34}\text{S}) = \frac{1.05457 \times 10^{-34} \text{ J s}}{(4\pi) \times (5.9328 \times 10^9 \text{ s}^{-1})} = 1.4145 \times 10^{-45} \text{ kg m}^2 = 8.5184 \times 10^{-19} \text{ u m}^2$$

The expression for the moment of inertia given in Table 13.1 may be rearranged as follows.

$$\begin{aligned} Im &= m_A m R^2 + m_C m R'^2 - (m_A R - m_C R')^2 \\ &= m_A m R^2 + m_C m R'^2 - m_A^2 R^2 + 2m_A m_C R R' - m_C^2 R'^2 \\ &= m_A (m_B + m_C) R^2 + m_C (m_A + m_B) R'^2 + 2m_A m_C R R' \end{aligned}$$

Let $m_C = m_{32s}$ and $m'_C = m_{34s}$

$$\frac{Im}{m_C} = \frac{m_A}{m_C} (m_B + m_C) R^2 + (m_A + m_B) R'^2 + 2m_A R R' \quad (a)$$

$$\frac{I'm'}{m'_C} = \frac{m_A}{m'_C} (m_B + m'_C) R^2 + (m_A + m_B) R'^2 + 2m_A R R' \quad (b)$$

Subtracting

$$\frac{Im}{m_C} - \frac{I'm'}{m'_C} = \left[\left(\frac{m_A}{m_C} \right) (m_B + m_C) - \left(\frac{m_A}{m'_C} \right) (m_B + m'_C) \right] R^2$$

Solving for R^2

$$R^2 = \frac{\left(\frac{Im}{m_C} - \frac{I'm'}{m'_C} \right)}{\left[\left(\frac{m_A}{m_C} \right) (m_B + m_C) - \left(\frac{m_A}{m'_C} \right) (m_B + m'_C) \right]} = \frac{m'_C Im - m_C I'm'}{m_B m_A (m'_C - m_C)}$$

Substituting the masses, with $m_A = m_O$, $m_B = m_C$, $m_C = m_{32s}$, and $m'_C = m_{34s}$

$$m = (15.9949 + 12.0000 + 31.9721) \text{ u} = 59.9670 \text{ u}$$

$$m' = (15.9949 + 12.0000 + 33.9679) \text{ u} = 61.9628 \text{ u}$$

$$\begin{aligned} R^2 &= \frac{(33.9679 \text{ u}) \times (8.3101 \times 10^{-19} \text{ u m}^2) \times (59.9670 \text{ u})}{(12.0000 \text{ u}) \times (15.9949 \text{ u}) \times (33.9679 \text{ u} - 31.9721 \text{ u})} \\ &\quad - \frac{(31.9721 \text{ u}) \times (8.5184 \times 10^{-19} \text{ u m}^2) \times (61.9628 \text{ u})}{(12.0000 \text{ u}) \times (15.9949 \text{ u}) \times (33.9679 \text{ u} - 31.9721 \text{ u})} \\ &= \frac{51.6446 \times 10^{-19} \text{ m}^2}{383.071} = 1.3482 \times 10^{-20} \text{ m}^2 \end{aligned}$$

$$R = 1.161 \bar{1} \times 10^{-10} \text{ m} = \boxed{116.1 \text{ pm}} = R_{OC}$$

Because the numerator of the expression for R^2 involves the difference between two rather large numbers of nearly the same magnitude, the number of significant figures in the answer for R is certainly no greater than 4. Having solved for R , either equation (a) or (b) above can be solved for R' . The result is

$$R' = 1.559 \times 10^{-10} \text{ m} = \boxed{155.9 \text{ pm}} = R_{CS}$$

E13.10(b) The wavenumber of a Stokes line in rotational Raman is

$$\tilde{\nu}_{\text{Stokes}} = \tilde{\nu}_i - 2B(2J + 3) \quad [13.42a]$$

where J is the initial (lower) rotational state. So

$$\tilde{\nu}_{\text{Stokes}} = 20\,623 \text{ cm}^{-1} - 2(1.4457 \text{ cm}^{-1}) \times [2(2) + 3] = \boxed{20\,603 \text{ cm}^{-1}}$$

E13.11(b) The separation of lines is $4B$, so $B = \frac{1}{4} \times (3.5312 \text{ cm}^{-1}) = 0.88280 \text{ cm}^{-1}$

Then we use $R = \left(\frac{\hbar}{4\pi m_{\text{eff}} c B} \right)^{1/2}$ [Exercise 13.8(a)]

with $m_{\text{eff}} = \frac{1}{2} m(^{19}\text{F}) = \frac{1}{2} \times (18.9984 \text{ u}) \times (1.6605 \times 10^{-27} \text{ kg u}^{-1}) = 1.577342 \times 10^{-26} \text{ kg}$

$$R = \left(\frac{1.0546 \times 10^{-34} \text{ J s}}{4\pi (1.577342 \times 10^{-26} \text{ kg}) \times (2.998 \times 10^{10} \text{ cm s}^{-1}) \times (0.88280 \text{ cm}^{-1})} \right)^{1/2}$$

$$= 1.41785 \times 10^{-10} \text{ m} = \boxed{141.78 \text{ pm}}$$

E13.12(b) Polar molecules show a pure rotational absorption spectrum. Therefore, select the polar molecules based on their well-known structures. Alternatively, determine the point groups of the molecules and use the rule that only molecules belonging to C_n , C_{nv} , and C_s may be polar, and in the case of C_n and C_{nv} , that dipole must lie along the rotation axis. Hence all are polar molecules.

Their point group symmetries are

(a) H_2O , C_{2v} , (b) H_2O_2 , C_2 , (c) NH_3 , C_{3v} , (d) N_2O , $C_{\infty v}$

All show a pure rotational spectrum.

E13.13(b) A molecule must be anisotropically polarizable to show a rotational Raman spectrum; all molecules except spherical rotors have this property. So CH_2Cl_2 , CH_3CH_3 , and N_2O can display rotational Raman spectra; SF_6 cannot.

E13.14(b) The angular frequency is

$$\omega = \left(\frac{k}{m} \right)^{1/2} = 2\pi\nu \quad \text{so} \quad k = (2\pi\nu)^2 m = (2\pi)^2 \times (3.0 \text{ s}^{-1})^2 \times (2.0 \times 10^{-3} \text{ kg})$$

$$k = \boxed{0.71 \text{ N m}^{-1}}$$

E13.15(b) $\omega = \left(\frac{k}{m_{\text{eff}}} \right)^{1/2}$ $\omega' = \left(\frac{k}{m'_{\text{eff}}} \right)^{1/2}$ [prime = $^2\text{H}^{37}\text{Cl}$]

The force constant, k , is assumed to be the same for both molecules. The fractional difference is

$$\frac{\omega' - \omega}{\omega} = \frac{\left(\frac{k}{m'_{\text{eff}}} \right)^{1/2} - \left(\frac{k}{m_{\text{eff}}} \right)^{1/2}}{\left(\frac{k}{m_{\text{eff}}} \right)^{1/2}} = \frac{\left(\frac{1}{m'_{\text{eff}}} \right)^{1/2} - \left(\frac{1}{m_{\text{eff}}} \right)^{1/2}}{\left(\frac{1}{m_{\text{eff}}} \right)^{1/2}} = \left(\frac{m_{\text{eff}}}{m'_{\text{eff}}} \right)^{1/2} - 1$$

$$\frac{\omega' - \omega}{\omega} = \left(\frac{m_{\text{eff}}}{m'_{\text{eff}}} \right)^{1/2} - 1 = \left\{ \frac{m_{\text{H}} m_{\text{Cl}}}{m_{\text{H}} + m_{\text{Cl}}} \times \frac{(m_{2\text{H}} + m_{37\text{Cl}})}{(m_{2\text{H}} \times m_{37\text{Cl}})} \right\}^{1/2} - 1$$

$$= \left\{ \frac{(1.0078 \text{ u}) \times (34.9688 \text{ u})}{(1.0078 \text{ u}) + (34.9688 \text{ u})} \times \frac{(2.0140 \text{ u}) + (36.9651 \text{ u})}{(2.0140 \text{ u}) \times (36.9651 \text{ u})} \right\}^{1/2} - 1$$

$$= -0.284$$

Thus the difference is 28.4 percent

E13.16(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

$$\begin{aligned} m_{\text{eff}}^{-1} &= m_1^{-1} + m_2^{-1} = (78.9183 \text{ u})^{-1} + (80.9163 \text{ u})^{-1} = 0.025\,029\,8 \text{ u}^{-1} \\ k &= \frac{[2\pi(2.998 \times 10^{10} \text{ cm s}^{-1}) \times (323.2 \text{ cm}^{-1})]^2 \times (1.66054 \times 10^{-27} \text{ kg u}^{-1})}{0.025\,029\,8 \text{ u}^{-1}} \\ &= \boxed{245.9 \text{ N m}^{-1}} \end{aligned}$$

E13.17(b) The ratio of the population of the ground state (N_0) to the first excited state (N_1) is

$$\frac{N_0}{N_1} = \exp\left(\frac{-h\nu}{kT}\right) = \exp\left(\frac{-hc\tilde{\nu}}{kT}\right)$$

$$\text{(a)} \quad \frac{N_0}{N_1} = \exp\left(\frac{-(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^{10} \text{ cm s}^{-1}) \times (321 \text{ cm}^{-1})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}\right) = \boxed{0.212}$$

$$\text{(b)} \quad \frac{N_0}{N_1} = \exp\left(\frac{-(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^{10} \text{ cm s}^{-1}) \times (321 \text{ cm}^{-1})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (800 \text{ K})}\right) = \boxed{0.561}$$

E13.18(b) The relation between vibrational frequency and wavenumber is

$$\omega = \left(\frac{k}{m_{\text{eff}}} \right)^{1/2} = 2\pi\nu = 2\pi c\tilde{\nu} \quad \text{so} \quad \tilde{\nu} = \frac{1}{2\pi c} \left(\frac{k}{m_{\text{eff}}} \right)^{1/2} = \frac{(km_{\text{eff}}^{-1})^{1/2}}{2\pi c}$$

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 13.18(a) are identical for the deuterium halide and the hydrogen halide.

For DF

$$\begin{aligned} m_{\text{eff}}^{-1} &= \frac{(2.0140 \text{ u})^{-1} + (18.9984 \text{ u})^{-1}}{1.66054 \times 10^{-27} \text{ kg u}^{-1}} = 3.3071 \times 10^{26} \text{ kg}^{-1} \\ \tilde{\nu} &= \frac{\{(3.3071 \times 10^{26} \text{ kg}^{-1}) \times (967.04 \text{ kg s}^{-2})\}^{1/2}}{2\pi(2.9979 \times 10^{10} \text{ cm s}^{-1})} = \boxed{3002.3 \text{ cm}^{-1}} \end{aligned}$$

For DCI

$$\begin{aligned} m_{\text{eff}}^{-1} &= \frac{(2.0140 \text{ u})^{-1} + (34.9688 \text{ u})^{-1}}{1.66054 \times 10^{-27} \text{ kg u}^{-1}} = 3.1624 \times 10^{26} \text{ kg}^{-1} \\ \tilde{\nu} &= \frac{\{(3.1624 \times 10^{26} \text{ kg}^{-1}) \times (515.59 \text{ kg s}^{-2})\}^{1/2}}{2\pi(2.9979 \times 10^{10} \text{ cm s}^{-1})} = \boxed{2143.7 \text{ cm}^{-1}} \end{aligned}$$

For DBr

$$m_{\text{eff}}^{-1} = \frac{(2.0140 \text{ u})^{-1} + (80.9163 \text{ u})^{-1}}{1.66054 \times 10^{-27} \text{ kg u}^{-1}} = 3.0646 \times 10^{26} \text{ kg}^{-1}$$

$$\tilde{\nu} = \frac{\{(3.0646 \times 10^{26} \text{ kg}^{-1}) \times (411.75 \text{ kg s}^{-2})\}^{1/2}}{2\pi(2.9979 \times 10^{10} \text{ cm s}^{-1})} = \boxed{1885.8 \text{ cm}^{-1}}$$

For DI

$$m_{\text{eff}}^{-1} = \frac{(2.0140 \text{ u})^{-1} + (126.9045 \text{ u})^{-1}}{1.66054 \times 10^{-27} \text{ kg u}^{-1}} = 3.0376 \times 10^{26} \text{ kg}^{-1}$$

$$\tilde{\nu} = \frac{\{(3.0376 \times 10^{26} \text{ kg}^{-1}) \times (314.21 \text{ kg s}^{-2})\}^{1/2}}{2\pi(2.9979 \times 10^{10} \text{ cm s}^{-1})} = \boxed{1640.1 \text{ cm}^{-1}}$$

E13.19(b) Data on three transitions are provided. Only two are necessary to obtain the value of $\tilde{\nu}$ and x_e . The third datum can then be used to check the accuracy of the calculated values.

$$\Delta G(\nu = 1 \leftarrow 0) = \tilde{\nu} - 2\tilde{\nu}x_e = 2345.15 \text{ cm}^{-1} \quad [13.57]$$

$$\Delta G(\nu = 2 \leftarrow 0) = 2\tilde{\nu} - 6\tilde{\nu}x_e = 4661.40 \text{ cm}^{-1} \quad [13.58]$$

Multiply the first equation by 3, then subtract the second.

$$\tilde{\nu} = (3) \times (2345.15 \text{ cm}^{-1}) - (4661.40 \text{ cm}^{-1}) = \boxed{2374.05 \text{ cm}^{-1}}$$

Then from the first equation

$$x_e = \frac{\tilde{\nu} - 2345.15 \text{ cm}^{-1}}{2\tilde{\nu}} = \frac{(2374.05 - 2345.15) \text{ cm}^{-1}}{(2) \times (2374.05 \text{ cm}^{-1})} = \boxed{6.087 \times 10^{-3}}$$

x_e data are usually reported as $x_e\tilde{\nu}$ which is

$$x_e\tilde{\nu} = 14.45 \text{ cm}^{-1}$$

$$\begin{aligned} \Delta G(\nu = 3 \leftarrow 0) &= 3\tilde{\nu} - 12\nu x_e = (3) \times (2374.05 \text{ cm}^{-1}) - (12) \times (14.45 \text{ cm}^{-1}) \\ &= 6948.74 \text{ cm}^{-1} \end{aligned}$$

which is close to the experimental value.

E13.20(b) $\Delta G_{\nu+1/2} = \tilde{\nu} - 2(\nu+1)x_e\tilde{\nu}$ [13.57] where $\Delta G_{\nu+1/2} = G(\nu+1) - G(\nu)$

Therefore, since

$$\Delta G_{\nu+1/2} = (1 - 2x_e)\tilde{\nu} - 2\nu x_e\tilde{\nu}$$

a plot of $\Delta G_{\nu+1/2}$ against ν should give a straight line which gives $(1 - 2x_e)\tilde{\nu}$ from the intercept at $\nu = 0$ and $-2x_e\tilde{\nu}$ from the slope. We draw up the following table

ν	0	1	2	3	4
$G(\nu)/\text{cm}^{-1}$	1144.83	3374.90	5525.51	7596.66	9588.35
$\Delta G_{\nu+1/2}/\text{cm}^{-1}$	2230.07	2150.61	2071.15	1991.69	

The points are plotted in Figure 13.1.

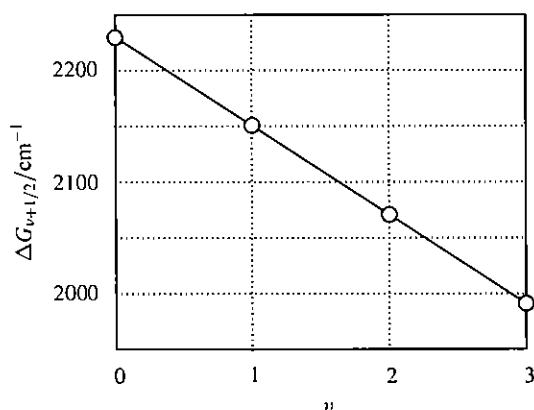


Figure 13.1

The intercept lies at 2230.51 and the slope = -76.65 cm^{-1} ; hence $x_e \tilde{\nu} = 39.83 \text{ cm}^{-1}$.

Since $\tilde{\nu} - 2x_e \tilde{\nu} = 2230.51 \text{ cm}^{-1}$ it follows that $\tilde{\nu} = 2310.16 \text{ cm}^{-1}$

The dissociation energy may be obtained by assuming that a Morse potential describes the molecule and that the constant D_e in the expression for the potential is an adequate first approximation for it. Then

$$D_e = \frac{\tilde{\nu}}{4x_e} [13.55] = \frac{\tilde{\nu}^2}{4x_e \tilde{\nu}} = \frac{(2310.16 \text{ cm}^{-1})^2}{(4) \times (39.83 \text{ cm}^{-1})} = 33.50 \times 10^3 \text{ cm}^{-1} = 4.15 \text{ eV}$$

However, the depth of the potential well D_e differs from D_0 , the dissociation energy of the bond, by the zero-point energy; hence

$$\begin{aligned} D_0 &= D_e - \frac{1}{2} \tilde{\nu} = (33.50 \times 10^3 \text{ cm}^{-1}) - \left(\frac{1}{2}\right) \times (2310.16 \text{ cm}^{-1}) \\ &= \boxed{3.235 \times 10^4 \text{ cm}^{-1}} = \boxed{4.01 \text{ eV}} \end{aligned}$$

E13.21(b) The wavenumber of an R-branch IR transition is

$$\tilde{\nu}_R = \tilde{\nu} + 2B(J+1) [13.62c]$$

where J is the initial (lower) rotational state. So

$$\tilde{\nu}_R = 2308.09 \text{ cm}^{-1} + 2(6.511 \text{ cm}^{-1}) \times (2+1) = \boxed{2347.16 \text{ cm}^{-1}}$$

- E13.22(b)** See Section 13.10. 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 ; (c) CH_3Cl

COMMENT. A more powerful method for determining infrared activity based on symmetry considerations is described in Section 13.15.

- E13.23(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) $\text{C}_6\text{H}_6\text{CH}_3$ has $3(16) - 6 = \boxed{42}$ normal modes.
 (c) $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$ is linear; it has $3(6) - 5 = \boxed{13}$ normal modes.

- E13.24(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

A''_2 and E' are IR active. We also see from the character table that E' and A'_1 correspond to the quadratic terms; hence A'_1 and E' 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 A_1 and E are IR active and that $A_1 + E$ are also Raman active. Thus all modes are observable in both the IR and the Raman spectra.

E13.25(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 **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 **Raman inactive**.

E13.26(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 **$A_{1g} + A_{2g} + E_{1u}$**

Solutions to problems

Solutions to numerical problems

P13.2

$$\begin{aligned}\frac{\delta\lambda}{\lambda} &= \frac{2}{c} \left(\frac{2kT \ln 2}{m} \right)^{1/2} \quad [13.17] \\ &= \left(\frac{2}{2.998 \times 10^8 \text{ m s}^{-1}} \right) \times \left(\frac{(2) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K}) \times (\ln 2)}{(m/u) \times (1.6605 \times 10^{-27} \text{ kg})} \right)^{1/2} \\ &= \frac{1.237 \times 10^{-5}}{(m/u)^{1/2}}\end{aligned}$$

(a) For $^1\text{H}^{35}\text{Cl}$, $m \approx 36 \text{ u}$, so $\frac{\delta\lambda}{\lambda} \approx \boxed{2.1 \times 10^{-6}}$

(b) For $^{127}\text{I}^{35}\text{Cl}$, $m \approx 162 \text{ u}$, so $\frac{\delta\lambda}{\lambda} \approx \boxed{9.7 \times 10^{-7}}$

For the second part of the problem, we also need

$$\frac{\delta\bar{\nu}}{\bar{\nu}} = \frac{\delta\nu}{\nu} = \frac{2}{c} \left(\frac{2kT \ln 2}{m} \right)^{1/2} \quad [13.17] = \frac{\delta\lambda}{\lambda} \quad \left[\frac{\delta\lambda}{\lambda} \ll 1 \right]$$

(a) For HCl , $\nu(\text{rotation}) \approx 2Bc \approx (2) \times (10.6 \text{ cm}^{-1}) \times (2.998 \times 10^{10} \text{ cm s}^{-1})$
 $\approx 6.4 \times 10^{11} \text{ s}^{-1}$ or $6.4 \times 10^{11} \text{ Hz}$

Therefore, $\delta\nu(\text{rotation}) \approx (2.1 \times 10^{-6}) \times (6.4 \times 10^{11} \text{ Hz}) = \boxed{1.3 \text{ MHz}}$

$\bar{\nu}(\text{vibration}) \approx 2991 \text{ cm}^{-1}$ [Table 13.2]; therefore

$\delta\bar{\nu}(\text{vibration}) \approx (2.1 \times 10^{-6}) \times (2991 \text{ cm}^{-1}) = \boxed{0.0063 \text{ cm}^{-1}}$

(b) For ICl , $\nu(\text{rotation}) \approx (2) \times (0.1142 \text{ cm}^{-1}) \times (2.998 \times 10^{10} \text{ cm s}^{-1}) \approx 6.8 \times 10^9 \text{ Hz}$

$\delta\nu(\text{rotation}) \approx (9.7 \times 10^{-7}) \times (6.8 \times 10^9 \text{ Hz}) = \boxed{6.6 \text{ kHz}}$

$\bar{\nu}(\text{vibration}) \approx 384 \text{ cm}^{-1}$

$\delta\bar{\nu}(\text{vibration}) \approx (9.7 \times 10^{-7}) \times (384 \text{ cm}^{-1}) \approx \boxed{0.0004 \text{ cm}^{-1}}$

COMMENT. ICl is a solid which melts at 27.2 °C and has a significant vapor pressure at 25 °C.

- P13.4** Rotational line separations are $2B$ (in wavenumber units), $2Bc$ (in frequency units), and $(2B)^{-1}$ in wavelength units. Hence the transitions are separated by $\boxed{596 \text{ GHz}}$, $\boxed{19.9 \text{ cm}^{-1}}$, and $\boxed{0.503 \text{ mm}}$. Ammonia is a symmetric rotor (section 13.4) and we know that

$$B = \frac{h}{4\pi c I_{\perp}} [13.30]$$

and from Table 13.1,

$$I_{\perp} = m_A R^2 (1 - \cos \theta) + \left(\frac{m_A m_B}{m} \right) R^2 (1 + 2 \cos \theta)$$

$m_A = 1.6735 \times 10^{-27} \text{ kg}$, $m_B = 2.3252 \times 10^{-26} \text{ kg}$, and $m = 2.8273 \times 10^{-26} \text{ kg}$ with $R = 101.4 \text{ pm}$ and $\theta = 106^{\circ}47'$, which gives

$$\begin{aligned} I_{\perp} &= (1.6735 \times 10^{-27} \text{ kg}) \times (101.4 \times 10^{-12} \text{ m})^2 \times (1 - \cos 106^{\circ}47') \\ &\quad + \left(\frac{(1.6735 \times 10^{-27}) \times (2.3252 \times 10^{-26} \text{ kg}^2)}{2.8273 \times 10^{-26} \text{ kg}} \right) \\ &\quad \times (101.4 \times 10^{-12} \text{ m})^2 \times (1 + 2 \cos 106^{\circ}47') \\ &= 2.8158 \times 10^{-47} \text{ kg m}^2 \end{aligned}$$

Therefore,

$$B = \frac{1.05457 \times 10^{-34} \text{ J s}}{(4\pi) \times (2.9979 \times 10^8 \text{ m s}^{-1}) \times (2.8158 \times 10^{-47} \text{ kg m}^2)} = 994.1 \text{ m}^{-1} = \boxed{9.941 \text{ cm}^{-1}}$$

which is in accord with the data.

- P13.6** Rotation about any axis perpendicular to the C_6 axis may be represented in its essentials by rotation of the pseudolinear molecule in Figure 13.2(a) about the x -axis in the figure.

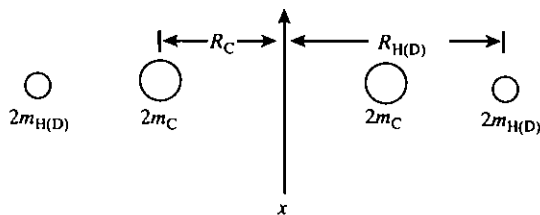


Figure 13.2(a)

The data allow for a determination of R_C and $R_{H(D)}$ which may be decomposed into R_{CC} and $R_{CH(D)}$.

$$I_H = 4m_H R_H^2 + 4m_C R_C^2 = 147.59 \times 10^{-47} \text{ kg m}^2$$

$$I_D = 4m_D R_D^2 + 4m_C R_C^2 = 178.45 \times 10^{-47} \text{ kg m}^2$$

Subtracting I_H from I_D (assume $R_H = R_D$) yields

$$4(m_D - m_H)R_H^2 = 30.86 \times 10^{-47} \text{ kg m}^2$$

$$4(2.01417 \text{ u} - 1.0078 \text{ u}) \times (1.66054 \times 10^{-27} \text{ kg u}^{-1}) \times (R_H^2) = 30.86 \times 10^{-47} \text{ kg m}^2$$

$$R_H^2 = 4.6169 \times 10^{-20} \text{ m}^2 \quad R_H = 2.149 \times 10^{-10} \text{ m}$$

$$\begin{aligned} R_C^2 &= \frac{(147.59 \times 10^{-47} \text{ kg m}^2) - (4m_H R_H^2)}{4m_C} \\ &= \frac{(147.59 \times 10^{-47} \text{ kg m}^2) - (4) \times (1.0078 \text{ u}) \times (1.66054 \times 10^{-27} \text{ kg u}^{-1}) \times (4.6169 \times 10^{-20} \text{ m}^2)}{(4) \times (12.011 \text{ u}) \times (1.66054 \times 10^{-27} \text{ kg u}^{-1})} \\ &= 1.4626 \times 10^{-20} \text{ m}^2 \\ R_C &= 1.209 \times 10^{-10} \text{ m} \end{aligned}$$

Figure 13.2(b) shows the relation between R_H , R_C , R_{CC} , and R_{CH} .

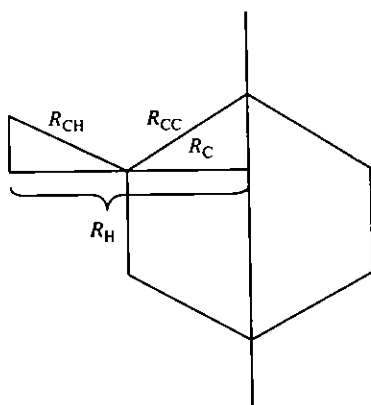


Figure 13.2(b)

$$R_{CC} = \frac{R_C}{\cos 30^\circ} = \frac{1.209 \times 10^{-10} \text{ m}}{0.8660} = 1.396 \times 10^{-10} \text{ m} = \boxed{139.6 \text{ pm}}$$

$$R_{CH} = \frac{R_H - R_C}{\cos 30^\circ} = \frac{0.940 \times 10^{-10}}{0.8660} = 1.085 \times 10^{-10} = \boxed{108.5 \text{ pm}}$$

$$R_{CD} = R_{CH}$$

COMMENT. These values are very close to the interatomic distances quoted by Herzberg in *Electronic Spectra and Electronic Structure of Polyatomic Molecules*, p. 666 (*Further reading*, Chapter 14), which are 139.7 and 108.4 pm respectively.

P13.8 $\tilde{\nu} = 2B(J + 1) [13.37] = 2B$

Hence, $B(^1\text{HCl}) = 10.4392 \text{ cm}^{-1}$, $B(^2\text{HCl}) = 5.3920 \text{ cm}^{-1}$

$$B = \frac{\hbar}{4\pi cI} [13.24] \quad I = m_{\text{eff}} R^2 \text{ [Table 13.1]}$$

$$R^2 = \frac{\hbar}{4\pi c m_{\text{eff}} B} = \frac{\hbar}{4\pi c} = 2.79927 \times 10^{-44} \text{ kg m}$$

$$m_{\text{eff}}(\text{HCl}) = \left(\frac{(1.007825 \text{ u}) \times (34.96885 \text{ u})}{(1.007825 \text{ u}) + (34.96885 \text{ u})} \right) \times (1.66054 \times 10^{-27} \text{ kg u}^{-1})$$

$$= 1.62665 \times 10^{-27} \text{ kg}$$

$$m_{\text{eff}}(\text{DCl}) = \left(\frac{(2.0140 \text{ u}) \times (34.96885 \text{ u})}{(2.0140 \text{ u}) + (34.96885 \text{ u})} \right) \times (1.66054 \times 10^{-27} \text{ kg u}^{-1})$$

$$= 3.1622 \times 10^{-27} \text{ kg}$$

$$R^2(\text{HCl}) = \frac{2.79927 \times 10^{-44} \text{ kg m}}{(1.62665 \times 10^{-27} \text{ kg}) \times (1.04392 \times 10^3 \text{ m}^{-1})} = 1.64848 \times 10^{-20} \text{ m}^2$$

$$R(\text{HCl}) = 1.28393 \times 10^{-10} \text{ m} = \boxed{128.393 \text{ pm}}$$

$$R^2(^2\text{HCl}) = \frac{2.79927 \times 10^{-44} \text{ kg m}}{(3.1622 \times 10^{-27} \text{ kg}) \times (5.3920 \times 10^2 \text{ m}^{-1})} = 1.6417 \times 10^{-20} \text{ m}^2$$

$$R(^2\text{HCl}) = 1.2813 \times 10^{-10} \text{ m} = \boxed{128.13 \text{ pm}}$$

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 are precise to 6 figures.

P13.10 From the equation for a linear rotor in Table 13.1 it is possible to show that $I_{\text{m}} = m_{\text{a}}m_{\text{c}}(R + R')^2 + m_{\text{a}}m_{\text{b}}R^2 + m_{\text{b}}m_{\text{c}}R'^2$.

$$\text{Thus, } I(^{16}\text{O}^{12}\text{C}^{32}\text{S}) = \left(\frac{m(^{16}\text{O})m(^{32}\text{S})}{m(^{16}\text{O}^{12}\text{C}^{32}\text{S})} \right) \times (R + R')^2 + \left(\frac{m(^{12}\text{C})\{m(^{16}\text{O})R^2 + m(^{32}\text{S})R'^2\}}{m(^{16}\text{O}^{12}\text{C}^{32}\text{S})} \right)$$

$$I(^{16}\text{O}^{12}\text{C}^{34}\text{S}) = \left(\frac{m(^{16}\text{O})m(^{34}\text{S})}{m(^{16}\text{O}^{12}\text{C}^{34}\text{S})} \right) \times (R + R')^2 + \left(\frac{m(^{12}\text{C})\{m(^{16}\text{O})R^2 + m(^{34}\text{S})R'^2\}}{m(^{16}\text{O}^{12}\text{C}^{34}\text{S})} \right)$$

$m(^{16}\text{O}) = 15.9949 \text{ u}$, $m(^{12}\text{C}) = 12.0000 \text{ u}$, $m(^{32}\text{S}) = 31.9721 \text{ u}$, and $m(^{34}\text{S}) = 33.9679 \text{ u}$. Hence,

$$I(^{16}\text{O}^{12}\text{C}^{32}\text{S})/\text{u} = (8.5279) \times (R + R')^2 + (0.20011) \times (15.9949R^2 + 31.9721R'^2)$$

$$I(^{16}\text{O}^{12}\text{C}^{34}\text{S})/\text{u} = (8.7684) \times (R + R')^2 + (0.19366) \times (15.9949R^2 + 33.9679R'^2)$$

The spectral data provides the experimental values of the moments of inertia based on the relation $\tilde{\nu} = 2cB(J+1)$ [13.37] with $B = h/4\pi cI$ [13.24]. 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

$$I(^{16}\text{O}^{12}\text{C}^{32}\text{S}) = 1.379\,98 \times 10^{-45} \text{ kg m}^2$$

$$I(^{16}\text{O}^{12}\text{C}^{34}\text{S}) = 1.414\,60 \times 10^{-45} \text{ kg m}^2$$

Therefore, after conversion of the atomic mass units to kg, the equations we must solve are

$$1.379\,98 \times 10^{-45} \text{ m}^2 = (1.4161 \times 10^{-26}) \times (R + R')^2 + (5.3150 \times 10^{-27} R^2) \\ + (1.0624 \times 10^{-26} R'^2)$$

$$1.414\,60 \times 10^{-45} \text{ m}^2 = (1.4560 \times 10^{-26}) \times (R + R')^2 + (5.1437 \times 10^{-27} R^2) \\ + (1.0923 \times 10^{-26} R'^2)$$

These two equations may be solved for R and R' . They are tedious to solve by hand, but straightforward. Exercise 13.9(b) illustrates the details of the solution. Readily available mathematical software can be used to quickly give the result. The outcome is $R = 116.28 \text{ pm}$ and $R' = 155.97 \text{ pm}$. 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 13.9(b) is similar to this problem; its starting point 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?

P13.12 The wavenumbers of the transitions with $\Delta v = +1$ are

$$\Delta G_{v+1/2} = \tilde{\nu} - 2(v+1)x_e\tilde{\nu} \text{ [13.57]} \quad \text{and} \quad D_e = \frac{\tilde{\nu}^2}{4x_e\tilde{\nu}} \text{ [13.55]}$$

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	281.502

The points are plotted in Figure 13.3.

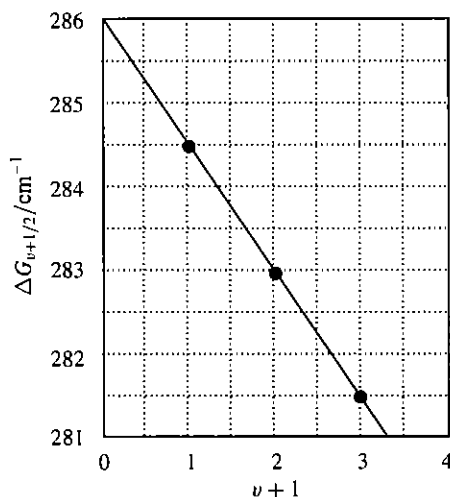


Figure 13.3

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

$$D_e = \frac{(286 \text{ cm}^{-1})^2}{(4) \times (0.750 \text{ cm}^{-1})} = 27\,300 \text{ cm}^{-1}, \quad \text{or} \quad 3.38 \text{ eV}$$

The zero-point level lies at 142.81 cm^{-1} and so $D_0 = 3.36 \text{ eV}$. Since

$$m_{\text{eff}} = \frac{(22.99) \times (126.90)}{(22.99) + (126.90)} \text{ u} = 19.464 \text{ u}$$

the force constant of the molecule is

$$\begin{aligned} k &= 4\pi^2 m_{\text{eff}} c^2 \tilde{\nu}^2 \text{ [Exercise 13.16(a)]} \\ &= (4\pi^2) \times (19.464) \times (1.6605 \times 10^{-27} \text{ kg}) \times [(2.998 \times 10^{10} \text{ cm s}^{-1}) \times (286 \text{ cm}^{-1})]^2 \\ &= 93.8 \text{ N m}^{-1} \end{aligned}$$

P13.14 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) $\tilde{\nu}_Q(J) = \tilde{\nu} \text{ [13.62b]} = 2143.26 \text{ cm}^{-1}$

(b) The zero-point energy is $\frac{1}{2}\tilde{\nu} = 1071.63 \text{ cm}^{-1}$. The molar zero-point energy in J mol^{-1} is

$$\begin{aligned} N_A h c \times (1071.63 \text{ cm}^{-1}) &= N_A h c \times (1.07163 \times 10^5 \text{ m}^{-1}) \\ &= 1.28195 \times 10^4 \text{ J mol}^{-1} = 12.8195 \text{ kJ mol}^{-1} \end{aligned}$$

$$(c) \quad k = 4\pi^2 \mu c^2 \tilde{\nu}^2$$

$$\mu(^{12}\text{C}^{16}\text{O}) = \frac{m_{\text{C}} m_{\text{O}}}{m_{\text{C}} + m_{\text{O}}} = \left(\frac{(12.0000 \text{ u}) \times (15.9949 \text{ u})}{(12.0000 \text{ u}) + (15.9949 \text{ u})} \right) \times (1.66054 \times 10^{-27} \text{ kg u}^{-1})$$

$$= 1.13852 \times 10^{-26} \text{ kg}$$

$$k = 4\pi^2 c^2 \times (1.13852 \times 10^{-26} \text{ kg}) \times (2.14326 \times 10^5 \text{ m}^{-1})^2 = \boxed{1.85563 \times 10^3 \text{ N m}^{-1}}$$

$$(d) \quad 4B \approx 7.655 \text{ cm}^{-1}$$

$$B \approx \boxed{1.91 \text{ cm}^{-1}} \quad [4 \text{ significant figures not justified}]$$

$$(e) \quad B = \frac{\hbar}{4\pi c I} [13.24] = \frac{\hbar}{4\pi c \mu R^2} [\text{Table 13.1}]$$

$$R^2 = \frac{\hbar}{4\pi c \mu B} = \frac{\hbar}{(4\pi c) \times (1.13852 \times 10^{-26} \text{ kg}) \times (191 \text{ m}^{-1})} = 1.287 \times 10^{-20} \text{ m}^2$$

$$R = 1.13 \times 10^{-10} \text{ m} = \boxed{113 \text{ pm}}$$

P13.16

$$V(R) = hcD_e \{1 - e^{-a(R-R_e)}\}^2 [13.54]$$

$$\tilde{\nu} = \frac{\omega}{2\pi c} = 936.8 \text{ cm}^{-1} \quad x_e \tilde{\nu} = 14.15 \text{ cm}^{-1}$$

$$a = \left(\frac{m_{\text{eff}}}{2hcD_e} \right)^{1/2} \omega \quad x_e = \frac{\hbar a^2}{2m_{\text{eff}} \omega} \quad D_e = \frac{\tilde{\nu}}{4x_e}$$

$$m_{\text{eff}}(\text{RbH}) \approx \frac{(1.008) \times (85.47)}{(1.008) + (85.47)} \text{ u} = 1.654 \times 10^{-27} \text{ kg}$$

$$D_e = \frac{\tilde{\nu}^2}{4x_e \tilde{\nu}} = \frac{(936.8 \text{ cm}^{-1})^2}{(4) \times (14.15 \text{ cm}^{-1})} = 15505 \text{ cm}^{-1} \quad (1.92 \text{ eV})$$

$$a = 2\pi \nu \left(\frac{m_{\text{eff}}}{2hcD_e} \right)^{1/2} [13.54] = 2\pi c \tilde{\nu} \left(\frac{m_{\text{eff}}}{2hcD_e} \right)^{1/2}$$

$$= (2\pi) \times (2.998 \times 10^{10} \text{ cm s}^{-1}) \times (936.8 \text{ cm}^{-1})$$

$$\times \left(\frac{1.654 \times 10^{-27} \text{ kg}}{(2) \times (15505 \text{ cm}^{-1}) \times (6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^{10} \text{ cm s}^{-1})} \right)^{1/2}$$

$$= 9.144 \times 10^9 \text{ m}^{-1} = 9.44 \text{ nm}^{-1} = \frac{1}{0.1094 \text{ nm}}$$

$$\text{Therefore, } \frac{V(R)}{hcD_e} = \{1 - e^{-(R-R_e)/(0.1094 \text{ nm})}\}^2$$

with $R_e = 236.7$ pm. We draw up the following table

R/pm	50	100	200	300	400	500	600	700	800
$V/(hcD_e)$	20.4	6.20	0.159	0.193	0.601	0.828	0.929	0.971	0.988

These points are plotted in Figure 13.4 as the line labeled $J = 0$

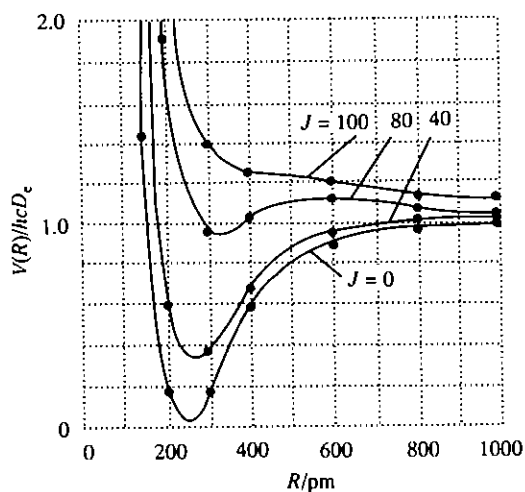


Figure 13.4

For the second part, we note that $B \propto \frac{1}{R^2}$ and write

$$V_J^* = V + hcB_e J(J+1) \times \left(\frac{R_e^2}{R^2} \right)$$

with B_e the equilibrium rotational constant, $B_e = 3.020 \text{ cm}^{-1}$.

We then draw up the following table using the values of V calculated above

R/pm	50	100	200	300	400	600	800	1000
$\frac{R_e}{R}$	4.73	2.37	1.18	0.79	0.59	0.39	0.30	0.24
$\frac{V}{hcD_e}$	20.4	6.20	0.159	0.193	0.601	0.929	0.988	1.000
$\frac{V_{40}^*}{hcD_e}$	27.5	7.99	0.606	0.392	0.713	0.979	1.016	1.016
$\frac{V_{80}^*}{hcD_e}$	48.7	13.3	1.93	0.979	1.043	1.13	1.099	1.069
$\frac{V_{100}^*}{hcD_e}$	64.5	17.2	2.91	1.42	1.29	1.24	1.16	1.11

These points are also plotted in Figure 13.4

- P13.18** (a) Vibrational wavenumbers ($\tilde{\nu}/\text{cm}^{-1}$) computed by PC Spartan Pro™ 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 in Figure 13.5.

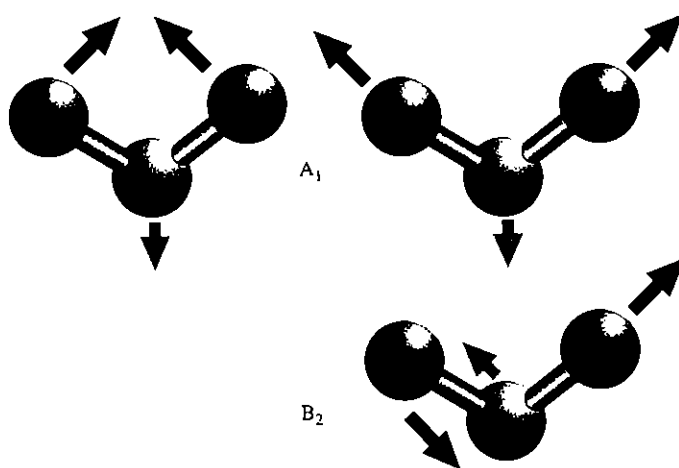


Figure 13.5

- (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 transitions: 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.).

- P13.20** 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 Figure 12.7. 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

P13.22 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 from 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 throughout:

$$\text{So } E = \frac{J^2(1 - \mu\omega^2/k)^2}{2\mu r_e^2} + \frac{\mu^2\omega^4 r_e^2}{2k(1 - \mu\omega^2/k)^2}.$$

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:

$$J = I\omega = \mu r^2 \omega \quad \text{so} \quad \omega = J/\mu r_c^2$$

which allows us to substitute expressions involving J for all ω s:

$$E \approx \frac{J^2}{2\mu r_c^2} - \frac{J^4}{\mu^2 r_c^6 k} + \frac{J^4}{2\mu^2 r_c^6 k}$$

(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 :

$$E \approx \frac{J^2}{2I} - \frac{J^4 \mu}{2I^3 k} \Rightarrow E \approx \frac{J(J+1)\hbar^2}{2I} - \frac{J^2(J+1)^2 \hbar^4 \mu}{2I^3 k}$$

Dividing by hc gives the rotational term, $F(J)$:

$$F(J) \approx \frac{J(J+1)\hbar^2}{2hcI} - \frac{J^2(J+1)^2 \hbar^4 \mu}{2hcI^3 k} = \frac{J(J+1)}{4\pi cI} - \frac{J^2(J+1)^2 \hbar^3 \mu}{4\pi cI^3 k}$$

where we have used $\hbar = h/2\pi$ to eliminate a common divisor of h . Now use the definition of the rotational constant,

$$B = \frac{\hbar^2}{4\pi cI} \Rightarrow F(J) \approx J(J+1)B - J^2(J+1)^2 B^3 \frac{16\pi^2 c^2 \mu}{k}$$

Finally, use the relationship between the force constant and vibrational wavenumber:

$$\left(\frac{k}{\mu}\right)^{1/2} = \omega_{\text{vib}} = 2\pi\nu = 2\pi c\tilde{\nu} \quad \text{so} \quad \frac{\mu}{k} = \frac{1}{4\pi^2 c^2 \tilde{\nu}^2}$$

leaving $F(J) \approx BJ(J+1) - \frac{4B^3}{\tilde{\nu}^2} J^2(J+1)^2 = BJ(J+1) - DJ^2(J+1)^2$ where $D = \frac{4B^3}{\tilde{\nu}^2}$.

P13.24 $N \propto g e^{-E/kT}$ [Boltzmann distribution, Chapters 2 and 16]

$$N_J \propto g_J e^{-E_J/kT} \propto (2J+1) e^{-hcBJ(J+1)/kT} \quad [g_J = 2J+1 \text{ for a diatomic rotor}]$$

The maximum population occurs when

$$\frac{d}{dJ} N_J \propto \left\{ 2 - (2J+1)^2 \times \left(\frac{hcB}{kT} \right) \right\} e^{-hcBJ(J+1)/kT} = 0$$

and, since the exponential can never be zero at a finite temperature, when

$$(2J+1)^2 \times \left(\frac{hcB}{kT} \right) = 2$$

$$\text{or when } J_{\text{max}} = \left(\frac{kT}{2hcB} \right)^{1/2} - \frac{1}{2}$$

For ICl, with $\frac{kT}{hc} = 207.22 \text{ cm}^{-1}$ (inside front cover)

$$J_{\max} = \left(\frac{207.22 \text{ cm}^{-1}}{0.2284 \text{ cm}^{-1}} \right)^{1/2} - \frac{1}{2} = \boxed{30}$$

For a spherical rotor, $N_J \propto (2J+1)^2 e^{-hcBJ(J+1)/kT}$ [$g_J = (2J+1)^2$]

and the greatest population occurs when

$$\frac{dN_J}{dJ} \propto \left(8J+4 - \frac{hcB(2J+1)^3}{kT} \right) e^{-hcBJ(J+1)/kT} = 0$$

which occurs when

$$4(2J+1) = \frac{hcB(2J+1)^3}{kT}$$

or at $J_{\max} = \boxed{\left(\frac{kT}{hcB} \right)^{1/2} - \frac{1}{2}}$

For CH_4 , $J_{\max} = \left(\frac{207.22 \text{ cm}^{-1}}{5.24 \text{ cm}^{-1}} \right)^{1/2} - \frac{1}{2} = \boxed{6}$

P13.26 The energy levels of a Morse oscillator, expressed as wavenumbers, are given by:

$$G(v) = \left(v + \frac{1}{2} \right) \tilde{\nu} - \left(v + \frac{1}{2} \right)^2 x_e \tilde{\nu} = \left(v + \frac{1}{2} \right) \tilde{\nu} - \left(v + \frac{1}{2} \right)^2 \tilde{\nu}^2 / 4D_e.$$

States are bound only if the energy is less than the well depth, D_e , also expressed as a wavenumber:

$$G(v) < D_e \quad \text{or} \quad \left(v + \frac{1}{2} \right) \tilde{\nu} - \left(v + \frac{1}{2} \right)^2 \tilde{\nu}^2 / 4D_e < D_e.$$

Solve for the maximum value of v by making the inequality into an equality:

$$\left(v + \frac{1}{2} \right)^2 \tilde{\nu}^2 / 4D_e - \left(v + \frac{1}{2} \right) \tilde{\nu} + D_e = 0.$$

Multiplying through by $4D_e$ results in an expression that can be factored by inspection into:

$$\left[\left(v + \frac{1}{2} \right) \tilde{\nu} - 2D_e \right]^2 = 0 \quad \text{so} \quad v + \frac{1}{2} = 2D_e / \tilde{\nu} \quad \text{and} \quad v = \boxed{2D_e / \tilde{\nu} - \frac{1}{2}}.$$

Of course, v is an integer, so its maximum value is really the greatest integer less than this quantity.

Solutions to applications

P13.28 (a) The molar absorption coefficient $\varepsilon(\tilde{\nu})$ is given by

$$\varepsilon(\tilde{\nu}) = \frac{A(\tilde{\nu})}{l[\text{CO}_2]} = \frac{RTA(\tilde{\nu})}{l x_{\text{CO}_2} p} \quad [13.4, 1.8, \text{ and } 1.15]$$

where $T = 298\text{ K}$, $l = 10\text{ cm}$, $p = 1\text{ bar}$, and $x_{\text{CO}_2} = 0.021$.

The absorption band originates with the $001 \leftarrow 000$ transition of the antisymmetric stretch vibrational mode at 2349 cm^{-1} (Figure 13.40). 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 13.3). The spectra reveals that the Q branch is missing so we conclude that the transition $\Delta J = 0$ is forbidden (Section 13.12) 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. See Figures 13.16(a), (b).

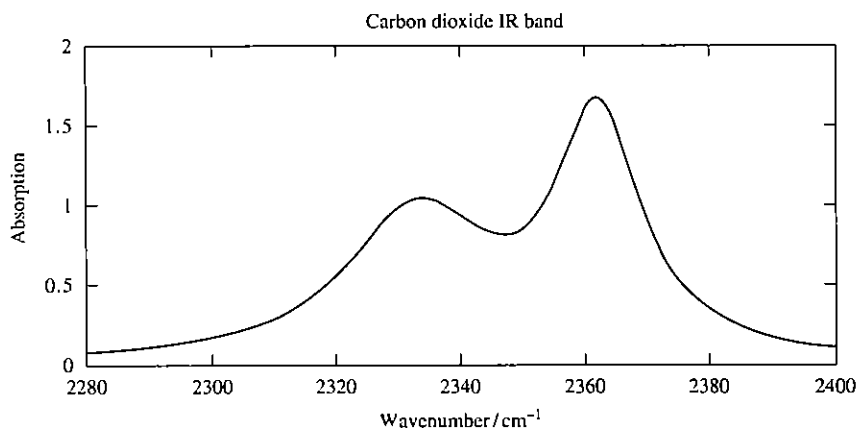


Figure 13.6(a)

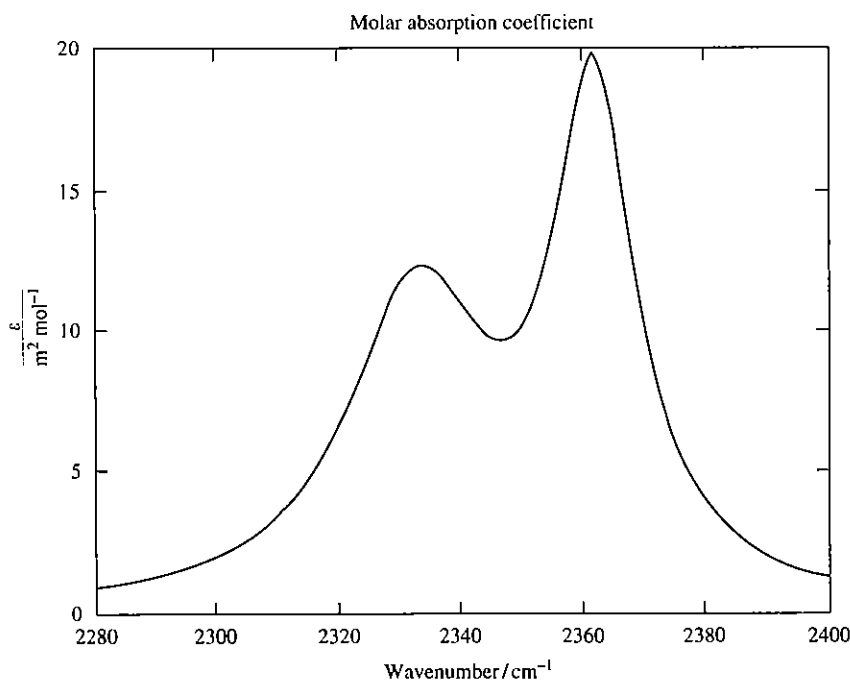


Figure 13.6(b)

- (b) $^{16}\text{O}-^{12}\text{C}-^{16}\text{O}$ 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 13.8). 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 $J = 0, 2, 4, \dots$. According to eqn 13.61, the energy of the $(0, J)$ state is

$$S(0, J) = \frac{1}{2}\tilde{\nu} + BJ(J+1),$$

where $\tilde{\nu} = 2349 \text{ cm}^{-1}$

$$I = \frac{2M_{\text{O}}R^2}{N_{\text{A}}} = \frac{2(0.01600 \text{ kg mol}^{-1})(116.2 \times 10^{-12} \text{ m})^2}{6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$= 7.175 \times 10^{-46} \text{ kg m}^2 \quad (\text{Table 13.1})$$

$$B = \frac{h}{8\pi^2 cI} \quad [13.24]$$

$$= \frac{6.626 \times 10^{-34} \text{ J s}}{8\pi^2 (2.998 \times 10^8 \text{ m s}^{-1})(7.175 \times 10^{-46} \text{ kg m}^2)}$$

$$= 39.02 \text{ m}^{-1} = 0.3902 \text{ cm}^{-1}$$

The transitions of the P and R branches occur at

$$\tilde{\nu}_{\text{P}} = \tilde{\nu} - 2BJ \quad [13.62b]$$

and

$$\tilde{\nu}_{\text{R}} = \tilde{\nu} + 2B(J+1) \quad [13.62c]$$

where $J = 0, 2, 4, 6, \dots$

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 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 Boltzmann distribution with a degeneracy of $2J+1$. The transition probability is also proportional to both a nuclear degeneracy factor (eqn 13.43) and a transition dipole moment, which is approximately independent of J . The former factors are absorbed into the constant of proportionality.

$$\text{transition probability} \propto (2J+1)e^{-S(0,J)hc/kT}$$

A plot of the right-hand-side of this equation against J at 298 K indicates a maximum transition probability at $J_{\text{max}} = 16$. We “normalize” the maximum in the predicted structure, and eliminate the constant of proportionality by examining the transition probability ratio:

$$\frac{\text{transition probability for } J\text{th state}}{\text{transition probability for } J_{\text{max}} \text{ state}} = \frac{(2J+1)e^{-S(0,J)hc/kT}}{33e^{-S(0,16)hc/RT}}$$

$$= \left(\frac{2J+1}{33}\right)e^{-(J^2+J-272)Bhc/kT}$$

A plot, Figure 13.6(c), of the above ratio against predicted wavenumbers can be compared to the ratio $A(\tilde{\nu})/A_{\text{max}}$ 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.

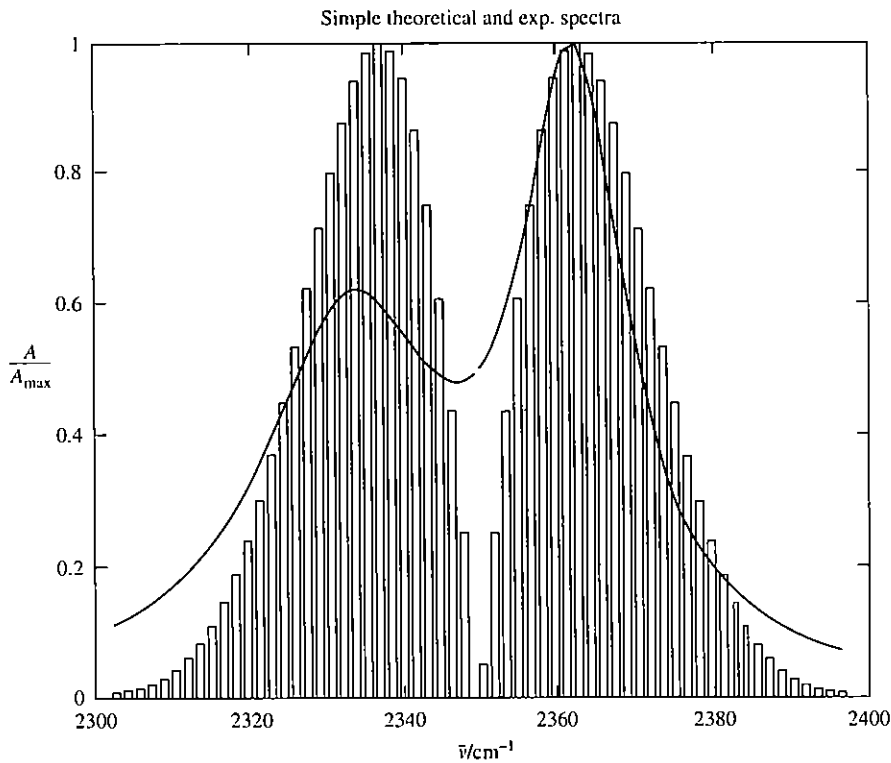


Figure 13.6(c)

(c) Using the equations of justification 13.1, we may write the relationship

$$A = \varepsilon(\tilde{\nu}) \int_0^h [\text{CO}_2] d\tilde{h}$$

The strong absorption of the band suggests that h should not be a very great length and that $[\text{CO}_2]$ should be constant between the Earth's surface and h . Consequently, the integration gives

$$\begin{aligned} A &= \varepsilon(\tilde{\nu})[\text{CO}_2]h \\ &= \varepsilon(\tilde{\nu})h \left\{ \frac{x_{\text{CO}_2} p}{RT} \right\} \quad \text{Dalton's law of partial pressures} \end{aligned}$$

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.

$$\begin{aligned} A &= \varepsilon(\tilde{\nu})h \left\{ \frac{(3.3 \times 10^{-4})(1 \times 10^5 \text{ Pa})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(288 \text{ K})} \right\} \\ &= (0.0138 \text{ m}^{-3} \text{ mol}) \varepsilon(\tilde{\nu})h \end{aligned}$$

$$\text{Transmittance} = 10^{-A} = 10^{-(0.0138 \text{ m}^{-3} \text{ mol}) \varepsilon(\tilde{\nu})h} \quad [13.3]$$

The transmittance surface plot, Figure 13.6(d), clearly shows that before a height of about 30 m has been reached all of the Earth's IR radiation in the 2320–2380 cm^{-1} range has been absorbed by atmospheric carbon dioxide.

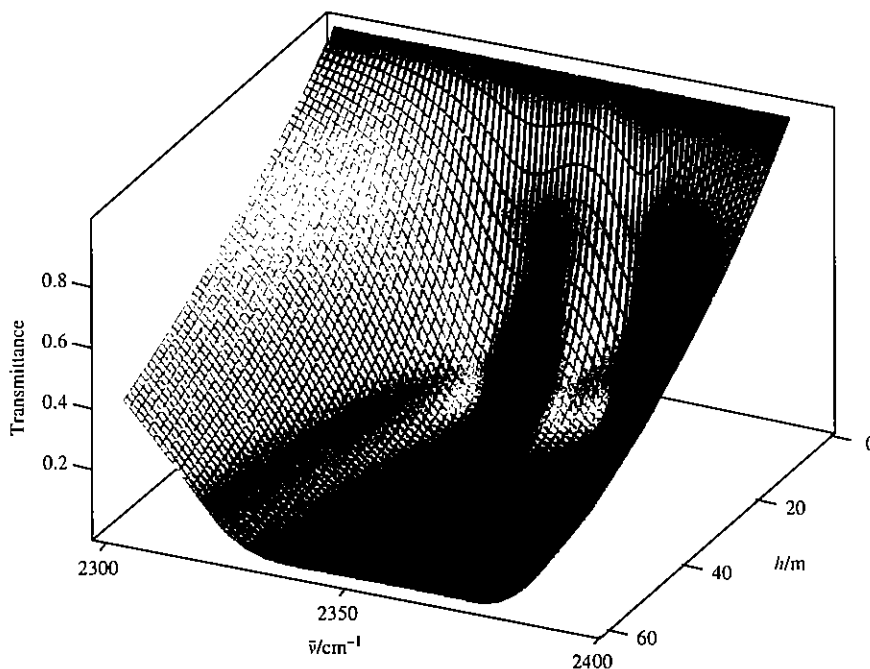


Figure 13.6(d)

See C.A. Meserole, F.M. Mulcahy, J. Lutz, and H.A. Yousif, *J. Chem. Ed.*, 74, 316 (1997).

- P13.30** The question of whether to use CN or CH within the interstellar cloud of constellation Ophiuchus for the determination of the temperature of the cosmic background radiation depends upon which one has a rotational spectrum that best spans blackbody radiation of 2.726 K. Given $B_0(\text{CH}) = 14.90 \text{ cm}^{-1}$, the rotational constant that is needed for the comparative analysis may be calculated from the 226.9 GHz spectral line of the Orion Nebula. Assuming that the line is for the $^{12}\text{C}^{14}\text{N}$ isotopic species and $J+1 \leftarrow J = 1$, which gives a reasonable estimate of the CN bond length (117.4 pm), the CN rotational constant is calculated as follows.

$$B_0 = \nu/c = \frac{\nu}{2c(J+1)} = \frac{\nu}{4c} \quad (1)$$

$$= 1.892 \text{ cm}^{-1} \quad (2)$$

Blackbody radiation at 2.726 K may be plotted against radiation wavenumber with suitable transformation of eqn 11.5.

$$\rho(\tilde{\nu}) = \frac{8\pi hc\tilde{\nu}^3}{e^{hc\tilde{\nu}/kT} - 1}$$

Spectral absorption lines of $^{12}\text{C}^{14}\text{N}$ and $^{12}\text{C}^1\text{H}$ are calculated with eqn 16.44.

$$\tilde{\nu}(J+1 \leftarrow J) = 2B(J+1) \quad J = 0, 1, 2, 3, \dots$$

The cosmic background radiation and molecular absorption lines are shown in the graph, Figure 13.7. It is evident that only CN spans the background radiation.

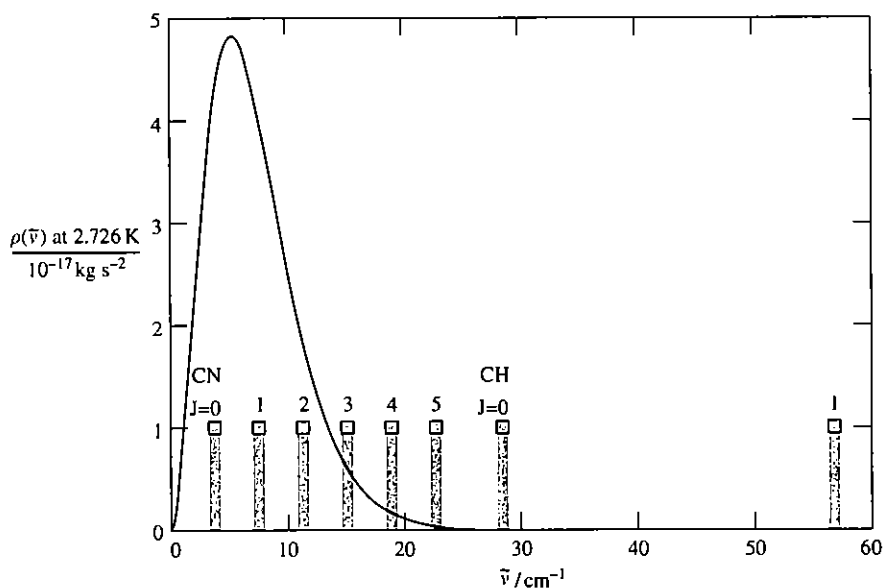


Figure 13.7

- P13.32** (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 Figure 13.8 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

$$\begin{aligned} R_C &= R/\sqrt{3} \\ I_C &= 3mR_C^2 = 3m(R/\sqrt{3})^2 = mR^2 \\ I_B &= 2mR_B^2 = 2m(R/2)^2 = mR^2/2 \end{aligned}$$

Therefore

$$I_C = 2I_B$$

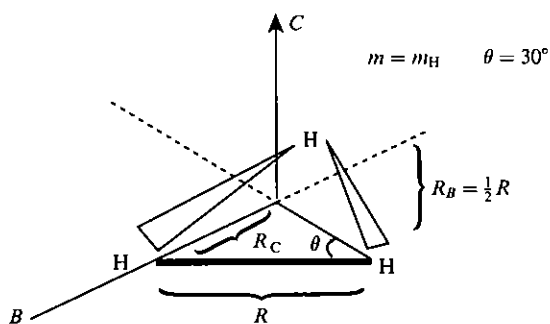


Figure 13.8

$$\begin{aligned}
 \text{(b)} \quad B &= \frac{h}{4\pi c I_B} = \frac{2h}{4\pi c m R^2} = \frac{h}{2\pi c m R^2} \quad [13.30] \\
 R &= \left(\frac{h}{2\pi c m B} \right)^{1/2} = \left(\frac{h N_A}{2\pi c M_H B} \right)^{1/2} \\
 &= \left(\frac{(1.0546 \times 10^{-34} \text{ J s}) \times (6.0221 \times 10^{23} \text{ mol}^{-1}) \times \left(\frac{10^{-2} \text{ m}}{\text{cm}} \right)}{2\pi (2.998 \times 10^8 \text{ m s}^{-1}) \times (0.001008 \text{ kg mol}^{-1}) \times (43.55 \text{ cm}^{-1})} \right)^{1/2} \\
 &= 8.764 \times 10^{-11} \text{ m} = \boxed{87.64 \text{ pm}}
 \end{aligned}$$

Alternatively the rotational constant C can be used to calculate R .

$$\begin{aligned}
 C &= \frac{h}{4\pi c I_C} = \frac{h}{4\pi c m R^2} \quad [13.30] \\
 R &= \left(\frac{h}{4\pi c m C} \right)^{1/2} = \left(\frac{h N_A}{4\pi c M_H C} \right)^{1/2} \\
 &= \left(\frac{(1.0546 \times 10^{-34} \text{ J s}) \times (6.0221 \times 10^{23} \text{ mol}^{-1}) \times \left(\frac{10^{-2} \text{ m}}{\text{cm}} \right)}{4\pi (2.998 \times 10^8 \text{ m s}^{-1}) \times (0.001008 \text{ kg mol}^{-1}) \times (20.71 \text{ cm}^{-1})} \right)^{1/2} \\
 &= 8.986 \times 10^{-11} \text{ m} = \boxed{89.86 \text{ pm}}
 \end{aligned}$$

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.

$$(R) \approx \frac{(87.64 + 89.86) \text{ pm}}{2} = \boxed{88.7 \text{ pm}}$$

$$\begin{aligned}
 B &= \frac{h}{2\pi c m R^2} = \frac{(1.0546 \times 10^{-34} \text{ J s}) \times (6.0221 \times 10^{23} \text{ mol}^{-1}) \times \left(\frac{10^{-2} \text{ m}}{\text{cm}} \right)}{2\pi (2.998 \times 10^8 \text{ m s}^{-1}) \times (0.001008 \text{ kg mol}^{-1}) \times (87.32 \times 10^{-12} \text{ m})^2} \\
 &= \boxed{43.87 \text{ cm}^{-1}}
 \end{aligned}$$

$$C = \frac{1}{2} B = \boxed{21.93 \text{ cm}^{-1}}$$

$$\frac{1}{m_{\text{eff}}} = \frac{3}{m} \quad \text{or} \quad m_{\text{eff}} = \frac{1}{3} m$$

Since $m_D = 2m_H$, $m_{\text{eff}, D} = 2m_H/3$

$$\begin{aligned}
 \tilde{\nu}_2(D_3^+) &= \left(\frac{m_{\text{eff}}(H_3)}{m_{\text{eff}}(D_3)} \right)^{1/2} \tilde{\nu}_2(H_3) \quad [13.51] = \left(\frac{m_H/3}{2m_H/3} \right)^{1/2} \tilde{\nu}_2(H_3) = \frac{\tilde{\nu}_2(H_2)}{2^{1/2}} \\
 &= \frac{2521.6 \text{ cm}^{-1}}{2^{1/2}} = \boxed{1783.0 \text{ cm}^{-1}}
 \end{aligned}$$

Since B and $C \propto \frac{1}{m}$, where $m = \text{mass of H or D}$

$$B(\text{D}_3^+) = B(\text{H}_3^+) \times \frac{M_{\text{H}}}{M_{\text{D}}} = 43.55 \text{ cm}^{-1} \times \left(\frac{1.008}{2.014} \right) = \boxed{21.80 \text{ cm}^{-1}}$$

$$C(\text{D}_3^+) = C(\text{H}_3^+) \times \frac{M_{\text{H}}}{M_{\text{D}}} = 20.71 \text{ cm}^{-1} \times \left(\frac{1.008}{2.014} \right) = \boxed{10.37 \text{ cm}^{-1}}$$



14

Spectroscopy 2: electronic transitions

Answers to discussion questions

D14.2 The Franck–Condon principle states that because electrons are so much lighter than nuclei, an electronic transition occurs so rapidly compared to vibrational motions that the internuclear distance is relatively unchanged as a result of the transition. This implies that the most probable transitions $\nu_f \leftarrow \nu_i$ 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?

D14.4 Color can arise by emission, absorption, or scattering of electromagnetic radiation by an object. Many molecules have electronic transitions that have wavelengths in the visible portion of the electromagnetic spectrum. When a substance emits radiation the perceived color of the object will be that of the emitted radiation and it may be an additive color resulting from the emission of more than one wavelength of radiation. When a substance absorbs radiation its color is determined by the subtraction of those wavelengths from white light. For example, absorption of red light results in the object being perceived as green. Scattering, including the diffraction that occurs when light falls on a material with a grid of variation in texture or refractive index having dimensions comparable to the wavelength of light, for example, a bird's plumage, may also form color.

D14.6 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.

D14.8 See Table 14.4 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 14.6(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 femtosecond 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 that would have been unimaginable before.

Solutions to exercises

E14.1(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 $u \times g = \boxed{u}$ since (apart from the complete core), one electron occupies a u orbital another occupies a g orbital.

E14.2(b) Use the Beer–Lambert law

$$\begin{aligned}\log \frac{I}{I_0} &= -\varepsilon[J]l = (-327 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) \times (2.22 \times 10^{-3} \text{ mol dm}^{-3}) \times (0.15 \text{ cm}) \\ &= -0.10889 \\ \frac{I}{I_1} &= 10^{-0.10889} = 0.778\end{aligned}$$

The reduction in intensity is $\boxed{22.2 \text{ percent}}$

E14.3(b)

$$\begin{aligned}\varepsilon &= -\frac{1}{[J]l} \log \frac{I}{I_0} [13.2, 13.3] \\ &= \frac{-1}{(6.67 \times 10^{-4} \text{ mol dm}^{-3}) \times (0.35 \text{ cm})} \log 0.655 = 787 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \\ &= 787 \times 10^3 \text{ cm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \quad [1 \text{ dm} = 10 \text{ cm}] \\ &= \boxed{7.9 \times 10^5 \text{ cm}^2 \text{ mol}^{-1}}\end{aligned}$$

E14.4(b) The Beer–Lambert law is

$$\begin{aligned}\log \frac{I}{I_0} &= -\varepsilon[J]l \quad \text{so} \quad [J] = \frac{-1}{\varepsilon l} \log \frac{I}{I_0} \\ [J] &= \frac{-1}{(323 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) \times (0.750 \text{ cm})} \log(1 - 0.523) = \boxed{1.33 \times 10^{-3} \text{ mol dm}^{-3}}\end{aligned}$$

- E14.5(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 center 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

$$A = \int \varepsilon d\tilde{\nu}$$

If the peak is triangular, this area is

$$\begin{aligned} A &= \frac{1}{2}(\text{base}) \times (\text{height}) \\ &= \frac{1}{2}[(199 \times 10^{-9} \text{ m})^{-1} - (275 \times 10^{-9} \text{ m})^{-1}] \times (2.25 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) \\ &= 1.5\bar{6} \times 10^{10} \text{ dm}^3 \text{ m}^{-1} \text{ mol}^{-1} \text{ cm}^{-1} = \frac{(1.5\bar{6} \times 10^9 \text{ dm}^3 \text{ m}^{-1} \text{ mol}^{-1} \text{ cm}^{-1}) \times (100 \text{ cm m}^{-1})}{10^3 \text{ dm}^3 \text{ m}^{-3}} \\ &= 1.5\bar{6} \times 10^9 \text{ m mol}^{-1} = \boxed{1.5\bar{6} \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-2}} \end{aligned}$$

- E14.6(b)** Modeling the π electrons of 1,3,5-hexatriene as free electrons in a linear box yields non-degenerate energy levels of

$$E_n = \frac{n^2 h^2}{8m_e L^2}$$

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

$$\Delta E_{\text{linear}} = \frac{(4^2 - 3^2)h^2}{8m_e(5R)^2}$$

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: $I = m_e R^2$. These energy levels are doubly degenerate, except for the non-degenerate $m_l = 0$. The six π electrons fill the $m_l = 0$ and ± 1 levels, so the lowest-energy transition is from $m_l = 1$ to $m_l = 2$

$$\Delta E_{\text{ring}} = \frac{(2^2 - 1^2)\hbar^2}{2m_e R^2} = \frac{(2^2 - 1^2)h^2}{8\pi^2 m_e R^2}$$

Comparing the two shows

$$\Delta E_{\text{linear}} = \frac{7}{25} \left(\frac{h^2}{8m_e R^2} \right) < \Delta E_{\text{ring}} = \frac{3}{\pi^2} \left(\frac{h^2}{8m_e R^2} \right)$$

Therefore, the lowest-energy absorption will rise in energy.

E14.7(b) The Beer–Lambert law is

$$\log \frac{I}{I_0} = -\varepsilon[J]l = \log T$$

so a plot (Figure 14.1) 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

$[\text{dye}]/(\text{mol dm}^{-3})$	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

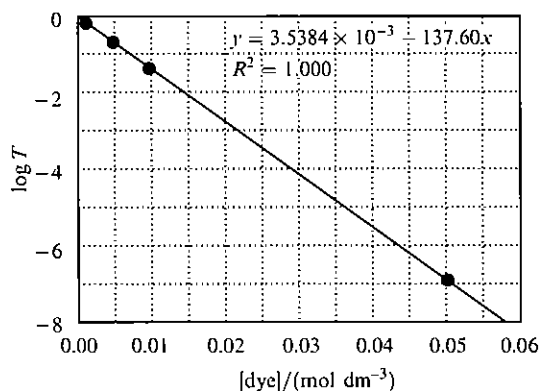


Figure 14.1

The molar absorptivity is

$$\varepsilon = -\frac{-138 \text{ dm}^3 \text{ mol}^{-1}}{0.250 \text{ cm}} = \boxed{522 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}}$$

E14.8(b) The Beer–Lambert law is

$$\log T = -\varepsilon[J]l \quad \text{so} \quad \varepsilon = \frac{-1}{[J]l} \log T$$

$$\varepsilon = \frac{-1}{(0.0155 \text{ mol dm}^{-3}) \times (0.250 \text{ cm})} \log 0.32 = \boxed{128 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}}$$

Now that we have ε , we can compute T of this solution with any size of cell

$$T = 10^{-\varepsilon[J]l} = 10^{-\{(128 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) \times (0.0155 \text{ mol dm}^{-3}) \times (0.450 \text{ cm})\}} = \boxed{0.13}$$

E14.9(b) The Beer–Lambert law is

$$\log \frac{I}{I_0} = -\varepsilon[J]l \quad \text{so} \quad l = -\frac{1}{\varepsilon[J]} \log \frac{I}{I_0}$$

$$(a) \quad l = -\frac{1}{(30 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) \times (1.0 \text{ mol dm}^{-3})} \times \log \frac{1}{2} = \boxed{0.010 \text{ cm}}$$

$$(b) \quad l = -\frac{1}{(30 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) \times (1.0 \text{ mol dm}^{-3})} \times \log 0.10 = \boxed{0.033 \text{ cm}}$$

E14.10(b) The integrated absorption coefficient is the area under an absorption peak

$$A = \int \varepsilon \, d\tilde{\nu}$$

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

$$A = \int_{-\infty}^{\infty} \varepsilon_{\max} \exp\left(\frac{-x^2}{a^2}\right) dx = \varepsilon_{\max} a \sqrt{\pi}$$

We must relate a to the half-width at half-height, $x_{1/2}$

$$\frac{1}{2}\varepsilon_{\max} = \varepsilon_{\max} \exp\left(\frac{-x_{1/2}^2}{a^2}\right) \quad \text{so} \quad \ln \frac{1}{2} = \frac{-x_{1/2}^2}{a^2} \quad \text{and} \quad a = \frac{x_{1/2}}{\sqrt{\ln 2}}$$

$$\begin{aligned} \text{So } A &= \varepsilon_{\max} x_{1/2} \left(\frac{\pi}{\ln 2}\right)^{1/2} = (1.54 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) \times (4233 \text{ cm}^{-1}) \times \left(\frac{\pi}{\ln 2}\right)^{1/2} \\ &= \boxed{1.39 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-2}} \end{aligned}$$

In SI base units

$$\begin{aligned} A &= \frac{(1.39 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-2}) \times (1000 \text{ cm}^3 \text{ dm}^{-3})}{100 \text{ cm m}^{-1}} \\ &= \boxed{1.39 \times 10^9 \text{ m mol}^{-1}} \end{aligned}$$

E14.11(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 **stronger** transition to a vibrationally excited state than to the vibrational ground state of the cation.

Solutions to problems

Solutions to numerical problems

P14.2 The energy of the dissociation products of the B state, $O(^3P)$ and $O(^1D)$ above the $v = 0$ state of the ground state is $7760\text{ cm}^{-1} + 49\,363\text{ cm}^{-1} = 57\,123\text{ cm}^{-1}$. One of these products, $O(^1D)$, has energy $15\,870\text{ cm}^{-1}$ above the energy of the ground-state atom, $O(^3P)$. Hence, the energy of two ground-state atoms, $2O(^3P)$ above the $v = 0$ state of the ground electronic state is $57\,123\text{ cm}^{-1} - 15\,870\text{ cm}^{-1} = 41\,253\text{ cm}^{-1} = \boxed{5.1147\text{ eV}}$. These energy relations are indicated (not to scale) in Figure 14.2 of the *Instructor's Solutions Manual*.

P14.4 We write $\varepsilon = \varepsilon_{\max} e^{-x^2} = \varepsilon_{\max} e^{-\tilde{\nu}^2/2\Gamma}$ the variable being $\tilde{\nu}$ and Γ being a constant. $\tilde{\nu}$ is measured from the band center, at which $\tilde{\nu} = 0$, $\varepsilon = \frac{1}{2}\varepsilon_{\max}$ when $\tilde{\nu}^2 = 2\Gamma \ln 2$. Therefore, the width at half height is

$$\Delta\tilde{\nu}_{1/2} = 2 \times (2\Gamma \ln 2)^{1/2}, \text{ implying that } \Gamma = \frac{\Delta\tilde{\nu}_{1/2}^2}{8 \ln 2}$$

Now we carry out the integration

$$\begin{aligned} A &= \int \varepsilon d\tilde{\nu} = \varepsilon_{\max} \int_{-\infty}^{\infty} e^{-\tilde{\nu}^2/2\Gamma} d\tilde{\nu} = \varepsilon_{\max} (2\Gamma\pi)^{1/2} \left[\int_{-\infty}^{\infty} e^{-x^2} dx = \pi^{1/2} \right] \\ &= \varepsilon_{\max} \left(\frac{2\pi \Delta\tilde{\nu}_{1/2}^2}{8 \ln 2} \right)^{1/2} = \left(\frac{\pi}{4 \ln 2} \right)^{1/2} \varepsilon_{\max} \Delta\tilde{\nu}_{1/2} = 1.0645 \varepsilon_{\max} \Delta\tilde{\nu}_{1/2} \end{aligned}$$

From Figure 14.50 of the text we estimate $\varepsilon_{\max} \approx 9.5\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ and $\Delta\tilde{\nu}_{1/2} \approx 4760\text{ cm}^{-1}$. Then

$$A = 1.0645 \times (9.5\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}) \times (4760\text{ cm}^{-1}) = \boxed{4.8 \times 10^4\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-2}}$$

The area under the curve on the printed page is about 1288 mm^2 , each mm^2 corresponds to about $190.5\text{ cm}^{-1} \times 0.189\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$, and so $\int \varepsilon d\tilde{\nu} \approx 4.64 \times 10^4\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-2}$. The agreement with the calculated value above is good.

P14.6 For a photon to induce a spectroscopic transition, the transition moment $\langle \mu \rangle$ must be nonzero. The Laporte selection rule forbids transitions that involve no change in parity. So transitions to the Π_u states are forbidden. (Note, these states may not even be reached by a vibronic transition, for these molecules have only one vibrational mode and it is centrosymmetric.)

We will judge transitions to the other states with the assistance of the $D_{\infty h}$ character table. The transition moment is the integral $\int \psi_f^* \mu \psi_i d\tau$, where the dipole moment operator has components proportional to the Cartesian coordinates. The integral vanishes unless the integrand, or at least some part of it, belongs to the totally symmetric representation of the molecule's point group. To find the character of the integrand, we multiply together the characters of its factors. Note that the μ_z has the same symmetry species as the ground state, namely A_{1u} , and the product of the ground state and μ_z has the A_{1g} symmetry species; since the symmetry species are mutually orthogonal, only a state with A_{1g} symmetry can be reached

from the ground state with z -polarized light. The $^2\Sigma_g^+$ state is such a state, so $^2\Sigma_g^+ \leftarrow ^2\Sigma_u^+$ is allowed. That leaves x - or y -polarized transitions to the $^2\Pi_g$ states to consider.

	E	$\infty C'_2$	$2C_\phi$	i	$\infty \sigma_v$	$2S_\phi$
$\Sigma_u^+ (A_{1u})$	1	-1	1	-1	1	-1
μ_x or $y (E_{1u})$	2	0	$2 \cos \phi$	-2	0	$2 \cos \phi$
$\Pi_g (E_{1g})$	2	0	$2 \cos \phi$	2	0	$-2 \cos \phi$
Integrand	4	0	$4 \cos^2 \phi$	4	0	$4 \cos^2 \phi$

The little orthogonality theorem (see the solution to Problem 12.18) gives the coefficient of A_{1g} in the integrand as

$$c_{A_{1g}} = (1/h) \Sigma_c g(C) \chi(C) = [4 + 0 + 2(4 \cos^2 \phi) + 4 + 0 + 2(4 \cos^2 \phi)]/\infty = 0.$$

So the integrand does not contain A_{1g} , and the transition to $^2\Pi_g$ would be forbidden.

P14.8 The weak absorption at $30\,000\text{ cm}^{-1}$ is typical of a carbonyl group. The strong $\text{C}=\text{C}$ absorption, which typically occurs at about 180 nm , has been shifted to longer wavelength (213 nm) because of the double bond and the CO group.

P14.10 The ratio of the transition probabilities of spontaneous emission to stimulated emission at a frequency ν is given by

$$A = \left(\frac{8\pi h \nu^3}{c^3} \right) B [13.11] = \frac{k}{\lambda^3} B, \text{ where } k \text{ is a constant and we have } \nu = \frac{c}{\lambda}.$$

Thus at 400 nm

$$A(400) = \frac{k}{(400)^3} B(400), \quad \text{and at } 500\text{ nm} \quad A(500) = \frac{k}{(500)^3} B(500)$$

$$\text{Then, } \frac{A(500)}{A(400)} = \left(\frac{(400)^3}{(500)^3} \right) \times \left(\frac{B(500)}{B(400)} \right) = \left(\frac{64}{125} \right) \times 10^{-5} = 5 \times 10^{-6}$$

Lifetimes and half-lives are inversely proportional to transition probabilities (rate constants) and hence

$$t_{1/2}(\text{T} \rightarrow \text{S}) = \frac{1}{5 \times 10^{-6}} t_{1/2}(\text{S}^* \rightarrow \text{S}) = (2 \times 10^5) \times (1.0 \times 10^{-9}\text{ s}) = 2 \times 10^{-4}\text{ s}$$

P14.12 The laser is delivering photons of energy

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\text{ J s}) \times (2.998 \times 10^8\text{ m s}^{-1})}{488 \times 10^{-9}\text{ m}} = 4.07 \times 10^{-19}\text{ J}$$

Since the laser is putting out 1.0 mJ of these photons every second, the rate of photon emission is:

$$r = \frac{1.0 \times 10^{-3}\text{ J s}^{-1}}{4.07 \times 10^{-19}\text{ J}} = 2.5 \times 10^{15}\text{ s}^{-1}$$

The time it takes the laser to deliver 10^6 photons (and therefore the time the dye remains fluorescent) is

$$t = \frac{10^6}{2.5 \times 10^{15} \text{ s}^{-1}} = \boxed{4 \times 10^{-10} \text{ s or } 0.4 \text{ ns}}$$

Solutions to theoretical problems

- P14.14** (a) Ethene (ethylene) belongs to D_{2h} . In this group the x , y , and z components of the dipole moment transform as B_{3u} , B_{2u} , and B_{1u} respectively. (See a more extensive set of character tables than in the text.) The π orbital is B_{1u} (like z , the axis perpendicular to the plane) and π^* is B_{3g} . Since $B_{3g} \times B_{1u} = B_{2u}$ and $B_{2u} \times B_{2u} = A_{1g}$, the transition is **allowed** (and is y -polarized).
- (b) Regard the CO group with its attached groups as locally C_{2v} . The dipole moment has components that transform as $A_1(z)$, $B_1(x)$, and $B_2(y)$, with the z -axis along the C=O direction and x perpendicular to the $R_2\text{CO}$ plane. The n orbital is p_y (in the $R_2\text{CO}$ plane), and hence transforms as B_2 . The π^* orbital is p_x (perpendicular to the $R_2\text{CO}$ plane), and hence transforms as B_1 . Since $\Gamma_f \times \Gamma_i = B_1 \times B_2 = A_2$, but no component of the dipole moment transforms as A_2 , the transition is **forbidden**.

P14.16
$$\mu = -e \int \psi_f^* x \psi_i dx$$

From Problem 9.15, $\mu_{10} = -e \int \psi_{1x} \psi_0 dx = -e \left[\frac{\hbar}{2(m_e k)^{1/2}} \right]^{1/2}$

Hence,
$$f = \frac{8\pi^2 m_e \nu}{3\hbar e^2} \times \frac{e^2 \hbar}{2(m_e k)^{1/2}} = \left[\frac{1}{3} \right] \left[2\pi \nu = \left(\frac{k}{m_e} \right)^{1/2} \right]$$

- P14.18** (a) Vibrational energy spacings of the **lower** state are determined by the spacing of the peaks of A. From the spectrum, $\bar{\nu} \approx 1800 \text{ cm}^{-1}$.
- (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.

- P14.20** (a) The Beer–Lambert Law is:

$$A = \log \frac{I_0}{I} = \varepsilon[J]l.$$

The absorbed intensity is:

$$I_{\text{abs}} = I_0 - I \quad \text{so} \quad I = I_0 - I_{\text{abs}}.$$

Substitute this expression into the Beer–Lambert law and solve for I_{abs} :

$$\log \frac{I_0}{I_0 - I_{\text{abs}}} = \varepsilon[J]l \quad \text{so} \quad I_0 - I_{\text{abs}} = I_0 \times 10^{-\varepsilon[J]l},$$

and
$$I_{\text{abs}} = \boxed{I_0 \times (1 - 10^{-\varepsilon[J]l})}.$$

(b) The problem states that $I_f(\tilde{\nu}_f)$ is proportional to ϕ_f and to $I_{\text{abs}}(\tilde{\nu})$, so:

$$I_f(\tilde{\nu}_f) \propto \phi_f I_0(\tilde{\nu}) \times (1 - 10^{\varepsilon[J]l}).$$

If the exponent is small, we can expand $1 - 10^{-\varepsilon[J]l}$ in a power series:

$$10^{-\varepsilon[J]l} = (e^{\ln 10})^{-\varepsilon[J]l} \approx 1 - \varepsilon[J]l \ln 10 + \dots,$$

$$\text{and } I_f(\tilde{\nu}_f) \propto \boxed{\phi_f I_0(\tilde{\nu}) \varepsilon[J]l \ln 10}$$

Solutions to applications

P14.22 There are three isosbestic wavelengths (wavenumbers). The presence of two or more isosbestic points is good evidence that only two solutes in equilibrium with each other are present. The solutes here being $\text{Her}(\text{CNS})_8$ and $\text{Her}(\text{OH})_8$.

P14.24 The following table summarizes AM1 calculations (an extended Hückel method) of the LUMO–HOMO separation in the 11-*cis* and 11-*trans* molecule (7) model of retinal. The -46.0° torsional angle between the first two alternate double bonds indicates that they are not coplanar. In contrast, the C11C12C13C14 torsion angle shows that the C11C12 double bond is close to coplanar with neighboring double bonds. The aromatic character of the alternating π -bond system is evidenced by contrasting the computed bond lengths at a single bond away from the π -system (C1–C2), a double bond (C11–C12), and a single bond between doubles (C12–C13) within the Lewis structure. We see a typical single bond length, a slightly elongated double bond length, and a bond length that is intermediate between a single and a double, respectively. The latter lengths are characteristic of aromaticity.

Conformation	11- <i>trans</i> (5)	11- <i>cis</i> (5)
$\Delta_f H^\circ / \text{kJ mol}^{-1}$	725.07	738.1
$E_{\text{LUMO}} / \text{eV}$	−5.142	−5.138
$E_{\text{HOMO}} / \text{eV}$	−10.770	−10.888
$\Delta E / \text{eV}$	(a) 5.628	(b) 5.750
λ / nm	(a) 220.3	(b) 215.6
C5C6C7C8 torsion angle/ $^\circ$	−44.5	−46.0
C11C12C13C14 torsion angle/ $^\circ$	179.7	−165.5
C1–C2/pm	153.2	153.2
C11–C12/pm	137.3	136.7
C12–C13/pm	1.420	1.421

(c) The lowest $\pi^* \leftarrow \pi$ transition occurs in the ultraviolet with the 11-*cis* transition at higher energy (higher frequency, lower wavelength). It is apparent that important interactions between retinal and a surrounding opsin molecule are responsible for reducing the transition energy to the observed strong absorption in the 400 to 600 nm visible range.

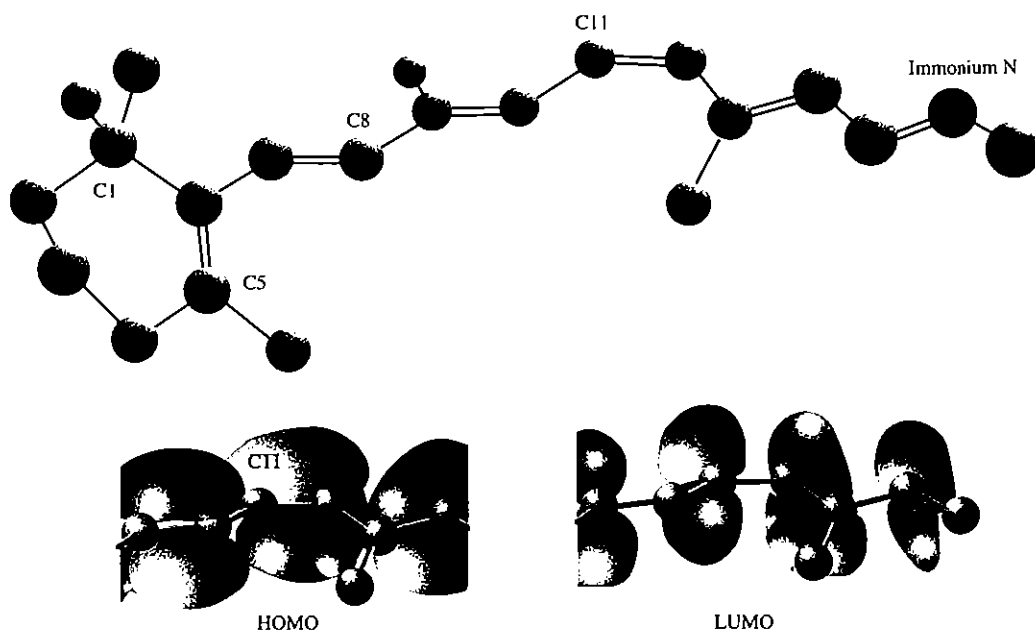


Figure 14.2

P14.26 The concentration of the hypothetical pure layer is

$$[\text{O}_3] = \frac{n}{V} = \frac{p}{RT} = \frac{1 \text{ atm}}{(0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}) \times (273 \text{ K})} = 4.46 \times 10^{-2} \text{ mol dm}^{-3}$$

So for 300 DU

$$A = \varepsilon cl = (476 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) \times (0.300 \text{ cm}) \times (4.46 \times 10^{-2} \text{ mol dm}^{-3}) = \boxed{6.37}$$

and for 100 DU

$$A = \varepsilon cl = (476 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) \times (0.100 \text{ cm}) \times (4.46 \times 10^{-2} \text{ mol dm}^{-3}) = \boxed{2.12}$$

P14.28 The reaction enthalpy for process (2) is

$$\Delta_f H^\ominus = \Delta_f H^\ominus(\text{Cl}) + \Delta_f H^\ominus(\text{OCIO}^+) + \Delta_f H^\ominus(\text{e}^-) - \Delta_f H^\ominus(\text{Cl}_2\text{O}_2)$$

$$\text{so } \Delta_f H^\ominus(\text{Cl}_2\text{O}_2) = \Delta_f H^\ominus(\text{Cl}) + \Delta_f H^\ominus(\text{OCIO}^+) + \Delta_f H^\ominus(\text{e}^-) - \Delta_f H^\ominus$$

$$\begin{aligned} \Delta_f H^\ominus(\text{Cl}_2\text{O}_2) &= (121.68 + 1096 + 0) \text{ kJ mol}^{-1} - (10.95 \text{ eV}) \times (96.485 \text{ kJ eV}^{-1}) \\ &= 161 \text{ kJ mol}^{-1} \end{aligned}$$

We see that the Cl_2O_2 in process (2) is different from that in process (1), for its heat of formation is $\boxed{28 \text{ kJ mol}^{-1}}$ greater. This is consistent with the computations, which say that ClOOC is likely to be the lowest-energy isomer. Experimentally we see that the Cl_2O_2 of process (2), which is not ClOOC , is not very much greater in energy than the lowest-energy isomer.

15

Spectroscopy 3: magnetic resonance

Answers to discussion questions

D15.2 Before the application of a pulse the magnetization vector, \mathbf{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 \mathbf{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 \mathbf{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 \mathbf{M} antiparallel to the static field. Now there are more β spins than α spins. A population inversion has occurred.

D15.4 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 Figure 15.46 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 Figure 15.12). At thermal equilibrium, the population of the $\alpha_A \alpha_X$ level is the greatest, and that of $\beta_A \beta_X$ 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 (Figure 15.50). 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 (Figure 15.46), the result is a two-dimensional spectrum that contains four groups of signals centered 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 centered on $(\delta_A\delta_A)$ and $(\delta_X\delta_X)$ 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 centered on $(\delta_A\delta_X)$ and $(\delta_X\delta_A)$ 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 15.52 shows a simple example of a proton COSY spectrum of isoleucine.

- D15.6** The ESR spectra of a spin probe, such as the di-*tert*-butyl nitroxide radical, broadens with restricted motion of the probe. This suggests that the width of spectral lines may correlate with the depth to which a probe may enter into a biopolymer crevice. Deep crevices are expected to severely restrict probe motion and broaden the spectral lines. Additionally, the splitting and center of ESR spectra of an oriented sample can provide information about the shape of the biopolymer-probe environment because the probe ESR signal is anisotropic and depends upon the orientation of the probe with the external magnetic field. Oriented biopolymers occur in lipid membranes and in muscle fibers.

Solutions to exercises

E15.1(b) For ^{19}F , $\frac{\mu}{\mu_N} = 2.62835$, $g = 5.2567$

$$\nu = \nu_L = \frac{\gamma \mathcal{B}}{2\pi} \quad \text{with} \quad \gamma = \frac{gI\mu_N}{\hbar}$$

$$\text{Hence, } \nu = \frac{gI\mu_N \mathcal{B}}{h} = \frac{(5.2567) \times (5.0508 \times 10^{-27} \text{ J T}^{-1}) \times (16.2 \text{ T})}{(6.626 \times 10^{-34} \text{ J s})}$$

$$= 6.49 \times 10^8 \text{ s}^{-1} = \boxed{649 \text{ MHz}}$$

E15.2(b) $E_{m_I} = -\gamma \hbar \mathcal{B} m_I = -gI\mu_N \mathcal{B} m_I$

$$m_I = 1, 0, -1$$

$$E_{m_I} = -(0.404) \times (5.0508 \times 10^{-27} \text{ J T}^{-1}) \times (11.50 \text{ T}) m_I$$

$$= -(2.3466 \times 10^{-26} \text{ J}) m_I$$

$$\boxed{-2.35 \times 10^{-26} \text{ J}, 0, +2.35 \times 10^{-26} \text{ J}}$$

E15.3(b) The energy separation between the two levels is

$$\begin{aligned}\Delta E = h\nu \quad \text{where } \nu &= \frac{\gamma \mathcal{B}}{2\pi} = \frac{(1.93 \times 10^7 \text{ T}^{-1} \text{ s}^{-1}) \times (15.4 \text{ T})}{2\pi} \\ &= 4.73 \times 10^7 \text{ s}^{-1} = \boxed{47.3 \text{ MHz}}\end{aligned}$$

E15.4(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 15.1(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 $\Delta E(+1 \rightarrow 0) = \Delta E(0 \rightarrow -1)$

$$\begin{aligned}\Delta E &= E_{m'_I} - E_{m_I} = -\gamma \hbar \mathcal{B} m'_I - (-\gamma \hbar \mathcal{B} m_I) \\ &= -\gamma \hbar \mathcal{B} (m'_I - m_I) = -\gamma \hbar \mathcal{B} \Delta m_I\end{aligned}$$

The allowed transitions correspond to $\Delta m_I = \pm 1$; hence

$$\begin{aligned}\Delta E = h\nu &= \gamma \hbar \mathcal{B} = g_I \mu_N \mathcal{B} = (0.4036) \times (5.051 \times 10^{-27} \text{ J T}^{-1}) \times (14.1 \text{ T}) \\ &= \boxed{2.88 \times 10^{-26} \text{ J}}\end{aligned}$$

(b) We assume that the electron g -value in the radical is equal to the free electron g -value, $g_e = 20023$. Then

$$\begin{aligned}\Delta E = h\nu &= g_e \mu_B \mathcal{B} [37] = (2.0023) \times (9.274 \times 10^{-24} \text{ J T}^{-1}) \times (0.300 \text{ T}) \\ &= \boxed{5.57 \times 10^{-24} \text{ J}}\end{aligned}$$

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.

E15.5(b) $\Delta E = h\nu = \gamma \hbar \mathcal{B} = g_I \mu_N \mathcal{B}$ [Solution to Exercise 15.1(a)]

$$\text{Hence, } \mathcal{B} = \frac{h\nu}{g_I \mu_N} = \frac{(6.626 \times 10^{-34} \text{ J Hz}^{-1}) \times (150.0 \times 10^6 \text{ Hz})}{(5.586) \times (5.051 \times 10^{-27} \text{ J T}^{-1})} = \boxed{3.523 \text{ T}}$$

E15.6(b) In all cases the selection rule $\Delta m_I = \pm 1$ is applied; hence (Exercise 15.4(b)(a))

$$\begin{aligned}B &= \frac{h\nu}{g_I \mu_N} = \frac{6.626 \times 10^{-34} \text{ J Hz}^{-1}}{5.0508 \times 10^{-27} \text{ J T}^{-1}} \times \frac{\nu}{g_I} \\ &= (1.3119 \times 10^{-7}) \times \left(\frac{\nu}{\text{Hz}} \right) \text{ T} = (0.13119) \times \left(\frac{\nu}{\text{MHz}} \right) \text{ T}\end{aligned}$$

We can draw up the following table

	\mathcal{B}/T	^{14}N	^{19}F	^{31}P
	g_I	0.40356	5.2567	2.2634
(a)	300 MHz	97.5	7.49	17.4
(b)	750 MHz	244	18.7	43.5

COMMENT. Magnetic fields above 20 T have not yet been obtained for use in NMR spectrometers. As discussed in the solution to Exercise 15.4(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.

E15.7(b) The relative population difference for spin $-\frac{1}{2}$ nuclei is given by

$$\begin{aligned}\frac{\delta N}{N} &= \frac{N_\alpha - N_\beta}{N_\alpha + N_\beta} \approx \frac{\gamma h \mathcal{B}}{2kT} = \frac{g_I \mu_N \mathcal{B}}{2kT} \quad [\text{Justification 15.1}] \\ &= \frac{1.405 (5.05 \times 10^{-27} \text{ J T}^{-1}) \mathcal{B}}{2 (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})} = 8.62 \times 10^{-7} (\mathcal{B}/\text{T})\end{aligned}$$

(a) For 0.50 T $\frac{\delta N}{N} = (8.62 \times 10^{-7}) \times (0.50) = \boxed{4.3 \times 10^{-7}}$

(b) For 2.5 T $\frac{\delta N}{N} = (8.62 \times 10^{-7}) \times (2.5) = \boxed{2.2 \times 10^{-6}}$

(c) For 15.5 T $\frac{\delta N}{N} = (8.62 \times 10^{-7}) \times (15.5) = \boxed{1.34 \times 10^{-5}}$

E15.8(b) The ground state has

$$m_I = +\frac{1}{2} = \alpha \text{ spin}, \quad m_I = -\frac{1}{2} = \beta \text{ spin}$$

Hence, with

$$\delta N = N_\alpha - N_\beta$$

$$\begin{aligned}\frac{\delta N}{N} &= \frac{N_\alpha - N_\beta}{N_\alpha + N_\beta} = \frac{N_\alpha - N_\alpha e^{-\Delta E/kT}}{N_\alpha + N_\alpha e^{-\Delta E/kT}} \quad [\text{Justification 15.1}] \\ &= \frac{1 - e^{-\Delta E/kT}}{1 + e^{-\Delta E/kT}} \approx \frac{1 - (1 - \Delta E/kT)}{1 + 1} \approx \frac{\Delta E}{2kT} = \frac{g_I \mu_N \mathcal{B}}{2kT} \quad [\text{for } \Delta E \ll kT]\end{aligned}$$

$$\delta N = \frac{Ng_I \mu_N \mathcal{B}}{2kT} = \frac{Nh\nu}{2kT}$$

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.

$$(a) \quad \delta = \frac{\nu - \nu^0}{\nu^0} \times 10^6 \text{ [15.8]}$$

Since both ν and ν^0 depend upon the magnetic field in the same manner, namely

$$\nu = \frac{gI\mu_N\mathcal{B}}{h} \text{ and } \nu^0 = \frac{gI\mu_N\mathcal{B}_0}{h} \text{ [Exercise 15.1(a)]}$$

δ is independent of both \mathcal{B} and ν .

(b) Rearranging [15.18], $\nu - \nu^0 = \nu^0\delta \times 10^{-6}$ and we see that the relative chemical shift is

$$\frac{\nu - \nu^0(800 \text{ MHz})}{\nu - \nu^0(60 \text{ MHz})} = \frac{(800 \text{ MHz})}{(60 \text{ MHz})} = \boxed{13}$$

COMMENT. This direct proportionality between $\nu - \nu^0$ and ν^0 is one of the major reasons for operating an NMR spectrometer at the highest frequencies possible.

$$\text{E15.9(b)} \quad \mathcal{B}_{\text{loc}} = (1 - \sigma)\mathcal{B}$$

$$\begin{aligned} |\Delta\mathcal{B}_{\text{loc}}| &= |(\Delta\sigma)|\mathcal{B} \approx |[\delta(\text{CH}_3) - \delta(\text{CH}_2)]|\mathcal{B} \\ &= |1.16 - 3.36| \times 10^{-6}\mathcal{B} = 2.20 \times 10^{-6}\mathcal{B} \end{aligned}$$

$$(a) \quad \mathcal{B} = 1.9 \text{ T}, |\Delta\mathcal{B}_{\text{loc}}| = (2.20 \times 10^{-6}) \times (1.9 \text{ T}) = \boxed{4.2 \times 10^{-6} \text{ T}}$$

$$(b) \quad \mathcal{B} = 16.5 \text{ T}, |\Delta\mathcal{B}_{\text{loc}}| = (2.20 \times 10^{-6}) \times (16.5 \text{ T}) = \boxed{3.63 \times 10^{-5} \text{ T}}$$

$$\text{E15.10(b)} \quad \nu - \nu^0 = \nu^0\delta \times 10^{-6}$$

$$\begin{aligned} |\Delta\nu| &\equiv (\nu - \nu^0)(\text{CH}_2) - (\nu - \nu^0)(\text{CH}_3) = \nu(\text{CH}_2) - \nu(\text{CH}_3) \\ &= \nu^0[\delta(\text{CH}_2) - \delta(\text{CH}_3)] \times 10^{-6} \\ &= (3.36 - 1.16) \times 10^{-6}\nu^0 = 2.20 \times 10^{-6}\nu^0 \end{aligned}$$

$$(a) \quad \nu^0 = 350 \text{ MHz} \quad |\Delta\nu| = (2.20 \times 10^{-6}) \times (350 \text{ MHz}) = 770 \text{ Hz} \text{ [Figure 15.1]}$$

$$(b) \quad \nu^0 = 650 \text{ MHz} \quad |\Delta\nu| = (2.20 \times 10^{-6}) \times (650 \text{ MHz}) = 1.43 \text{ kHz}$$

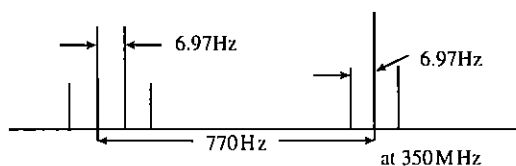


Figure 15.1

At 650 MHz, the spin-spin splitting remains the same at 6.97 Hz, but as $\Delta\nu$ has increased to 1.43 kHz, the splitting appears narrower on the δ scale.

E15.11(b) The difference in resonance frequencies is

$$\Delta\nu = (\nu^0 \times 10^{-6}) \Delta\delta = (350 \text{ s}^{-1}) \times (6.8 - 5.5) = 4.6 \times 10^2 \text{ s}^{-1}$$

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

$$\text{rate} = (2\pi \Delta\delta) = 2\pi (4.6 \times 10^2 \text{ s}^{-1}) = \boxed{2.9 \times 10^3 \text{ s}^{-1}}$$

E15.12(b) $\nu = \frac{g\mu_N\mathcal{B}}{h}$ [Solution to exercise 15.1(a)]

$$\text{Hence, } \frac{\nu(^{31}\text{P})}{\nu(^1\text{H})} = \frac{g(^{31}\text{P})}{g(^1\text{H})}$$

$$\text{or } \nu(^{31}\text{P}) = \frac{2.2634}{5.5857} \times 500 \text{ MHz} = \boxed{203 \text{ MHz}}$$

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 15.6). The lines are spaced $\frac{5.5857}{2.2634} = 2.47$ times greater in the phosphorus region than the proton region. The spectrum is sketched in Figure 15.2.

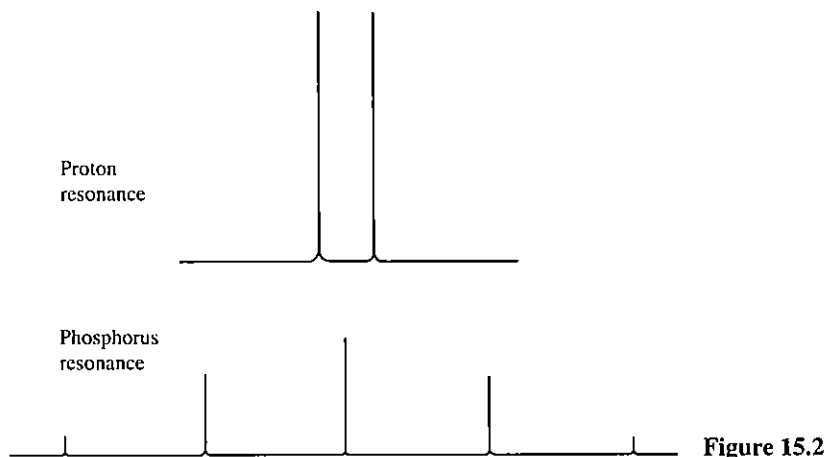


Figure 15.2

E15.13(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).

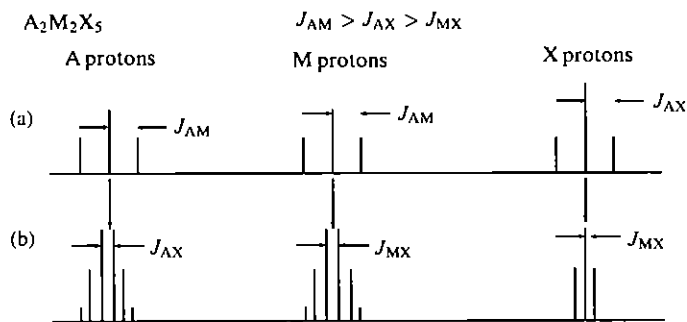


Figure 15.3

The X resonance will be split into a less widely spaced triplet (by the two A protons); each peak of that triplet will be split into a narrowly spaced triplet (by the two M protons). (See Figure 15.3.)

Only the splitting of the central peak of Figure 15.3(a) is shown in Figure 15.3(b).

E15.14(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.

E15.15(b) Precession in the rotating frame follows

$$\nu_L = \frac{\gamma \mathcal{B}_1}{2\pi} \quad \text{or} \quad \omega_L = \gamma \mathcal{B}_1$$

Since ω is an angular frequency, the angle through which the magnetization vector rotates is

$$\theta = \gamma \mathcal{B}_1 t = \frac{g_I \mu_N}{\hbar} \mathcal{B}_1 t$$

$$\text{So } \mathcal{B}_1 = \frac{\theta \hbar}{g_I \mu_N t} = \frac{(\pi) \times (1.0546 \times 10^{-34} \text{ J s})}{(5.586) \times (5.0508 \times 10^{-27} \text{ J T}^{-1}) \times (12.5 \times 10^{-6} \text{ s})} = \boxed{9.40 \times 10^{-4} \text{ T}}$$

$$\text{a } 90^\circ \text{ pulse requires } \frac{1}{2} \times 12.5 \mu\text{s} = \boxed{6.25 \mu\text{s}}$$

$$\begin{aligned} \text{E15.16(b)} \quad \mathcal{B} &= \frac{h\nu}{g_e \mu_B} = \frac{hc}{g_e \mu_B \lambda} \\ &= \frac{(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1})}{(2) \times (9.274 \times 10^{-24} \text{ J T}^{-1}) \times (8 \times 10^{-3} \text{ m})} = \boxed{1.3 \text{ T}} \end{aligned}$$

E15.17(b) The g factor is given by

$$g = \frac{h\nu}{\mu_B \mathcal{B}}; \quad \frac{h}{\mu_B} = \frac{6.62608 \times 10^{-34} \text{ J s}}{9.2740 \times 10^{-24} \text{ J T}^{-1}} = 7.1448 \times 10^{-11} \text{ T Hz}^{-1} = 71.448 \text{ mT GHz}^{-1}$$

$$g = \frac{71.448 \text{ mT GHz}^{-1} \times 9.2482 \text{ GHz}}{330.02 \text{ mT}} = \boxed{2.0022}$$

- E15.18(b)** The hyperfine coupling constant for each proton is 2.2 mT , the difference between adjacent lines in the spectrum. The g value is given by

$$g = \frac{h\nu}{\mu_B \mathcal{B}} = \frac{(71.448 \text{ mT GHz}^{-1}) \times (9.332 \text{ GHz})}{334.7 \text{ mT}} = 1.992$$

- E15.19(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 center, namely

$$328.865, 330.975, 331.735, 331.755, 333.845, 333.865, 334.625, \text{ and } 336.735 \text{ mT}$$

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.

- E15.20(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.

- E15.21(b)** The hyperfine coupling constant for each proton is 2.2 mT , the difference between adjacent lines in the spectrum. The g value is given by

$$g = \frac{h\nu}{\mu_B \mathcal{B}} \text{ so } \mathcal{B} = \frac{h\nu}{\mu_B g}, \quad \frac{h}{\mu_B} = 71.448 \text{ mT GHz}^{-1}$$

$$(a) \quad \mathcal{B} = \frac{(71.448 \text{ mT GHz}^{-1}) \times (9.312 \text{ GHz})}{2.0024} = 332.3 \text{ mT}$$

$$(b) \quad \mathcal{B} = \frac{(71.448 \text{ mT GHz}^{-1}) \times (33.88 \text{ GHz})}{2.0024} = 1209 \text{ mT}$$

- E15.22(b)** Two nuclei of spin $I = 1$ give five lines in the intensity ratio 1:2:3:2:1 (Figure 15.4).

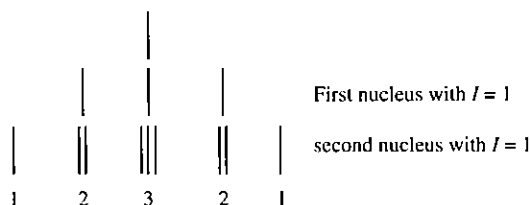


Figure 15.4

- E15.23(b)** The X nucleus produces four lines of equal intensity. Three H nuclei split each into a 1:3:3:1 quartet. The three D nuclei split each line into a septet with relative intensities 1:3:6:7:6:3:1 (see Exercise 15.20(a)). (See Figure 15.5.)

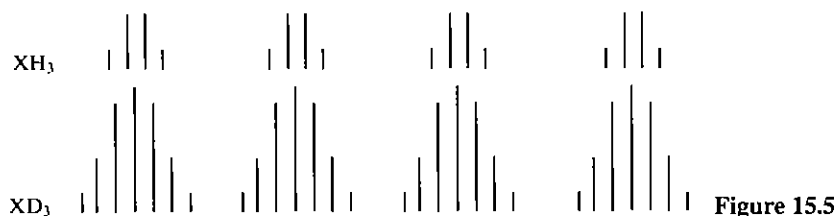


Figure 15.5

Solutions to problems

Solutions to numerical problems

P15.2

$$\tau_J \approx \frac{1}{2\pi\delta\nu} = \frac{1}{(2\pi) \times ((5.2 - 4.0) \times 10^{-6}) \times (60 \times 10^6 \text{ Hz})}$$

$$\approx 2.2 \text{ ms, corresponding to a jump rate of } 450 \text{ s}^{-1}.$$

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 22)

$$\text{rate} \propto e^{-E_a/RT}$$

$$\text{Then, } \ln \left[\frac{\text{rate}(T')}{\text{rate}(T)} \right] = \frac{-E_a}{R} \left(\frac{1}{T'} - \frac{1}{T} \right)$$

$$\text{and therefore } E_a = \frac{R \ln(r'/r)}{\frac{1}{T} - \frac{1}{T'}} = \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln \frac{2.3 \times 10^3}{450}}{\frac{1}{280 \text{ K}} - \frac{1}{300 \text{ K}}} = \boxed{57 \text{ kJ mol}^{-1}}$$

P15.4

The three rotational conformations of $\text{F}_2\text{BrC}-\text{CBrCl}_2$ are shown in Figure 15.6. In conformation I, the two F atoms are equivalent. However, in conformations II and III they are non-equivalent. At low temperature, the molecular residence time in conformation I is longer (because this conformation has the lowest repulsive energy of the large bromine atoms) than that of conformations II and III, which have equal residence times. With its longer residence time, we expect that the NMR signal intensity of conformation I should be stronger and we can conclude that it is the low-temperature singlet. It is a singlet because equivalent atoms do not have detectable spin-spin couplings.

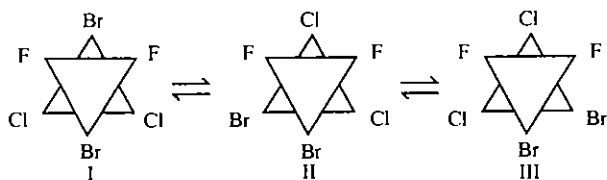


Figure 15.6

The fluorines of conformations II and III are non-equivalent, so their coupling is observed at low-temperature. Fluorine has a nuclear spin of $1/2$, so we expect a doublet for each fluorine. These are observed with strong geminal coupling of 160 Hz. As temperature increases, the rate of rotation between II and III increases and the two fluorines become equivalent in these conformations, though remaining distinct from I. The doublets collapse to singlets. With a further temperature increase to -30°C , and above, the rate of rotation about the C—C bond becomes so rapid that the residence times of the three conformations become equal. The very short residence times produce an average NMR signal that is a singlet and the fluorines appear totally equivalent.

The spectra shown in Figure 15.63 of the text for conformations II and III show both spin–spin coupling and differences in chemical shift. The spin–spin splitting is 160 Hz. The difference in chemical shift can be estimated from the separation between the doublet centers, Δ

$$\Delta = (J^2 + \delta\nu^2)^{1/2}$$

Δ is estimated from the figure to be 210 Hz. This yields for $\delta\nu$, the chemical shift,

$$\begin{aligned}\delta\nu &= (\Delta^2 - J^2)^{1/2} \\ &= (210^2 - 160^2)^{1/2} \text{ Hz} \approx 140 \text{ Hz}\end{aligned}$$

Collapse to a single line will occur when the rate of interconversion satisfies

$$\begin{aligned}k &\approx \frac{1}{\tau} \approx \frac{\pi\Delta}{\sqrt{2}} [15.29] \\ k &= \frac{\pi \times 200 \text{ s}^{-1}}{\sqrt{2}} \approx \boxed{4 \times 10^2 \text{ s}^{-1}}\end{aligned}$$

The relative intensities, I , of the lines at -80°C can be used to estimate the energy difference ($E_{\text{II}} - E_{\text{I}}$) between conformation I and conformations II and III. We assume that the relative intensities of the lines are proportional to the populations of conformers and that these populations follow the Boltzmann distribution (Chapters 2 and 16). Then

$$\begin{aligned}\frac{I_{\text{I}}}{I_{\text{II}}} &= \frac{e^{-E_{\text{I}}/RT}}{e^{-E_{\text{II}}/RT}} = e^{(E_{\text{II}} - E_{\text{I}})/RT} \\ E_{\text{II}} - E_{\text{I}} &= RT \ln \left(\frac{I_{\text{I}}}{I_{\text{II}}} \right) = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times (273 - 80) \text{ K} \ln(10) \\ &= 3.7 \times 10^3 \text{ J mol}^{-1} = \boxed{3.7 \text{ kJ mol}^{-1}}\end{aligned}$$

This energy difference is not, however, the rotational energy barrier between the rotational isomers. The latter can be estimated from the rate of interconversion between the isomers as a function of temperature. That rate of interconversion is roughly $4 \times 10^2 \text{ s}^{-1}$ at -30°C . At -60°C , as estimated from the line width at that temperature [13.19], it is roughly $1/3$ of that value, or $\sim 1.3 \times 10^2 \text{ s}^{-1}$. Assuming that the rate of interconversion satisfies an Arrhenius type of behavior, $k \propto e^{-E_a/RT}$, where E_a is the rotational energy barrier,

$$\frac{k(-30^\circ\text{C})}{k(-60^\circ\text{C})} = 3 = e^{\left[-\frac{E_a}{R} \left(\frac{1}{213\text{K}} - \frac{1}{213\text{K}} \right) \right]}$$

$$E_a = \frac{R \ln 3}{\left(\frac{1}{213 \text{ K}} - \frac{1}{243 \text{ K}}\right)} = 1.6 \times 10^4 \text{ J mol}^{-1} = \boxed{16 \text{ kJ mol}^{-1}}$$

This value is typical of the rotational barriers observed in compounds of this kind.

- P15.6** (a) The Karplus equation [15.27] for $^3J_{\text{HH}}$ is a linear equation in $\cos \phi$ and $\cos 2\phi$. The experimentally determined equation for $^3J_{\text{SnSn}}$ is a linear equation in $^3J_{\text{HH}}$. In general, if $F(f)$ is linear in f , and if $f(x)$ is linear in x , then $F(x)$ is linear. So we expect $^3J_{\text{SnSn}}$ to be linear in $\cos \phi$ and $\cos 2\phi$. This is demonstrated in (b).

(b) $^3J_{\text{SnSn}}/\text{Hz} = 78.86(^3J_{\text{HH}}/\text{Hz}) + 27.84$

Inserting the Karplus equation for $^3J_{\text{HH}}$ we obtain

$$^3J_{\text{SnSn}}/\text{Hz} = 78.86\{A + B \cos \phi + C \cos 2\phi\} + 27.84. \text{ Using } A = 7, B = -1, \text{ and } C = 5, \text{ we obtain}$$

$$^3J_{\text{SnSn}}/\text{Hz} = \boxed{580 - 79 \cos \phi + 395 \cos 2\phi}$$

The plot of $^3J_{\text{SnSn}}$ is shown in Figure 15.7.

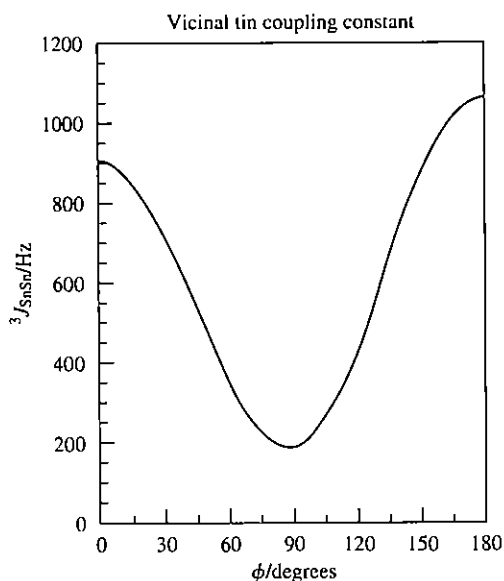
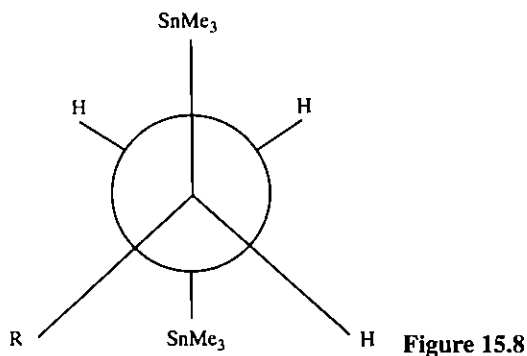


Figure 15.7

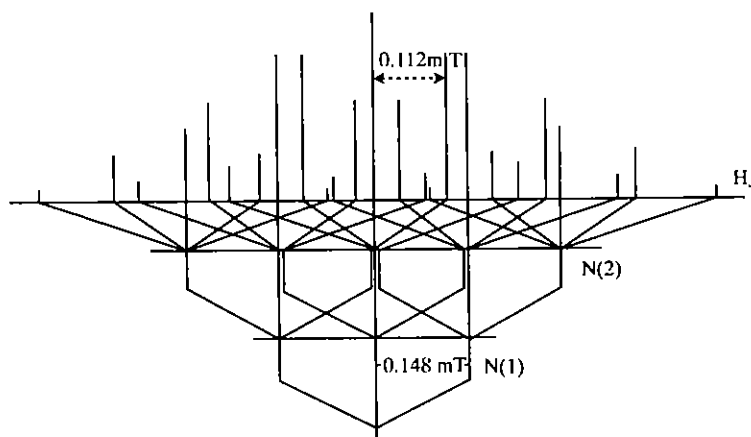
- (c) A staggered configuration (Figure 15.8) with the SnMe_3 groups *trans* to each other is the preferred configuration. The SnMe_3 repulsions are then at a minimum.

P15.8

$$\begin{aligned} g &= \frac{h\nu}{\mu_B \mathcal{B}_0} [15.40] = \frac{(7.14478 \times 10^{-11} \text{ T}) \times (\nu / \text{Hz})}{\mathcal{B}_0} \\ &= \frac{(7.14478 \times 10^{-11} \text{ T}) \times (9.302 \times 10^9)}{\mathcal{B}_0} = \frac{0.66461}{\mathcal{B}_0/T} \\ g_{\parallel} &= \frac{0.66461}{0.33364} = \boxed{1.992} \quad g_{\perp} = \frac{0.66461}{0.33194} = \boxed{2.002} \end{aligned}$$



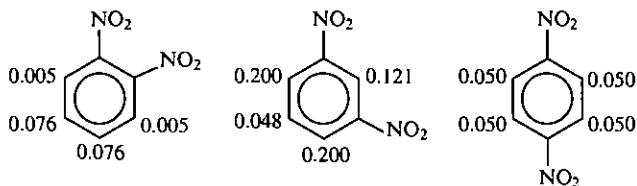
- P15.10** Construct the spectrum by taking into account first the two equivalent ^{14}N splitting (producing a $1:2:3:2:1$ quintet) and then the splitting of each of these lines into a $1:4:6:4:1$ quintet by the four equivalent protons. The resulting 25-line spectrum is shown in Figure 15.9. Note that Pascal's triangle does not apply to the intensities of the quintet due to ^{14}N , but does apply to the quintet due to the protons.

**Figure 15.9**

- P15.12** For C_6H_6^- , $a = Q\rho$ with $Q = 2.25 \text{ mT}$ [15.43]. 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

$$\rho = \frac{a}{Q} = \frac{a}{2.25 \text{ mT}}$$

Hence, we can construct the following maps



Solutions to theoretical problems

- P15.14** (a) The table displays experimental ^{13}C chemical shifts and computed* atomic charges on the carbon atom *para* to a number of substituents in substituted benzenes. Two sets of charges are shown, one derived by fitting the electrostatic potential and the other by Mulliken population analysis.

Substituent	OH	CH ₃	H	CF ₃	CN	NO ₂
δ	130.1	128.4	128.5	128.9	129.1	129.4
Electrostatic charge/ <i>e</i>	-0.1305	-0.1273	-0.0757	-0.0227	-0.0152	-0.0541
Mulliken charge/ <i>e</i>	-0.1175	-0.1089	-0.1021	-0.0665	-0.0805	-0.0392

*Semi-empirical, PM3 level, PC Spartan ProTM

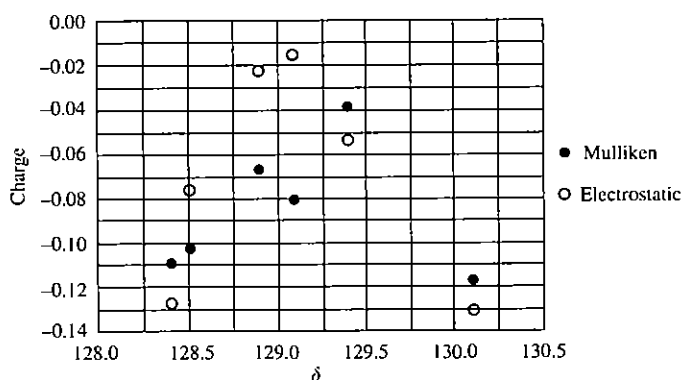


Figure 15.10

- (b) Neither set of charges correlates well to the chemical shifts. If one removes phenol from the data set, a correlation would be apparent, particularly for the Mulliken charges.
- (c) The diamagnetic local contribution to shielding is roughly proportional to the electron density on the atom. The extent to which the *para*-carbon atom is affected by electron-donating or withdrawing groups on the other side of the benzene ring is reflected in the net charge on the atom. If the diamagnetic local contribution dominated, then the more positive the atom, the greater the deshielding and the greater the chemical shift δ would be. That no such correlation is observed leads to several possible hypotheses: for example, the diamagnetic local contribution is not the dominant contribution in these molecules (or not in all of these molecules), or the computation is not sufficiently accurate to provide meaningful atomic charges.

- P15.16** Equation 15.39 may be written

$$\mathcal{B} = k(1 - 3 \cos^2 \theta)$$

where k is a constant independent of angle. Thus

$$\begin{aligned}
 \langle \mathcal{B} \rangle &\propto \int_0^\pi (1 - 3 \cos^2 \theta) \sin \theta d\theta \int_0^{2\pi} d\phi \\
 &\propto \int_1^{-1} (1 - 3x^2) dx \times 2\pi \quad [x = \cos \theta, dx = -\sin \theta d\theta] \\
 &\propto (x - x^3) \Big|_1^{-1} = 0
 \end{aligned}$$

P15.18 We have seen (Problem 15.17) that, if $G \propto \cos \omega_0 t$, then $I(\omega) \propto \frac{1}{[1 + (\omega_0 - \omega)^2 \tau^2]}$

which peaks at $\omega \approx \omega_0$. Therefore, if

$$G(t) \propto a \cos \omega_1 t + b \cos \omega_2 t$$

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 $\omega \approx \omega_2$.

Solutions to applications

P15.20 Methionine-105 is in the vicinity of both typtophan-28 and tyrosine-23 but the latter two residues are not in the vicinity of each other. The methionine residue may lay between them as represented in the figure.

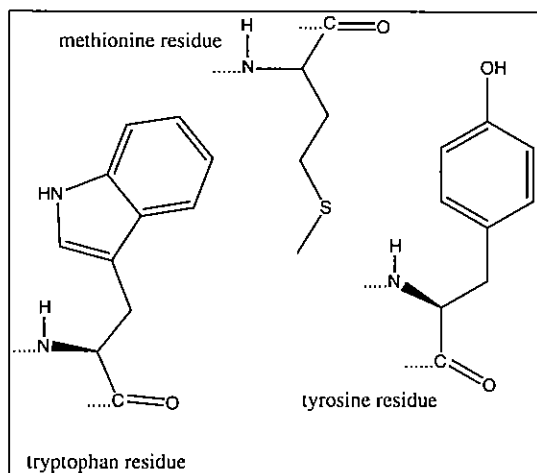
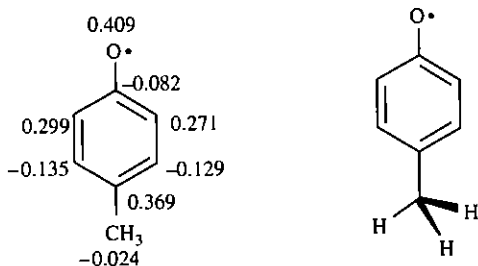


Figure 15.11

P15.22 At, say, room temperature, the tumbling rate of benzene, the small molecule, in a mobile solvent, may be close to the Larmor frequency, and hence its spin-lattice relaxation time will be short. As the temperature increases, the tumbling rate may increase well beyond the Larmor frequency, resulting in an increased spin-lattice relaxation time.

For the large oligopeptide at room temperature, the tumbling rate may be well below the Larmor frequency, but with increasing temperature it will approach the Larmor frequency due to the increased thermal motion of the molecule combined with the decreased viscosity of the solvent. Therefore, the spin-lattice relaxation time may decrease.

- P15.24** (a) The first figure displays spin densities computed by molecular modeling software (*ab initio*, density functional theory, Gaussian 98TM).



- (b) First, note that the software assigned slightly different values to the two protons *ortho* to the oxygen and to the two protons *meta* to the oxygen. This is undoubtedly a computational artifact, a result of the minimum-energy structure having one methyl proton in the plane of the ring, which makes the right and left side of the ring slightly non-equivalent. (See second figure.) In fact, fast internal rotation makes the two halves of the ring equivalent. We will take the spin density at the *ortho* carbons to be 0.285 and those of the *meta* carbons to be -0.132 . Predict the form of the spectrum by using the McConnell equation (15.43) for the splittings. The two *ortho* protons give rise to a 1:2:1 triplet with splitting $0.285 \times 2.25 \text{ mT} = 0.64 \text{ mT}$; these will in turn be split by the two *meta* protons into 1:2:1 triplets with splitting

$$0.132 \times 2.25 \text{ mT} = 0.297 \text{ mT} = 0.297 \text{ mT}.$$

And finally, these lines will be seen to be further split by the three methyl protons into 1:3:3:1 quartets with splittings 1.045 mT. Note that the McConnell relation cannot be applied to calculate these latter splittings, but the software generates them directly from calculated spin densities on the methyl hydrogens. The computed splittings agree well with experiment at the *ortho* positions (0.60 mT) and at the methyl hydrogens (1.19 mT), but less well at the *meta* positions (0.145 mT).

P15.26 We use $\nu = \frac{\gamma N \mathcal{B}_{\text{loc}}}{2\pi} = \frac{\gamma N}{2\pi} (1 - \sigma) \mathcal{B}$ [15.17]

where \mathcal{B} is the applied field.

Because shielding constants are quite small (a few parts per million) compared to 1, we may write for the purposes of this calculation

$$\begin{aligned} \nu &= \frac{\gamma N \mathcal{B}}{2\pi} \\ \nu_L - \nu_R &= 100 \text{ Hz} = \frac{\gamma N}{2\pi} (\mathcal{B}_L - \mathcal{B}_R) \\ \mathcal{B}_L - \mathcal{B}_R &= \frac{2\pi \times 100 \text{ s}^{-1}}{\gamma N} \\ &= \frac{2\pi \times 100 \text{ s}^{-1}}{26.752 \times 10^7 \text{ T}^{-1} \text{ s}^{-1}} = 2.35 \times 10^{-6} \text{ T} \\ &= 2.35 \mu\text{T} \end{aligned}$$

The field gradient required is then

$$\frac{2.35 \mu\text{T}}{0.08 \text{ m}} = \boxed{29 \mu\text{T m}^{-1}}$$

Note that knowledge of the spectrometer frequency, applied field, and the numerical value of the chemical shift (because constant) is not required.

16

Statistical thermodynamics 1: the concepts

Answers to discussion questions

- D16.2** See Figure 16.11 and 16.13, *Illustration* 16.4, Self-test 16.6 in the text and the solution to Exercise 16.8(a)
- D16.4** The simple zipper model for the conversion of a polypeptide helical (*h*) chain to a random coil (*c*) begins with nucleation whereby an *h* residue makes an independent transition to a *c* residue with a probability that depends upon σs where $\sigma < 1$ and *s* is the stability parameter. After the nucleation conversion, only residues adjacent to a *c* undergo the *h* to *c* transition and they do so non-cooperatively with a probability that depends upon the stability parameter. The Zimm–Brag model allows for multiple nucleation sites.
- D16.6** 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.

Solutions to exercises

E16.1(b)
$$n_i = \frac{N e^{-\beta \epsilon_i}}{q} \quad \text{where } q = \sum_j e^{-\beta \epsilon_j}$$

Thus

$$\frac{n_2}{n_1} = \frac{e^{-\beta \epsilon_2}}{e^{-\beta \epsilon_1}} = e^{-\beta(\epsilon_2 - \epsilon_1)} = e^{-\beta \Delta \epsilon} = e^{-\Delta \epsilon / kT}$$

Given $\frac{n_2}{n_1} = \frac{1}{2}$, $\Delta \epsilon = 300 \text{ cm}^{-1}$

$$k = (1.380\,66 \times 10^{-23} \text{ J K}^{-1}) \times \left(\frac{1 \text{ cm}^{-1}}{1.9864 \times 10^{-23} \text{ J}} \right) = 0.695\,06 \text{ cm}^{-1} \text{ K}^{-1}$$

$$\frac{n_2}{n_1} = e^{-\Delta \epsilon / kT}$$

$$\ln \left(\frac{n_2}{n_1} \right) = -\Delta \epsilon / kT$$

$$T = \frac{-\Delta \epsilon}{k \ln(n_2/n_1)} = \frac{\Delta \epsilon}{k \ln(n_1/n_2)}$$

$$= \frac{300 \text{ cm}^{-1}}{(0.695\,06 \text{ cm}^{-1} \text{ K}^{-1}) \ln(2)} = 622.7 \text{ K} \approx \boxed{623 \text{ K}}$$

$$\begin{aligned}
 \text{E16.2(b)} \quad (a) \quad \Lambda &= h \left(\frac{\beta}{2\pi m} \right)^{1/2} [16.19] = h \left(\frac{1}{2\pi mkT} \right)^{1/2} \\
 &= (6.626 \times 10^{-34} \text{ J s}) \\
 &\quad \times \left(\frac{1}{(2\pi) \times (39.95) \times (1.6605 \times 10^{-27} \text{ kg}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times T} \right)^{1/2} \\
 &= \frac{276 \text{ pm}}{(T/\text{K})^{1/2}}
 \end{aligned}$$

$$(b) \quad q = \frac{V}{\Lambda^3} [16.19] = \frac{(1.00 \times 10^{-6} \text{ m}^3) \times (T/\text{K})^{3/2}}{(2.76 \times 10^{-10} \text{ m})^3} = 4.76 \times 10^{22} (T/\text{K})^{3/2}$$

$$(i) \quad T = 300 \text{ K}, \quad \Lambda = 1.59 \times 10^{-11} \text{ m} = \boxed{15.9 \text{ pm}}, \quad q = \boxed{2.47 \times 10^{26}}$$

$$(ii) \quad T = 3000 \text{ K}, \quad \Lambda = \boxed{5.04 \text{ pm}}, \quad q = \boxed{7.82 \times 10^{27}}$$

Question. At what temperature does the thermal wavelength of an argon atom become comparable to its diameter?

E16.3(b) The translational partition function is

$$q_{\text{tr}} = \frac{V}{h^3} (2\pi kT\pi m)^{3/2}$$

$$\text{so } \frac{q_{\text{Xe}}}{q_{\text{He}}} = \left(\frac{m_{\text{Xe}}}{m_{\text{He}}} \right)^{3/2} = \left(\frac{131.3 \text{ u}}{4.003 \text{ u}} \right)^{3/2} = \boxed{187.9}$$

$$\text{E16.4(b)} \quad q = \sum_{\text{levels}} g_j e^{-\beta \epsilon_j} = 2 + 3e^{-\beta \epsilon_1} + 2e^{-\beta \epsilon_2}$$

$$\beta \epsilon = \frac{hc\tilde{\nu}}{kT} = \frac{1.4388(\tilde{\nu}/\text{cm}^{-1})}{T/\text{K}}$$

$$\text{Thus } q = 2 + 3e^{-(1.4388 \times 1250/2000)} + 2e^{-(1.4388 \times 1300/2000)}$$

$$= 2 + 1.2207 + 0.7850 = \boxed{4.006}$$

$$\text{E16.5(b)} \quad E = U - U(0) = -\frac{N}{q} \frac{dq}{d\beta} = -\frac{N}{q} \frac{d}{d\beta} (2 + 3e^{-\beta \epsilon_1} + 2e^{-\beta \epsilon_2})$$

$$= -\frac{N}{q} (-3\epsilon_1 e^{-\beta \epsilon_1} - 2\epsilon_2 e^{-\beta \epsilon_2}) = \frac{Nhc}{q} (3\tilde{\nu}_1 e^{-\beta hc\tilde{\nu}_1} + 2\tilde{\nu}_2 e^{-\beta hc\tilde{\nu}_2})$$

$$= \left(\frac{N_{\text{A}} hc}{4.006} \right) \times \left\{ 3(1250 \text{ cm}^{-1}) \times \left(e^{-(1.4388 \times 1250/2000)} \right) \right.$$

$$\left. + 2(1300 \text{ cm}^{-1}) \times \left(e^{-(1.4388 \times 1300/2000)} \right) \right\}$$

$$= \left(\frac{N_{\text{A}} hc}{4.006} \right) \times (2546 \text{ cm}^{-1})$$

$$= (6.022 \times 10^{23} \text{ mol}^{-1}) \times (6.626 \times 10^{-34} \text{ J s}) \times (2.9979 \times 10^{10} \text{ cm s}^{-1}) \times (2546 \text{ cm}^{-1})/4.006$$

$$= \boxed{7.605 \text{ kJ mol}^{-1}}$$

- E16.6(b)** In fact there are two upper states, but one upper level. And of course the answer is different if the question asks when 15 percent of the molecules are in the upper level, or if it asks when 15 percent 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

$$\frac{n_2}{n_1} = \exp\left(\frac{-\Delta E}{kT}\right) = \exp\left(\frac{-hc\tilde{\nu}}{kT}\right) \quad \text{so} \quad \ln \frac{n_2}{n_1} = \frac{-hc\tilde{\nu}}{kT}$$

$$\text{Thus } T = \frac{-hc\tilde{\nu}}{k \ln(n_2/n_1)}$$

Having 15 percent of the molecules in the upper level means

$$\frac{2n_2}{n_1} = \frac{0.15}{1 - 0.15} \quad \text{so} \quad \frac{n_2}{n_1} = 0.088$$

$$\begin{aligned} \text{and } T &= \frac{-(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^{10} \text{ cm s}^{-1}) \times (360 \text{ cm}^{-1})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (\ln 0.088)} \\ &= \boxed{213 \text{ K}} \end{aligned}$$

- E16.7(b)** The energies of the states relative to the energy of the state with $m_l = 0$ are $-\gamma_N \hbar \mathcal{B}$, 0 , $+\gamma_N \hbar \mathcal{B}$, where $\gamma_N \hbar = 2.04 \times 10^{-27} \text{ J T}^{-1}$. With respect to the lowest level they are 0 , $\gamma_N \hbar$, $2\gamma_N \hbar$.

The partition function is

$$q = \sum_{\text{states}} e^{-E_{\text{state}}/kT}$$

where the energies are measured with respect to the lowest energy. So in this case

$$q = 1 + \exp\left(\frac{-\gamma_N \hbar \mathcal{B}}{kT}\right) + \exp\left(\frac{-2\gamma_N \hbar \mathcal{B}}{kT}\right)$$

As \mathcal{B} is increased at any given T , q decays from $q = 3$ toward $q = 1$ as shown in Figure 16.1(a).

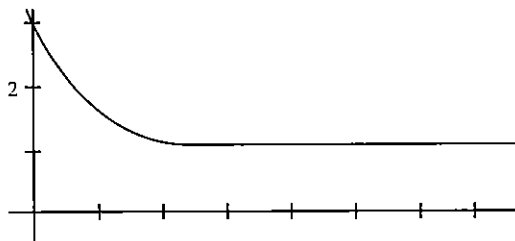


Figure 16.1(a)

The average energy (measured with respect to the lowest state) is

$$\langle E \rangle = \frac{\sum_{\text{states}} E_{\text{state}} e^{-E_{\text{state}}/kT}}{q} = \frac{1 + \gamma_N \hbar \mathcal{B} \exp(-\gamma_N \hbar \mathcal{B}/kT) + 2\gamma_N \hbar \mathcal{B} \exp(-2\gamma_N \hbar \mathcal{B}/kT)}{1 + \exp(-\gamma_N \hbar \mathcal{B}/kT) + \exp(-2\gamma_N \hbar \mathcal{B}/kT)}$$

The expression for the mean energy measured based on zero spin having zero energy becomes

$$E = \frac{\gamma_N \hbar \mathcal{B} - \gamma_N \hbar \mathcal{B} \exp(-2\gamma_N \hbar \mathcal{B}/kT)}{1 + \exp(-\gamma_N \hbar \mathcal{B}/kT) + \exp(-2\gamma_N \hbar \mathcal{B}/kT)} = \frac{\gamma_N \hbar \mathcal{B} (1 - \exp(-2\gamma_N \hbar \mathcal{B}/kT))}{1 + \exp(-\gamma_N \hbar \mathcal{B}/kT) + \exp(-2\gamma_N \hbar \mathcal{B}/kT)}$$

As \mathcal{B} is increased at constant T , the mean energy varies as shown in Figure 16.1(b).

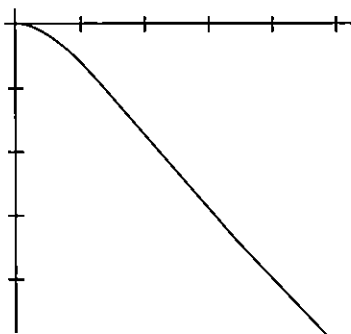


Figure 16.1(b)

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 $\frac{\gamma_N \hbar \mathcal{B}}{k} = \frac{(2.04 \times 10^{-27} \text{ J T}^{-1}) \times (20.0 \text{ T})}{1.381 \times 10^{-23} \text{ J K}^{-1}} = 2.95 \times 10^{-3} \text{ K}$

so the populations are

(a) $\exp\left(\frac{-2.95 \times 10^{-3} \text{ K}}{1.0 \text{ K}}\right) = \boxed{0.997}$ and $\exp\left(\frac{2(-2.95 \times 10^{-3} \text{ K})}{1.0 \text{ K}}\right) = \boxed{0.994}$

(b) $\exp\left(\frac{-2.95 \times 10^{-3} \text{ K}}{298}\right) = \boxed{0.99999}$
and $\exp\left(\frac{2(-2.95 \times 10^{-3} \text{ K})}{298}\right) = \boxed{0.99998}$

E16.8(b) (a) The ratio of populations is given by the Boltzmann factor

$$\frac{n_2}{n_1} = \exp\left(\frac{-\Delta E}{kT}\right) = e^{-25.0 \text{ K}/T} \quad \text{and} \quad \frac{n_3}{n_1} = e^{-50.0 \text{ K}/T}$$

(1) At 1.00 K

$$\frac{n_2}{n_1} = \exp\left(\frac{-25.0 \text{ K}}{1.00 \text{ K}}\right) = \boxed{1.39 \times 10^{-11}}$$

$$\text{and } \frac{n_3}{n_1} = \exp\left(\frac{-50.0 \text{ K}}{1.00 \text{ K}}\right) = \boxed{1.93 \times 10^{-22}}$$

(2) At 25.0 K

$$\frac{n_2}{n_1} = \exp\left(\frac{-25.0 \text{ K}}{25.0 \text{ K}}\right) = \boxed{0.368} \quad \text{and} \quad \frac{n_3}{n_1} = \exp\left(\frac{-50.0 \text{ K}}{25.0 \text{ K}}\right) = \boxed{0.135}$$

(3) At 100 K

$$\frac{n_2}{n_1} = \exp\left(\frac{-25.0 \text{ K}}{100 \text{ K}}\right) = \boxed{0.779} \quad \text{and} \quad \frac{n_3}{n_1} = \exp\left(\frac{-50.0 \text{ K}}{100 \text{ K}}\right) = \boxed{0.607}$$

(b) The molecular partition function is

$$q = \sum_{\text{states}} e^{-E_{\text{state}}/kT} = 1 + e^{-25.0 \text{ K}/T} + e^{-50.0 \text{ K}/T}$$

At 25.0 K, we note that $e^{-25.0 \text{ K}/T} = e^{-1}$ and $e^{-50.0 \text{ K}/T} = e^{-2}$

$$q = 1 + e^{-1} + e^{-2} = \boxed{1.503}$$

(c) The molar internal energy is

$$U_m = U_m(0) - \frac{N_A}{q} \left(\frac{\partial q}{\partial \beta} \right) \quad \text{where } \beta = (kT)^{-1}$$

$$\text{So } U_m = U_m(0) - \frac{N_A}{q} (-25.0 \text{ K}) k (e^{-25.0 \text{ K}/T} + 2e^{-50.0 \text{ K}/T})$$

At 25.0 K

$$\begin{aligned} U_m - U_m(0) &= - \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (-25.0 \text{ K}) \times (1.381 \times 10^{-23} \text{ J K}^{-1})}{1.503} \\ &\quad \times (e^{-1} + 2e^{-2}) \\ &= \boxed{88.3 \text{ J mol}^{-1}} \end{aligned}$$

(d) The molar heat capacity is

$$\begin{aligned} C_{V,m} &= \left(\frac{\partial U_m}{\partial T} \right)_V = N_A (25.0 \text{ K}) k \frac{\partial}{\partial T} \frac{1}{q} (e^{-25.0 \text{ K}/T} + 2e^{-50.0 \text{ K}/T}) \\ &= N_A (25.0 \text{ K}) k \times \left(\frac{25.0 \text{ K}}{qT^2} (e^{-25.0 \text{ K}/T} + 4e^{-50.0 \text{ K}/T}) \right. \\ &\quad \left. - \frac{1}{q^2} (e^{-25.0 \text{ K}/T} + 2e^{-50.0 \text{ K}/T}) \frac{\partial q}{\partial T} \right) \end{aligned}$$

$$\text{where } \frac{\partial q}{\partial T} = \frac{25.0 \text{ K}}{T^2} (e^{-25.0 \text{ K}/T} + 2e^{-50.0 \text{ K}/T})$$

$$\text{so } C_{V,m} = \frac{N_A(25.0 \text{ K})^2 k}{T^2 q} \left(e^{-25.0 \text{ K}/T} + 4e^{-50.0 \text{ K}/T} - \frac{(e^{-25.0 \text{ K}/T} + 2e^{-50.0 \text{ K}/T})^2}{q} \right)$$

At 25.0 K

$$\begin{aligned} C_{V,m} &= \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (25.0 \text{ K})^2 \times (1.381 \times 10^{-23} \text{ J K}^{-1})}{(25.0 \text{ K})^2 \times (1.503)} \\ &\quad \times \left(e^{-1} + 4e^{-2} - \frac{(e^{-1} + 2e^{-2})^2}{1.503} \right) \\ &= \boxed{3.53 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

(e) The molar entropy is

$$S_m = \frac{U_m - U_m(0)}{T} + N_A k \ln q$$

At 25.0 K

$$\begin{aligned} S_m &= \frac{88.3 \text{ J mol}^{-1}}{25.0 \text{ K}} + (6.022 \times 10^{23} \text{ mol}^{-1}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \ln 1.503 \\ &= \boxed{6.92 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

$$\text{E16.9(b)} \quad \frac{n_1}{n_0} = \frac{g_1 e^{-\varepsilon_1/kT}}{g_0 e^{-\varepsilon_0/kT}} = g_1 e^{-\Delta\varepsilon/kT} = 3e^{-hcB/kT}$$

Set $\frac{n_1}{n_0} = \frac{1}{e}$ and solve for T .

$$\ln\left(\frac{1}{e}\right) = \ln 3 + \left(\frac{-hcB}{kT}\right)$$

$$\begin{aligned} T &= \frac{hcB}{k(1 + \ln 3)} \\ &= \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^{10} \text{ cm s}^{-1} \times 10.593 \text{ cm}^{-1}}{+1.381 \times 10^{-23} \text{ J K}^{-1} \times (1 + 1.0986)} \\ &= \boxed{7.26 \text{ K}} \end{aligned}$$

E16.10(b) The Sackur–Tetrode equation gives the entropy of a monatomic gas as

$$S = nR \ln \left(\frac{e^{5/2} kT}{p \Lambda^3} \right) \quad \text{where } \Lambda = \frac{h}{\sqrt{2kT\pi m}}$$

(a) At 100 K

$$\begin{aligned} \Lambda &= \frac{6.626 \times 10^{-34} \text{ J s}}{\left\{ 2(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (100 \text{ K}) \times \pi(131.3 \text{ u}) \times (1.66054 \times 10^{-27} \text{ kg u}^{-1}) \right\}^{1/2}} \\ &= 1.52 \times 10^{-11} \text{ m} \end{aligned}$$

$$\begin{aligned}\text{and } S_m &= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left(\frac{e^{5/2} (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (100 \text{ K})}{(1.013 \times 10^5 \text{ Pa}) \times (1.52 \times 10^{-11} \text{ m})^3} \right) \\ &= \boxed{147 \text{ J K}^{-1} \text{ mol}^{-1}}\end{aligned}$$

(b) At 298.15 K

$$\begin{aligned}\Lambda &= \frac{6.626 \times 10^{-34} \text{ J s}}{\left\{ 2(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298.15 \text{ K}) \times \pi (131.3 \text{ u}) \times (1.66054 \times 10^{-27} \text{ kg u}^{-1}) \right\}^{1/2}} \\ &= 8.822 \times 10^{-12} \text{ m}\end{aligned}$$

and

$$\begin{aligned}S_m &= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left(\frac{e^{5/2} (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298.15 \text{ K})}{(1.013 \times 10^5 \text{ Pa}) \times (8.822 \times 10^{-12} \text{ m})^3} \right) \\ &= \boxed{169.6 \text{ J K}^{-1} \text{ mol}^{-1}}\end{aligned}$$

E16.11(b)

$$q = \frac{1}{1 - e^{-\beta \epsilon}} = \frac{1}{1 - e^{-hc\beta \tilde{\nu}}}$$

$$hc\beta \tilde{\nu} = \frac{(1.4388 \text{ cm K}) \times (321 \text{ cm}^{-1})}{600 \text{ K}} = 0.76976$$

$$\text{Thus } q = \frac{1}{1 - e^{-0.76976}} = 1.86\bar{3}$$

The internal energy due to vibrational excitation is

$$\begin{aligned}U - U(0) &= \frac{N\epsilon e^{-\beta \epsilon}}{1 - e^{-\beta \epsilon}} \\ &= \frac{Nhc\tilde{\nu} e^{-hc\beta \tilde{\nu}}}{1 - e^{-hc\beta \tilde{\nu}}} = \frac{Nhc\tilde{\nu}}{e^{hc\beta \tilde{\nu}} - 1} = (0.86\bar{3}) \times (Nhc) \times (321 \text{ cm}^{-1})\end{aligned}$$

$$\begin{aligned}\text{and hence } \frac{S_m}{N_A k} &= \frac{U - U(0)}{N_A k T} + \ln q = (0.86\bar{3}) \times \left(\frac{hc}{kT} \right) \times (321 \text{ cm}^{-1}) + \ln(1.86\bar{3}) \\ &= \frac{(0.86\bar{3}) \times (1.4388 \text{ K cm}) \times (321 \text{ cm}^{-1})}{600 \text{ K}} + \ln(1.86\bar{3}) \\ &= 0.66\bar{4} + 0.6219\bar{9} = 1.28\bar{6}\end{aligned}$$

$$\text{and } S_m = 1.28\bar{6}R = \boxed{10.7 \text{ J K}^{-1} \text{ mol}^{-1}}$$

E16.12(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 (a) CO₂ gas.

Solutions to problems

Solutions to numerical problems

P16.2 Although He is a liquid at these temperatures ($T_b = 4.22$ K), we will test it as if it were a perfect gas with no interaction potential

$$p_i = \frac{N_i}{N} = g_i e^{-\beta \varepsilon_i} / q \quad [16.6a]$$

$$\varepsilon_i = \frac{h^2}{8mX^2} (n_x^2 + n_y^2 + n_z^2) \quad [16.16]; \quad q = \frac{V}{\Lambda^3}; \quad \Lambda = h \left(\frac{\beta}{2\pi m} \right)^{1/2} \quad [16.19]$$

Ground state $n_x = n_y = n_z = 1$; $g = 1$

First excited state

$$\left. \begin{array}{ll} n_x = n_y = 1; & n_z = 2 \\ n_x = n_z = 1; & n_y = 2 \\ n_y = n_z = 1; & n_x = 2 \end{array} \right\} g = 3$$

$$\begin{aligned} q &= \frac{V}{\Lambda^3} = \frac{V}{h^3} (2\pi m k T)^{3/2} \\ &= \frac{(1 \text{ cm}^3) \times \left(\frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \right) \times [2\pi (1.381 \times 10^{-23} \text{ J K}^{-1})]^{3/2} \times (mT)^{3/2}}{(6.626 \times 10^{-34} \text{ J s})^3} \\ &= 2.28 \times 10^{60} \text{ kg}^{-3/2} \text{ K}^{-3/2} (mT)^{3/2} \end{aligned}$$

$$\begin{aligned} \beta \varepsilon_{\text{1st excited}} &= \left(\frac{1}{kT} \right) \times \left(\frac{h^2}{8mX^2} \right) (6) \\ &= \frac{6 (6.626 \times 10^{-34} \text{ J s})^2}{8 (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (0.01 \text{ m})^2 mT} \frac{1}{mT} \\ &= \frac{2.38 \times 10^{-40} \text{ kg K}}{mT} \end{aligned}$$

$$p_{\text{1st excited}} = \frac{3e^{-\left(\frac{2.38 \times 10^{-40} \text{ kg K}}{mT} \right)}}{(2.78 \times 10^{60} \text{ kg}^{-3/2} \text{ K}^{-3/2}) \times (mT)^{3/2}}$$

Isotope	m/kg	T/K	$p_{\text{1st excited}}$	Occupancy $= pN = 10^{22} p$
^4He	6.64×10^{-27}	0.0010	6.30×10^{-17}	6.30×10^5
		2.0	7.04×10^{-22}	7
		4.0	2.49×10^{-22}	2
^3He	5.01×10^{-27}	0.0010	9.63×10^{-17}	9.63×10^5
		2.0	1.08×10^{-21}	11
		4.0	3.81×10^{-22}	4

These results may at first seem to contradict the expected common sense result that the populations of excited states increase as the temperature increases, but the energy separations of these states is so small that even a slight increase in temperature promotes the particles to much higher quantum states.

P16.4 $S = k \ln W$ or $W = e^{S/k}$ [16.34]

$$\left(\frac{\partial W}{\partial V}\right)_{T,N} = \frac{W}{k} \left(\frac{\partial S}{\partial V}\right)_{T,N}$$

$$S = nR \ln \frac{e^{5/2} V}{N \Lambda^3} = nR \left[\ln V + \ln \frac{e^{5/2}}{N \Lambda^3} \right]$$

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = nR \left(\frac{\partial \ln V}{\partial V}\right)_{T,N} = \frac{nR}{V} = \frac{NR}{N_A V}$$

$$\left(\frac{\partial W}{\partial V}\right)_{T,N} = \frac{NRW}{N_A k V} = \frac{NW}{V}$$

$$\begin{aligned} \frac{\Delta W}{W} &\approx N \frac{\Delta V}{V} = \frac{pV}{kT} \frac{\Delta V}{V} \\ &\approx \frac{(1 \times 10^5 \text{ Pa}) \times (20 \text{ m}^3) \times (1 \times 10^{-5})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (300 \text{ K})} \\ &\approx \boxed{4.8 \times 10^{21}} \end{aligned}$$

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 $126 \text{ J K}^{-1} \text{ mol}^{-1}$. Therefore,

$$\begin{aligned} S &= nS_m = \left(\frac{pV}{RT}\right) S_m = \frac{(1 \times 10^5 \text{ Pa}) \times (20 \text{ m}^3) \times (126 \text{ J K}^{-1} \text{ mol}^{-1})}{(8.315 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} \\ &= 1.02 \times 10^5 \text{ J K}^{-1} \end{aligned}$$

$$\frac{S}{k} = \frac{1.02 \times 10^5 \text{ J K}^{-1}}{1.381 \times 10^{-23} \text{ J K}^{-1}} = 7.36 \times 10^{27}$$

$$W = e^{S/k} = e^{7.36 \times 10^{27}} = 10^{3.20 \times 10^{27}}$$

P16.6 $\frac{n_1}{n_0} = \frac{g_1 e^{-\epsilon_1/kT}}{g_0 e^{-\epsilon_0/kT}} = \frac{4}{2} \times e^{-\Delta\epsilon/kT} = \frac{4}{2} \times e^{-hc\tilde{\nu}/kT} = 2e^{-\{(1.4388 \times 450)/300\}} = 0.23$

The observed ratio is $0.30/0.70 = 0.43$. Hence the populations are not at equilibrium.

P16.8 First we evaluate the partition function

$$q = \sum_j g_j e^{-\beta \epsilon_j} [16.9] = \sum_j g_j e^{-hc\beta \tilde{\nu}_j}$$

$$\text{At } 3287^\circ\text{C} = 3560\text{ K}, \quad hc\beta = \frac{1.43877\text{ cm K}}{3560\text{ K}} = 4.041 \times 10^{-4}\text{ cm}$$

$$\begin{aligned} q &= 5 + 7e^{-\{(4.041 \times 10^{-4}\text{ cm}) \times (170\text{ cm}^{-1})\}} + 9e^{-\{(4.041 \times 10^{-4}\text{ cm}) \times (387\text{ cm}^{-1})\}} \\ &\quad + 3e^{-\{(4.041 \times 10^{-4}\text{ cm}) \times (6557\text{ cm}^{-1})\}} \\ &= (5) + (7) \times (0.934) + (9) \times (0.855) + (3) \times (0.0707) = 19.445 \end{aligned}$$

The fractions of molecules in the various states are

$$\begin{aligned} p_j &= \frac{g_j e^{-\beta \epsilon_j}}{q} \quad [16.7] = \frac{g_j e^{-hc\beta \tilde{\nu}_j}}{q} \\ p(^3F_2) &= \frac{5}{19.445} = \boxed{0.257} \quad p(^3F_3) = \frac{(7) \times (0.934)}{19.445} = \boxed{0.336} \\ p(^3F_4) &= \frac{(9) \times (0.855)}{19.445} = \boxed{0.396} \quad p(^4F_1) = \frac{(3) \times (0.0707)}{19.445} = \boxed{0.011} \end{aligned}$$

COMMENT. $\sum_j p_j = 1$. Note that the most highly populated level is not the ground state.

P16.10 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

$$\begin{aligned} q &= 1 + 3 \exp\left(-\frac{(6.626 \times 10^{-34}\text{ J s}) \times (2.998 \times 10^{10}\text{ cm s}^{-1}) \times (557.1\text{ cm}^{-1})}{(1.381 \times 10^{-23}\text{ J K}^{-1}) \times (298\text{ K})}\right) + \dots \\ &= \boxed{1.209} \end{aligned}$$

At 1000 K

$$\begin{aligned} q &= 1 + 3 \exp\left(-\frac{(6.626 \times 10^{-34}\text{ J s}) \times (2.998 \times 10^{10}\text{ cm s}^{-1}) \times (557.1\text{ cm}^{-1})}{(1.381 \times 10^{-23}\text{ J K}^{-1}) \times (1000\text{ K})}\right) + \dots \\ &= \boxed{3.004} \end{aligned}$$

P16.12 (a) Total entropy, $S = S_1 + S_2 = (5.69 + 11.63)\text{ J K}^{-1} = 17.32\text{ J K}^{-1}$

$$\begin{aligned} W &= e^{S/k} = e^{17.32\text{ J K}^{-1}/1.381 \times 10^{-23}} \quad [16.34] \\ &= e^{1.254 \times 10^{24}} = 10^{5.44 \times 10^{23}} \end{aligned}$$

(b) Total entropy, $S = 2\text{ mol } (9.03\text{ J K}^{-1}\text{ mol}^{-1}) = 18.06\text{ J K}^{-1}$

$$\begin{aligned} W &= e^{S/k} = e^{18.06\text{ J K}^{-1}/1.381 \times 10^{-23}\text{ J K}^{-1}} \\ &= e^{1.31 \times 10^{24}} = 10^{5.69 \times 10^{23}} \end{aligned}$$

The final temperature is not the average because the molar heat capacity of graphite increases with temperature. At 298 K, it is $8.54 \text{ J K}^{-1} \text{ mol}^{-1}$, whereas at 498 K it is $14.64 \text{ J K}^{-1} \text{ mol}^{-1}$.

(c) At constant internal energy and volume the condition for spontaneity is $\Delta S_{U,V} > 0$. Since

$$W_{(b)} > W_{(a)}, \text{ the process part (b) is spontaneous}$$

Solutions to theoretical problems

P16.14 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	0	1	9
7	1	0	0	0	0	0	0	0	1	0	72
7	0	1	0	0	0	0	0	1	0	0	72
7	0	0	1	0	0	0	1	0	0	0	72
7	0	0	0	1	1	0	0	0	0	0	72
6	2	0	0	0	0	0	0	1	0	0	252
6	0	2	0	0	0	1	0	0	0	0	252
6	0	0	3	0	0	0	0	0	0	0	84
6	1	0	0	2	0	0	0	0	0	0	252
6	1	1	0	0	0	0	1	0	0	0	504
6	1	0	1	0	1	0	0	0	0	0	504
6	0	1	1	1	0	0	0	0	0	0	504
5	3	0	0	0	0	0	1	0	0	0	504
5	0	3	1	0	0	0	0	0	0	0	504
5	2	1	0	0	1	0	0	0	0	0	1512
5	2	0	1	1	0	0	0	0	0	0	1512
5	1	2	0	1	0	0	0	0	0	0	1512
5	1	1	2	0	0	0	0	0	0	0	1512
4	4	0	0	0	1	0	0	0	0	0	630
4	3	1	0	1	0	0	0	0	0	0	2520
4	3	0	2	0	0	0	0	0	0	0	1260
4	2	2	1	0	0	0	0	0	0	0	3780
3	5	0	0	1	0	0	0	0	0	0	504
3	4	1	1	0	0	0	0	0	0	0	2520
2	6	0	1	0	0	0	0	0	0	0	252
2	5	2	0	0	0	0	0	0	0	0	756
1	7	1	0	0	0	0	0	0	0	0	72
0	9	0	0	0	0	0	0	0	0	0	1

The most probable configuration is the "almost exponential" $\{4, 2, 2, 1, 0, 0, 0, 0, 0\}$

P16.16 (a) $q = \sum_j g_j e^{-\beta \epsilon_j} = 1 + 3e^{-\beta \epsilon} = 1 + 3e^{-\epsilon/kT}$
 at $T = \frac{\epsilon}{k}$, $q = 1 + 3e^{-1} = 2.104$

$$\begin{aligned}
 \text{(b)} \quad U_m - U_m(0) &= E = -\frac{N_A}{q} \frac{dq}{d\beta} = \frac{N_A}{q} (3\epsilon e^{-\beta\epsilon}) \\
 &= \frac{N_A}{q} (3RT e^{-1}) = \frac{3RT}{2.104} = \boxed{0.5245 RT}
 \end{aligned}$$

A numerical value cannot be obtained for the energy without specific knowledge of the temperature, but that is not required for the heat capacity or the entropy.

$$C_V = \left(\frac{\partial U_m}{\partial T} \right)_V = \left(\frac{\partial E}{\partial T} \right)_V$$

$$\text{Since } \frac{d}{dT} = \frac{d\beta}{dT} \times \frac{d}{d\beta} = -\frac{1}{kT^2} \frac{d}{d\beta} = -k\beta^2 \frac{d}{d\beta}$$

$$\begin{aligned}
 C_V &= -k\beta^2 \left(\frac{\partial E}{\partial \beta} \right)_V = -k\beta^2 (3\epsilon N_A) \frac{\partial}{\partial \beta} \left(\frac{e^{-\beta\epsilon}}{q} \right) \\
 &= -k\beta^2 (3\epsilon N_A) \frac{\partial}{\partial \beta} \left(\frac{e^{-\beta\epsilon}}{1 + 3e^{-\beta\epsilon}} \right) \\
 &= -k\beta^2 (3\epsilon N_A) \left[\frac{(1 + 3e^{-\beta\epsilon}) \times (-\epsilon)e^{-\beta\epsilon} - e^{-\beta\epsilon} (-3\epsilon e^{-\beta\epsilon})}{(1 + 3e^{-\beta\epsilon})^2} \right] \\
 &= -k\beta^2 (3\epsilon N_A) \left[\frac{-\epsilon e^{-\beta\epsilon} - 3\epsilon e^{-2\beta\epsilon} + 3\epsilon e^{-2\beta\epsilon}}{(1 + 3e^{-\beta\epsilon})^2} \right] \\
 &= -k\beta^2 (3\epsilon N_A) \left[\frac{-\epsilon e^{-\beta\epsilon}}{(1 + 3e^{-\beta\epsilon})^2} \right] \\
 &= \frac{3R\epsilon^2 e^{-\beta\epsilon}}{(kT)^2 (1 + 3e^{-\beta\epsilon})^2}
 \end{aligned}$$

$$\text{For } \epsilon = kT, \quad C_V = \frac{3Re^{-1}}{(1 + 3e^{-1})^2} = \frac{3R}{e(1 + (3/e))^2} = \boxed{2.074 \text{ J K}^{-1} \text{ mol}^{-1}}$$

Note that taking the derivative of $0.5245 RT$ with regard to T does not give the correct answer. That is because the temperature dependence of q is not taken into account by that process.

$$\frac{\partial}{\partial T} (0.5245 RT) = 0.5245 R = 4.361 \text{ J K}^{-1} \text{ mol}^{-1}$$

and this is not the correct value.

The calculation of S does not require taking another derivative, so we can use $E = 0.5245 RT$

$$S_m = \frac{E}{T} + R \ln q = 0.5245 R + R \ln(2.104) = \boxed{10.55 \text{ J K}^{-1} \text{ mol}^{-1}}$$

P16.18 (a) The form of Stirling's approximation used in the text in the derivation of the Boltzmann distribution is

$$\ln x! = x \ln x - x \quad [16.2] \quad \text{or} \quad \ln N! = N \ln N - N$$

and $\ln n_i! = n_i \ln n_i - n_i$ which then leads to [N is cancelled by $-\sum_i n_i$]

$$\ln W = N \ln N - \sum_i n_i \ln n_i \quad [16.3]$$

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 $\ln x! = (x + \frac{1}{2}) \ln x - x + \frac{1}{2} \ln 2\pi$ [Comment 16.2],

Since the method of undetermined multipliers requires only (*Further Information* 16.1) $d \ln W$, only the terms $d \ln n_i!$ survive. The constant term, $\frac{1}{2} \ln 2\pi$, drops out, as do all terms d 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

$$\begin{aligned} \frac{\partial}{\partial n_i} (n_i \ln n_i) &= 1 + \ln n_i \approx \ln n_i [\text{large } n_i] \\ \frac{\partial}{\partial n_i} \left(\frac{1}{2} \ln n_i \right) &= \frac{1}{2n_i} \end{aligned}$$

Whereas $\ln n_i$ increases as n_i increases, $1/2n_i$ decreases and in the limit becomes negligible. For $n_i = 1 \times 10^6$, $\ln n_i = 13.8$, $1/2n_i = 5 \times 10^{-7}$; 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

P16.20
$$\frac{p(h)}{p(h_0)} = \frac{N(h)/V}{N(h_0)/V} = e^{-[(\epsilon(h) - \epsilon(h_0))/kT]} \quad [16.6a]$$

$$= e^{-mg(h-h_0)/kT}$$

For $p(0) \equiv p_0$,

$$\boxed{\frac{p(h)}{p_0} = e^{-mgh/kt}}$$

$$\frac{N(8.0 \text{ km})}{N(0)} = \frac{N(8.0 \text{ km})/V}{N(0)/V} = e^{\frac{-M(\text{O}_2)gh}{RT}}$$

$$\begin{aligned} \frac{N(8.0 \text{ km})}{N(0)} [\text{O}_2] &= e^{-\left\{ \frac{(0.032 \text{ kg mol}^{-1}) \times (9.81 \text{ m s}^{-2}) \times (8.0 \times 10^3 \text{ m})}{(8.315 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} \right\}} \\ &= \boxed{0.36} \text{ for O}_2 \end{aligned}$$

$$\begin{aligned} \frac{N(8.0 \text{ km})}{N(0)} [\text{H}_2\text{O}] &= e^{-\left\{ \frac{(0.018 \text{ kg mol}^{-1}) \times (9.81 \text{ m s}^{-2}) \times (8.0 \times 10^3 \text{ m})}{(8.315 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} \right\}} \\ &= \boxed{0.57} \text{ for H}_2\text{O} \end{aligned}$$

- P16.22** (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:

$$E_n = \left(1 - \frac{1}{n^2}\right) hcR_H, \quad n = 1, 2, 3, \dots, \infty,$$

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 10.11). 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.

$$q_E = \sum_{n=1}^{\infty} g_n e^{-E_n/kT} = 2 \sum_{n=1}^{\infty} n^2 e^{-\left(1 - \frac{1}{n^2}\right)C},$$

where $C = hcR_H/kT_{\text{photosphere}} = 27.301$. q_E , when written as an infinite sum, is infinitely large because $\lim_{n \rightarrow \infty} \{n^2 e^{-(1 - 1/n^2)C}\} = \lim_{n \rightarrow \infty} \{n^2 e^{-C}\} = e^{-C} \lim_{n \rightarrow \infty} (n^2) = \infty$. 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 13.18) is given by:

$$\delta E_n = \frac{h}{2\pi\tau} = \frac{z_n h}{2\pi},$$

where z_n = collisional frequency of n th state of atomic perfect gas

$$= \frac{\sqrt{2}\sigma_n \bar{c} p}{kT} = \frac{\sqrt{2}\sigma_n \bar{c} \rho N_A}{M_H} \quad [21.11(b)]$$

$$\bar{c} = \text{mean speed} = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}} = 1.106 \times 10^4 \text{ ms}^{-1} \quad [21.7]$$

σ_n = collisional cross-section of n th state (Figure 21.9)

$$\begin{aligned} &= \pi((r)_n + a_0)^2 \\ &= \pi a_0^2 \left(\frac{3n^2 + 2}{2}\right)^2 \quad (\text{Example 10.2}) \end{aligned}$$

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 $0 \leq E < E_{\infty} - \delta E$ 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

$$\begin{aligned} E_{n_{\text{max}}} &= E_{\infty} - \delta E_{n_{\text{max}}} \\ \left(1 - \frac{1}{n_{\text{max}}^2}\right) hcR_H &= hcR_H - \frac{\sqrt{2}\pi a_0^2 \left(\frac{3n_{\text{max}}^2 + 2}{2}\right)^2 \bar{c} \rho N_A h}{2\pi M_H} \end{aligned}$$

with $\rho = 1.99 \times 10^{-4} \text{ kg m}^{-3}$ and $M_H = 0.001 \text{ kg mol}^{-1}$.

The root function of a calculator or mathematical software may be used to solve this equation for n_{\max} :

$$n_{\max} = 28 \text{ for atomic hydrogen of the photosphere}$$

Furthermore, examination of the partition function terms $n = 2, 3, \dots, n_{\max}$ indicates that they are negligibly small and may be discarded. The point is that very large n values should not be included in q_E because they do not reflect reality.

$$\rho_n = \frac{2n^2 e^{-E_n/kT}}{q_E} \quad \text{where} \quad T = 5780 \text{ K [eqn 16.6]}$$

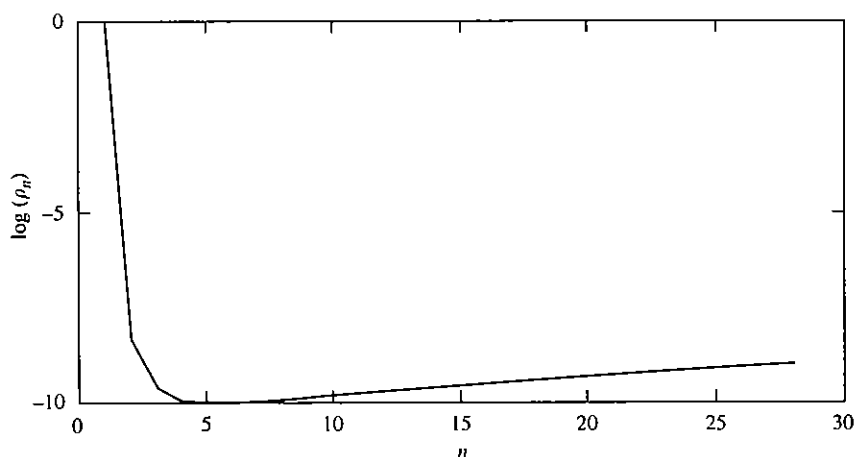


Figure 16.2

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 lower energy. The photosphere may show significant deviations from equilibrium.

See S. J. Strickler, *J. Chem. Ed.*, 43, 364 (1966).

P16.24 (a) $q = 1 + \sum_{i=1}^n N_i K_i$

But, $K_1 = \sigma e^{-\Delta G/RT} = \sigma s$

$$K_2 = K_1 s = \sigma s^2$$

$$K_3 = K_1 s^2 = \sigma s^3$$

\vdots

$$K_i = K_1 s^{i-1} = \sigma s^i$$

Therefore,

$$q = 1 + \sum_{i=1}^n N_i \sigma s^i$$

To show that $N_i = n - i + 1$ consider the following figure of n positions having an “X” label.

$$\begin{array}{ccccccc}
 1 & 2 & 3 & \dots & y_L & & \\
 X & X & X & \dots & X & \dots & X \quad \dots \quad X \quad X \\
 & & & & & y_R & \dots \quad n-1 \quad n
 \end{array}$$

Starting from the left, there are a total of y_L groups of i positions where y_L is limited because an additional group of i would extend beyond the n th position. There are more groups of i . We may start from the right and count off groups of i until reaching position y_R where y_R is limited because an additional group of i would be identical to the group starting at y_L . In fact, $y_R = n - y_L + (i - 1)$. Consequently,

$$N_i = y_L + y_R = y_L + n - \{y_L + (i - 1)\} = n - i + 1$$

$$(b) \quad q = 1 + \sum_{i=1}^n N_i \sigma s^i$$

$$\frac{dq}{ds} = \sum_{i=1}^n i N_i \sigma s^{i-1} = s^{-1} \sum_{i=1}^n i N_i \sigma s^i$$

$$\text{and } \sum_{i=1}^n i N_i \sigma s^i = \frac{dq}{ds}$$

We may substitute the above expression into the equation for the degree of conversion, θ , that is given in the box.

$$\theta = \left(\frac{1}{nq} \right) \sum_{i=1}^n i N_i \sigma s^i = \frac{s}{nq} \frac{dq}{ds}$$

Since $dq/q = d(\ln q)$ and $ds/s = d(\ln s)$, the expression becomes

$$\theta = \left(\frac{1}{n} \right) \frac{d(\ln q)}{d(\ln s)}$$

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Statistical thermodynamics 2: applications

Answers to discussion questions

- D17.2** The symmetry number, σ , is a correction factor to prevent the over-counting of rotational states when computing the high temperature form of the rotational partition function. An elementary interpretation of σ is that it recognizes that in a homonuclear diatomic molecule AA the orientations AA' and $A'A$ are indistinguishable, and should not be counted twice, so the quantity $q = kT/hcB$ is replaced by $q = kT/\sigma hcB$ with $\sigma = 2$. A more sophisticated interpretation is that the Pauli principle allows only certain rotational states to be occupied, and the symmetry factor adjusts the high temperature form of the partition function (which is derived by taking a sum over all states), to account for this restriction. In either case the symmetry number is equal to the number of indistinguishable orientations of the molecule. More formally, it is equal to the order of the rotational subgroup of the molecule. (See Chapter 12.)
- D17.4** The temperature is always high enough for the mean translational energy to be $\frac{3}{2}kT$, the equipartition value (provided the gas is above its condensation temperature). Therefore, the molar constant-volume heat capacity for translation is $C_{V,m}^T = \frac{3}{2}R$.

Translation is the only mode of motion for a monatomic gas, so for such a gas $C_{V,m} = \frac{3}{2}R = 12.47 \text{ J K}^{-1} \text{ mol}^{-1}$. 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 $T \gg \theta_R$) we can use the equipartition value kT for the mean rotational energy (for a linear rotor) to obtain $C_{V,m} = R$. 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 $T \gg \theta_R$. 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 17.26a for a linear molecule). The resulting expression is plotted in Figure 17.10 of the text. Because the translational contribution is always present, we can expect the molar heat capacity of a gas of diatomic molecules ($C_{V,m}^T + C_{V,m}^R$) to change from $\frac{3}{2}R$ to $\frac{5}{2}R$ as the temperature is increased above θ_R .

Molecular vibrations contribute to the heat capacity, but only when the temperature is high enough for them to be significantly excited. For each vibrational mode, the equipartition mean energy is kT , so the maximum contribution to the molar heat capacity is R . However, it is very unusual for the vibrations to be so highly excited that equipartition is valid, and it is more appropriate to use the full expression for the vibrational heat capacity which is obtained by differentiating eqn 17.28. The curve in Figure 17.12 of the

text shows how the vibrational heat capacity depends on temperature. Note that even when the temperature is only slightly above the vibrational temperature, the heat capacity is close to its equipartition value.

The total heat capacity of a molecular substance is the sum of each contribution (Figure 17.13 of the text). When equipartition is valid (when the temperature is well above the characteristic temperature of the mode $T \gg \theta_M$) we can estimate the heat capacity by counting the numbers of modes that are active. In gases, all three translational modes are always active and contribute $\frac{3}{2}R$ to the molar heat capacity. If we denote the number of active rotational modes by ν_R^* (so for most molecules at normal temperatures $\nu_R^* = 2$ for linear molecules, and 3 for nonlinear molecules), then the rotational contribution is $\frac{1}{2}\nu_R^*R$. If the temperature is high enough for ν_V^* vibrational modes to be active the vibrational contribution to the molar heat capacity is ν_V^*R . In most cases $\nu_V \approx 0$. It follows that the total molar heat capacity is

$$C_{V,m} = \frac{1}{2}(3 + \nu_R^* + 2\nu_V^*)R$$

D17.6 The pair distribution function is a statistical method for studying the complex properties of liquids. It is especially important because, being a Fourier transform of the intensity distribution of scattered radiation, the function relates directly to experimental observation. Equations, which use both the pair distribution function and the intermolecular potential, have been derived for the computation of both equilibrium thermodynamic properties and the equation of state for model liquids [17.50 and 17.51]. However, the computational demands of these equations make the Monte Carlo method and methods of molecular dynamics attractive. The Monte Carlo method randomly displaces molecules and accepts, or rejects, the new molecular configuration with a Boltzmann factor test, which has a potential energy change exponent. Thermodynamic properties are computed as a weighted average of the properties of acceptable configurations. Molecular dynamic methods use Newtonian equations of motion and model intermolecular potentials to compute the motion of molecules as a function of time. Since molecular rotational and vibrational motion occur on the order of 10^{13} Hz, the time increment for calculations is taken to be about 10^{-15} s (a femtosecond, fs). Properties are computed as time averages.

Solutions to exercises

E17.1(b) $C_{V,m} = \frac{1}{2}(3 + \nu_R^* + 2\nu_V^*)R$ [17.35]

with a mode active if $T > \theta_M$.

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

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

(c) CO_2 : $C_{V,m} = \frac{1}{2}(3 + 2 + 0)R = \frac{5}{2}R$ [experimental = $4.5R$]

Consultation of the Herzberg references in *Further reading*, Chapters 13 and 14, turns up only one vibrational mode among these molecules whose frequency is low enough to have a vibrational temperature near room temperature. That mode was in C_2H_6 , corresponding to the “internal rotation” of CH_3 groups. The discrepancies between the estimates and the experimental values suggest that there are vibrational modes in each molecule that contribute to the heat capacity—albeit not to the full equipartition value—that our estimates have classified as inactive.

E17.2(b) The equipartition theorem would predict a contribution to molar heat capacity of $\frac{1}{2}R$ for every translational and rotational degree of freedom and R for each vibrational mode. For an ideal gas, $C_{p,m} = R + C_{V,m}$. So for CO_2

With vibrations

$$C_{V,m}/R = 3 \left(\frac{1}{2} \right) + 2 \left(\frac{1}{2} \right) = (3 \times 4 - 6) = 6.5 \quad \text{and} \quad \gamma = \frac{7.5}{6.5} = \boxed{1.15}$$

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

$$\text{Experimental } \gamma = \frac{37.11 \text{ J mol}^{-1} \text{ K}^{-1}}{(37.11 - 8.3145) \text{ J mol}^{-1} \text{ K}^{-1}} = \boxed{1.29}$$

The experimental result is closer to that obtained by neglecting vibrations, but not so close that vibrations can be neglected entirely.

E17.3(b) The rotational partition function of a linear molecule is [Table 17.3]

$$q^R = \frac{0.6950}{\sigma} \times \frac{T/\text{K}}{(B/\text{cm}^{-1})} = \frac{(0.6950) \times (T/\text{K})}{2 \times 1.4457} = 0.2404(T/\text{K})$$

$$\text{(a) At } 25^\circ\text{C: } q^R = (0.2403) \times (298) = \boxed{71.6}$$

$$\text{(b) At } 250^\circ\text{C: } q^R = (0.2403) \times (523) = \boxed{126}$$

E17.4(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).

$$\text{(a) CO}_2\text{: full group } D_{\infty h}\text{; subgroup } C_2\text{; hence } \sigma = \boxed{2}$$

$$\text{(b) O}_3\text{: full group } C_{2v}\text{; subgroup } C_2\text{; } \sigma = \boxed{2}$$

$$\text{(c) SO}_3\text{: full group } D_{3h}\text{; subgroup } \{E, C_3, C_3^2, 3C_2\}\text{; } \sigma = \boxed{6}$$

$$\text{(d) SF}_6\text{: full group } O_h\text{; subgroup } O\text{; } \sigma = \boxed{24}$$

$$\text{(e) Al}_2\text{Cl}_6\text{: full group } D_{2d}\text{; subgroup } D_2\text{; } \sigma = \boxed{4}$$

E17.5(b) The rotational partition function of a non-linear molecule is [Table 17.3]

$$q^R = \frac{1.0270}{\sigma} \frac{(T/\text{K})^{3/2}}{(ABC/\text{cm}^{-3})^{1/2}} = \frac{1.0270 \times 298^{3/2}}{(2) \times (2.02736 \times 0.34417 \times 0.293535)^{1/2}} [\sigma = 2] = \boxed{5837}$$

The high-temperature approximation is valid if $T > \theta_R$, where

$$\begin{aligned} \theta_R &= \frac{hc(ABC)^{1/3}}{k} \\ &= \frac{(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^{10} \text{ cm s}^{-1}) \times [(2.02736) \times (0.34417) \times (0.293535) \text{ cm}^{-3}]^{1/3}}{1.381 \times 10^{-23} \text{ J K}^{-1}} \\ &= \boxed{0.8479 \text{ K}} \end{aligned}$$

$$\text{E17.6(b)} \quad q^R = 5837 \text{ [Exercise 17.5(b)]}$$

All rotational modes of SO₂ are active at 25 °C; therefore

$$\begin{aligned}
 U_m^R - U_m^R(0) &= E^R = \frac{3}{2}RT \\
 S_m^R &= \frac{E^R}{T} + R \ln q^R \\
 &= \frac{3}{2}R + R \ln(5837) = \boxed{84.57 \text{ J K}^{-1} \text{ mol}^{-1}}
 \end{aligned}$$

E17.7(b) (a) The partition function is

$$q = \sum_{\text{states}} e^{-E_{\text{state}}/kT} = \sum_{\text{levels}} g e^{-E_{\text{level}}/kT}$$

where g is the degeneracy of the level. For rotations of a symmetric rotor such as CH₃CN, 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

$$q = 1 + \sum_{J=1}^{\infty} (2J+1) e^{-\{hcBJ(J+1)/kT\}} \left(1 + 2 \sum_{K=1}^J e^{-\{hc(A-B)K^2/kT\}} \right)$$

To evaluate this sum explicitly, we set up the following columns in a spreadsheet (values for $A = 5.28 \text{ cm}^{-1}$, $B = 5.2412 \text{ cm}^{-1}$, and $T = 298.15 \text{ K}$)

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 labeled 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 ($\sigma = 3$). At 298 K, $q^R = \boxed{2.50 \times 10^3}$. A similar computation at $T = 500 \text{ K}$ yields $q^R = \boxed{5.43 \times 10^3}$.

(b) The rotational partition function of a nonlinear molecule is [Table 17.3 with $B = C$]

$$q^R = \frac{1.0270}{\sigma} \frac{(T/\text{K})^{3/2}}{(ABC/\text{cm}^{-3})^{1/2}} = \frac{1.0270}{3} \frac{(T/\text{K})^{3/2}}{(5.28 \times 0.307 \times 0.307)^{1/2}} = 0.485 \times (T/\text{K})^{3/2}$$

$$\text{At } 298 \text{ K, } q^R = 0.485 \times 298^{3/2} = \boxed{2.50 \times 10^3}$$

$$\text{At } 500 \text{ K, } q^R = 0.485 \times 500^{3/2} = \boxed{5.43 \times 10^3}$$

The high-temperature approximation is certainly valid here.

E17.8(b) The rotational partition function of a nonlinear molecule is [Table 17.3]

$$q^R = \frac{1.0270}{\sigma} \frac{(T/\text{K})^{3/2}}{(ABC/\text{cm}^{-3})^{1/2}} = \frac{1.0270 \times (T/\text{K})^{3/2}}{(3.1752 \times 0.3951 \times 0.3505)^{1/2}} = 1.549 \times (T/\text{K})^{3/2}$$

(a) At 25 °C, $q^R = 1.549 \times (298)^{3/2} = \boxed{7.97 \times 10^3}$

(b) At 100 °C, $q^R = 1.549 \times (373)^{3/2} = \boxed{1.12 \times 10^4}$

E17.9(b) The molar entropy of a collection of oscillators is given by

$$S_m = \frac{U_m - U_m(0)}{T} + k \ln Q \quad [17.1] = \frac{N_A \langle \epsilon \rangle}{T} + R \ln q$$

where $\langle \epsilon \rangle = \frac{hc\bar{\nu}}{e^{\beta hc\bar{\nu}} - 1} = k \frac{\theta_V}{e^{\theta_V/T} - 1}$ [17.28], $q = \frac{1}{1 - e^{-\beta hc\bar{\nu}}} = \frac{1}{1 - e^{-\theta_V/T}}$ [17.19]

and θ_V is the vibrational temperature $hc\bar{\nu}/k$. Thus

$$S_m = \frac{R(\theta_V/T)}{e^{\theta_V/T} - 1} - R \ln(1 - e^{-\theta_V/T})$$

A plot of S_m/R versus T/θ_V is shown in Figure 17.1.

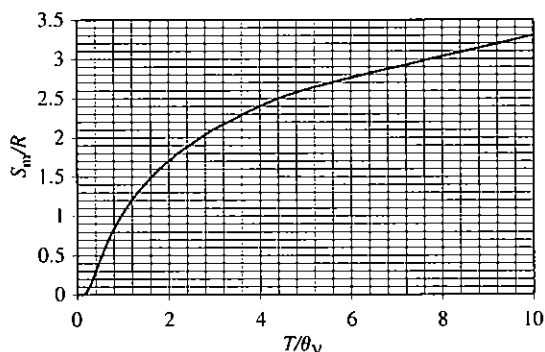


Figure 17.1

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.

$\bar{\nu}/\text{cm}^{-1}$	θ_V/K	$T = 298 \text{ K}$		$T = 500 \text{ K}$	
		T/θ_V	S_m/R	T/θ_V	S_m/R
612	880	0.336	0.216	0.568	0.554
729	1049	0.284	0.138	0.479	0.425
1974	2839	0.105	0.000 766	0.176	0.0229
3287	4728	0.0630	0.000 002 17	0.106	0.000 818
3374	4853	0.0614	0.000 001 46	0.103	0.000 652

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, $S_m = 0.708R = \boxed{5.88 \text{ J mol}^{-1} \text{ K}^{-1}}$

(b) At 500 K, $S_m = 1.982R = \boxed{16.48 \text{ J mol}^{-1} \text{ K}^{-1}}$

E17.10(b) The contributions of rotational and vibrational modes of motion to the molar Gibbs energy depend on the molecular partition functions

$$G_m - G_m(0) = -RT \ln q \quad [17.9; \text{also see Comment to Exercise 17.6(a)}]$$

The rotational partition function of a nonlinear molecule is given by

$$q^R = \frac{1}{\sigma} \left(\frac{kT}{hc} \right)^{3/2} \left(\frac{\pi}{ABC} \right)^{1/2} = \frac{1.0270}{\sigma} \left(\frac{(T/\text{K})^3}{ABC/\text{cm}^{-3}} \right)^{1/2}$$

and the vibrational partition function for each vibrational mode is given by

$$q^V = \frac{1}{1 - e^{-\theta/T}} \quad \text{where } \theta = \frac{hc\tilde{\nu}}{k} = \frac{1.4388 (\tilde{\nu}/\text{cm}^{-1})}{(T/\text{K})}$$

$$\text{At 298 K} \quad q^R = \frac{1.0270}{2} \left(\frac{298^3}{(3.553) \times (0.4452) \times (0.3948)} \right)^{1/2} = 3.35 \times 10^3$$

and

$$\begin{aligned} G_m^R - G_m^R(0) &= -(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K}) \ln 3.35 \times 10^3 \\ &= -20.1 \times 10^3 \text{ J mol}^{-1} = \boxed{-20.1 \text{ kJ mol}^{-1}} \end{aligned}$$

The vibrational partition functions are so small that we are better off taking

$$\ln q^V = -\ln(1 - e^{-\theta/T}) \approx e^{-\theta/T}$$

$$\ln q_1^V \approx e^{-\{1.4388(1110)/298\}} = 4.70 \times 10^{-3}$$

$$\ln q_2^V \approx e^{-\{1.4388(705)/298\}} = 3.32 \times 10^{-2}$$

$$\ln q_3^V \approx e^{-\{1.4388(1042)/298\}} = 6.53 \times 10^{-3}$$

$$\text{so } G_m^V - G_m^V(0) = -(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K})$$

$$\times (4.70 \times 10^{-3} + 3.32 \times 10^{-2} + 6.53 \times 10^{-3})$$

$$= -110 \text{ J mol}^{-1} = \boxed{-0.110 \text{ kJ mol}^{-1}}$$

$$\text{E17.11(b)} \quad q = \sum_j g_j e^{-\beta \epsilon_j}, \quad \text{where } g = (2S + 1) \times \begin{cases} 1 & \text{for } \Sigma \text{ states} \\ 2 & \text{for } \Pi, \Delta, \dots \text{ states} \end{cases}$$

The $^3\Sigma$ term is triply degenerate (from spin), and the $^1\Delta$ term is doubly (orbitally) degenerate. Hence

$$q = 3 + 2e^{-\beta \epsilon}$$

At 400 K

$$\beta \epsilon = \frac{(1.4388 \text{ cm K}) \times (7918.1 \text{ cm}^{-1})}{400 \text{ K}} = 28.48$$

Therefore, the contribution to G_m is

$$\begin{aligned} G_m - G_m(0) &= -RT \ln q \text{ [Table 17.4 for one mole]} \\ -RT \ln q &= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K}) \times \ln(3 + 2 \times e^{-28.48}) \\ &= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K}) \times (\ln 3) = \boxed{3.65 \text{ kJ mol}^{-1}} \end{aligned}$$

COMMENT. The contribution of the excited state is negligible at this temperature.

E17.12(b) The degeneracy of a species with $S = \frac{5}{2}$ is 6. The electronic contribution to molar entropy is

$$S_m = \frac{U_m - U_m(0)}{T} + R \ln q = R \ln q$$

(The term involving the internal energy is proportional to a temperature-derivative of the partition function, which in turn depends on excited state contributions to the partition function; those contributions are negligible.)

$$S_m = (8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \ln 6 = \boxed{14.9 \text{ J mol}^{-1} \text{ K}^{-1}}$$

E17.13(b) Use $S_m = R \ln s$ [17.52b]

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.

E17.14(b) We need to calculate

$$K = \prod_j \left(\frac{q_{j,m}^\ominus}{N_A} \right)^{\nu_j} \times e^{-\Delta E_0/RT} \text{ [17.54b]} = \frac{q_m^\ominus(^{79}\text{Br}_2) q_m^\ominus(^{81}\text{Br}_2)}{q_m^\ominus(^{79}\text{Br}^{81}\text{Br})^2} e^{-\Delta E_0/RT}$$

Each of these partition functions is a product

$$q_m^{\ominus} = q_m^T q^R q^V q^E$$

with all $q^E = 1$.

The ratio of the translational partition functions is virtually 1 (because the masses nearly cancel; explicit calculation gives 0.999). The same is true of the vibrational partition functions. Although the moments of inertia cancel in the rotational partition functions, the two homonuclear species each have $\sigma = 2$, so

$$\frac{q^R(^{79}\text{Br}_2)q^R(^{81}\text{Br}_2)}{q^R(^{79}\text{Br}^{81}\text{Br})^2} = 0.25$$

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

P17.2

$$\Delta\varepsilon = \varepsilon = g\mu_B B \text{ [15.42]}$$

$$q = 1 + e^{-\beta\varepsilon}$$

$$C_{V,m}/R = \frac{x^2 e^{-x}}{(1 + e^{-x})^2} \text{ [Problem 17.1], } x = 2\mu_B B\beta \text{ [} g = 2 \text{ for electrons]}$$

Therefore, if $B = 5.0 \text{ T}$,

$$x = \frac{(2) \times (9.274 \times 10^{-24} \text{ J T}^{-1}) \times (5.0 \text{ T})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times T} = \frac{6.72}{T/\text{K}}$$

(a) $T = 50 \text{ K}$, $x = 0.134$, $C_V = 4.47 \times 10^{-3} R$, implying that $C_V = 3.7 \times 10^{-2} \text{ J K}^{-1} \text{ mol}^{-1}$. Since the equipartition value is about $3R$ [$v_R^* = 3$, $v_V^* \approx 0$], the field brings about a change of about

$$\boxed{0.1 \text{ per cent}}$$

(b) $T = 298 \text{ K}$, $x = 2.26 \times 10^{-2}$, $C_V = 1.3 \times 10^{-4} R$, implying that $C_V = 1.1 \text{ mJ K}^{-1} \text{ mol}^{-1}$, a change of about

$$\boxed{4 \times 10^{-3} \text{ per cent}}$$

Question. What percentage change would a magnetic field of 1 kT cause?

P17.4

$$q = 1 + 5e^{-\beta\varepsilon} \quad [g_J = 2J + 1]$$

$$\varepsilon = E(J = 2) - E(J = 0) = 6hcB \quad [E = hcBJ(J + 1)]$$

$$\frac{U - U(0)}{N} = -\frac{1}{q} \frac{\partial q}{\partial \beta} = \frac{5\varepsilon e^{-\beta\varepsilon}}{1 + 5e^{-\beta\varepsilon}}$$

$$C_{V,m} = -k\beta^2 \left(\frac{\partial U_m}{\partial \beta} \right)_V \text{ [17.31a]}$$

$$C_{V,m}/R = \frac{5\varepsilon^2\beta^2e^{-\beta\varepsilon}}{(1+5e^{-\beta\varepsilon})^2} = \frac{180(hcB\beta)^2e^{-6hcB\beta}}{(1+5e^{-6hcB\beta})^2}$$

$$\frac{hcB}{k} = 1.4388 \text{ cm K} \times 60.864 \text{ cm}^{-1} = 87.571 \text{ K}$$

Hence,

$$C_{V,m}/R = \frac{1.380 \times 10^6 e^{-525.4 \text{ K}/T}}{(1 + 5e^{-525.4 \text{ K}/T}) \times (T/\text{K})^2}$$

We draw up the following table

T/K	50	100	150	200	250	300	350	400	450	500
$C_{V,m}/R$	0.02	0.68	1.40	1.35	1.04	0.76	0.56	0.42	0.32	0.26

These points are plotted in Figure 17.2.

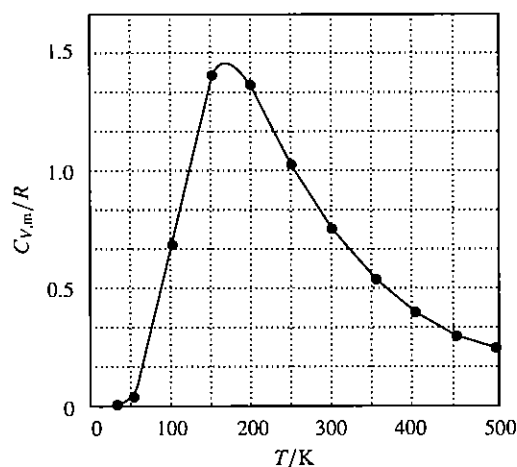


Figure 17.2

P17.6

$$\frac{q_m^T}{N_A} = 2.561 \times 10^{-2} \times (T/\text{K})^{5/2} \times (M/\text{g mol}^{-1})^{3/2} \text{ [Table 17.3]}$$

$$= (2.561 \times 10^{-2}) \times (298)^{5/2} \times (28.02)^{3/2} = 5.823 \times 10^6$$

$$q^R = \frac{0.6950}{\sigma} \times \frac{T/\text{K}}{(B/\text{cm}^{-1})} = \frac{0.6950}{2} \times \frac{298}{1.9987} = 51.81 \text{ [Table 17.3]}$$

$$q^V = \frac{1}{1 - e^{-\theta_V/T}} \text{ [Table 17.3]}$$

$$\text{where } \theta_V = \frac{hc\bar{\nu}}{k} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^{10} \text{ cm s}^{-1} \times 2358 \text{ cm}^{-1}}{1.381 \times 10^{-23} \text{ J K}^{-1}} = 3392 \text{ K}$$

$$\text{so } q^V = \frac{1}{1 - e^{-3392\text{K}/298\text{K}}} = 1.00$$

Therefore

$$\frac{q_m^\ominus}{N_A} = (5.823 \times 10^6) \times (51.81) \times (1.00) = 3.02 \times 10^8$$

$$U_m - U_m(0) = \frac{3}{2}RT + RT = \frac{5}{2}RT \quad [T \gg \theta_T, \theta_R]$$

Hence

$$\begin{aligned} S_m^\ominus &= \frac{U_m - U_m(0)}{T} + R \left(\ln \frac{q_m^\ominus}{N_A} + 1 \right) \\ &= \frac{5}{2}R + R \{ \ln 3.02 \times 10^8 + 1 \} = 23.03R = \boxed{191.4 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

The difference between the experimental and calculated values is negligible, indicating that the residual entropy is negligible.

P17.8 The vibrational temperature is defined by

$$k\theta_V = hc\tilde{\nu},$$

so a vibration with θ_V less than 1000 K has a wavenumber less than

$$\tilde{\nu} = \frac{k\theta_V}{hc} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (1000 \text{ K})}{(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^{10} \text{ cm s}^{-1})} = 695.2 \text{ cm}^{-1}$$

There are seven such wavenumbers listed among those for C_{60} : two T_{1u} , a T_{2u} , a G_u , and three H_u . The number of *modes* involved, ν_V^* , must take into account the degeneracy of these vibrational energies

$$\nu_V^* = 2(3) + 1(3) + 1(4) + 3(5) = \boxed{28}$$

The molar heat capacity of a molecule is roughly

$$\begin{aligned} C_{V,m} &= \frac{1}{2}(3 + \nu_R^* + 2\nu_V^*)R [17.35] = \frac{1}{2}(3 + 3 + 2 \times 28)R = 31R = 31(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \\ &= \boxed{258 \text{ J mol}^{-1} \text{ K}^{-1}} \end{aligned}$$

P17.10

$$K = \frac{q_m^\ominus(\text{CHD}_3)q_m^\ominus(\text{DCI})}{q_m^\ominus(\text{CD}_4)q_m^\ominus(\text{HCl})} e^{-\beta \Delta E_0} [17.54; N_A \text{ factors cancel}]$$

Use partition function expressions from Table 17.3. The ratio of translational partition functions is

$$\frac{q_m^T(\text{CHD}_3)q_m^T(\text{DCI})}{q_m^T(\text{CD}_4)q_m^T(\text{HCl})} = \left(\frac{M(\text{CHD}_3)M(\text{DCI})}{M(\text{CD}_4)M(\text{HCl})} \right)^{3/2} = \left(\frac{19.06 \times 37.46}{20.07 \times 36.46} \right)^{3/2} = 0.964$$

The ratio of rotational partition functions is

$$\begin{aligned} \frac{q^R(\text{CHD}_3)q^R(\text{DCI})}{q^R(\text{CD}_4)q^R(\text{HCl})} &= \frac{\sigma(\text{CD}_4)}{\sigma(\text{CHD}_3)} \frac{(B(\text{CD}_4)/\text{cm}^{-1})^{3/2} B(\text{HCl})/\text{cm}^{-1}}{(A(\text{CHD}_3)B(\text{CHD}_3)^2/\text{cm}^{-3})^{1/2} B(\text{DCI})/\text{cm}^{-1}} \\ &= \frac{12}{3} \times \frac{2.63^{3/2} \times 10.59}{(2.63 \times 3.282)^{1/2} \times 5.445} = 6.24 \end{aligned}$$

The ratio of vibrational partition functions (call it Q for convenience below) is

$$Q = \frac{q^{\text{V}}(\text{CHD}_3)q^{\text{V}}(\text{DCI})}{q^{\text{V}}(\text{CD}_4)q^{\text{V}}(\text{HCl})} = \frac{q(2993)q(2142)q(1003)^3q(1291)^2q(1036)^2q(2145)}{q(2109)q(1092)^2q(2259)^3q(996)^3q(2991)}$$

$$\text{where } q(x) = \frac{1}{1 - e^{-1.4388x/(T/K)}}.$$

We also require ΔE_0 , which is equal to the difference in zero point energies

$$\begin{aligned}\frac{\Delta E_0}{hc} &= \frac{1}{2} \{ (2993 + 2142 + 3 \times 1003 + 2 \times 1291 + 2 \times 1036 + 2145) \\ &\quad - (2109 + 2 \times 1092 + 3 \times 2259 + 3 \times 996 + 2991) \} \text{ cm}^{-1} \\ &= -1053 \text{ cm}^{-1}\end{aligned}$$

So the exponent in the energy term is

$$-\beta \Delta E_0 = -\frac{\Delta E_0}{kT} = -\frac{hc}{k} \times \frac{\Delta E_0}{hc} \times \frac{1}{T} = -\frac{1.4388 \times (-1053)}{T/K} = +\frac{1515}{T/K}$$

Hence,

$$K = 0.964 \times 6.24 \times Q e^{+1515/(T/K)} = 6.02 Q e^{+1515/(T/K)}$$

We can now evaluate K (on a computer), and obtain the following values

T/K	300	400	500	600	700	800	900	1000
K	945	273	132	83	61	49	42	37

The values of K are plotted in Figure 17.3.

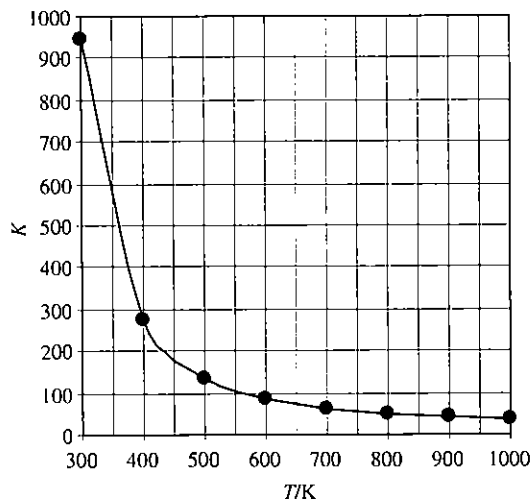


Figure 17.3

Solutions to theoretical problems

P17.12 A Sackur–Tetrode type of equation describes the translational entropy of the gas. Here

$$q^T = q_x^T q_y^T \quad \text{with } q_x^T = \left(\frac{2\pi m}{\beta h^2} \right)^{1/2} X \quad [16.15]$$

where X is the length of the surface. Therefore,

$$q^T = \left(\frac{2\pi m}{\beta h^2} \right) XY = \frac{2\pi m \sigma}{\beta h^2}, \quad \sigma = XY$$

$$U_m - U_m(0) = -\frac{N_A}{q} \left(\frac{\partial q}{\partial \beta} \right) = RT \quad [\text{or by equipartition}]$$

$$S_m = \frac{U_m - U_m(0)}{T} + R(\ln q_m - \ln N_A + 1) \left[q_m = \frac{q}{n} \right]$$

$$= R + R \ln \left(\frac{eq_m}{N_A} \right) = R \ln \left(\frac{e^2 q_m}{N_A} \right)$$

$$= \boxed{R \ln \left(\frac{2\pi e^2 m \sigma_m}{h^2 N_A \beta} \right)} \left[\sigma_m = \frac{\sigma}{n} \right]$$

Call this molar entropy of the mobile two-dimensional film S_{m2} . The molar entropy of condensation is the difference between this entropy and that of a (three-dimensional) gas:

$$\Delta S_m = S_{m2} - S_{m3}.$$

The three-dimensional value is given by the Sackur–Tetrode equation

$$S_m = R \ln \left\{ e^{5/2} \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2} \frac{V_m}{N_A} \right\}$$

$$\text{So } \Delta S_m = R \ln \frac{e^2 (2\pi m / h^2 \beta) \times (\sigma_m / N_A)}{e^{5/2} (2\pi m / h^2 \beta)^{3/2} \times (V_m / N_A)} = \boxed{R \ln \left\{ \left(\frac{\sigma_m}{V_m} \right) \times \left(\frac{h^2 \beta}{2\pi m e} \right)^{1/2} \right\}}$$

P17.14 Begin with the partition function of an oscillator (Table 17.3)

$$q = \frac{1}{1 - e^{-x}}, \quad x = \frac{\theta_v}{T} = hc\bar{\nu}\beta = \hbar\omega\beta$$

Expressions for internal energy and other thermodynamic functions are in Table 17.4.

$$U - U(0) = -\frac{N}{q} \left(\frac{\partial q}{\partial \beta} \right)_v = -N(1 - e^{-x}) \frac{d}{d\beta} (1 - e^{-x})^{-1} = \frac{N\hbar\omega e^{-x}}{1 - e^{-x}} = \boxed{\frac{N\hbar\omega}{e^x - 1}}$$

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = -k\beta^2 \frac{\partial U}{\partial \beta} \quad [17.31a] = -k\beta^2 \hbar\omega \frac{\partial U}{\partial x}$$

$$= k(\beta\hbar\omega)^2 N \left\{ \frac{e^x}{(e^x - 1)^2} \right\} = \boxed{kN \left\{ \frac{x^2 e^x}{(e^x - 1)^2} \right\}}$$

$$H - H(0) = U - U(0) \text{ [} q \text{ is independent of } V \text{]} = \boxed{\frac{N\hbar\omega}{e^x - 1}}$$

$$S = \frac{U - U(0)}{T} + nR \ln q = \frac{Nkxe^{-x}}{1 - e^{-x}} - Nk \ln(1 - e^{-x})$$

$$= \boxed{Nk \left(\frac{x}{e^x - 1} - \ln(1 - e^{-x}) \right)}$$

$$A - A(0) = G - G(0) = -nRT \ln q = \boxed{NkT \ln(1 - e^{-x})}$$

The functions are plotted in Figure 17.4.

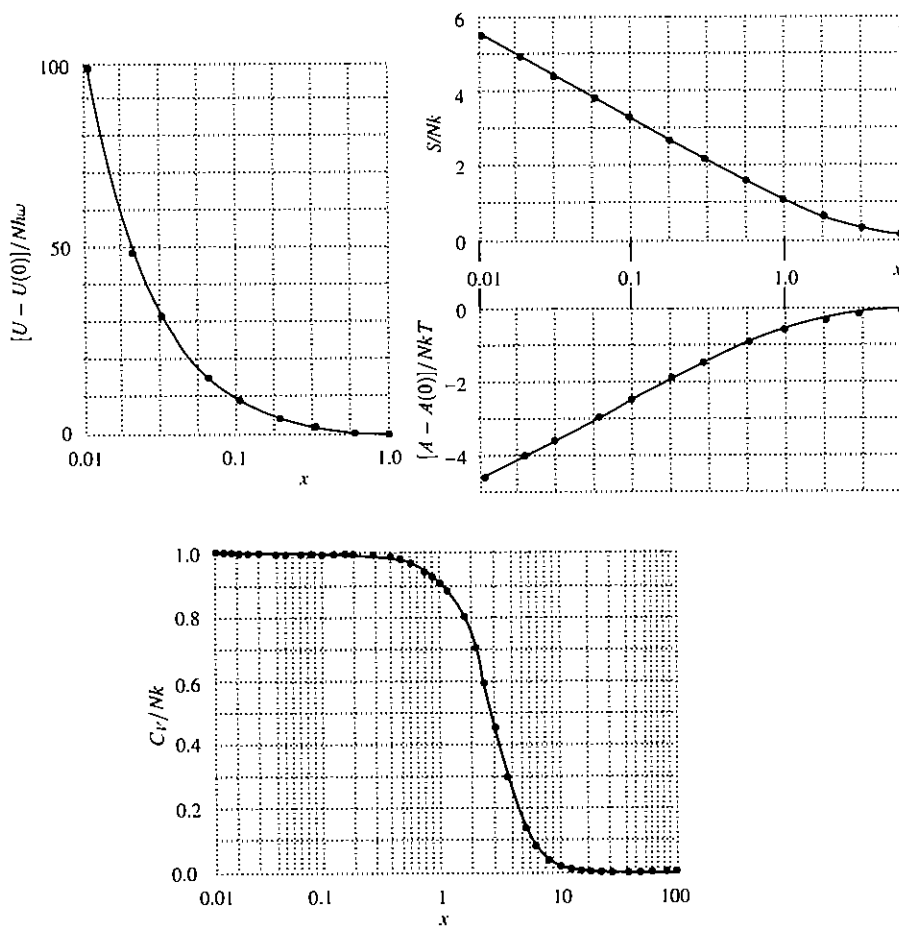


Figure 17.4

P17.16 (a)
$$\frac{N_J}{N} = \frac{g_J e^{-\epsilon_J/kT}}{\sum_J g_J e^{-\epsilon_J/kT}} = \frac{g_J e^{-\epsilon_J/kT}}{q}$$

For a linear molecule $g_J = 2J + 1$ and $\epsilon_J = hcBJ(J + 1)$ [Sections 13.5(c) and d)]. Therefore,

$$N_J \propto (2J + 1) e^{-hcBJ(J+1)/kT}$$

(b) J_{\max} occurs when $dN_J/dJ = 0$.

$$\frac{dN_J}{dJ} = \frac{N}{q} \frac{d}{dJ} \left\{ (2J+1) e^{-\left(\frac{hcBJ(J+1)}{kT}\right)} \right\} = 0$$

$$2 - (2J_{\max} + 1) \left(\frac{hcB}{kT} \right) (2J_{\max} + 1) = 0$$

$$2J_{\max} + 1 = \left(\frac{2kT}{hcB} \right)^{1/2}$$

$$\boxed{J_{\max} = \left(\frac{kT}{2hcB} \right)^{1/2} - \frac{1}{2}}$$

(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.

$$\begin{aligned} T &\approx \frac{hcB}{2k} (2J_{\max} + 1)^2 \\ &\approx \frac{(6.626 \times 10^{-34} \text{ J s}) \times (3.000 \times 10^8 \text{ m s}^{-1}) \times (10.593 \text{ cm}^{-1}) \times \left(\frac{10^2 \text{ cm}}{\text{m}} \right) \times (7)^2}{2(1.38066 \times 10^{-23} \text{ J K}^{-1})} \end{aligned}$$

$$\boxed{T \approx 374 \text{ K}}$$

(d) For a spherical rotor $g_J = (2J+1)^2$ and $\epsilon_J = hcBJ(J+1)$ [Sections 13.5(c) and (d)]. Therefore

$$N_J \propto (2J+1)^2 e^{-hcBJ(J+1)/kT}$$

J_{\max} occurs when $dN_J/dJ = 0$.

$$\frac{dN_J}{dJ} = \frac{N}{q} \frac{d}{dJ} \left\{ (2J+1)^2 e^{-\left(\frac{hcBJ(J+1)}{kT}\right)} \right\} = 0$$

$$2(2J_{\max} + 1) \times 2 - (2J_{\max} + 1)^2 \left(\frac{hcB}{kT} \right) (2J_{\max} + 1) = 0$$

Divide both sides by $2J_{\max} + 1$:

$$4 - (2J_{\max} + 1)^2 \left(\frac{hcB}{kT} \right) = 0$$

$$2J_{\max} + 1 = \left(\frac{4kT}{hcB} \right)^{1/2}$$

$$\boxed{J_{\max} = \left(\frac{kT}{hcB} \right)^{1/2} - \frac{1}{2}}$$

P17.18 (a) $U - U(0) = -\frac{N}{q} \frac{\partial q}{\partial \beta} = -\frac{N}{q} \sum \epsilon_j e^{-\beta \epsilon_j} = \frac{NkT}{q} \dot{q} = \boxed{nRT \left(\frac{\dot{q}}{q} \right)}$

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T} \right)_V = \frac{\partial \beta}{\partial T} \left(\frac{\partial U}{\partial \beta} \right)_V = \frac{1}{kT^2} \frac{\partial}{\partial \beta} \left(\frac{N}{q} \sum \epsilon_j e^{-\beta \epsilon_j} \right) \\ &= \left(\frac{N}{kT^2} \right) \times \left[\frac{1}{q} \sum \epsilon_j^2 e^{-\beta \epsilon_j} + \frac{1}{q^2} \left(\frac{\partial q}{\partial \beta} \right) \sum \epsilon_j e^{-\beta \epsilon_j} \right] \\ &= \left(\frac{N}{kT^2} \right) \times \left[\frac{1}{q} \sum \epsilon_j^2 e^{-\beta \epsilon_j} - \frac{1}{q^2} \left(\sum \epsilon_j e^{-\beta \epsilon_j} \right)^2 \right] \\ &= \left(\frac{N}{kT^2} \right) \times \left[\frac{k^2 T^2 \ddot{q}}{q} - \frac{k^2 T^2}{q^2} \dot{q}^2 \right] \\ &= \boxed{nR \left\{ \frac{\ddot{q}}{q} - \left(\frac{\dot{q}}{q} \right)^2 \right\}} \end{aligned}$$

$$S = \frac{U - U(0)}{T} + nR \ln \left(\frac{q}{N} + 1 \right) = \boxed{nR \left(\frac{\dot{q}}{q} + \ln \frac{eq}{N} \right)}$$

(b) At 5000 K, $\frac{kT}{hc} = 3475 \text{ cm}^{-1}$. We form the sums

$$q = \sum_j e^{-\beta \epsilon_j} = 1 + e^{-21870/3475} + 3e^{-21870/3475} + \dots = 1.0167$$

$$\begin{aligned} \dot{q} &= \sum_j \frac{\epsilon_j}{kT} e^{-\beta \epsilon_j} = \frac{hc}{kT} \sum_j \tilde{\nu}_j e^{-\beta \epsilon_j} \\ &= \left(\frac{1}{3475} \right) \times \{0 + 21850 e^{-21850/3475} + 3 \times 21870 e^{-21870/3475} + \dots\} = 0.1057 \end{aligned}$$

$$\begin{aligned} \ddot{q} &= \sum_j \left(\frac{\epsilon_j}{kT} \right)^2 e^{-\beta \epsilon_j} = \left(\frac{hc}{kT} \right)^2 \sum_j \tilde{\nu}_j^2 e^{-\beta \epsilon_j} \\ &= \left(\frac{1}{3475} \right)^2 \times \{0 + 21850^2 e^{-21850/3475} + 3 \times 21870^2 e^{-21870/3475} + \dots\} = 0.6719 \end{aligned}$$

The electronic contribution to the molar constant-volume heat capacity is

$$\begin{aligned} C_{V,m} &= R \left\{ \frac{\ddot{q}}{q} - \left(\frac{\dot{q}}{q} \right)^2 \right\} \\ &= 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times \left\{ \frac{0.6719}{1.0167} - \left(\frac{0.1057}{1.0167} \right)^2 \right\} = \boxed{5.41 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

P17.20 The derivation of

$$C_V = \frac{kN\beta^2}{2} \zeta(\beta)$$

given in P17.19 is completely general. That is, it makes no use of the fact that the energies and degeneracies in question were those of a linear rotor. The derivation and therefore the result can apply equally well to a nonlinear rotor, to electronic energy levels, or to the vibrational energy levels involved in P17.20.

To evaluate contributions of individual excitations to the heat capacity, we re-write $\zeta(\beta)$ in notation associated with vibrational energy levels

$$\zeta(\beta) = \frac{1}{q^2} \sum_{\nu, \nu'} \{\varepsilon(\nu) - \varepsilon(\nu')\}^2 g(\nu) g(\nu') e^{-\beta[\varepsilon(\nu) + \varepsilon(\nu')]} = \frac{1}{q^2} \sum_{\nu, \nu'} \{\varepsilon(\nu) - \varepsilon(\nu')\}^2 e^{-\beta[\varepsilon(\nu) + \varepsilon(\nu')]}$$

where the levels are nondegenerate, or at least are treated as such because vibrational modes are treated one by one. The energy levels are

$$\varepsilon(\nu) = hc\tilde{\nu}\nu = \theta_V k\nu \quad \text{so} \quad \beta\varepsilon(\nu) = \theta_V \nu / T.$$

The total heat capacity and the contributions of several transitions are plotted in Figure 17.5. For vibration, one can compute q and the total C_V/R analytically, using expressions from Tables 17.3 and 17.5 respectively:

$$q = \frac{1}{1 - e^{-\theta_V/T}} \quad \text{and} \quad \frac{C_{V,m}}{R} = \left(\frac{\theta_V}{T}\right)^2 \frac{e^{-\theta_V/T}}{(1 - e^{-\theta_V/T})^2}$$

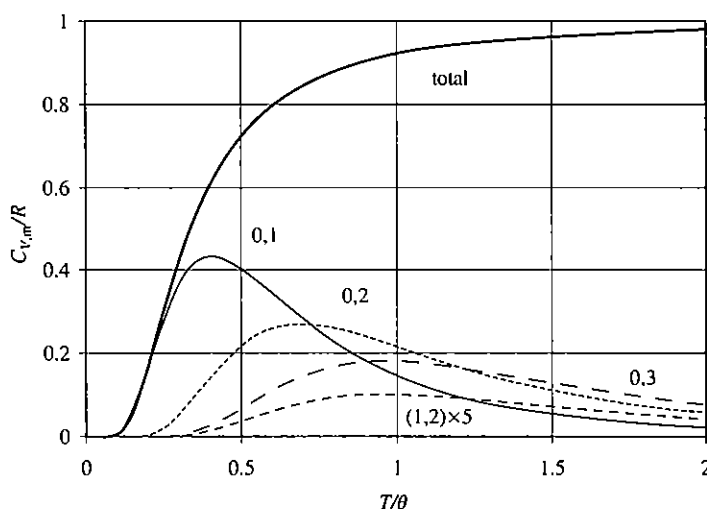


Figure 17.5

P17.22

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

$$(a) \quad C_{V,m} = \frac{1}{2}R(3 + v_R^* + 2v_V^*) = \frac{1}{2}R(3 + 2) = \frac{5}{2}R$$

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

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

$$(b) \quad C_{V,m} = \frac{1}{2}R(3 + 2) = \frac{5}{2}R, \quad \gamma = 1.40, \quad c_s = \left(\frac{1.40RT}{M} \right)^{1/2}$$

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

$$C_{p,m} = 3R + R = 4R, \quad \gamma = \frac{4}{3}, \quad c_s = \left(\frac{4RT}{3M} \right)^{1/2}$$

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

$$c_s = \left(\frac{(1.40) \times (2.48 \text{ kJ mol}^{-1})}{29 \times 10^{-3} \text{ mol}^{-1}} \right)^{1/2} = 350 \text{ m s}^{-1}$$

Solutions to applications

P17.24 (a) The heat capacity is

$$C_V = -k\beta^2 \left(\frac{\partial E}{\partial \beta} \right)_V \quad [17.31a].$$

First express E as a function of β :

$$E = \frac{N\epsilon e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}}$$

$$\text{Hence } \frac{C_V}{-k\beta^2} = \left(\frac{\partial E}{\partial \beta} \right)_V = \frac{1}{1 + e^{-\beta\epsilon}} \times (-N\epsilon^2 e^{-\beta\epsilon}) - \frac{N\epsilon}{(1 + e^{-\beta\epsilon})^2} \times (-\epsilon e^{-\beta\epsilon})$$

Collecting terms over a common denominator yields

$$C_V = \frac{kN\beta^2 \epsilon^2 e^{-\beta\epsilon}}{(1 + e^{-\beta\epsilon})^2} (1 + e^{-\beta\epsilon} - e^{-\beta\epsilon}) = \frac{kN\beta^2 \epsilon^2 e^{-\beta\epsilon}}{(1 + e^{-\beta\epsilon})^2} = \frac{kN(1/kT)^2 \epsilon^2 e^{-\epsilon/kT}}{(1 + e^{-\epsilon/kT})^2}$$

Multiply through by $e^{2\epsilon/kT} / e^{2\epsilon/kT}$:

$$C_V = \frac{kN(1/kT)^2 \epsilon^2 e^{\epsilon/kT}}{(e^{\epsilon/kT} + 1)^2}$$

The desired expression uses molar rather than molecular quantities:

$$N = N_A, \quad R = N_A k, \quad \text{and} \quad \epsilon/k = \epsilon_m/R$$

$$\text{so } C_{V,m} = \frac{R(\varepsilon_m/RT)^2 e^{\varepsilon_m/RT}}{(1 + e^{\varepsilon_m/RT})^2}$$

(b) It is convenient to plot $C_{V,m}$ (in units of R) as a function of x where $x = kT/\varepsilon = RT/\varepsilon_m$.

$$C_{V,m} = \frac{R e^{-1/x}}{x^2 (1 + e^{-1/x})^2}$$

The molar heat capacity is plotted in Figure 17.6.

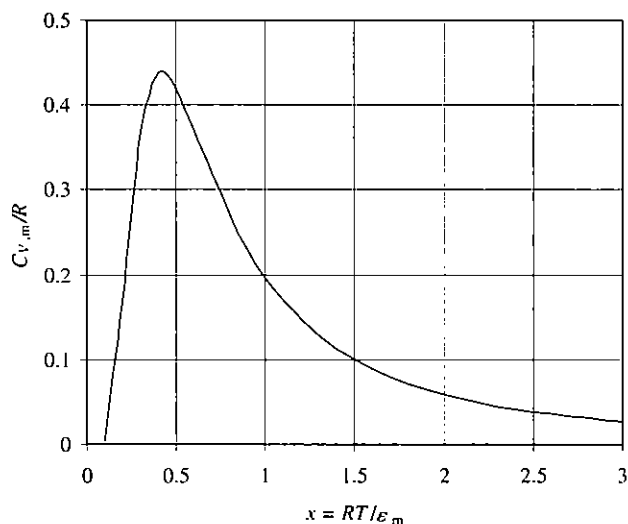


Figure 17.6

(c) The above plot indicates a maximum heat capacity at about $0.43 R$ at value for x of about 0.4 . The $X - Y$ trace feature of mathematical software may be used to find the more accurate value for x of 0.417 . A formula for the maximum is determined by the criterion that $dC_{V,m}/dx = 0$ at the maximum.

$$\begin{aligned} \frac{d(C_{V,m}/R)}{dx} &= \frac{d}{dx} \left\{ \frac{e^{-1/x}}{x^2 (1 + e^{-1/x})^2} \right\} \\ &= \frac{e^{-1/x}}{x^4 (1 + e^{-1/x})^2} - \frac{2e^{-1/x}}{x^3 (1 + e^{-1/x})^2} - \frac{2e^{-2/x}}{x^4 (1 + e^{-1/x})^3} \\ &= \frac{e^{-1/x}}{x^4 (1 + e^{-1/x})^3} \{ 1 - e^{-1/x} - 2x(1 + e^{-1/x}) - 2e^{-1/x} \} \\ &= \frac{e^{-1/x}}{x^4 (1 + e^{-1/x})^3} \{ 1 - 2x - (1 + 2x)e^{-1/x} \} \end{aligned}$$

Thus, $C_{V,m}$ is a maximum when $x = x_{\max}$ satisfies the equation

$$1 - 2x_{\max} - (1 + 2x_{\max})e^{-1/x_{\max}} = 0$$

This is a transcendental equation so it is necessary to solve for x_{\max} with a numerical method. x_{\max} may be numerically determined with the numeric solver application of the modern scientific calculator. The Given/Find solve block of Mathcad can be used or a graph containing plots of $f(x) = 1 - x$ and $g(x) = (1 + 2x)e^{-1/x}$ may be prepared. The intercept of $f(x)$ and $g(x)$ determines x_{\max} . Alternatively, expand $e^{-1/x}$ in a Taylor series around $x = 0.4$ within the above equation,

discard second order and higher terms (linearize), and solve for x . All methods yield $x_{\max} \approx 0.417$.
The following presents a Mathcad solution

```
x := 2      Estimate for following Solve Block
Given      1 - 2 · x - (1 + 2 · x) · e-1/x = 0    x > 0    x := Find(x)
x = 0.417
```

P17.26 The standard molar Gibbs energy is given by

$$G_m^\ominus - G_m^\ominus(0) = RT \ln \frac{q_m^\ominus}{N_A} \quad \text{where} \quad \frac{q_m^\ominus}{N_A} = \frac{q_m^{\text{T}\ominus}}{N_A} q^{\text{R}} q^{\text{V}} q^{\text{E}} \quad [17.53]$$

Translation (see Table 17.3 for all partition functions):

$$\begin{aligned} \frac{q_m^{\text{T}\ominus}}{N_A} &= 2.561 \times 10^{-2} (T/\text{K})^{5/2} (M/\text{g mol}^{-1})^{3/2} \\ &= 2.561 \times 10^{-2} \times (200.0)^{5/2} \times (102.9)^{3/2} = 1.512 \times 10^7 \end{aligned}$$

Rotation of a nonlinear molecule:

$$\begin{aligned} q^{\text{R}} &= \frac{1}{\sigma} \left(\frac{kT}{hc} \right)^{3/2} \left(\frac{\pi}{ABC} \right)^{1/2} = \frac{1.0270}{\sigma} \times \frac{(T/\text{K})^{3/2}}{(ABC/\text{cm}^{-3})^{1/2}} \\ &= \frac{1.0270}{2} \times \frac{[(200.0) \times (2.998 \times 10^{10} \text{ cm s}^{-1})]^3}{[(13\,109.4) \times (2409.8) \times (2139.7) \times (10^6 \text{ s}^{-1})^3/\text{cm}^{-3}]^{1/2}} = 2.900 \times 10^4 \end{aligned}$$

Vibration

$$q_1^{\text{V}} = \frac{1}{1 - \exp\left(\frac{-1.4388(\tilde{\nu}/\text{cm}^{-1})}{T/\text{K}}\right)} = \frac{1}{1 - \exp\left(\frac{-1.4388(753)}{200.0}\right)} = 1.004$$

$$q_2^{\text{V}} = \frac{1}{1 - \exp\left(\frac{-1.4388(542)}{200.0}\right)} = 1.021$$

$$q_3^{\text{V}} = \frac{1}{1 - \exp\left(\frac{-1.4388(310)}{200.0}\right)} = 1.120$$

$$q_4^{\text{V}} = \frac{1}{1 - \exp\left(\frac{-1.4388(127)}{200.0}\right)} = 1.670$$

$$q_5^{\text{V}} = \frac{1}{1 - \exp\left(\frac{-1.4388(646)}{200.0}\right)} = 1.010$$

$$q_6^V = \frac{1}{1 - \exp\left(\frac{-1.4388(419)}{200.0}\right)} = 1.052$$

$$q^V = \prod_{i=1}^6 q_i^V = 2.037$$

Putting it all together yields

$$G_m^\circ - G_m^\circ(0) = (8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \times (200.0 \text{ K}) \\ \times \ln[(1.512 \times 10^7) \times (2.900 \times 10^4) \times (2.037) \times (1)]$$

$$G_m^\circ - G_m^\circ(0) = 4.576 \times 10^4 \text{ J mol}^{-1} = \boxed{45.76 \text{ kJ mol}^{-1}}$$

18

Molecular interactions

Answers to discussion questions

D18.2 When the applied field changes direction slowly, the permanent dipole moment has time to reorientate—the whole molecule rotates into a new direction—and 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 18.3*, 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.

D18.4 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).

D18.6 The increase in entropy of a solution when hydrophobic molecules or groups in molecules cluster together and reduce their structural demands on the solvent (water) is the origin of the hydrophobic interaction that tends to stabilize clustering of hydrophobic groups in solution. A manifestation of the hydrophobic interaction is the clustering together of hydrophobic groups in biological macromolecules. For example,

the side chains of amino acids that are used to form the polypeptide chains of proteins are hydrophobic, and the hydrophobic interaction is a major contributor to the tertiary structure of polypeptides. At first thought, this clustering would seem to be a nonspontaneous process as the clustering of the solute results in a decrease in entropy of the solute. However, the clustering of the solute results in greater freedom of movement of the solvent molecules and an accompanying increase in disorder and entropy of the solvent. The total entropy of the system has increased and the process is spontaneous.

Solutions to exercises

E18.1(b) A molecule that has a center of symmetry cannot be polar. $\text{SO}_3(D_{3h})$ and $\text{XeF}_4(D_{4h})$ cannot be polar. SF_4 (see-saw, C_{2v}) may be polar.

E18.2(b)
$$\mu = (\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta)^{1/2} \quad [18.2a]$$
$$= [(1.5)^2 + (0.80)^2 + (2) \times (1.5) \times (0.80) \times (\cos 109.5^\circ)]^{1/2} \text{ D} = \boxed{1.4 \text{ D}}$$

E18.3(b) The components of the dipole moment vector are

$$\mu_x = \sum_i q_i x_i = (4e) \times (0) + (-2e) \times (162 \text{ pm})$$
$$+ (-2e) \times (143 \text{ pm}) \times (\cos 30^\circ) = (-572 \text{ pm})e$$

and $\mu_y = \sum_i q_i y_i = (4e) \times (0) + (-2e) \times (0) + (-2e) \times (143 \text{ pm}) \times (\sin 30^\circ) = (-143 \text{ pm})e$

The magnitude is

$$\mu = (\mu_x^2 + \mu_y^2)^{1/2} = ((-570)^2 + (-143)^2)^{1/2} \text{ pm } e = (590 \text{ pm})e$$
$$= (590 \times 10^{-12} \text{ m}) \times (1.602 \times 10^{-19} \text{ C}) = \boxed{9.45 \times 10^{-29} \text{ C m}}$$

and the direction is $\theta = \tan^{-1} \frac{\mu_y}{\mu_x} = \tan^{-1} \frac{-143 \text{ pm } e}{-572 \text{ pm } e} = \boxed{194.0^\circ}$ from the x -axis (i.e. 14.0° below the negative x -axis).

E18.4(b) The molar polarization depends on the polarizability through

$$P_m = \frac{N_A}{3\epsilon_0} \left(\alpha + \frac{\mu^2}{3kT} \right)$$

This is a linear equation in T^{-1} with slope

$$m = \frac{N_A \mu^2}{9\epsilon_0 k} \quad \text{so} \quad \mu = \left(\frac{9\epsilon_0 k m}{N_A} \right)^{1/2} = (4.275 \times 10^{-29} \text{ C m}) \times (m/(\text{m}^3 \text{ mol}^{-1} \text{ K}))^{1/2}$$

and with y -intercept

$$b = \frac{N_A \alpha}{3\epsilon_0} \quad \text{so} \quad \alpha = \frac{3\epsilon_0 b}{N_A} = (4.411 \times 10^{-35} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}) b/(\text{m}^3 \text{ mol}^{-1})$$

Since the molar polarization is linearly dependent on T^{-1} , we can obtain the slope m and the intercept b

$$m = \frac{P_{m,2} - P_{m,1}}{T_1^{-1} - T_2^{-1}} = \frac{(75.74 - 71.43) \text{ cm}^3 \text{ mol}^{-1}}{(320.0 \text{ K})^{-1} - (421.7 \text{ K})^{-1}} = 5.72 \times 10^3 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$$

$$\begin{aligned} \text{and } b &= P_m - mT^{-1} = 75.74 \text{ cm}^3 \text{ mol}^{-1} - (5.72 \times 10^3 \text{ cm}^3 \text{ mol}^{-1} \text{ K}) \times (320.0 \text{ K})^{-1} \\ &= 57.9 \text{ cm}^3 \text{ mol}^{-1} \end{aligned}$$

It follows that

$$\mu = (4.275 \times 10^{-29} \text{ C m}) \times (5.72 \times 10^{-3})^{1/2} = \boxed{3.23 \times 10^{-30} \text{ C m}}$$

and

$$\alpha = (4.411 \times 10^{-35} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}) \times (57.9 \times 10^{-6}) = \boxed{2.55 \times 10^{-39} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}}$$

E18.5(b) The relative permittivity is related to the molar polarization through

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{\rho P_m}{M} \equiv C \quad \text{so} \quad \epsilon_r = \frac{2C + 1}{1 - C},$$

$$C = \frac{(1.92 \text{ g cm}^{-3}) \times (32.16 \text{ cm}^3 \text{ mol}^{-1})}{85.0 \text{ g mol}^{-1}} = 0.726$$

$$\epsilon_r = \frac{2 \times (0.726) + 1}{1 - 0.726} = \boxed{8.97}$$

E18.6(b) The induced dipole moment is

$$\begin{aligned} \mu^* &= \alpha \epsilon = 4\pi \epsilon_0 \alpha' \epsilon \\ &= 4\pi (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (2.22 \times 10^{-30} \text{ m}^3) \times (15.0 \times 10^3 \text{ V m}^{-1}) \\ &= \boxed{3.71 \times 10^{-36} \text{ C m}} \end{aligned}$$

E18.7(b) If the permanent dipole moment is negligible, the polarizability can be computed from the molar polarization

$$P_m = \frac{N_A \alpha}{3\epsilon_0} \quad \text{so} \quad \alpha = \frac{3\epsilon_0 P_m}{N_A}$$

and the molar polarization from the refractive index

$$\begin{aligned} \frac{\rho P_m}{M} &= \frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{n_r^2 - 1}{n_r^2 + 2} \quad \text{so} \quad \alpha = \frac{3\epsilon_0 M}{N_A \rho} \left(\frac{n_r^2 - 1}{n_r^2 + 2} \right) \\ \alpha &= \frac{3 \times (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (65.5 \text{ g mol}^{-1})}{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (2.99 \times 10^6 \text{ g m}^{-3})} \times \left(\frac{1.622^2 - 1}{1.622^2 + 2} \right) \\ &= \boxed{3.40 \times 10^{-40} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}} \end{aligned}$$

E18.8(b) The solution to Exercise 18.7(a) showed that

$$\alpha = \left(\frac{3\epsilon_0 M}{\rho N_A} \right) \times \left(\frac{n_r^2 - 1}{n_r^2 + 2} \right) \quad \text{or} \quad \alpha' = \left(\frac{3M}{4\pi\rho N_A} \right) \times \left(\frac{n_r^2 - 1}{n_r^2 + 2} \right)$$

which may be solved for n_r to yield

$$n_r = \left(\frac{\beta' + 2\alpha'}{\beta' - \alpha'} \right)^{1/2} \quad \text{with } \beta' = \frac{3M}{4\pi\rho N_A}$$

$$\beta' = \frac{(3) \times (72.3 \text{ g mol}^{-1})}{(4\pi) \times (0.865 \times 10^6 \text{ g m}^{-3}) \times (6.022 \times 10^{23} \text{ mol}^{-1})} = 3.314 \times 10^{-29} \text{ m}^3$$

$$n_r = \left(\frac{33.14 + 2 \times 2.2}{33.14 - 2.2} \right)^{1/2} = \boxed{1.10}$$

E18.9(b) The relative permittivity is related to the molar polarization through

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{\rho P_m}{M} \equiv C \quad \text{so} \quad \epsilon_r = \frac{2C + 1}{1 - C}$$

The molar polarization depends on the polarizability through

$$P_m = \frac{N_A}{3\epsilon_0} \left(\alpha + \frac{\mu^2}{3kT} \right) \quad \text{so} \quad C = \frac{\rho N_A}{3\epsilon_0 M} \left(4\pi\epsilon_0\alpha' + \frac{\mu^2}{3kT} \right)$$

$$C = \frac{(1491 \text{ kg m}^{-3}) \times (6.022 \times 10^{23} \text{ mol}^{-1})}{3(8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (157.01 \times 10^{-3} \text{ kg mol}^{-1})}$$

$$\times \left(4\pi(8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (1.5 \times 10^{-29} \text{ m}^3) \right.$$

$$\left. + \frac{(5.17 \times 10^{-30} \text{ C m})^2}{3(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})} \right)$$

$$C = 0.83 \quad \text{and} \quad \epsilon_r = \frac{2(0.83) + 1}{1 - 0.83} = \boxed{16}$$

E18.10(b)
$$V_m = \frac{M}{\rho} = \frac{18.02 \text{ g mol}^{-1}}{999.4 \times 10^3 \text{ g m}^{-3}} = 1.803 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

$$\frac{2\gamma V_m}{rRT} = \frac{2(7.275 \times 10^{-2} \text{ N m}^{-1}) \times (1.803 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})}{(20.0 \times 10^{-9} \text{ m}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (308.2 \text{ K})}$$

$$= 5.119 \times 10^{-2}$$

$$p = (5.623 \text{ kPa}) e^{0.05119} = \boxed{5.92 \text{ kPa}}$$

E18.11(b)
$$\gamma = \frac{1}{2} \rho g h r = \frac{1}{2} (0.9956 \text{ g cm}^{-3}) \times (9.807 \text{ m s}^{-2}) \times (9.11 \times 10^{-2} \text{ m})$$

$$\times (0.16 \times 10^{-3} \text{ m}) \times \left(\frac{1000 \text{ kg m}^{-3}}{\text{g cm}^{-3}} \right)$$

$$= \boxed{7.12 \times 10^{-2} \text{ N m}^{-1}}$$

$$\text{E18.12(b)} \quad p_{\text{in}} - p_{\text{out}} = \frac{2\gamma}{r} [18.38] = \frac{(2) \times (22.39 \times 10^{-3} \text{ N m}^{-1})}{2.20 \times 10^{-7} \text{ m}} = \boxed{2.04 \times 10^5 \text{ Pa}}$$

Solutions to problems

Solutions to numerical problems

P18.2 The energy of the dipole $-\mu_1\epsilon$. To flip it over requires a change in energy of $2\mu_1\epsilon$. This will occur when the energy of interaction of the dipole with the induced dipole of the Ar atom equals $2\mu_1\epsilon$. The magnitude of the dipole-induced-dipole interaction is

$$V = \frac{\mu_1^2 \alpha'_2}{\pi \epsilon_0 r^6} [18.24] = 2\mu_1\epsilon \text{ [after flipping over]}$$

$$r^6 = \frac{\mu_1 \alpha'_2}{2\pi \epsilon_0 \epsilon} = \frac{(6.17 \times 10^{-30} \text{ C m}) \times (1.66 \times 10^{-30} \text{ m}^3)}{(2\pi) \times (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (1.0 \times 10^3 \text{ V m}^{-1})}$$

$$= 1.84 \times 10^{-52} \text{ m}^6$$

$$r = 2.4 \times 10^{-9} \text{ m} = \boxed{2.4 \text{ nm}}$$

COMMENT. This distance is about 24 times the radius of the Ar atom.

$$\text{P18.4} \quad P_{\text{m}} = \left(\frac{M}{\rho}\right) \times \left(\frac{\epsilon_r - 1}{\epsilon_r + 2}\right) \quad \text{and} \quad P_{\text{m}} = \frac{4\pi}{3} N_A \alpha' + \frac{N_A \mu^2}{9\epsilon_0 kT} [18.14 \text{ and } 18.15 \text{ with } \alpha = 4\pi \epsilon_0 \alpha']$$

The data have been corrected for the variation in methanol density, so use $\rho = 0.791 \text{ g cm}^{-3}$ for all entries. Obtain μ and α' from the liquid range ($\theta > -95^\circ\text{C}$) results, but note that some molecular rotation occurs even below the freezing point (thus the -110°C value is close to the -80°C value).

Draw up the following table using $M = 32.0 \text{ g mol}^{-1}$.

$\theta/^\circ\text{C}$	-80	-50	-20	0	20
T/K	193	223	253	273	293
$\frac{1000}{T/\text{K}}$	5.18	4.48	3.95	3.66	3.41
ϵ_r	57	49	42	38	34
$\frac{\epsilon_r - 1}{\epsilon_r + 2}$	0.949	0.941	0.932	0.925	0.917
$P_{\text{m}}/(\text{cm}^3 \text{ mol}^{-1})$	38.4	38.1	37.7	37.4	37.1

P_{m} is plotted against $1/T$ in Figure 18.1.

The extrapolated intercept at $1/T = 0$ is 34.8 (not shown in the figure) and the slope is 721 (from a least-squares analysis). It follows that

$$\alpha' = \frac{3P_{\text{m}}(\text{at intercept})}{4\pi N_A} = \frac{(3) \times (35.0 \text{ cm}^3 \text{ mol}^{-1})}{(4\pi) \times (6.022 \times 10^{23} \text{ mol}^{-1})} = \boxed{1.38 \times 10^{-23} \text{ cm}^3}$$

$$\mu = (1.282 \times 10^{-2} \text{ D}) \times (721)^{1/2} \text{ [from Problem 18.3]} = \boxed{0.34 \text{ D}}$$

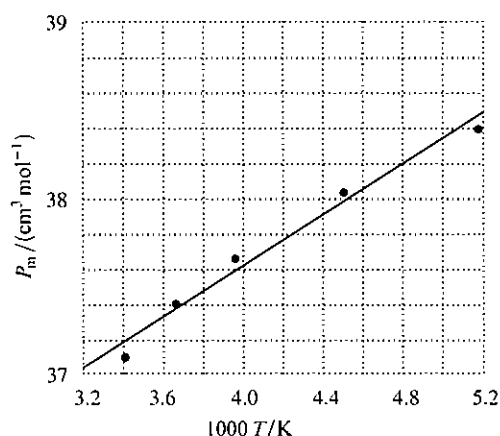


Figure 18.1

The jump in ϵ_r which occurs below the melting temperature suggests that the molecules can rotate while the sample is still solid.

P18.6

$$P_m = \frac{4\pi}{3} N_A \alpha' + \frac{N_A \mu^2}{9\epsilon_0 kT} \quad [18.15, \text{ with } \alpha = 4\pi\epsilon_0\alpha']$$

Draw up the following table

T/K	384.3	420.1	444.7	484.1	522.0
$1000/(T/K)$	2.602	2.380	2.249	2.066	1.916
$P_m/(\text{cm}^3 \text{mol}^{-1})$	57.4	53.5	50.1	46.8	43.1

The points are plotted in Figure 18.2.

The extrapolated (least-squares) intercept is $3.44 \text{ cm}^3 \text{mol}^{-1}$; the slope is 2.084×10^4 .

$$\mu = (1.282 \times 10^{-2} \text{ D}) \times (\text{slope})^{1/2} [\text{Problem 18.3}] = \boxed{1.85 \text{ D}}$$

$$\alpha' = \frac{3P_m(\text{at intercept})}{4\pi N_A} = \frac{(3) \times (3.44 \text{ cm}^3 \text{mol}^{-1})}{(4\pi) \times (6.022 \times 10^{23} \text{mol}^{-1})} = \boxed{1.36 \times 10^{-24} \text{ cm}^3}$$

COMMENT. The agreement of the value of μ with Table 18.1 is exact, but the polarizability volumes differ by about 8 percent.

P18.8

An electric dipole moment may be considered as charge $+q$ and $-q$ separated by a distance l such that

$$\mu = ql \quad \text{so} \quad q = \mu/l = \frac{(1.77 \text{ D}) \times (3.336 \times 10^{-30} \text{ C m/D})}{299 \times 10^{-12} \text{ m}} = 1.97 \times 10^{-20} \text{ C}$$

In units of the electron charge

$$q/e = (1.97 \times 10^{-20} \text{ C}) / (1.602 \times 10^{-19} \text{ C}) = \boxed{0.123}$$

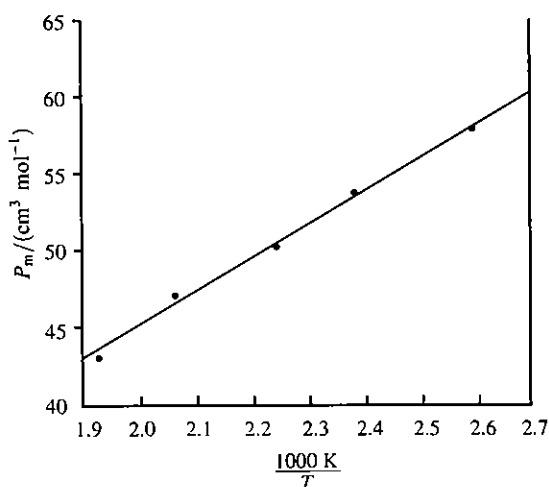


Figure 18.2

Solutions to theoretical problems

- P18.10** (a) Consider the arrangement shown in Figure 18.3(a). There are a total of $3 \times 3 = 9$ Coulombic interactions at the distances shown. The total potential energy of interaction of the two quadrupoles is

$$\begin{aligned}
 V &= \frac{q_1 q_2}{4\pi\epsilon_0} \times \left[\left(\frac{1}{r} - \frac{2}{r-l} + \frac{1}{r-2l} \right) - 2 \left(\frac{1}{r+l} - \frac{2}{r} + \frac{1}{r-l} \right) \right. \\
 &\quad \left. + \left(\frac{1}{r+2l} - \frac{2}{r+l} + \frac{1}{r} \right) \right] \\
 &= \frac{q_1 q_2}{4\pi\epsilon_0 r} \times \left[\left(1 - \frac{2}{1-\lambda} + \frac{1}{1-2\lambda} \right) - 2 \left(\frac{1}{1+\lambda} - 2 + \frac{1}{1-\lambda} \right) \right. \\
 &\quad \left. + \left(\frac{1}{1+2\lambda} - \frac{2}{1+\lambda} + 1 \right) \right] \quad \left(\lambda = \frac{l}{r} \ll 1 \right)
 \end{aligned}$$

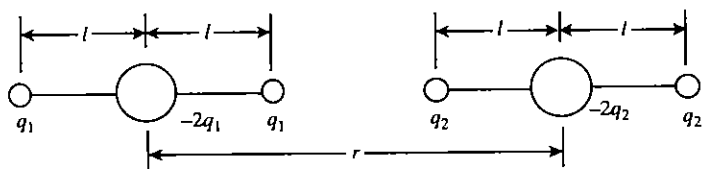


Figure 18.3(a)

Expand each term using

$$\frac{1}{1+x} = 1 - x + x^2 - x^3 + x^4 - \dots$$

and keep up to λ^4 (the preceding terms cancel). The result is

$$V = \frac{q_1 q_2}{4\pi\epsilon_0 r} \times 24\lambda^4 = \frac{6q_1 q_2 l^4}{\pi\epsilon_0 r^5}$$

Define the quadrupole moments of the two distributions as

$$Q_1 = q_1 l^2, \quad Q_2 = q_2 l^2$$

and hence obtain
$$V = \frac{6Q_1 Q_2}{\pi \epsilon_0} \times \frac{1}{r^5}$$

- (b) Consider Figure 18.3(b). There are three different distances, r , r' , and r'' . Three interactions are at r , four at r' , and two at r'' .

$$r' = (r^2 + l^2)^{1/2} = r(1 + \lambda^2)^{1/2} \approx r \left(1 + \frac{\lambda^2}{2} - \frac{\lambda^4}{8} + \dots \right)$$

$$r'' = (r^2 + 4l^2)^{1/2} = r(1 + 4\lambda^2)^{1/2} \approx r(1 + 2\lambda^2 - 2\lambda^4 + \dots)$$

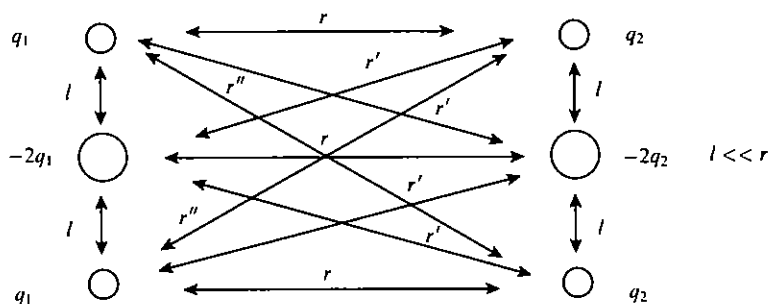


Figure 18.3(b)

$$\begin{aligned} V &= \frac{q_1 q_2}{4\pi \epsilon_0} \times \left[\left(\frac{1}{r} - \frac{2}{r'} + \frac{1}{r''} \right) - 2 \left(\frac{2}{r'} - \frac{4}{r} + \frac{2}{r'} \right) + \left(\frac{1}{r''} - \frac{2}{r'} + \frac{1}{r} \right) \right] \\ &= \left(\frac{2q_1 q_2}{4\pi \epsilon_0} \right) \times \left(\frac{3}{r} - \frac{4}{r'} + \frac{1}{r''} \right) = \left(\frac{2q_1 q_2}{4\pi \epsilon_0 r} \right) \times \left(3 - 4 \frac{r}{r'} + \frac{r}{r''} \right) \end{aligned}$$

Substituting for r' and r'' in terms of r and λ from above we obtain (dropping terms beyond λ^4)

$$\begin{aligned} V &= V_0 \left(3 - \frac{4}{\left(1 + \frac{\lambda^2}{2} - \frac{\lambda^4}{8} \right)} + \frac{1}{(1 + 2\lambda^2 - 2\lambda^4)} \right) \quad \left[V_0 = \frac{2q_1 q_2}{4\pi \epsilon_0 r} \right] \\ &= V_0 \left[3 - 4 \left(1 - \frac{\lambda^2}{2} + \frac{\lambda^4}{8} + \frac{\lambda^4}{4} \right) + (1 - 2\lambda^2 + 2\lambda^4 + 4\lambda^4) \right] \end{aligned}$$

The terms in λ^0 and λ^2 cancel leaving

$$V = V_0 \left(6 - \frac{3}{2} \right) \lambda^4 = \frac{9}{2} V_0 \lambda^4 = \frac{9q_1 q_2 \lambda^4}{4\pi \epsilon_0 r} = \frac{9q_1 q_2 l^4}{4\pi \epsilon_0 r^5} = \boxed{\frac{9Q_1 Q_2}{4\pi \epsilon_0 r^5}}$$

- P18.12** The dimers should have a zero dipole moment. The strong molecular interactions in the pure liquid probably break up the dimers and produce hydrogen-bonded groups of molecules with a chain-like structure. In very dilute benzene solutions, the molecules should behave much like those in the gas and should tend to form planar dimers. Hence the relative permittivity should decrease as the dilution increases.

- P18.14** An 'exponential-6' Lennard-Jones potential has the form

$$V = 4\varepsilon \left[Ae^{-r/\sigma} - \left(\frac{\sigma}{r}\right)^6 \right]$$

and is sketched in Figure 18.4.

The minimum occurs where

$$\frac{dV}{dr} = 4\varepsilon \left(\frac{-A}{\sigma} e^{-r/\sigma} + \frac{6\sigma^6}{r^7} \right) = 0$$

which occurs at the solution of

$$\frac{\sigma^7}{r^7} = \frac{A}{6} e^{-r/\sigma}$$

Solve this equation numerically. As an example, when $A = \sigma = 1$, a minimum occurs at $r =$ 1.63

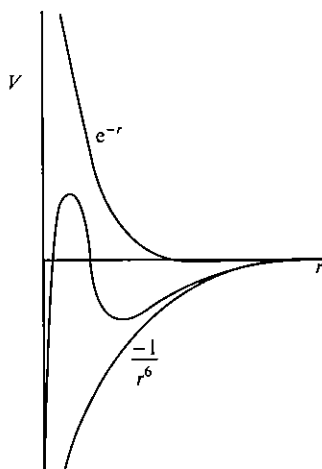


Figure 18.4

- P18.16** Refer to Figure 18.5(a).

The scattering angle is $\theta = \pi - 2\alpha$ if specular reflection occurs in the collision (angle of impact equal to angle of departure from the surface). For $b \leq R_1 + R_2$, $\sin \alpha = b/(R_1 + R_2)$.

$$\theta = \begin{cases} \pi - 2 \arcsin \left(\frac{b}{R_1 + R_2} \right) & b \leq R_1 + R_2 \\ 0 & b > R_1 + R_2 \end{cases}$$

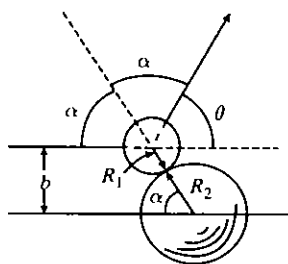


Figure 18.5(a)

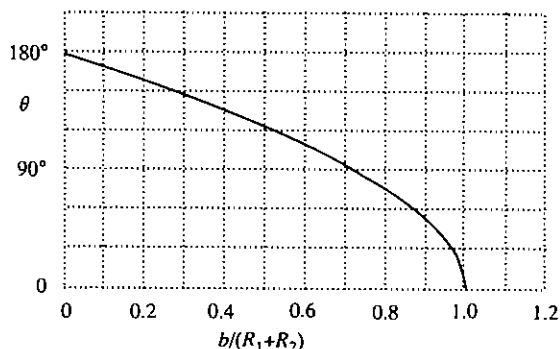


Figure 18.5(b)

The function is plotted in the Fig 18.5(b).

P18.18 The interaction is a dipole–induced-dipole interaction. The energy is given by eqn 18.24:

$$V = -\frac{\mu_1^2 \alpha'_2}{4\pi \epsilon_0 r^6} = -\frac{[(2.7 \text{ D})(3.336 \times 10^{-30} \text{ C m D}^{-1})]^2 (1.04 \times 10^{-29} \text{ m}^3)}{4\pi (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1})(4.0 \times 10^{-9} \text{ m})^6}$$

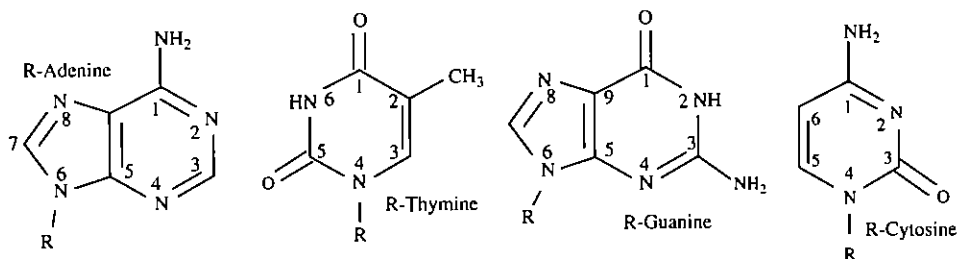
$$V = \boxed{-1.8 \times 10^{-27} \text{ J} = -1.1 \times 10^{-3} \text{ J mol}^{-1}}$$

COMMENT. This value seems exceedingly small. The distance suggested in the problem may be too large compared to typical values.

Solutions to applications

- P18.20** (a) The table displays computed electrostatic charges (semi-empirical, PM3 level, PC Spartan) of the DNA bases, modified by addition of a methyl group to the position at which the base binds to the DNA backbone. (That is, R = methyl for the computations displayed, but R = DNA backbone in DNA.) See the first set of structures for numbering.
- (b) and (c) On purely electrostatic grounds, one would expect the most positively charged hydrogen atoms of one molecule to bind to the most negatively charged atoms of another. The figure below depicts hydrogen atoms as black lines, and has thicker gray lines for the most positively charged hydrogens (those with a charge of at least 0.200); they also happen to be the hydrogens bound to electronegative atoms. The figure also has light gray type for the atoms with the greatest negative charges

(more negative than -0.400), with a gray ball on the most negative carbon atoms. In principle, then, any of the thick gray lines of one molecule can line up next to any of the atoms in light gray type of its bonding partner. In practice, the carbon atoms are not good binding sites for steric reasons.

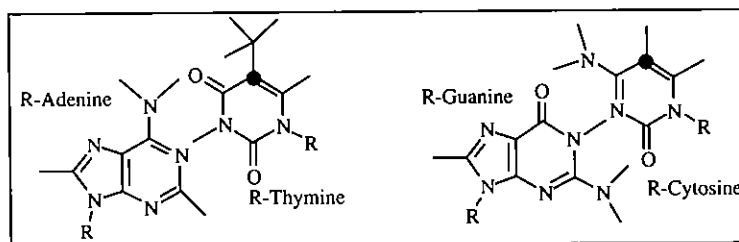


R-Adenine		R-Thymine		R-Guanine		R-Cytosine	
atom	charge	atom	charge	atom	charge	atom	charge
C1	0.905	C1	0.885	C1	0.720	C1	0.961
amino N	-0.656	O of C1	-0.580	O of C1	-0.524	amino N	-0.709
amino H [†]	0.288	C2	-0.554	N2	-0.473	amino H [†]	0.291
N2	-0.914	C2 methyl C	0.180	H of H2	0.233	N2	-0.901
C3	0.785	C2 methyl H	-0.003	C3	0.794	C3	0.993
H of C3	-0.020	C3	0.173	amino N	-0.693	O of C3	-0.609
N4	-0.835	H of C3	0.111	amino H [†]	0.288	N4	-0.286
C5	0.639	N4	-0.390	N4	-0.757	methyl C*	0.119
N6	-0.183	N4 methyl C*	0.211	C5	0.325	methyl H* [†]	0.017
methyl C*	0.113	N4 methyl H* [†]	0.002	N6	0.079	C5	0.205
methyl H* [†]	0.022	C5	0.836	methyl C*	-0.008	H of C5	0.103
C7	0.320	O of C5	-0.596	methyl H* [†]	0.043	C6	-0.684
H of C7	0.056	N6	-0.540	C7	0.130	H of C6	0.174
N8	-0.584	H of N6	0.264	H of C7	0.086		
C9	-0.268			N8	-0.470		
				C9	-0.146		

* part of R group, so not really available for hydrogen bonding in DNA

† table displays average charge of atoms that are chemically equivalent

- (d) The naturally occurring pairs are shown below. These configurations are quite accessible sterically, and they have the further advantage of multiple hydrogen bonds.



(e) See above

- P18.22** (a) The hydrocarbons in question form a homologous series. They are straight-chain alkanes of the formula C_nH_{2n+2} , or $R-H$ where $R = C_nH_{2n+1}$. Draw up the following table:

n	1	2	3	4	5
π	0.5	1.0	1.5	2.0	2.5

The relationship here is evident by inspection: $\pi = n/2$, so we predict for the seven-carbon hydrocarbon in question:

$$\pi = 7/2 = \boxed{3.5}.$$

- (b) The plot, shown in Figure 18.6, is consistent with a linear relationship, for $R^2 = 0.997$ is close to unity. The best linear fit is:

$$\log K = -1.95 - 1.49\pi,$$

so $\boxed{\text{slope} = -1.49}$ and $\boxed{\text{intercept} = -1.95}$.

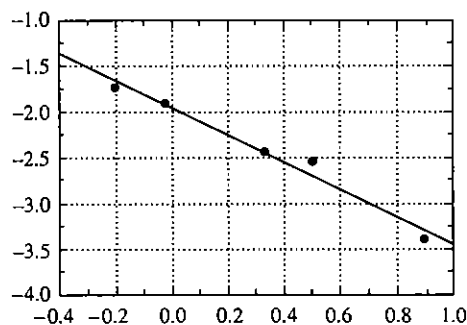


Figure 18.6

- (c) If we know π for the substituent $R = H$, then we can use the linear SAR just derived. Our best estimate of π can be obtained by considering the zero-carbon "alkane" H_2 , whose radical H ought to have a hydrophobicity constant $\pi = 0/2 = 0$. This value yields

$$\log K = -1.95 - 1.49(0) = -1.95 \text{ so } K = 10^{-1.95} = \boxed{1.12 \times 10^{-2}}.$$

Note: the assumption that $R = H$ is part of the homologous series of straight-chain alkanes is a reasonable but questionable one.

19

Materials 1: macromolecules and aggregates

Answers to discussion questions

- D19.2** First, try to understand why different molar mass averages might give different numerical values. Polymers are unlike small molecules in that all small molecules of the same species have nearly identical masses. Polymers vary widely in mass because they can vary in the number of monomeric units they contain. Depending on how a polymer is synthesized and purified, it is entirely possible for one macromolecule to contain 2 monomer units and another 100. We call a polymer sample *polydisperse* if there is a large variation in mass among the molecules of the sample; conversely, a sample is *monodisperse* if its range of masses is narrow.

Even for small molecules, *the* molar mass is an average (over isotopic variants); however, the details of the averaging process make a negligible difference when the distribution of molar masses is narrow. But the different averages can give significantly different answers for highly polydisperse samples. Why should experiments yield one average or another?

The differences in averages are in the weighting factors. We see that the weighting factor for \overline{M}_n is the number of molecules that have a particular mass and (from eqn 19.2) that the weighting factor in \overline{M}_w is the mass fraction of a sample that has a particular mass. Different measurement techniques yield different weighting factors because they are sensitive to different factors (or, more accurately, different combinations of factors). The intensity of a mass spectrometry peak, for instance, is proportional to the number of molecules of a given mass. Some techniques, like light scattering, are more sensitive to the size (volume) and shape of particles, and some, like sedimentation, are more sensitive to the mass. (Discussions in the text reveal, however, that the measurements capture a complicated function of size, shape, mass, and number.)

Experimental techniques for the study of polydisperse polymer solutions are sensitive to a wide range of properties. Osmometry, measuring a colligative property, is sensitive to the number of molecules N_i that have molar mass M_i . Consequently, average osmotic properties depend upon the number average molar mass. Light scattering depends upon molecular size and shape, which indirectly depend upon mass, so weight average molar mass becomes important. Other mass averages become important when the technique is sensitive to intermolecular attractions and repulsions, molecular entanglements, gravitational and centrifuge effects.

- D19.4** (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 $v = n/N$.

- (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 (Figure 19.15 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 $n l$ 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 neighbor (Figure 19.16). In a hypothetical one-dimensional freely jointed chain all the residues lie in a straight line, and the angle between neighbors 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.

D19.6 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.

D19.8 Using symbols that relate to surface properties ($G(\sigma)$, $S(\sigma)$, $n_j(\sigma)$, Γ_j , etc.) and the symbol c for the surfactant concentration in the bulk solution,

$$dG = -SdT + Vdp + \gamma d\sigma + \sum_j \mu_j dn_j \quad (\text{Justification 19.7})$$

$$\left(\frac{\partial S}{\partial \sigma}\right)_{T,p,n_j} = -\left(\frac{\partial \gamma}{\partial T}\right)_{p,\sigma,n_j} \quad (\text{Maxwell Relationship})$$

This equation does not give a definitive indication of whether entropy changes are positive (increase) or negative (decrease) when surface area increases at the interface, or when $\Gamma_j > 0$, because the partial derivative of the surface tension with respect to temperature may be either positive or negative. However, the partial of the surface tension (also called interfacial tension) with respect to temperature is usually negative so it seems most likely that the entropy of the interface increases when the surface area increases. The equation for the enthalpy change with surface changes is

$$H = G + TS$$

$$\left(\frac{\partial H}{\partial \sigma}\right)_{T,p,n_j} = \left(\frac{\partial G}{\partial \sigma}\right)_{T,p,n_j} + T \left(\frac{\partial S}{\partial \sigma}\right)_{T,p,n_j} = \gamma - T \left(\frac{\partial \gamma}{\partial T}\right)_{p,\sigma,n_j}$$

Surface tension is always positive and the partial with respect to temperature is usually negative so the enthalpy change is positive for increasing surface area.

Although it is difficult to find general statements concerning thermodynamic properties of surfactants at solution interfaces, a surfactant that forms an ideal solution with one phase and is insoluble in the second phase is expected to exhibit a negative entropy change upon adsorbing at the solution interface. This would happen because the surfactant molecules are relatively disordered in the bulk solution. Upon adsorption, the molecules become self-aligned and ordered. With spontaneous adsorption the free energy of adsorption is negative and, since $\Delta G = \Delta H - T\Delta S$ for an isothermal process, we expect that $\Delta_{\text{ads}}H$ should be exothermic to the extent that $\Delta_{\text{ads}}H < T\Delta_{\text{ads}}S < 0$.

Solutions to exercises

E19.1(b) The number-average molar mass is (eqn 19.1)

$$\bar{M}_n = \frac{1}{N} \sum N_i M_i = \frac{[3 \times (62) + 2 \times (78)] \text{ kg mol}^{-1}}{5} = \boxed{68 \text{ kg mol}^{-1}}$$

The mass-average molar mass is (eqn 19.3)

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{3 \times (62)^2 + 2 \times (78)^2}{3 \times (62) + 2 \times (78)} \text{ kg mol}^{-1} = \boxed{69 \text{ kg mol}^{-1}}$$

E19.2(b) For a random coil, the radius of gyration is (19.33)

$$R_g = l(N/6)^{1/2} \text{ so } N = 6(R_g/l)^2 = 6 \times (18.9 \text{ nm}/0.450 \text{ nm})^2 = \boxed{1.06 \times 10^4}$$

E19.3(b) (a) Osmometry gives the number-average molar mass, so

$$\begin{aligned} \bar{M}_n &= \frac{N_1 M_1 + N_2 M_2}{N_1 + N_2} = \frac{(m_1/M_1) M_1 + (m_2/M_2) M_2}{(m_1/M_1) + (m_2/M_2)} = \frac{m_1 + m_2}{(m_1/M_1) + (m_2/M_2)} \\ &= \frac{100 \text{ g}}{\left(\frac{25 \text{ g}}{22 \text{ kg mol}^{-1}}\right) + \left(\frac{75 \text{ g}}{22/3 \text{ kg mol}^{-1}}\right)} [\text{assume } 100 \text{ g of solution}] = \boxed{8.8 \text{ kg mol}^{-1}} \end{aligned}$$

(b) Light-scattering gives the mass-average molar mass, so

$$\bar{M}_w = \frac{m_1 M_1 + m_2 M_2}{m_1 + m_2} = \frac{(25) \times (22) + (75) \times (22/3)}{25 + 75} \text{ kg mol}^{-1} = \boxed{11 \text{ kg mol}^{-1}}$$

E19.4(b) The formula for the rotational correlation time is

$$\begin{aligned} \tau &= \frac{4\pi a^3 \eta}{3kT} \\ \eta(\text{H}_2\text{O}, 20^\circ\text{C}) &= 1.00 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1} [\text{CRC Handbook}] \\ \tau &= \frac{4\pi \times (4.5 \times 10^{-9} \text{ m})^3 \times 1.00 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}}{3 \times 1.381 \times 10^{-23} \text{ J K}^{-1} \times 293 \text{ K}} = \boxed{9.4 \times 10^{-8} \text{ s}} \end{aligned}$$

E19.5(b) The effective mass of the particles is

$$m_{\text{eff}} = bm = (1 - \rho v_s)m \quad [19.14] = m - \rho v_s m = v\rho_p - v\rho = v(\rho_p - \rho)$$

where v is the particle volume and ρ_p is the particle density. Equating the forces

$$m_{\text{eff}} r \omega^2 = fs = 6\pi \eta a s \quad [19.15, 19.12]$$

$$\text{or } v(\rho_p - \rho)r\omega^2 = \frac{4}{3}\pi a^3(\rho_p - \rho)r\omega^2 = 6\pi \eta a s$$

Solving for s yields

$$s = \frac{2a^2(\rho_p - \rho)r\omega^2}{9\eta}$$

$$\text{Thus, the relative rates of sedimentation are } \frac{s_2}{s_1} = \frac{a_2^2(\rho_p - \rho)_2}{a_1^2(\rho_p - \rho)_1} = \left(\frac{a_2}{a_1}\right)^2 \frac{(\rho_p - \rho)_2}{(\rho_p - \rho)_1}.$$

The value of this ratio depends on the density of the solution. For example, in a dilute aqueous solution with $\rho = 1.01 \text{ g cm}^{-3}$, the difference in polymer densities matters in that the factor involving densities is significantly different than 1:

$$\frac{s_2}{s_1} = (8.4)^2 \frac{(1.10 - 1.01)_2}{(1.18 - 1.01)_1} = \boxed{37}$$

In a less dense organic solution, for example a dilute solution in octane with $\rho = 0.71 \text{ g cm}^{-3}$, the density difference has a smaller effect, for the factor involving densities is closer to 1:

$$\frac{s_2}{s_1} = (8.4)^2 \frac{(1.10 - 0.71)_2}{(1.18 - 0.71)_1} = \boxed{59}$$

In both cases, the larger particle sediments faster.

E19.6(b) The molar mass is related to the sedimentation constant through eqns 19.19 and 19.14:

$$\overline{M} = \frac{SRT}{bD} = \frac{SRT}{(1 - \rho v_s)D}$$

where we have assumed the data refer to aqueous solution at 298 K.

$$\begin{aligned} \overline{M}_n &= \frac{(7.46 \times 10^{-13} \text{ s}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{[1 - (1000 \text{ kg m}^{-3}) \times (8.01 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1})] \times (7.72 \times 10^{-11} \text{ m}^2 \text{ s}^{-1})} \\ &= \boxed{120 \text{ kg mol}^{-1}} \end{aligned}$$

E19.7(b) See the solution to Exercise 19.5(b). In place of the centrifugal force $m_{\text{eff}}r^2$ we have the gravitational force $m_{\text{eff}}g$. The rest of the analysis is similar, leading to

$$s = \frac{2a^2(\rho_p - \rho)g}{9\eta} = \frac{(2) \times (15.5 \times 10^{-6} \text{ m})^2 \times (1250 - 1000) \text{ kg m}^{-3} \times (9.81 \text{ m s}^{-2})}{(9) \times (8.9 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1})} = \boxed{1.47 \times 10^{-4} \text{ m s}^{-1}}$$

E19.8(b) The molar mass is related to the sedimentation constant through eqns 19.19 and 19.14:

$$\bar{M} = \frac{SRT}{bD} = \frac{SRT}{(1 - \rho v_s)D}$$

Assuming that the data refer to an aqueous solution,

$$\bar{M} = \frac{(5.1 \times 10^{-13} \text{ s}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293 \text{ K})}{[1 - (0.997 \text{ g cm}^{-3}) \times (0.721 \text{ cm}^3 \text{ g}^{-1})] \times (7.9 \times 10^{-11} \text{ m}^2 \text{ s}^{-1})} = \boxed{56 \text{ kg mol}^{-1}}$$

E19.9(b) In a sedimentation experiment, the weight-average molar mass is given by (eqn 19.20)

$$\bar{M}_w = \frac{2RT}{(r_2^2 - r_1^2)b\omega^2} \ln \frac{c_2}{c_1} \quad \text{so} \quad \ln \frac{c_2}{c_1} = \frac{\bar{M}_w(r_2^2 - r_1^2)b\omega^2}{2RT}$$

This implies that

$$\ln c = \frac{\bar{M}_w r^2 b \omega^2}{2RT} + \text{constant}$$

so the plot of $\ln c$ versus r^2 has a slope m equal to

$$m = \frac{\bar{M}_w b \omega^2}{2RT} \quad \text{and} \quad \bar{M}_w = \frac{2RTm}{b\omega^2}$$

$$\begin{aligned} \bar{M}_w &= \frac{2 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293 \text{ K}) \times (821 \text{ cm}^{-2}) \times (100 \text{ cm m}^{-1})^2}{[1 - (1000 \text{ kg m}^{-3}) \times (7.2 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1})] \times [(1080 \text{ s}^{-1}) \times (2\pi)]^2} \\ &= \boxed{3.1 \times 10^3 \text{ kg mol}^{-1}} \end{aligned}$$

E19.10(b) The centrifugal acceleration is

$$a = r\omega^2 \text{ so } a/g = r\omega^2/g$$

$$a/g = \frac{(5.50 \text{ cm}) \times [2\pi \times (1.32 \times 10^3 \text{ s}^{-1})]^2}{(100 \text{ cm m}^{-1}) \times (9.81 \text{ m s}^{-2})} = \boxed{3.86 \times 10^5}$$

E19.11(b) For a random coil, the rms separation is [19.31]

$$R_{\text{rms}} = N^{1/2}l = (1200)^{1/2} \times (1.125 \text{ nm}) = \boxed{38.97 \text{ nm}}$$

E19.12(b) Polypropylene is $-(\text{CH}(\text{CH}_3)\text{CH}_2)-_N$, where N is given by

$$N = \frac{M_{\text{polymer}}}{M_{\text{monomer}}} = \frac{174 \text{ kg mol}^{-1}}{42.1 \times 10^{-3} \text{ kg mol}^{-1}} = 4.13 \times 10^3$$

The repeat length l is the length of two C–C bonds. The contour length is [19.30]

$$R_c = Nl = (4.13 \times 10^3) \times (2 \times 1.53 \times 10^{-10} \text{ m}) = \boxed{1.26 \times 10^{-6} \text{ m}}$$

The rms separation is [19.31]

$$R_{\text{rms}} = lN^{1/2} = (2 \times 1.53 \times 10^{-10} \text{ m}) \times (4.13 \times 10^3)^{1/2} = \boxed{1.97 \times 10^{-8} \text{ m}} = 19.7 \text{ nm}$$

Solutions to problems

Solutions to numerical problems

P19.2 From eqn 19.20, we can relate concentration ratios to the molar mass

$$\ln \frac{c_1}{c_2} = \frac{\overline{M}_w b \omega^2 (r_1^2 - r_2^2)}{2RT} = \frac{2\pi^2 \overline{M}_w b v^2 (r_1^2 - r_2^2)}{RT}$$

and hence

$$\begin{aligned} v &= \left(\frac{RT \ln \left(\frac{c_1}{c_2} \right)}{2\pi^2 \overline{M}_w b (r_1^2 - r_2^2)} \right)^{1/2} \\ &= \left(\frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (\ln 5)}{2\pi^2 \times (1 \times 10^2 \text{ kg mol}^{-1}) \times (1 - 0.75) \times (7.0^2 - 5.0^2) \times 10^{-4} \text{ m}^2} \right)^{1/2} \\ &= 58 \text{ Hz, or } \boxed{3500 \text{ rpm}} \end{aligned}$$

Question. What would the concentration gradient be in this system with a speed of operation of 70 000 rpm in an ultracentrifuge?

P19.4 We need to determine the intrinsic viscosity from a plot of $((\eta/\eta_0) - 1)/(c/(\text{g dm}^{-3}))$ against c , extrapolated to $c = 0$ as in Example 19.5. Then from the relation

$$[\eta] = K \overline{M}_V^a \quad [19.25]$$

with K and a from Table 19.4, the viscosity average molar mass \overline{M}_V may be calculated. η/η_0 values are determined from the times of flow using the relation

$$\frac{\eta}{\eta_0} = \frac{t}{t_0} \times \frac{\rho}{\rho_0} \approx \frac{t}{t_0} \quad [19.24]$$

noting that in the limit as c approaches 0 the approximation becomes exact. As explained in Example 19.5, $[\eta]$ can also be determined from the limit of $(1/c) \ln (\eta/\eta_0)$ as c approaches 0.

We draw up the following table

$c/(\text{g dm}^{-3})$	0.000	2.22	5.00	8.00	10.00
t/s	208.2	248.1	303.4	371.8	421.3
η/η_0	—	1.192	1.457	1.786	2.024
$\frac{100[(\eta/\eta_0) - 1]}{c/(\text{g dm}^{-3})}$	—	8.63	9.15	9.82	10.24
$\ln(\eta/\eta_0)$	—	0.1753	0.3766	0.5799	0.7048
$\frac{100 \ln(\eta/\eta_0)}{c/(\text{g dm}^{-3})}$	—	7.89	7.52	7.24	7.05

The points are plotted in Figure 19.1.

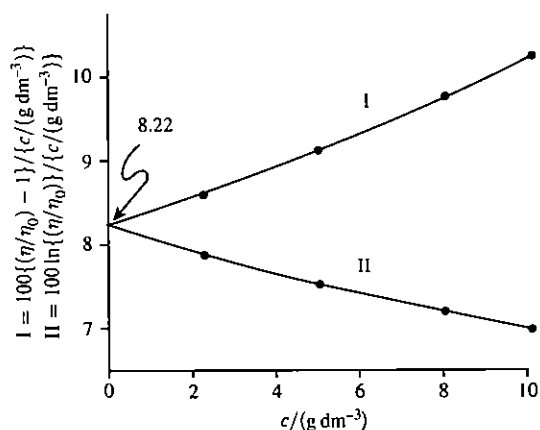


Figure 19.1

The intercept as determined from the simultaneous extrapolation of both plots is $0.0822 \text{ dm}^3 \text{ g}^{-1}$.

$$\frac{\bar{M}_V}{\text{g mol}^{-1}} = \left(\frac{[\eta]}{K} \right)^{1/a} = \left(\frac{0.0822 \text{ dm}^3 \text{ g}^{-1}}{9.5 \times 10^{-6} \text{ dm}^3 \text{ g}^{-1}} \right)^{1/0.74} = \boxed{2.1 \times 10^5}$$

P19.6 The relationship (eqn 19.25) between $[\eta]$ and \bar{M}_V can be transformed into a linear one

$$\ln[\eta] = \ln K + a \ln \bar{M}_V$$

so a plot of $\ln[\eta]$ versus $\ln \bar{M}_V$ will have a slope of a and a y -intercept of $\ln K$. The transformed data and plot are shown below (Figure 19.2)

$\bar{M}_V/(\text{kg mol}^{-1})$	10.0	19.8	106	249	359	860	1800	5470	9720	56 800
$[\eta]/(\text{cm}^3 \text{ g}^{-1})$	8.90	11.9	28.1	44.0	51.2	77.6	113.9	195	275	667
$\ln \bar{M}_V/(\text{kg mol}^{-1})$	2.30	2.99	4.66	5.52	5.88	6.76	7.509	8.61	9.18	10.90
$\ln[\eta]/(\text{cm}^3 \text{ g}^{-1})$	2.19	2.48	3.34	3.78	3.94	4.35	4.749	5.27	5.62	6.500

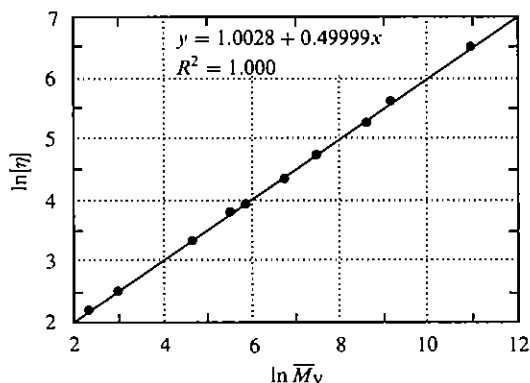


Figure 19.2

Thus $a = 0.500$ and $K = e^{1.0028} \text{ cm}^3 \text{ g}^{-1} \text{ kg}^{-1/2} \text{ mol}^{1/2} = 2.73 \text{ cm}^3 \text{ g}^{-1} \text{ kg}^{-1/2} \text{ mol}^{1/2}$

Solving for \bar{M}_V yields

$$\bar{M}_V = \left(\frac{[\eta]}{K} \right)^{1/a} = \left(\frac{100 \text{ cm}^3 \text{ g}^{-1}}{2.73 \text{ cm}^3 \text{ g}^{-1} \text{ kg}^{-1/2} \text{ mol}^{1/2}} \right)^2 = 1.34 \times 10^3 \text{ kg mol}^{-1}$$

P19.8 See section 5.5(e) and Example 5.4.

$$\frac{\Pi}{c} = \frac{RT}{\bar{M}_n} \left(1 + B \frac{c}{\bar{M}_n} + \dots \right) \text{ [Example 5.4, with } \Pi = \rho gh \text{]}$$

Therefore, to determine \bar{M}_n and B we need to plot Π/c against c . We draw up the following table

$c/(\text{g dm}^{-3})$	1.21	2.72	5.08	6.60
$(\Pi/c)/(\text{Pa/g dm}^{-3})$	111	118	129	136

The points are plotted in Figure 19.3

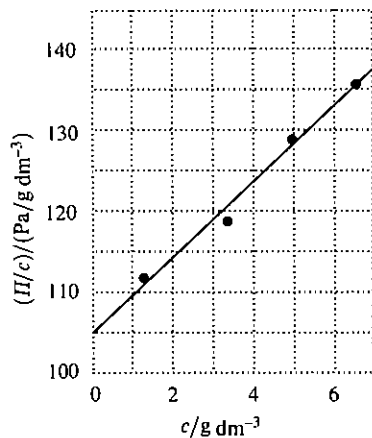


Figure 19.3

A least-squares analysis gives an intercept of 105.4 and a slope of 4.64 . It follows that

$$\frac{RT}{\overline{M}_n} = 105.4 \text{ Pa g}^{-1} \text{ dm}^3 = 105.4 \text{ Pa kg}^{-1} \text{ m}^3$$

$$\text{and hence that } \overline{M}_n = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293 \text{ K})}{105.4 \text{ Pa kg}^{-1} \text{ m}^3} = \boxed{23.1 \text{ kg mol}^{-1}}$$

The slope of the graph is equal to RTB/\overline{M}_n^2 , so

$$\frac{RTB}{\overline{M}_n^2} = 4.64 \text{ Pa g}^{-2} \text{ dm}^6 = 4.64 \text{ Pa kg}^{-2} \text{ m}^6$$

$$\text{Therefore, } B = \frac{(23.1 \text{ kg mol}^{-1})^2 \times (4.64 \text{ Pa kg}^{-2} \text{ m}^6)}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293 \text{ K})} = \boxed{1.02 \text{ m}^3 \text{ mol}^{-1}}$$

P19.10 The glass transition temperature T_g is the temperature at which internal bond rotations freeze. In effect, the easier such rotations are, the lower T_g . Internal rotations are more difficult for polymers that have bulky side chains than for polymers without such chains because the side chains of neighboring molecules can impede each others' motion. Of the four polymers in this problem, polystyrene has the largest side chain (phenyl) and the largest T_g . The chlorine atoms in poly(vinyl chloride) interfere with each other's motion more than the smaller hydrogen atoms that hang from the carbon backbone of polyethylene. Poly(oxyethylene), like polyethylene, has only hydrogen atoms protruding from its backbone; however, poly(oxyethylene) has fewer hydrogen protrusions and a still lower T_g than polyethylene.

Solutions to theoretical problems

$$\begin{aligned} \text{P19.12} \quad \text{SI unit}(\eta/\rho) &= \text{SI unit}(\eta)/\text{SI unit}(\rho) = (\text{Pa})/(\text{kg m}^{-3}) = (\text{N m}^{-2})/(\text{kg m}^{-3}) \\ &= (\text{kg m}^{-1} \text{ s}^{-1})/(\text{kg m}^{-3}) = \text{m}^2 \text{ s}^{-1} \end{aligned}$$

We begin by simplifying Poiseuille's formula with the assumptions that $p_2 = p_0$, $p_1 = p_2 + \Delta p$ where $\Delta p < p_2$, and $\Delta p^2 \ll 2p_2 \Delta p$ so the second order term may be discarded.

$$\begin{aligned} \frac{dV}{dt} &= \frac{(p_1^2 - p_2^2) \pi r^4}{16 l \eta p_0} = \frac{\{(p_2 + \Delta p)^2 - p_2^2\} \pi r^4}{16 l \eta p_0} \\ &= \frac{(p_2^2 + 2p_2 \Delta p + \Delta p^2 - p_2^2) \pi r^4}{16 l \eta p_0} \approx \frac{\Delta p \pi r^4}{8 l \eta} \end{aligned}$$

When gravity is the driving force for fluid flow, $\Delta p = F_{\text{gravity}}/(\pi r^2) = mgl/(\pi r^2 l) = \rho gl$ where g is the gravitational acceleration and $dV/dt = V/t = \pi r^2 l/t$.

$$\begin{aligned} \frac{\pi r^2 l}{t} &= \frac{\rho gl \pi r^4}{8 l \eta} \\ \frac{\eta/\rho}{t} &= \frac{gr^2}{8 l} = \text{constant} \end{aligned}$$

Dividing by the identical expression for a reference liquid gives eqn 19.24.

$$\frac{(\eta/\rho)l_0}{(\eta/\rho)_0l} = 1 \text{ or } \frac{(\eta/\rho)}{(\eta/\rho)_0} = \frac{l}{l_0}$$

This shows that the drainage time is governed by the kinematic viscosity (η/ρ) .

P19.14 Eqn 19.26 gives the probability of finding the end of an N -step one-dimensional random walk at a distance n_l from the start,

$$P = \left(\frac{2}{\pi N} \right)^{1/2} e^{-n^2/2N}.$$

We generalize to a continuous version:

$$dP_x = \left(\frac{2}{\pi N} \right)^{1/2} e^{-n_x^2/2N} dn_x.$$

Physically, it is more fundamental to talk of the probability of finding the end "at" a given distance $x = n_x l$ rather than a given number of steps away. $dx = l dn_x$. Hence, the probability of finding the end of the polymer in an interval between x and $x + dx$ is

$$dP_x = \left(\frac{2}{\pi N l^2} \right)^{1/2} e^{-x^2/2N l^2} dx.$$

Building our three-dimensional chain from one-dimensional random walks, we have

$$dP_x dP_y dP_z = \left(\frac{6}{\pi N l^2} \right)^{3/2} e^{-3(x^2+y^2+z^2)/2N l^2} dx dy dz$$

(Note that in this step we have replaced N with $N/3$. This allows us to continue to regard N as the total number of units in the polymer, so the number of steps in each dimension, divided equally among this number, becomes $N/3$.) Now change variables to spherical polar coordinates:

$$r^2 = x^2 + y^2 + z^2 \quad \text{and} \quad dx dy dz = r^2 \sin \theta dr d\theta d\phi,$$

$$\text{so } dP_x dP_y dP_z = \left(\frac{6}{\pi N l^2} \right)^{3/2} e^{-3r^2/2N l^2} r^2 \sin \theta dr d\theta d\phi.$$

To find the probability of finding the ends of the polymer at a distance between r and $r + dr$ regardless of angle, integrate over the angles and divide by 8, as stated in the problem, to restrict the integration to positive x, y, z :

$$\begin{aligned} \int_{\substack{\text{positive} \\ x,y,z \\ \text{directions}}} dP_x dP_y dP_z &= \frac{1}{8} \left(\frac{6}{\pi N l^2} \right)^{3/2} e^{-3r^2/2N l^2} r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \\ &= \frac{4}{8} \pi \left(\frac{6}{\pi N l^2} \right)^{3/2} e^{-3r^2/2N l^2} r^2 dr \end{aligned}$$

Defining $a = \left(\frac{3}{2Nl^2}\right)^{1/2}$ allows us to complete the derivation:

$$\int_{\substack{\text{positive} \\ x,y,z \\ \text{directions}}} dP_x dP_y dP_z = f(r) dr \text{ where } f(r) = \boxed{4\pi \left(\frac{a}{\pi^{1/2}}\right)^3 e^{-3r^2/2Nl^2} r^2}.$$

P19.16 A simple procedure is to generate numbers in the range 1 to 8, and to step north for a 1 or 2, east for 3 or 4, south for 5 or 6, and west for 7 or 8 on a uniform grid. One such walk is shown in Figure 19.4.

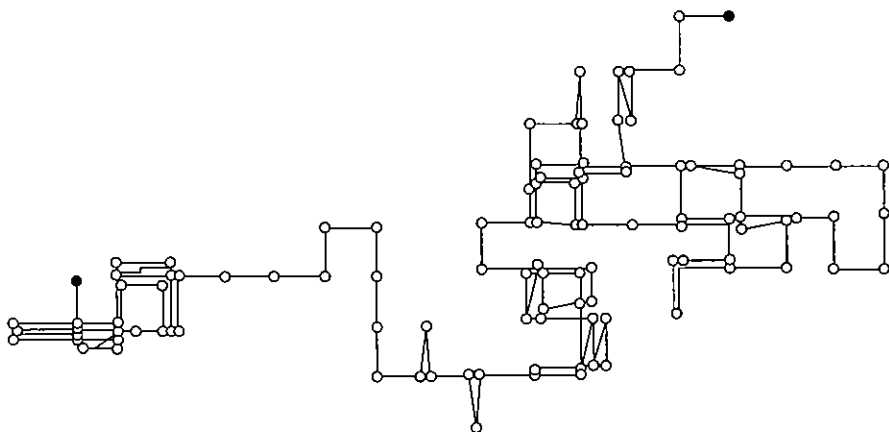


Figure 19.4

Roughly, they would appear to vary as $N^{1/2}$

P19.18 The volume of a spherical molecule of radius a is

$$v_{\text{mol}} = \frac{4\pi a^3}{3}$$

The smallest distance possible between centers of two such molecules is $2a$, so the excluded volume is

$$v_p = \frac{4\pi (2a)^3}{3} = 8v_{\text{mol}}$$

$$\text{so } B = \frac{1}{2} N_A v_p = 4N_A v_{\text{mol}} = \frac{16\pi}{2} N_A a_{\text{eff}}^3 = \frac{16\pi}{3} N_A \gamma^3 R_g^3$$

$$\text{(a) } R_g = \left(\frac{N}{6}\right)^{1/2} l \quad [19.33]$$

$$\begin{aligned} \text{so } B &= \frac{16\pi}{3 \times 6^{3/2}} \gamma^3 l^3 N^{3/2} N_A = \boxed{4.22 \times 10^{23} \text{ mol}^{-1} \times (l N^{1/2} \gamma)^3} \\ &= (4.22 \times 10^{23} \text{ mol}^{-1}) \times [(154 \times 10^{-12} \text{ m}) \times (4000)^{1/2}]^3 = \boxed{0.39 \text{ m}^3 \text{ mol}^{-1}} \end{aligned}$$

$$(b) \quad R_g = 2^{1/2} \times R_g(\text{free}) \quad [19.36]$$

$$\begin{aligned} \text{so } B &= 2^{3/2} \times B(\text{free}) = \boxed{1.19 \times 10^{24} \text{ mol}^{-1} \times (1N^{1/2})^3} \\ &= 2^{3/2} \times (0.39 \text{ m}^3 \text{ mol}^{-1}) = \boxed{1.1 \text{ m}^3 \text{ mol}^{-1}} \end{aligned}$$

P19.20 Given that $G = U - TS - tl$ and $dU = TdS + tdI$, we take the differential, obtaining

$$\begin{aligned} dG &= dU - TdS - SdT - ldt - tdl \\ &= TdS + tdI - TdS - SdT - ldt - tdl = \boxed{-SdT - ldt} \end{aligned}$$

Since $A = U - TS$, we have $A = G + tl$,

$$\text{so } dA = dG + tdl + ldt = -SdT - ldt + tdl + ldt = \boxed{-SdT + tdl}$$

Since dA and dG are both exact differentials

$$\left(\frac{\partial S}{\partial l}\right)_T = -\left(\frac{\partial t}{\partial T}\right)_l \quad \text{and} \quad \left(\frac{\partial S}{\partial t}\right)_T = \left(\frac{\partial l}{\partial T}\right)_t$$

Since $dU = TdS + tdI$ [given],

$$\left(\frac{\partial U}{\partial l}\right)_T = T\left(\frac{\partial S}{\partial l}\right)_T + t = \boxed{-T\left(\frac{\partial t}{\partial T}\right)_l + t} \quad [\text{Maxwell relation above}]$$

Solutions to applications

P19.22 Molecular mechanics computations with the AMBER force field using the HyperChem package are reported below. The value of the total potential energy will vary between different force fields, as will the shape of the potential energy surface. The local energy minimum at $\phi = -179.6^\circ$ and $\psi = -4.1^\circ$ is found to have a potential energy equal to $28.64 \text{ kJ mol}^{-1}$ when $R = \text{H}$. This value is used as a reference to calculate energy differences (ΔE) on the potential energy surface. ΔE values give the relative stability of different conformations with higher values indicating energetically unstable conformations. Similarly, ΔE values were calculated with respect to the local energy minimum at $\phi = -152.3^\circ$ and $\psi = 163.2^\circ$ when $R = \text{CH}_3$.

	initial		optimized		$E/(\text{kJ mol}^{-1})$	$\Delta E/(\text{kJ mol}^{-1})$
	$\phi/^\circ$	$\psi/^\circ$	$\phi/^\circ$	$\psi/^\circ$		
(a) $R = \text{H}$	75	-65	-176.0	8.3	28.765	0.126
	180	180	180	180	32.154	3.515
	65	35	-179.6	-4.1	28.639	0.000
(b) $R = \text{CH}_3$	75	-65	54.5	19.7	46.338	7.531
	180	180	-152.3	163.2	38.807	0.000
	65	35	52.9	24.1	46.250	7.443

The computations were set up by using the software's "model build" command, that is, initially setting default values for bond lengths and angles except for the specified initial values of ϕ and ψ . Care must be taken to build the proper chirality at the central carbon when $R = \text{CH}_3$. Then the constraints

were removed, and the entire structure was allowed to relax to a minimum energy. Not all of the initial conformations relaxed to the same final conformation. The different final conformations appear to represent local energy minima. It ought not to be surprising that there are several such minima in even a short peptide chain that contains several nearly free internal rotations. It is instructive to compare the all trans ($\phi = \psi = 180^\circ$) initial conformation in the $R = H$ and $R = CH_3$ cases. In the former, neither angle changes, but the resulting structure is not the lowest-energy structure. In the latter, the methyl group appears to push the planes of the peptide link away from each other (albeit not far) due to steric effects; however, the resulting energy is lower than that of the other conformations examined.

Two of the initial conformations of each molecule converge to the same energy minimum. These energy wells are rather broad and the exact angle at which the computation stops within the minimum depends upon details of convergence criteria used in the iterative methodology of the software as well as details of the force field. Both sets of computations also found a second local energy minimum.

An alternative method for studying the energy dependence on ϕ and ψ involves a method like that specified above but with the AMBER computation performed at fixed values of both angles. Figure 19.5 summarizes a set of computations with $-180^\circ < \phi < 180^\circ$ and $\psi = 90^\circ$. To characterize the energy surface, one would carry out similar calculations for several values of ψ .

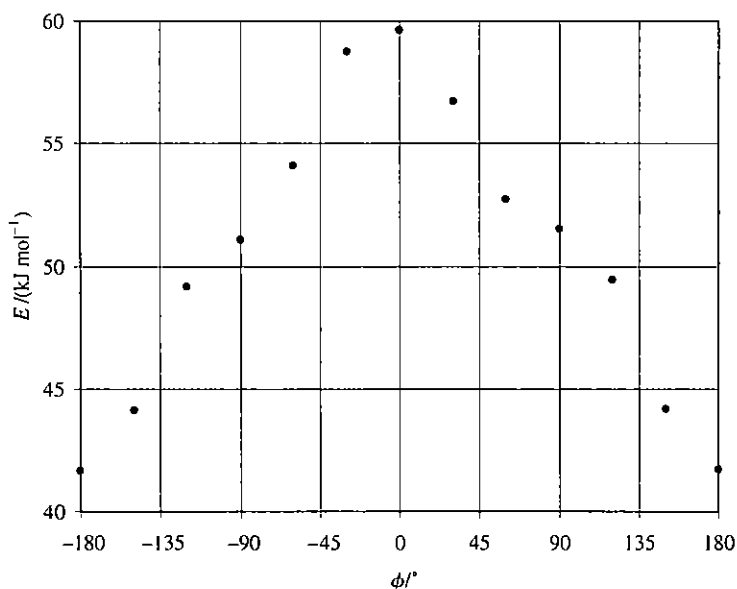


Figure 19.5

- P19.24** Assume the solute particles are solid spheres and see how well R_g calculated on the basis of that assumption agrees with experimental values.

$$R_g/\text{nm} = 0.05690 \times \left\{ (v_s/\text{cm}^3 \text{ g}^{-1}) \times (M/\text{g mol}^{-1})^{1/3} \right\} \quad [\text{P19.17}]$$

and draw up the following table

	$M/(\text{g mol}^{-1})$	$v_s/(\text{cm}^3 \text{ g}^{-1})$	$(R_g/\text{nm})_{\text{calc}}$	$(R_g/\text{nm})_{\text{expt}}$
Serum albumin	66×10^3	0.752	2.09	2.98
Bushy stunt virus	10.6×10^6	0.741	11.3	12.0
DNA	4×10^6	0.556	7.43	117.0

Therefore, serum albumin and bushy stunt virus resemble solid spheres, but DNA does not.

P19.26 Rearrange eqn 19.20 to yield

$$\ln c = \text{const.} + \frac{\overline{M}_w b \omega^2 r^2}{2RT}$$

so a plot of $\ln c$ against r^2 should be a straight line of slope $\frac{\overline{M}_w b \omega^2}{2RT}$. We construct 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 Figure 19.6. The least-squares slope is -0.623 .

Therefore

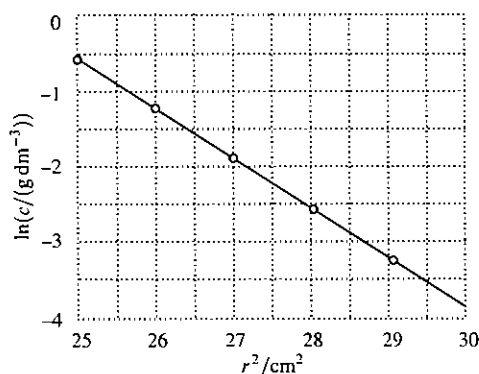


Figure 19.6

$$\frac{\overline{M}_w(1 - \rho v_s)\omega^2}{2RT} = -0.623 \text{ cm}^{-2} = -0.623 \times 10^4 \text{ m}^{-2}$$

It follows that

$$\overline{M}_w = \frac{(-0.623 \times 10^4 \text{ m}^{-2}) \times (2) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293 \text{ K})}{\{(1) - (1.001 \text{ g cm}^{-3}) \times (1.112 \text{ cm}^3 \text{ g}^{-1})\} \times [(2\pi) \times (322 \text{ s}^{-1})]^2} = \boxed{65.6 \text{ kg mol}^{-1}}$$

P19.28 The sedimentation constant S must first be calculated from the experimental data (eqn 19.16).

$$S = \frac{s}{r\omega^2} = \frac{1}{\omega^2} \frac{d \ln r}{dt} [\text{P19.1}]$$

Therefore, the slope of a plot of $\ln r$ against t will be related to S . We draw up the following table.

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
$\ln(r/\text{cm})$	1.813	1.817	1.821	1.826	1.830	1.834	1.838

The least-squares slope is $1.408 \times 10^{-5} \text{ s}^{-1}$, so

$$S = \frac{\text{slope}}{\omega^2} = \frac{1.408 \times 10^{-5} \text{ s}^{-1}}{[(2\pi) \times (50 \times 10^3 / 60 \text{ s})]^2} = 5.14 \times 10^{-13} \text{ s} = \boxed{5.14 \text{ Sv}}$$

$$\begin{aligned} \text{Then } \overline{M}_n &= \frac{SRT}{bD} [19.19] = \frac{(5.14 \times 10^{-13} \text{ s}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293 \text{ K})}{(1 - 0.9981 \times 0.728) \times (7.62 \times 10^{-11} \text{ m}^2 \text{ s})} \\ &= \boxed{60.1 \text{ kg mol}^{-1}} \end{aligned}$$

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 19.3 we can obtain the dimensions of the molecular ellipsoid.

$$f = \frac{kT}{D} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (293 \text{ K})}{7.62 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}} = 5.31 \times 10^{-11} \text{ kg s}^{-1}$$

$$\begin{aligned} V_m &= (0.728 \text{ cm}^3 \text{ g}^{-1}) \times (60.1 \times 10^3 \text{ g mol}^{-1}) = 43.8 \times 10^3 \text{ cm}^3 \text{ mol}^{-1} \\ &= 4.38 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1} \end{aligned}$$

$$\text{Then, } a = \left(\frac{3V_m}{4\pi N_A} \right)^{1/3} = \left(\frac{(3) \times (4.38 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1})}{(4\pi) \times (6.022 \times 10^{23} \text{ mol}^{-1})} \right)^{1/3} = 2.59 \text{ nm}$$

$$f_0 = 6\pi a\eta = (6\pi) \times (2.59 \times 10^{-9} \text{ m}) \times (1.00 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}) = 4.89 \times 10^{-11} \text{ kg s}^{-1}$$

$$\text{which gives } \frac{f}{f_0} = \frac{5.31}{4.89} = 1.09$$

Therefore, the molecule is either prolate or oblate, with an axial ratio of about 2.8 (Table 19.3).

P19.30 (a) $S/k_B = \ln(W)$

$$\Delta S/k_B = \ln(W_{\text{circular}}) - \ln(W_{\text{ideal chain}})$$

W_{circular} is the configuration weight of the DNA molecule that has joined ends ($n=0$) while $W_{\text{ideal chain}}$ is the configuration weight for the molecule chain for which no segment has a constraint and two possible configurations (right-pointing and left-pointing, see Justification 19.3). $W_{\text{ideal chain}}$ for a molecule of N segments equals 2^N .

$$W_{\text{circular}} = \frac{N!}{(N/2)!(N/2)!}$$

$$\begin{aligned}
\ln(W_{\text{circular}}) &= \ln(N!) - 2 \ln\{(N/2)!\} \\
&= \ln(2\pi)^{1/2} + \left(N + \frac{1}{2}\right) \ln(N) - N \\
&\quad - 2 \left\{ \ln(2\pi)^{1/2} + \left(\frac{N}{2} + \frac{1}{2}\right) \ln\left(\frac{N}{2}\right) - \frac{N}{2} \right\} \quad (\text{Stirling's approx.}) \\
&= \ln \left\{ 2^N \left(\frac{2}{\pi N} \right)^{\frac{1}{2}} \right\} \\
\Delta S/k_B &= \ln \left\{ 2^N \left(\frac{2}{\pi N} \right)^{\frac{1}{2}} \right\} - \ln(2^N) \\
\Delta S/k_B &= \ln \left(\frac{2}{\pi N} \right)^{\frac{1}{2}}
\end{aligned}$$

Since $2/\pi N < 1$, entropy decreases in forming the closed circular (cc)DNA. The following graph, Figure 19.7, shows the dependence of ΔS upon N with a plot of $f(N) = \ln(1/N)^{1/2}$ (i.e. $\Delta S/k_B - \ln(2/\pi)^{1/2}$).

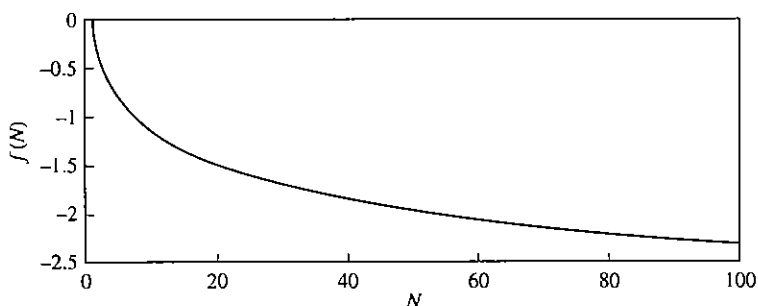


Figure 19.7

- (b) (i) A continuous, normalized Gaussian function, which is also called the normal distribution or the bell-curve, has the form: $f(x) = (1/(2\pi\sigma^2)^{1/2})e^{-(x-\langle x \rangle)^2/2\sigma^2}$ where $-\infty < x < \infty$. $\langle x \rangle$ is the mean value of x and σ is the standard deviation. It can be shown that $\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$.

The discrete energy distribution for a twisted ccDNA molecule is:

$$p_i = e^{-\beta \epsilon_i} / q [16.7] = e^{-\beta k i^2} / q \quad \text{where } k \text{ is an empirical constant and } i = 0, \pm 1, \pm 2, \dots$$

Because it has an exponent in i^2 , which is comparable to x^2 in the above Gaussian function, the energy distribution has the form of a Gaussian function with a maximum value that is centered upon $i = 0$. The standard deviation of the discrete Gaussian distribution is found by comparing the two equations. It is $\sigma = (1/2\beta k)^{1/2}$.

- (ii) The following MathCad worksheet plots the energy distribution at several values of the unitless temperature $T_{\text{ratio}} = 1/\beta k = k_B T/k$. Bar plots (histograms), Figure 19.8(a), are appropriate for discrete distributions in which the argument takes on specific values only ($i = 0, \pm 1, \pm 2, \pm 3, \dots$). Even though the argument is not defined for non-integer values of i , the last graph, Figure 19.8(b) presents line plots with the understanding of discrete values. This reduces the visual confusion of overlapping bars from multiple plots. The plots show that at higher temperatures there are fewer molecules in the lowest energy state $i = 0$ and a greater number of molecules in the high energy states.

$$N_{\max} := 10 \quad i := -N_{\max}..N_{\max} \quad q(T_{\text{ratio}}) := \sum_{i=-75}^{75} e^{-i^2/T_{\text{ratio}}} \quad p(T_{\text{ratio}}, i) := \frac{e^{-i^2/T_{\text{ratio}}}}{q(T_{\text{ratio}})}$$

- (iii) Cannot be completed unless k is specified. See Figure 19.8 for variation of p with i at several temperatures.

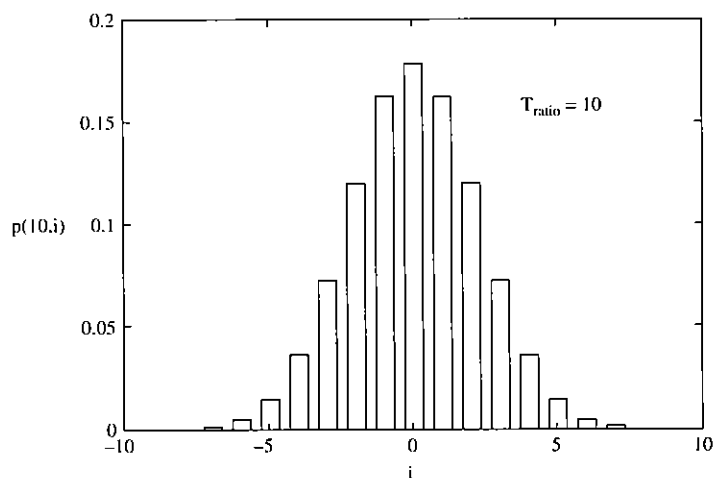


Figure 19.8

- P19.32** (a) The increase in temperature with the hydrophobic chain length is a result of the increased strength of the van der Waals interaction between long unsaturated portions of the chains that can interlock well with each other. The introduction of double bonds in the chains can affect the interlocking of the parallel chains by putting kinks in the chains, thereby decreasing the strength of the van der Waals interactions between chains. Double bonds can be either *cis* or *trans*. Only *cis*-double bonds produce a kink, but most fatty acids are the *cis*-isomer. So we expect that the transition temperatures will decrease in rough proportion to the number of C=C bonds.
- (b) The addition of cholesterol is expected to increase the temperature of the transition from the liquid crystalline state to the liquid state by altering the conformations of the hydrocarbon chains. Cholesterol stabilizes extended chain conformations of adjacent hydrocarbon sections by van der Waals interactions relative to the coiled conformations that predominate when cholesterol is absent. The extended chains can pack better than coiled arrangements. However the lower transition temperature, that from the solid crystalline state to the liquid crystalline form, is probably decreased upon addition of cholesterol; its presence prevents the hydrophobic chains from freezing into a solid array by disrupting their packing. This will also spread the melting point over a range of temperatures.

P19.34 (a) $\frac{\eta}{\eta^*} = \frac{t}{t^*} \approx 1 + [\eta]c + k'[\eta]^2 c^2$

Define $F = \frac{t/t^* - 1}{c} = [\eta] + k'[\eta]^2 c$

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 ($R = 0.99954$) yields

$$[\eta] = 0.08566 \text{ dm}^3 \text{ g}^{-1} = \boxed{0.086 \text{ dm}^3 \text{ g}^{-1}}; \text{ standard deviation} = 0.00020 \text{ dm}^3 \text{ g}^{-1}$$

$$k'[\eta]^2 = 0.002688 \text{ dm}^6 \text{ g}^{-2}; \text{ standard deviation} = 0.000057 \text{ dm}^6 \text{ g}^{-2}$$

Then

$$k' = \frac{0.002\,688\,\text{dm}^6\,\text{g}^{-2}}{(0.085\,66\,\text{dm}^3\,\text{g}^{-1})^2} = \boxed{0.37}$$

(2) In cyclohexane: Linear regression ($R = 0.981\,98$) yields

$$[\eta] = 0.041\,50\,\text{dm}^3\,\text{g}^{-1} = \boxed{0.042\,\text{dm}^3\,\text{g}^{-1}}; \text{ standard deviation} = 0.000\,18\,\text{dm}^3\,\text{g}^{-1}$$

$$k'[\eta]^2 = 0.006\,001\,\text{dm}^6\,\text{g}^{-2}; \text{ standard deviation} = 0.000\,116\,\text{dm}^6\,\text{g}^{-2}$$

Then

$$k' = \frac{0.000\,6001\,\text{dm}^6\,\text{g}^{-2}}{(0.041\,50\,\text{dm}^3\,\text{g}^{-1})^2} = \boxed{0.35}$$

$$(b) \quad [\eta] = K\bar{M}_v^a \quad \text{or} \quad \bar{M}_v = \left(\frac{[\eta]}{K}\right)^{1/a}$$

(1) In toluene

$$\bar{M}_v = \left(\frac{0.085\,66\,\text{dm}^3\,\text{g}^{-1}}{1.15 \times 10^{-5}\,\text{dm}^3\,\text{g}^{-1}}\right)^{(1/0.72)} \text{ g mol}^{-1} = \boxed{2.4 \times 10^5\,\text{g mol}^{-1}}$$

(2) In cyclohexane

$$\bar{M}_v = \left(\frac{0.041\,50\,\text{dm}^3\,\text{g}^{-1}}{8.2 \times 10^{-5}\,\text{dm}^3\,\text{g}^{-1}}\right)^{(1/(1/2))} \text{ g mol}^{-1} = \boxed{2.6 \times 10^5\,\text{g mol}^{-1}}$$

$$(c) \quad [\eta]/(\text{dm}^3\,\text{g}^{-1}) = \Phi(r_{\text{rms}}/\text{m})^3/M, \quad \Phi = 2.84 \times 10^{26}$$

$$r_{\text{rms}} = \left(\frac{[\eta]M}{\Phi}\right)^{1/3} \text{ m, where } r_{\text{rms}} = \langle r^2 \rangle^{1/2}$$

$$(1) \text{ In toluene: } r_{\text{rms}} = \left(\frac{0.085\,66 \times 2.39 \times 10^5}{2.84 \times 10^{26}}\right)^{1/3} \text{ m} = \boxed{42\,\text{nm}}$$

$$(2) \text{ In cyclohexane: } r_{\text{rms}} = \left(\frac{0.041\,50 \times 2.56 \times 10^5}{2.84 \times 10^{26}}\right)^{1/3} \text{ m} = \boxed{33\,\text{nm}}$$

$$(d) \quad M(\text{styrene}) = 104\,\text{g mol}^{-1}$$

Average number of monomeric units, $\langle n \rangle$ is

$$\langle n \rangle = \frac{\bar{M}_v}{M(\text{styrene})}$$

$$(1) \text{ In toluene } \langle n \rangle = \frac{2.39 \times 10^5\,\text{g mol}^{-1}}{104\,\text{g mol}^{-1}} = \boxed{2.3 \times 10^3}$$

$$(2) \text{ In cyclohexane: } \langle n \rangle = \frac{2.56 \times 10^5\,\text{g mol}^{-1}}{104\,\text{g mol}^{-1}} = \boxed{2.5 \times 10^3}$$

(e) Consider the geometry in Figure 19.9

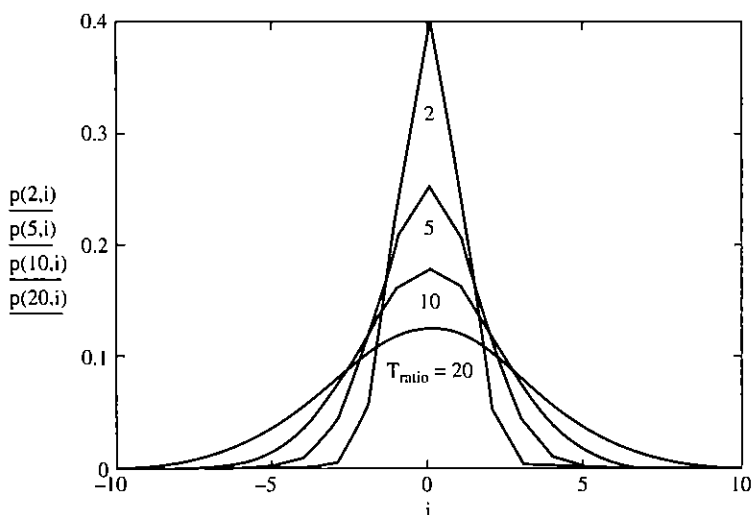


Figure 19.9

For a polymer molecule consisting of $\langle n \rangle$ monomers, the maximum molecular length, L_{\max} , is

$$\begin{aligned} L_{\max} &= 2l \langle n \rangle \cos \theta \\ &= 2(0.154 \text{ nm}) \langle n \rangle \cos 35^\circ \\ &= (0.2507 \text{ nm}) \langle n \rangle \end{aligned}$$

$$\text{In toluene: } L_{\max} = (0.2507 \text{ nm}) \times (2.30 \times 10^3) = \boxed{5.8 \times 10^2 \text{ nm}}$$

$$\text{In cyclohexane: } L_{\max} = (0.2507 \text{ nm}) \times (2.46 \times 10^3) = \boxed{6.2 \times 10^2 \text{ nm}}$$

$$(f) \quad R_g = \left(\frac{\langle n \rangle}{3} \right)^{1/2} l = (0.0889 \text{ nm}) \langle n \rangle^{1/2}$$

$$\text{Kirkwood-Riseman: } r_{\text{rms}}^{\text{KR}} = \left(\frac{[\eta]M}{\Phi} \right)^{1/3} = \left(\frac{[\eta]M}{2.84 \times 10^{26}} \right)^{1/3}$$

$$\text{constrained coil: } r_{\text{rms}} = (2\langle n \rangle)^{1/2} l [19.36] \text{ or } \langle n \rangle^{1/2} l [19.31]$$

Solvent	$\langle n \rangle$	R_g/nm	$r_{\text{rms}}^{\text{KR}}/\text{nm}$	$r_{\text{rms}}^{\text{cc}}/\text{nm}$
Toluene	2.30×10^3	$\boxed{4.3}$	42	$\boxed{10.4 \text{ or } 7.4}$
Cyclohexane	2.46×10^3	$\boxed{4.4}$	33	$\boxed{10.8 \text{ or } 7.6}$

(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.

20

Materials 2: the solid state

Answers to discussion questions

D20.2 We can use the Debye–Scherrer powder diffraction method, follow the procedure of Example 20.3, 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 center.
2. From the known radius of the camera, convert the distances to angles.
3. Calculate $\sin^2 \theta$.
4. Find the common factor $A = \lambda^2/4a^2$ 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 Figure 20.22 of the text. For body-centered cubic, diffraction lines corresponding to $h + k + l$ that are odd will be absent. For face-centered cubic, only lines for which h , k , and l are either all even or all odd will be present, others will be absent.
7. Solve $A = \lambda^2/4a^2$ for a .

D20.4 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 $F_{hkl} = |F_{hkl}|e^{i\alpha}$ 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):

$$P(r) = \frac{1}{V} \sum_{hkl} |F_{hkl}|^2 e^{-2\pi i(hx+ky+lz)}$$

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.

D20.6 In a face-centered cubic close-packed lattice, there is an octahedral hole in the center. The rock-salt structure can be thought of as being derived from an fcc structure of Cl^- ions in which Na^+ ions have filled the octahedral holes.

The caesium-chloride structure can be considered to be derived from the ccp structure by having Cl^- ions occupy all the primitive lattice points and octahedral sites, with all tetrahedral sites occupied by Cs^+ ions. This is 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.

- D20.8** Semiconductors generally have lower electrical conductivity than most metals. Additionally, the conductivity of semiconductors increases as the temperature is raised whereas that of metals decreases. The difference occurs because of the relative balance between the excitation of electrons into electrical conductance and the scattering of electrons off the conductance path by collisions with vibrating atoms. The scattering process predominates with increasing temperature of a metal. The excitation process predominates for the semiconductor.

The electronic structure of solids consists of allowed energy bands. The highest energy band of a metal is partially filled. Being approximately filled to the Fermi level only, there is no gap of forbidden energies for excitation. It is easy to promote electrons from the filled level in which all random vector momentums are occupied to levels in which there is a preferred vector momentum. This provides high electrical conductivity. The energy difference between the top of the band and the Fermi level helps to explain their appearance. If sufficiently wide, all incident visible light can be both absorbed and emitted. This gives many metals their shiny, "silver" luster. A narrow width may result in color as a range of visible frequencies are preferentially emitted. An example is the reddish color of copper.

Semiconductors have a band gap, E_g , between a filled valence band and an approximately unfilled conductance band above it. Significant energy is needed to promote electrons to the conductance band. The energy may be provided thermally with the application of higher temperature, with electromagnetic radiation of frequency above $\nu_{\min} = E_g/h$, or with an applied voltage. The visual appearance of a semiconductor is approximated with ν_{\min} . For example, electromagnetic radiation with more energy than green light is absorbed by cadmium sulfide (see *Illustration 20.2*) so the yellow, orange and red visible light are predominately reflected and seen as a yellow-orange color by an observer.

- D20.10** The most obvious difference is that there is no magnetic analog of electric charge; hence, there are no magnetic 'ions.' Both electric and magnetic moments exist and these can be either permanent or induced. Induced magnetic moments in the entire sample can be either parallel or antiparallel to the applied field producing them (paramagnetic or diamagnetic moments), whereas in the electric case they are always parallel. Magnetization, M , is the analog of polarization, P . Although both magnetization and induced dipole moment are proportional to the fields producing them, they are not analogous quantities, neither are volume magnetic susceptibility, χ , and electric polarizability, α . The magnetic quantities refer to the sample as a whole, the electric quantities to the molecules. Molar magnetic susceptibility is analogous to molar polarization as can be seen by comparing eqns 20.30 and 18.15 and magnetizability is analogous to electric polarizability.

Solutions to exercises

- E20.1(b)** $\left(\frac{1}{2}, 0, \frac{1}{2}\right)$ is the midpoint of a face. All face midpoints are alike, including $\left(\frac{1}{2}, \frac{1}{2}, 0\right)$ 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.

E20.2(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 $(31\bar{3})$ and (643)

E20.3(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 $(h/a, k/a, l/a)$.

$$d_{121} = \frac{523 \text{ pm}}{(1 + 2^2 + 1)^{1/2}} = 214 \text{ pm}$$

$$d_{221} = \frac{523 \text{ pm}}{(2^2 + 2^2 + 1)^{1/2}} = 174 \text{ pm}$$

$$d_{244} = \frac{523 \text{ pm}}{(2^2 + 4^2 + 4^2)^{1/2}} = 87.2 \text{ pm}$$

E20.4(b) The Bragg law is

$$n\lambda = 2d \sin \theta$$

Assuming the angle given is for a first-order reflection, the wavelength must be

$$\lambda = 2(128.2 \text{ pm}) \sin 19.76^\circ = 86.7 \text{ pm}$$

E20.5(b) Combining the Bragg law with Miller indices yields, for a cubic cell

$$\sin \theta_{hkl} = \frac{\lambda}{2a} (h^2 + k^2 + l^2)^{1/2}$$

In a face-centered 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

- E20.6(b)** In a circular camera, the distance between adjacent lines is $D = R\Delta(2\theta)$, where R is the radius of the camera (distance from sample to film) and θ is the diffraction angle. Combining these quantities with the Bragg law ($\lambda = 2d \sin \theta$, relating the glancing angle to the wavelength and separation of planes), we get

$$D = 2R\Delta\theta = 2R\Delta\left(\sin^{-1} \frac{\lambda}{2d}\right)$$

$$= 2(5.74 \text{ cm}) \times \left(\sin^{-1} \frac{96.035}{2(82.3 \text{ pm})} - \sin^{-1} \frac{95.401 \text{ pm}}{2(82.3 \text{ pm})}\right) = \boxed{0.054 \text{ cm}}$$

- E20.7(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

$$V = 2 \left(\frac{1}{2} a \times a \sin 60^\circ \right) c = a^2 c \sin 60^\circ = (1692.9 \text{ pm})^2 \times (506.96 \text{ pm}) \times \sin 60^\circ$$

$$= 1.2582 \times 10^9 \text{ pm}^3 = \boxed{1.2582 \text{ nm}^3}$$

- E20.8(b)** The volume of an orthorhombic unit cell is

$$V = abc = (589 \text{ pm}) \times (822 \text{ pm}) \times (798 \text{ pm}) = \frac{3.86 \times 10^8 \text{ pm}^3}{(10^{10} \text{ pm cm}^{-1})^3} = 3.86 \times 10^{-22} \text{ cm}^3$$

The mass per formula unit is

$$m = \frac{135.01 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 2.24 \times 10^{-22} \text{ g}$$

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

$$\rho = \frac{Nm}{V} \quad \text{so} \quad N = \frac{\rho V}{m} = \frac{(2.9 \text{ g cm}^{-3}) \times (3.86 \times 10^{-22} \text{ cm}^3)}{2.24 \times 10^{-22} \text{ g}} = \boxed{5}$$

A more accurate density, then, is

$$\rho = \frac{5(2.24 \times 10^{-22} \text{ g})}{3.86 \times 10^{-22} \text{ cm}^3} = \boxed{2.90 \text{ g cm}^{-3}}$$

- E20.9(b)** The distance between the origin and the plane which intersects coordinate axes at $(h/a, k/b, l/c)$ is given by

$$d_{hkl} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-1/2} = \left(\frac{3^2}{(679 \text{ pm})^2} + \frac{2^2}{(879 \text{ pm})^2} + \frac{2^2}{(860 \text{ pm})^2} \right)^{-1/2}$$

$$d_{322} = \boxed{182 \text{ pm}}$$

- E20.10(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-centered cubic cell and would be absent from a body-centered 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

$$\theta_{hkl} = \sin^{-1} \left(\frac{\lambda}{2a} (h^2 + k^2 + l^2)^{1/2} \right) = \sin^{-1} (0.176 (h^2 + k^2 + l^2)^{1/2})$$

$$\theta_{100} = \sin^{-1} (0.176 (1^2 + 0 + 0)^{1/2}) = 10.1^\circ \text{ (checks)}$$

$$\theta_{110} = \sin^{-1} (0.176 (1^2 + 1^2 + 0)^{1/2}) = 14.4^\circ \text{ (checks)}$$

$$\theta_{200} = \sin^{-1} (0.176 (2^2 + 0 + 0)^{1/2}) = 20.6^\circ \text{ (checks)}$$

These angles predicted for a simple cubic fit those observed, confirming the hypothesis of a simple lattice; the reflections are due to the (100) , (110) , (111) , and (200) planes.

E20.11(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 origin 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

E20.12(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 body-centered cubic

E20.13(b) The structure factor is given by

$$F_{hkl} = \sum_i f_i e^{i\phi_i} \quad \text{where} \quad \phi_i = 2\pi (hx_i + ky_i + lz_i)$$

All eight of the vertices of the cube are shared by eight cubes, so each vertex has a scattering factor of $f/8$.

The coordinates of all vertices are integers, so the phase ϕ is a multiple of 2π and $e^{i\phi} = 1$. The body-center point belongs exclusively to one unit cell, so its scattering factor is f . The phase is

$$\phi = 2\pi \left(\frac{1}{2}h + \frac{1}{2}k + \frac{1}{2}l \right) = \pi(h + k + l)$$

When $h + k + l$ is even, ϕ is a multiple of 2π and $e^{i\phi} = 1$; when $h + k + l$ is odd, ϕ is π + a multiple of 2π and $e^{i\phi} = -1$. So $e^{i\phi} = (-1)^{h+k+l}$ and

$$\begin{aligned} F_{hkl} &= 8(f/8)(1) + f(-1)^{h+k+l} \\ &= \boxed{2f \text{ for } h+k+l \text{ even} \quad \text{and} \quad 0 \text{ for } h+k+l \text{ odd}} \end{aligned}$$

E20.14(b) There are two smaller (white) triangles to each larger (gray) 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 $2N A/4$, for N of the larger triangles. The total space is then $(NA + (NA/2)) = 3NA/2$. Therefore the fraction filled is $NA/(3NA/2) = \boxed{2/3}$

E20.15(b) See Figure 20.1.

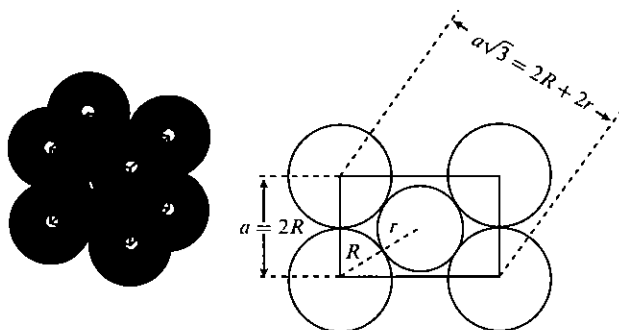


Figure 20.1

The body diagonal of a cube is $a\sqrt{3}$. Hence

$$a\sqrt{3} = 2R + 2r \quad \text{or} \quad \sqrt{3}R = R + r \quad [a = 2R]$$

$$\frac{r}{R} = \boxed{0.732}$$

E20.16(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 $(\sqrt{2} - 1) \times (138 \text{ pm}) = \boxed{57 \text{ pm}}$.

(b) The smallest ion that can have 8-fold coordination with it has a radius of $(\sqrt{3} - 1) \times (151 \text{ pm}) = \boxed{111 \text{ pm}}$.

- E20.17(b)** The diagonal of the face that has a lattice point in its center is equal to $4r$, where r is the radius of the atom. The relationship between this diagonal and the edge length a is

$$4r = a\sqrt{2} \quad \text{so} \quad a = 2\sqrt{2}r$$

The volume of the unit cell is a^3 , and each cell contains 2 atoms. (Each of the 8 vertices is shared among 8 cells; each of the 2 face points is shared by 2 cells.) So the packing fraction is

$$\frac{2V_{\text{atom}}}{V_{\text{cell}}} = \frac{2(4/3)\pi r^3}{(2\sqrt{2}r)^3} = \frac{\pi}{3(2)^{3/2}} = \boxed{0.370}$$

- E20.18(b)** The volume of an atomic crystal is proportional to the cube of the atomic radius divided by the packing fraction. The packing fraction 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 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.)

- E20.19(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 (\vec{AB} and \vec{BA}); don't forget the AA zero vectors for the center point of the diagram. See Figure 20.2 for C_6H_6 .

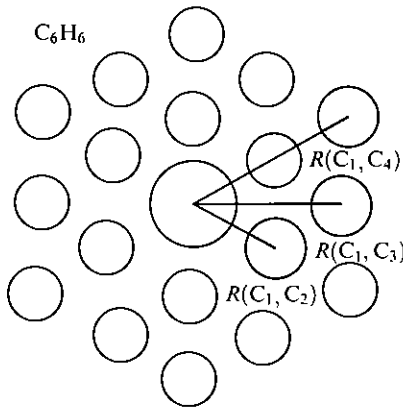
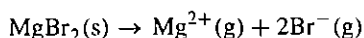


Figure 20.2

- E20.20(b)** Combine $E = \frac{1}{2}kT$ and $E = \frac{1}{2}mv^2 = \frac{h^2}{2m\lambda^2}$, to obtain

$$\lambda = \frac{h}{(mkT)^{1/2}} = \frac{6.626 \times 10^{-34} \text{ J s}}{[(1.675 \times 10^{-27} \text{ kg}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (300 \text{ K})]^{1/2}} = \boxed{252 \text{ pm}}$$

E20.21(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



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

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

So the lattice enthalpy is

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

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

E20.22(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).)

E20.23(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

$$\text{strain} = \frac{\text{stress}}{E} = \frac{mg}{\pi(d/2)^2 E} = \frac{4mg}{\pi d^2 E} = \frac{4(10.0 \text{ kg})(9.8 \text{ m s}^{-2})}{\pi(0.10 \times 10^{-3} \text{ m})^2(215 \times 10^9 \text{ Pa})} = \boxed{5.8 \times 10^{-2}}$$

The wire would stretch by 5.8%.

E20.24(b) Poisson's ratio is defined as:

$$\nu_p = \frac{\text{transverse strain}}{\text{normal strain}}$$

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 percent, resulting in a contraction by 0.41×2.0 percent, or 0.82 percent, 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:

$$\Delta V = (1.003 - 1)(1.0 \text{ dm}^3) = \boxed{0.003 \text{ dm}^3}$$

E20.25(b) p-type; the dopant, gallium, belongs to Group 13, whereas germanium belongs to Group 14.

$$\text{E20.26(b)} \quad E_g = h\nu_{\min} \quad \text{and} \quad \nu_{\min} = E_g/h = \frac{1.12 \text{ eV}}{6.626 \times 10^{-34} \text{ J s}} \left(\frac{1.602 \times 10^{-19} \text{ J}}{1 \text{ eV}} \right) = 2.71 \times 10^{14} \text{ Hz}$$

$$\text{E20.27(b)} \quad m = g_e \{S(S+1)\}^{1/2} \mu_B \quad [20.34, \text{ with } S \text{ in place of } s]$$

Therefore, since $m = 4.00 \mu_B$

$$S(S+1) = \left(\frac{1}{4}\right) \times (4.00)^2 = 4.00, \quad \text{implying that } S = 1.56$$

Thus $S \approx \frac{3}{2}$, implying three unpaired spins.

In actuality most Mn^{2+} compounds have 5 unpaired spins.

$$\begin{aligned} \text{E20.28(b)} \quad \chi_m &= \chi V_m = \frac{\chi M}{\rho} = \frac{(-7.9 \times 10^{-6}) \times (84.15 \text{ g mol}^{-1})}{0.811 \text{ g cm}^{-3}} \\ &= \boxed{-8.2 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}} = \boxed{-8.2 \times 10^{-10} \text{ m}^3 \text{ mol}^{-1}} \end{aligned}$$

E20.29(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,

$$\begin{aligned} \chi_m &= (6.022 \times 10^{23} \text{ mol}^{-1}) \times (2.0023)^2 \times (4\pi \times 10^{-7} \text{ T}^2 \text{ J}^{-1} \text{ m}^3) \\ &\quad \times \frac{(9.274 \times 10^{-24} \text{ J T}^{-1})^2 \times \left(\frac{1}{2}\right) \times \left(\frac{1}{2} + 1\right)}{3(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})} \\ &= \boxed{1.58 \times 10^{-8} \text{ m}^3 \text{ mol}^{-1}} \end{aligned}$$

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 favored by higher pressure. The dimer has no unpaired electrons, so the dimerization reaction effectively reduced the number of paramagnetic species.

E20.30(b) The molar susceptibility is given by

$$\chi_m = \frac{N_A g_e^2 \mu_0 \mu_B^2 S(S+1)}{3kT} \quad \text{so} \quad S(S+1) = \frac{3kT \chi_m}{N_A g_e^2 \mu_0 \mu_B^2}$$

$$S(S+1) = \frac{3(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (2.0023)^2}$$

$$\times \frac{(6.00 \times 10^{-8} \text{ m}^3 \text{ mol}^{-1})}{(4\pi \times 10^{-7} \text{ T}^2 \text{ J}^{-1} \text{ m}^3) \times (9.274 \times 10^{-24} \text{ J T}^{-1})^2}$$

$$= 2.84 \quad \text{so} \quad S = \frac{-1 + \sqrt{1 + 4(2.84)}}{2} = 1.26$$

corresponding to $\boxed{2.52}$ effective unpaired spins. The theoretical number is $\boxed{2}$. The magnetic moments in a crystal are close together, and they interact rather strongly. The discrepancy is most likely due to an interaction among the magnetic moments.

E20.31(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

$$\chi_m = \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (2.0023)^2 \times (4\pi \times 10^{-7} \text{ T}^2 \text{ J}^{-1} \text{ m}^3)}{3(1.381 \times 10^{-23} \text{ J K}^{-1})}$$

$$\times \frac{(9.274 \times 10^{-24} \text{ J T}^{-1})^2 \times (2.5) \times (2.5 + 1)}{(298 \text{ K})}$$

$$= \boxed{1.85 \times 10^{-7} \text{ m}^3 \text{ mol}^{-1}}$$

E20.32(b) The orientational energy of an electron spin system in a magnetic field is

$$E = g_e \mu_B M_S \mathcal{B}$$

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

$$r = \exp\left(\frac{-g_e \mu_B M_S \mathcal{B}}{kT}\right) = \exp\left(\frac{-(2.0023) \times (9.274 \times 10^{-24} \text{ J T}^{-1}) \times (1) \times (15.0 \text{ T})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}\right) = \boxed{0.935}$$

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

- P20.2** A large separation between the sixth and seventh lines relative to the separation between the fifth and sixth lines is characteristic of a simple (primitive) cubic lattice. This is readily seen without indexing the lines. The conclusion that the unit cell is simple cubic is then confirmed by the presence of reflections from (100) planes.

$$d_{100} = a [20.1] = \frac{\lambda}{2 \sin \theta} [20.5]$$

$$a = \frac{154 \text{ pm}}{(2) \times (0.225)} = \boxed{342 \text{ pm}}$$

- P20.4** 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 $A = \lambda^2/4a^2$ 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. Solve $A = \lambda^2/4a^2$ 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-centered cubic possibility

(hkl)	(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-centered cubic possibility

(hkl)	(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 20.2 and Figure 20.22).

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-centered cubic or body-centered 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-centered cubic and body-centered cubic possibilities is found in the above table. Successive reflective planes are determined with the rules found in Figure 20.22.

$$\text{fcc possibility : } A_{\text{av.}} = 0.0478, \quad \sigma_A = 0.0063 \text{ (13 percent)}$$

$$\text{bcc possibility : } A_{\text{av.}} = 0.0611, \quad \sigma_A = 0.0016 \text{ (6 percent)}$$

These standard deviations (σ_A) indicate that the cell type is body-centered 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 percent confidence. This yields a better average value for A .

$$A_{\text{av.}} = 0.0598, \quad \sigma_A = 0.0016 \text{ (3 percent)}$$

$$\text{Then } a = \frac{\lambda}{2A^{1/2}} = \frac{154 \text{ pm}}{(2) \times (0.0598)^{1/2}} = 315 \text{ pm}$$

$$4R = \sqrt{3}a, \quad \text{so } \boxed{R = 136 \text{ pm}} \text{ [Fig. 20.1 above with } r = R]$$

(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-centered cubic possibility

(hkl)	(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-centered cubic possibility

(hkl)	(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.

$$\text{fcc possibility : } A_{\text{av.}} = 0.0448, \quad \sigma_A = 0.0010 \text{ (2 percent)}$$

$$\text{bcc possibility : } A_{\text{av.}} = 0.0579, \quad \sigma_A = 0.0063 \text{ (11 percent)}$$

The standard deviations indicate that the cell type is face-centered cubic

$$\text{Then } a = \frac{\lambda}{2A^{1/2}} = \frac{154 \text{ pm}}{(2) \times (0.0448)^{1/2}} = \boxed{364 \text{ pm}}$$

$$4R = \sqrt{2}a, \quad \text{so } R = \boxed{129 \text{ pm}}$$

P20.6 When a very narrow X-ray beam (with a spread of wavelengths) is directed on the center of a genuine pearl, all the crystallites are irradiated parallel to a trigonal axis and the result is a Laue photograph with 6-fold 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).)

P20.8

$$\theta(100 \text{ K}) = 22^\circ 2' 25'', \quad \theta(300 \text{ K}) = 21^\circ 57' 59''$$

$$\sin \theta(100 \text{ K}) = 0.37526, \quad \sin \theta(300 \text{ K}) = 0.37406$$

$$\frac{\sin \theta(300 \text{ K})}{\sin \theta(100 \text{ K})} = 0.99681 = \frac{a(100 \text{ K})}{a(300 \text{ K})} \text{ [see Problem 21.7]}$$

$$a(300 \text{ K}) = \frac{\lambda \sqrt{3}}{2 \sin \theta} = \frac{(154.062 \text{ pm}) \times \sqrt{3}}{(2) \times (0.37406)} = 356.67 \text{ pm}$$

$$a(100 \text{ K}) = (0.99681) \times (356.67 \text{ pm}) = 355.53 \text{ pm}$$

$$\frac{\delta a}{a} = \frac{356.67 - 355.53}{355.53} = 3.206 \times 10^{-3}$$

$$\frac{\delta V}{V} = \frac{356.67^3 - 355.53^3}{355.53^3} = 9.650 \times 10^{-3}$$

$$\alpha_{\text{volume}} = \frac{1}{V} \frac{\delta V}{\delta T} = \frac{9.650 \times 10^{-3}}{200 \text{ K}} = \boxed{4.8 \times 10^{-5} \text{ K}^{-1}}$$

$$\alpha_{\text{volume}} = \frac{1}{a} \frac{\delta a}{\delta T} = \frac{3.206 \times 10^{-3}}{200 \text{ K}} = \boxed{1.6 \times 10^{-5} \text{ K}^{-1}}$$

P20.10 $V = abc \sin \beta$

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 $\rho = NM/VN_A = 2M/(1.662b^3 N_A)$ 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, $a = \boxed{834 \text{ pm}}$, $b = \boxed{606 \text{ pm}}$, $c = \boxed{870 \text{ pm}}$

P20.12 As in Example 20.4 of the text we use

$$\rho(x) = \frac{1}{V} \left\{ F_0 + 2 \sum_{h=1}^{\infty} F_h \cos(2\pi hx) \right\}$$

Because V is unknown we work with

$$V\rho(x) \equiv f(x)$$

$$\begin{aligned} f(x) = & 30 + 16.4 \cos(2\pi x) + 13 \cos(4\pi x) + 8.2 \cos(6\pi x) + 11 \cos(8\pi x) \\ & - 4.8 \cos(10\pi x) + 10.8 \cos(12\pi x) + 6.4 \cos(14\pi x) - 2 \cos(16\pi x) \\ & + 2.2 \cos(18\pi x) + 13 \cos(20\pi x) + 10.4 \cos(22\pi x) - 8.6 \cos(24\pi x) \\ & - 2.4 \cos(26\pi x) + 0.2 \cos(28\pi x) + 4.2 \cos(30\pi x) \end{aligned}$$

A plot of $V\rho(x) \equiv f(x)$ is shown in Figure 20.3.

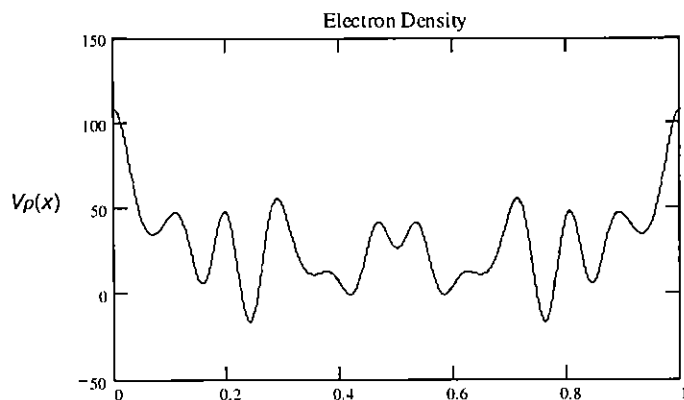


Figure 20.3

P20.14 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 $\text{CuC}_7\text{H}_{13}\text{N}_5\text{O}_8\text{S}$, so its molar mass is

$$M = 63.546 + 7(12.011) + 13(1.008) + 5(14.007) + 8(15.999) + 32.066 \text{ g mol}^{-1} \\ = 390.82 \text{ g mol}^{-1}$$

The number of monomer units, then, is the mass of the unit cell divided by the mass of the monomer

$$N = \frac{mN_A}{M} = \frac{(2.577 \times 10^{-21} \text{ g}) \times (6.022 \times 10^{23} \text{ mol}^{-1})}{390.82 \text{ g mol}^{-1}} = 3.97 \quad \text{or} \quad \boxed{4}$$

P20.16 The problem asks for an estimate of $\Delta_f H^\circ(\text{CaCl})$. A Born–Haber cycle would envision formation of $\text{CaCl}(\text{s})$ from its elements as sublimation of $\text{Ca}(\text{s})$, ionization of $\text{Ca}(\text{g})$, atomization of $\text{Cl}_2(\text{g})$ electron gain of $\text{Cl}(\text{g})$, and formation of $\text{CaCl}(\text{s})$ from gaseous ions. Therefore

$$\Delta_f H^\circ(\text{CaCl}, \text{s}) = \Delta_{\text{sub}} H^\circ(\text{Ca}, \text{s}) + \Delta_{\text{ion}} H^\circ(\text{Ca}, \text{g}) + 2\Delta_f H^\circ(\text{Cl}, \text{g}) \\ + 2\Delta_{\text{eg}} H^\circ(\text{Cl}, \text{g}) - \Delta_L H^\circ(\text{CaCl}, \text{s})$$

Before we can estimate the lattice enthalpy of CaCl , we select a lattice with the aid of the radius-ratio rule. The ionic radius for Cl^- is 181 pm; 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 20.15) as giving the negative of the lattice enthalpy

$$\Delta_L H^\circ \approx \frac{A|z_1 z_2| N_A e^2}{4\pi \epsilon_0 d} \left(1 - \frac{d^*}{d} \right)$$

The distance d is

$$d = (138 + 181) \text{ pm} = 319 \text{ pm}$$

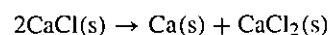
$$\text{so } \Delta_L H^\circ \approx \frac{(1.763) \times |(1)(-1)| \times (6.022 \times 10^{23} \text{ mol}^{-1}) \times (1.602 \times 10^{-9} \text{ C})^2}{4\pi (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (319 \times 10^{-12} \text{ m})} \left(1 - \frac{34.5 \text{ pm}}{319 \text{ pm}} \right)$$

$$\Delta_L H^\circ \approx 6.85 \times 10^5 \text{ J mol}^{-1} = 685 \text{ kJ mol}^{-1}$$

The enthalpy of formation, then, is

$$\Delta_f H^\circ(\text{CaCl}, \text{s}) \approx [176 + 589.7 + 2(121.7 - 348.7) - 685] \text{ kJ mol}^{-1} = \boxed{-373 \text{ kJ mol}^{-1}}$$

Although formation of $\text{CaCl}(\text{s})$ from its elements is exothermic, formation of $\text{CaCl}_2(\text{s})$ is still more favored energetically. Consider the reaction

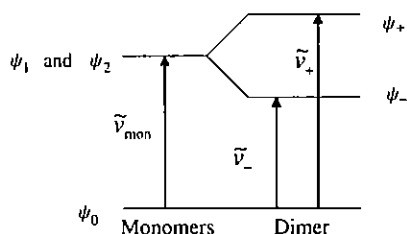


for which $\Delta H^\ominus = \Delta_f H^\ominus(\text{Ca}) + \Delta_f H^\ominus(\text{CaCl}_2) - 2\Delta_f H^\ominus(\text{CaCl})$

$$\approx [0 - 795.8 - 2(-373)] \text{ kJ mol}^{-1}$$

$$\Delta H^\ominus \approx -50 \text{ kJ mol}^{-1}$$

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 neighboring 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} , $\Delta_f H^\ominus(\text{CaCl})$ to -446 kJ mol^{-1} and the final reaction enthalpy to $+96 \text{ kJ mol}^{-1}$.

P20.18**Figure 20.4(a)**

$$\begin{aligned} \text{(a)} \quad \mu_{+or-} &= \langle \psi_{+or-} | \mu | \psi_0 \rangle = \langle c_{+or-,1} \psi_1 + c_{+or-,2} \psi_2 | \mu | \psi_0 \rangle \\ &= c_{+or-,1} \langle \psi_1 | \mu | \psi_0 \rangle + c_{+or-,2} \langle \psi_2 | \mu | \psi_0 \rangle \end{aligned}$$

But $\langle \psi_1 | \mu | \psi_0 \rangle = \langle \psi_2 | \mu | \psi_0 \rangle = \mu_{\text{mon}}$, so

$$\mu_{+or-} = (c_{+or-,1} + c_{+or-,2}) \mu_{\text{mon}}$$

$$\begin{aligned} \text{(b)} \quad \hat{H} \psi_{+or-} &= \tilde{\nu}_{+or-} \psi_{+or-} \quad \text{and} \quad (\hat{H} - \tilde{\nu}_{+or-}) \psi_{+or-} = 0 \\ \begin{pmatrix} \tilde{\nu}_{\text{mon}} - \tilde{\nu}_{+or-} & \beta \\ \beta & \tilde{\nu}_{\text{mon}} - \tilde{\nu}_{+or-} \end{pmatrix} \psi_{+or-} &= 0 \quad \text{where} \quad \beta = \frac{\mu_{\text{mon}}^2}{4\pi\epsilon_0\hbar c r^3} (1 - 3\cos^2\theta) \\ \begin{pmatrix} x_{+or-} & 1 \\ 1 & x_{+or-} \end{pmatrix} \psi_{+or-} &= 0 \quad \text{where} \quad x_{+or-} = (\tilde{\nu}_{\text{mon}} - \tilde{\nu}_{+or-})/\beta \\ \begin{vmatrix} x_{+or-} & 1 \\ 1 & x_{+or-} \end{vmatrix} &= x_{+or-}^2 - 1 = 0 \\ x_{+or-} &= (\tilde{\nu}_{\text{mon}} - \tilde{\nu}_{+or-})/\beta = \pm 1 \quad \text{and} \quad \tilde{\nu}_{+or-} = \tilde{\nu}_{\text{mon}} \pm \beta \\ \tilde{\nu}_+ &= \tilde{\nu}_{\text{mon}} - \beta \quad \text{and} \quad \tilde{\nu}_- = \tilde{\nu}_{\text{mon}} + \beta \end{aligned}$$

The ratio of μ_+^2/μ_-^2 (and the relative intensities of the dimer transitions) doesn't depend upon β or θ because $\mu_+ = 0$. To see this, we use the coefficients of the normalized wavefunctions for ψ_+ and ψ_- and the overlap integral $S = \langle \psi_1 | \psi_2 \rangle$.

$$\begin{pmatrix} x_{+or-} & 1 \\ 1 & x_{+or-} \end{pmatrix} \begin{pmatrix} c_{+or-,1} \\ c_{+or-,2} \end{pmatrix} = 0 \quad \text{where} \quad x_{+or-} = \pm 1$$

$$x_{+or-} c_{+or-,1} + c_{+or-,2} = 0$$

$$c_{+or-,2} = -x_{+or-} c_{+or-,1}$$

(i)

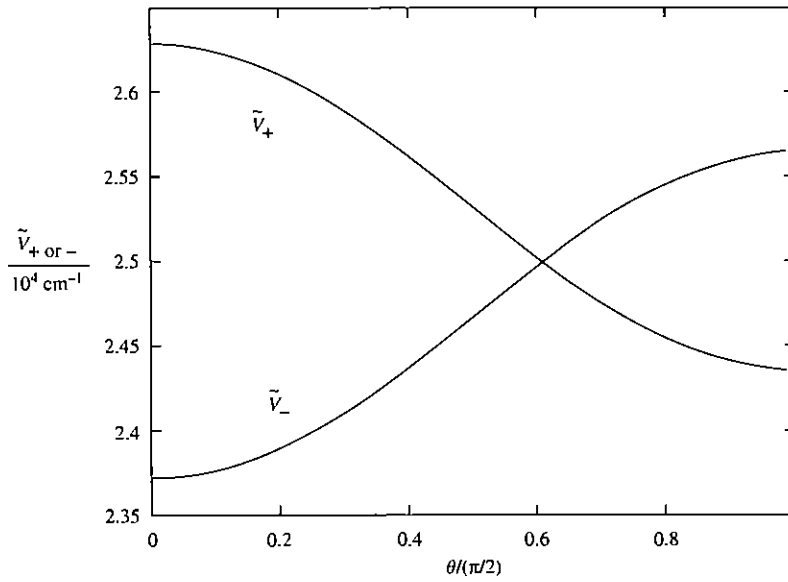


Figure 20.4(b)

The coefficients must also satisfy the normalization condition.

$$\begin{aligned}
 \langle \psi_{+or-} | \psi_{+or-} \rangle &= \langle c_{+or-,1} \psi_1 + c_{+or-,2} \psi_2 | c_{+or-,1} \psi_1 + c_{+or-,2} \psi_2 \rangle \\
 &= c_{+or-,1}^2 + c_{+or-,2}^2 + 2c_{+or-,1}c_{+or-,2}S \\
 &= c_{+or-,1}^2 + c_{+or-,1}^2 - 2x_{+or-}c_{+or-,1}^2S = 1
 \end{aligned} \tag{ii}$$

Thus,

$$c_{+,1} = \frac{1}{\{2(1-S)\}^{1/2}} \quad c_{+,2} = -c_{+,1}$$

and

$$c_{-,1} = \frac{1}{\{2(1+S)\}^{1/2}} \quad c_{-,2} = c_{-,1}$$

$$\frac{\mu_+^2}{\mu_-^2} = \left(\frac{\mu_+}{\mu_-} \right)^2 = \left(\frac{(c_{+,1} + c_{+,2}) \mu_{\text{mon}}}{(c_{-,1} + c_{-,2}) \mu_{\text{mon}}} \right)^2 = \left(\frac{c_{+,1} - c_{+,1}}{c_{-,1} + c_{-,1}} \right)^2 = 0$$

(c) The secular determinant for N monomers has the dimension $N \times N$.

$$\begin{vmatrix}
 \tilde{v}_{\text{mon}} - \tilde{v}_{\text{dimer}} & V & 0 & \cdots \\
 V & \tilde{v}_{\text{mon}} - \tilde{v}_{\text{dimer}} & V & \cdots \\
 0 & V & \tilde{v}_{\text{mon}} - \tilde{v}_{\text{dimer}} & \cdots \\
 \vdots & \vdots & \vdots & \ddots
 \end{vmatrix} = 0$$

$$\tilde{v}_{\text{dimer}} = \tilde{v}_{\text{mon}} + 2V \cos \left(\frac{k\pi}{N+1} \right) \quad k = 1, 2, 3, \dots, N \quad [20.21]$$

$$V = \beta(0) = \frac{\mu_{\text{mon}}^2}{4\pi\epsilon_0\hbar c r^3} (1 - 3\cos^2 0) = \frac{-\mu_{\text{mon}}^2}{2\pi\epsilon_0\hbar c r^3}$$

The plot in Figure 20.4(c) shows the dimer transitions for $\theta = 0$ and $N = 15$. The shape of the transition distribution changes slightly with N and transition energies are symmetrically distributed around the monomer transition. The lowest energy transition changes only slightly with N giving a value that goes to $25\,000\text{ cm}^{-1} + 2V = 25\,000\text{ cm}^{-1} + 2 \times (-1289\text{ cm}^{-1}) = 22\,422\text{ cm}^{-1}$ as $N \rightarrow \infty$.

Since the model considers only nearest neighbor interactions, the transition dipole moment of the lowest energy transition doesn't depend upon the size of the chain.

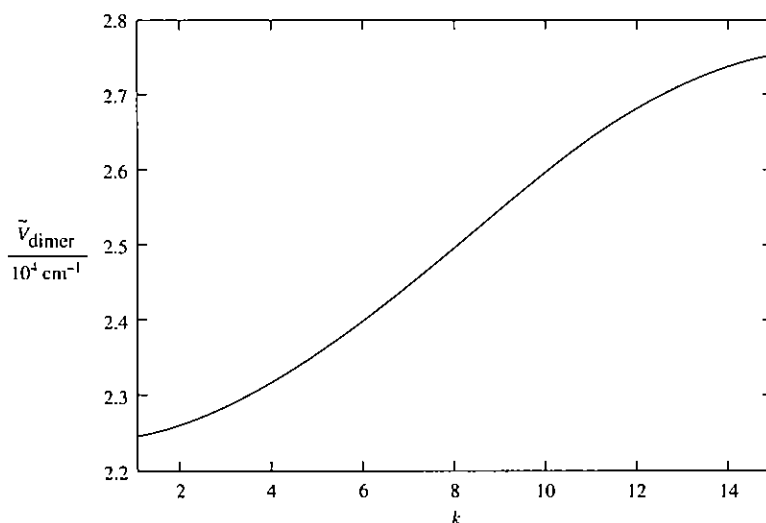


Figure 20.4(c)

P20.20 The relationship between critical temperature and critical magnetic field is given by

$$H_c(T) = H_c(0) \left(1 - \frac{T^2}{T_c^2}\right)$$

Solving for T gives the critical temperature for a given magnetic field:

$$T = T_c \left(1 - \frac{H_c(T)}{H_c(0)}\right)^{1/2} = (7.19\text{ K}) \times \left(1 - \frac{20 \times 10^3\text{ A m}^{-1}}{63901\text{ A m}^{-1}}\right)^{1/2} = \boxed{6.0\text{ K}}$$

Solutions to theoretical problems

P20.22 Consider for simplicity the two-dimensional lattice and planes shown in Figure 20.5.

The (hk) planes cut the a and b axes at a/h and b/k , and we have

$$\sin \alpha = \frac{d}{(a/h)} = \frac{hd}{a}, \quad \cos \alpha = \frac{d}{(b/k)} = \frac{kd}{b}$$

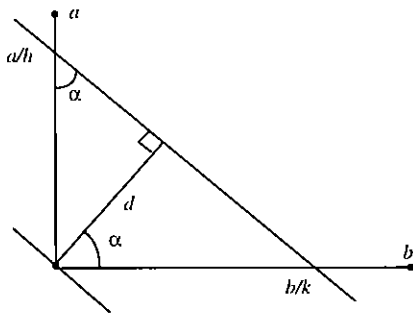


Figure 20.5

Then, since $\sin^2 \alpha + \cos^2 \alpha = 1$, we can write

$$\left(\frac{hd}{a}\right)^2 + \left(\frac{kd}{b}\right)^2 = 1$$

and therefore

$$\frac{1}{d^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2$$

The same argument extends by analogy (or further trigonometry) to three dimensions, to give

$$\frac{1}{d^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2$$

P20.24

$$f = \frac{NV_a}{V_c}$$

where N is the number of atoms in each unit cell, V_a their individual volumes, and V_c the volume of the unit cell itself. Refer to Figure 20.6.

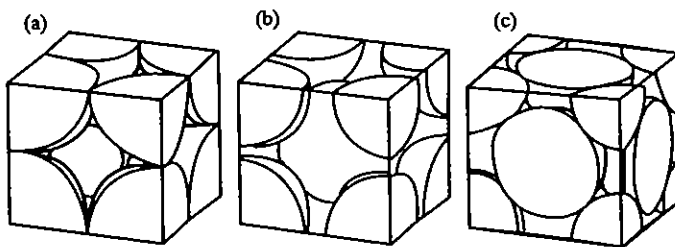


Figure 20.6

$$(a) \quad N = 1, \quad V_a = \frac{4}{3}\pi r^3, \quad V_c = (2R)^3$$

$$f = \frac{\left(\frac{4}{3}\pi R^3\right)}{(2R)^3} = \frac{\pi}{6} = \boxed{0.5236}$$

$$(b) \quad N = 1, \quad V_a = \frac{4}{3}\pi r^3, \quad V_c = \left(\frac{4R}{\sqrt{3}}\right)^3 \quad [\text{body diagonal of a unit cube is } \sqrt{3}]$$

$$f = \frac{2 \times (4/3)\pi R^3}{(4R/\sqrt{3})^3} = \frac{\pi\sqrt{3}}{8} = \boxed{0.6802}$$

$$(c) \quad N = 4, \quad V_a = \frac{4}{3}\pi R^3, \quad V_c = (2\sqrt{2}R)^3$$

$$f = \frac{4 \times (4/3)\pi R^3}{(2\sqrt{2}R)^3} = \frac{\pi}{3\sqrt{2}} = \boxed{0.7405}$$

P20.26

$$F_{hkl} = \sum_i f_i e^{2\pi i(hx_i + ky_i + lz_i)} \quad [20.7]$$

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).

$$\begin{aligned} F_{hkl} &= \frac{1}{8}f_A \left\{ 1 + e^{2\pi ih} + e^{2\pi ik} + e^{2\pi il} + e^{2\pi i(h+k)} + e^{2\pi i(h+l)} + e^{2\pi i(k+l)} + e^{2\pi i(h+k+l)} \right\} \\ &\quad + f_B e^{2\pi i(h+k+l)} \\ &= f_A + (-1)^{(h+k+l)} f_B \quad [h, k, l \text{ are all integers, } e^{i\pi} = -1] \end{aligned}$$

$$(a) \quad f_A = f, \quad f_B = 0; \quad F_{hkl} = f \quad \boxed{\text{no systematic absences}}$$

$$(b) \quad f_B = \frac{1}{2}f_A; \quad F_{hkl} = f_A \left[1 + \frac{1}{2}(-1)^{(h+k+l)} \right]$$

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 alternation of intensity ($I \propto F^2$) according to whether $h+k+l$ is odd or even.

$$(c) \quad f_A = f_B = f; \quad F_{h+k+l} = f \{ 1 + (-1)^{h+k+l} \} = 0 \quad \text{if } h+k+l \text{ is odd.}$$

Thus, all $h+k+l$ odd lines are missing.

P20.28

(a) The density of energy levels is:

$$\rho(E) = \frac{dk}{dE} = \left(\frac{dE}{dk} \right)^{-1}$$

$$\text{where } \frac{dE}{dk} = \frac{d}{dk} \left(\alpha + 2\beta \cos \frac{k\pi}{N+1} \right) = -\frac{2\pi\beta}{N+1} \sin \frac{k\pi}{N+1}$$

$$\text{so } \rho(E) = -\frac{N+1}{2\pi\beta} \left(\sin \frac{k\pi}{N+1} \right)^{-1}$$

Unlike the expression just derived, the relationship the problem asks us to derive has no trigonometric functions and it contains E and α within a square root. This comparison suggests that the trigonometric identity $\sin^2 \theta + \cos^2 \theta = 1$ will be of use here. Let $\theta = k\pi/(N+1)$; then

$$\sin \theta = (1 - \cos^2 \theta)^{1/2}$$

however, $\cos \theta$ is related to the energy

$$E = \alpha + 2\beta \cos \theta \quad \text{so} \quad \cos \theta = \frac{E - \alpha}{2\beta}$$

$$\text{and } \sin \theta = \left[1 - \left(\frac{E - \alpha}{2\beta} \right)^2 \right]^{1/2}$$

$$\text{Finally, } \boxed{\rho(E) = \frac{-(N+1)/2\pi\beta}{[1 - (E - \alpha/2\beta)^2]^{1/2}}}$$

- (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.

P20.30 If a substance responds nonlinearly to an electric field E , then it induces a dipole moment:

$$\mu = \alpha E + \beta E^2.$$

If the electric field is oscillating at two frequencies, we can write the electric field as

$$E = E_1 \cos \omega_1 t + E_2 \cos \omega_2 t,$$

and the nonlinear response as

$$\beta E^2 = \beta(E_1 \cos \omega_1 t + E_2 \cos \omega_2 t)^2,$$

$$\beta E^2 = \beta(E_1^2 \cos^2 \omega_1 t + E_2^2 \cos^2 \omega_2 t + 2E_1 E_2 \cos \omega_1 t \cos \omega_2 t).$$

Application of trigonometric identities allows a product of cosines to be re-written as a sum:

$$\cos A \cos B = \frac{1}{2} \cos(A - B) + \frac{1}{2} \cos(A + B).$$

Using this result (a special case of which applies to the \cos^2 terms), yields:

$$\beta E^2 = \frac{1}{2} \beta [E_1^2 (1 + \cos 2\omega_1 t) + E_2^2 (1 + \cos 2\omega_2 t) + 2E_1 E_2 (\cos(\omega_1 + \omega_2)t + \cos(\omega_1 - \omega_2)t)].$$

This expression includes responses at twice the original frequencies as well as at the sum and difference frequencies.

P20.32 $\text{N}_2\text{O}_4(\text{g}) \xrightleftharpoons{K} 2\text{NO}_2(\text{g})$

$$(1 - \alpha)n \quad 2\alpha n \quad \text{amounts}$$

$$\frac{1 - \alpha}{1 + \alpha} \quad \frac{2\alpha}{1 + \alpha} \quad \text{mole fractions}$$

$$\left(\frac{1-\alpha}{1+\alpha}\right)p \quad \left(\frac{2\alpha}{1+\alpha}\right)p \quad \text{partial pressures } [p \equiv p/p^\ominus \text{ here}]$$

$$K = \frac{(2\alpha/1+\alpha)^2 p}{(1-\alpha/1+\alpha)} = \frac{4\alpha^2}{1-\alpha^2} p$$

Now solve for α .

$$\alpha^2 = \frac{K}{4p + K}, \quad \alpha = \left(\frac{K}{4p + K}\right)^{1/2}$$

The degree of dimerization is $d = 1 - \alpha = 1 - \left(\frac{K}{4p + K}\right)^{1/2} = \boxed{1 - \left(\frac{1}{4(p/K) + 1}\right)^{1/2}}$

The susceptibility varies in proportion to $\alpha = 1 - d$. As pressure increases, α decreases, and the susceptibility decreases.

To determine the effect of temperature we need $\Delta_r H \approx \Delta_r H^\ominus$ for the reaction above.

$$\Delta_r H^\ominus = 2 \times (33.18 \text{ kJ mol}^{-1}) - 9.16 \text{ kJ mol}^{-1} = +57.2 \text{ kJ mol}^{-1}$$

A positive $\Delta_r H^\ominus$ indicates that $\text{NO}_2(\text{g})$ is favored as the temperature increases; hence the susceptibility increases with temperature.

Solutions to applications

- P20.34** The density of a face-centered cubic crystal is $4m/V$ where m is the mass of the unit hung on each lattice point and V is the volume of the unit cell. (The 4 comes from the fact that each of the cell's 8 vertices is shared by 8 cells, and each of the cell's 6 faces is shared by 2 cells.)

$$\text{So } \rho = \frac{4m}{a^3} = \frac{4M}{N_A a^3} \text{ and } M = \frac{1}{4} \rho N_A a^3$$

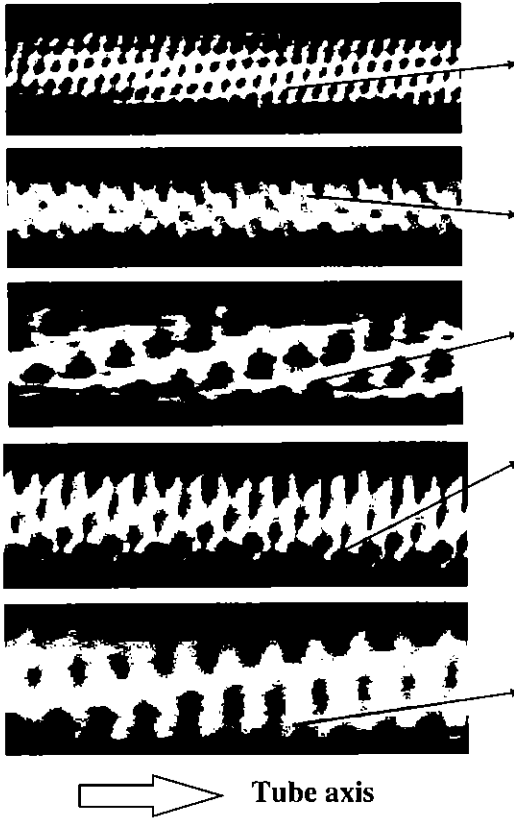
$$M = \frac{1}{4} (1.287 \text{ g cm}^{-3}) \times (6.022 \times 10^{23} \text{ mol}^{-1}) \times (12.3 \times 10^{-7} \text{ cm})^3$$

$$= \boxed{3.61 \times 10^5 \text{ g mol}^{-1}}$$

- P20.36** Single-walled carbon nanotubes (SWNT) may be either conductors or semiconductors depending upon the tube diameter and the chiral angle of the fused benzene rings with respect to the tube axis. Van der Waals forces cause SWNT to stick together in clumps, which are normally mixtures of conductors and semiconductors. SWNT stick to many surfaces and they bend, or drape, around nano-sized features that are upon a surface.

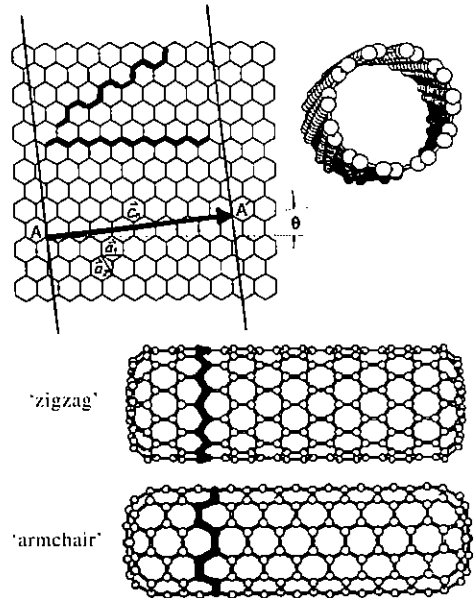
Only the semiconductor SWNT are suitable for the preparation of field-effect transistors (FET) so IBM researchers (*Science*, April 27, 2001) have developed a destructive technique for eliminating conducting tubes from conductor/semiconductor clumps with a current burst. The technique can also be used to remove the outer layers of multiwalled tubes that consist of multiple concentric tubes about a common axis. Bandgaps increase as the diameter of multiwalled tubes is decreased which means that the destructive technique can be used to tailor a semiconductor tube to specific requirements.

large variety of chiral angles

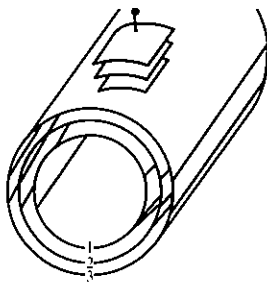


http://online.itp.ucsb.edu/online/qhall_c98/dekker/oh/18.html

Various types of nanotubes



http://online.itp.ucsb.edu/online/qhall_c98/dekker/oh/08.html



Multiwalled Nanotubes have diameters between 1 nm and 30 nm with an interlayer spacing of 0.34 nm.

http://online.itp.ucsb.edu/online/qhall_c98/dekker/oh/05.html

Figure 20.7(a)

Here is a list of ideas for producing transistors with SWNT.

Cees Dekker and students (S.J. Tans *et al.*, *Nature*, **393**, 49 (1998)) have draped a semiconducting carbon nanotube over metal electrodes that are 400 nm apart atop a silicon surface coated with silicon dioxide. A bias voltage between the electrodes provides the source and drain of an FET. The silicon serves as a gate electrode. By adjusting the magnitude of an electric field applied to the gate, current flow across the nanotube may be turned on and off.

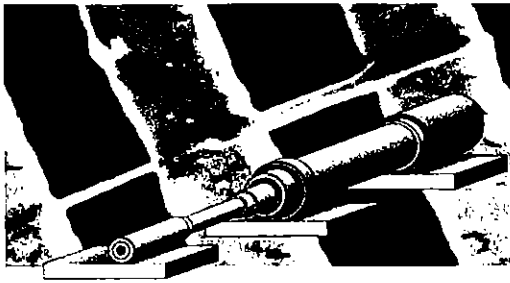
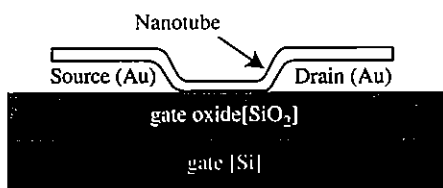


Figure 20.7(b)



<http://www.research.ibm.com/nanoscience/fet.html>

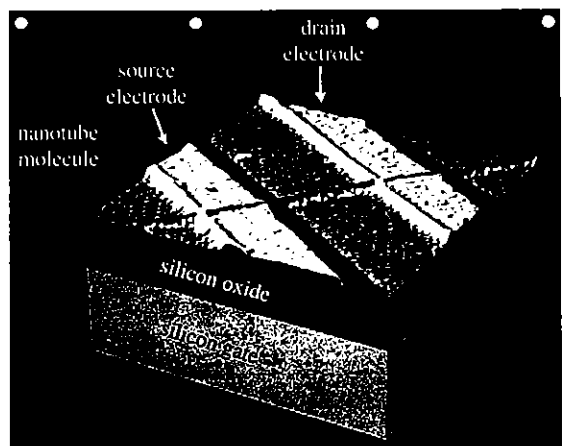
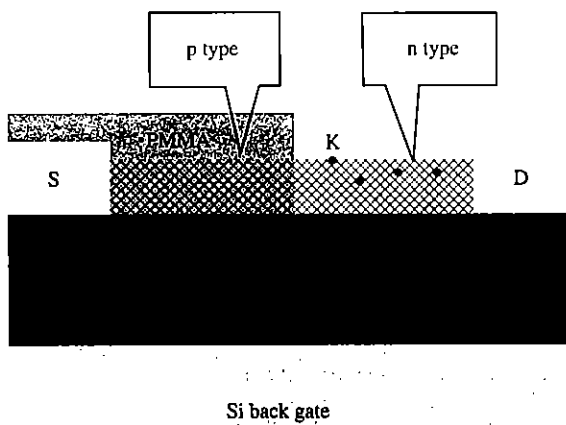


Figure 20.7(c)



<http://www.usc.edu/dept/ee/People/Faculty/Zhou/zhougrou/research.html> Figure 20.7(d)

A section of a single nanotube may be exposed to potassium vapor to produce a p–n junction.

A single-electron transistor (SET) has been prepared by Cees Dekker and coworkers (*Science*, **293**, 76, (2001)) with a conducting nanotube. The SET is prepared by putting two bends in a tube with the tip of an AFM. Bending causes two buckles that, at a distance of 20 nm, serves as a conductance barrier. When an appropriate voltage is applied to the gate below the barrier, electrons tunnel one at a time across the barrier.

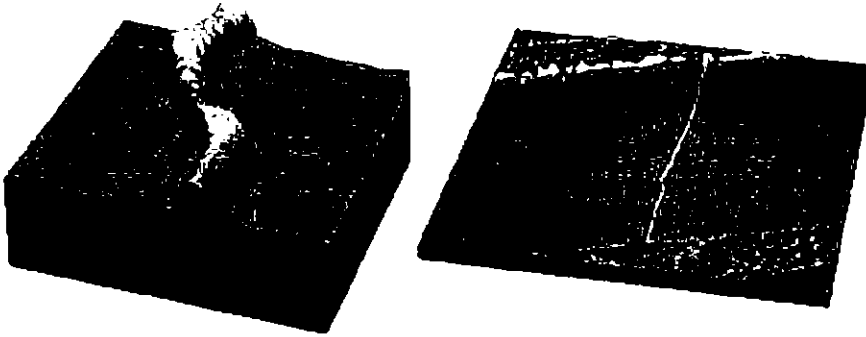
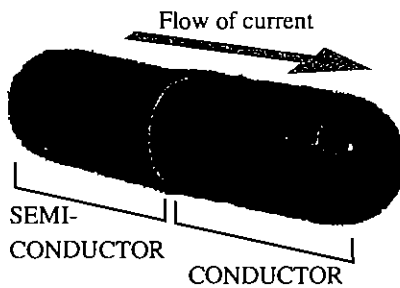


Figure 20.7(e)

A semiconductor tube may be fused to a conductor tube to produce a SET similar to an SET.



<http://www.geocities.com/fikrethasmer/physics/electronic/electronic.html>

Figure 20.7(f)

PART 3 Change

21

Molecules in motion

Answers to discussion questions

- D21.2** 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, also 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 (Figure 21.11 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.

D21.4 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_3O_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 (Figure 21.16a 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 $\text{H}_2\text{O} \cdots \text{H}^+ \cdots \text{OH}_2$ (Figure 21.16b). Shortly after this reorganization has occurred, a new H_3O_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 (Figure 21.16c). According to this model, there is no coordinated motion of a proton along a chain of molecules, simply a very rapid hopping between neighboring 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.

D21.6 The maximum flux in mediated transport is achieved at very high concentrations of the transported species. Under such conditions, the transported species A flood the carrier species C, pushing practically all of the latter into the form of the AC complex. (The mathematical condition for saturation of the flux at J_{\max} is that $[A] \gg K$, the equilibrium constant for dissociation of the AC complex; this condition puts practically all C into the complex, regardless of its inherent stability.) The value of J_{\max} depends on the concentration of carrier species, $[C]_0$. For a given value of $[C]_0$, J_{\max} represents the transport capacity of the “fleet” of carriers. The oversupply of A keeps the carriers transporting at full capacity.

Solutions to exercises

E21.1(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 $\boxed{1}$

E21.2(b) (a) The mean speed can be calculated from the formula derived in Example 21.1.

$$\bar{c} = \left(\frac{8RT}{\pi M} \right)^{1/2} = \left(\frac{8 \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{\pi \times (28.02 \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} = \boxed{4.75 \times 10^2 \text{ m s}^{-1}}$$

- (b) The mean free path is calculated from $\lambda = kT/(2^{1/2}\sigma p)$ [21.13] with $\sigma = \pi d^2 = \pi \times (3.95 \times 10^{-10} \text{ m})^2 = 4.90 \times 10^{-19} \text{ m}^2$

$$\begin{aligned}\text{Then, } \lambda &= \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}{2^{1/2} \times (4.90 \times 10^{-19} \text{ m}^2) \times (1 \times 10^{-9} \text{ Torr}) \times \left(\frac{1 \text{ atm}}{760 \text{ Torr}}\right) \times \left(\frac{1.013 \times 10^5 \text{ Pa}}{1 \text{ atm}}\right)} \\ &= \boxed{4 \times 10^4 \text{ m}}\end{aligned}$$

- (c) The collision frequency could be calculated from eqn 21.11, but is most easily obtained from eqn 21.12, since λ and \bar{c} have already been calculated

$$z = \frac{\bar{c}}{\lambda} = \frac{4.75 \times 10^2 \text{ m s}^{-1}}{4.46 \times 10^4 \text{ m}} = \boxed{1 \times 10^{-2} \text{ s}^{-1}}$$

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.

E21.3(b) $p = \frac{kT}{2^{1/2}\sigma\lambda}$ [21.13]

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

$$p = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}{(2^{1/2}) \times (0.36 \times 10^{-18} \text{ m}^2) \times (0.34 \times 10^{-9} \text{ m})} = \boxed{2.4 \times 10^7 \text{ Pa}}$$

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.

- E21.4(b)** The mean free path is

$$\lambda = \frac{kT}{2^{1/2}\sigma p} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (217 \text{ K})}{2^{1/2} \left[0.43 \times (10^{-9} \text{ m})^2\right] \times (12.1 \times 10^3 \text{ Pa atm}^{-1})} = \boxed{4.1 \times 10^{-7} \text{ m}}$$

- E21.5(b)** Obtain data from Exercise 21.4(b)

The expression for z obtained in Exercise 21.5(a) is $z = [16/(\pi mkT)]^{1/2} \sigma p$

Substituting $\sigma = 0.43 \text{ nm}^2$, $p = 12.1 \times 10^3 \text{ Pa}$, $m = (28.02 \text{ u})$, and $T = 217 \text{ K}$ we obtain

$$\begin{aligned}z &= \frac{4 \times (0.43 \times 10^{-18} \text{ m}^2) \times (12.1 \times 10^3 \text{ Pa})}{[\pi \times (28.02) \times (1.6605 \times 10^{-27} \text{ kg}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (217 \text{ K})]^{1/2}} \\ &= \boxed{9.9 \times 10^8 \text{ s}^{-1}}\end{aligned}$$

- E21.6(b)** The mean free path is

$$\lambda = \frac{kT}{2^{1/2}\sigma p} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (25 + 273) \text{ K}}{2^{1/2} \left[0.52 \times (10^{-9} \text{ m})^2\right] p} = \frac{5.50 \times 10^{-3} \text{ m Pa}}{p}$$

$$(a) \quad \lambda = \frac{5.50 \times 10^{-3} \text{ m Pa}}{(15 \text{ atm}) \times (1.013 \times 10^5 \text{ Pa atm}^{-1})} = \boxed{3.7 \times 10^{-9} \text{ m}}$$

$$(b) \quad \lambda = \frac{5.50 \times 10^{-3} \text{ m Pa}}{(1.0 \text{ bar}) \times (10^5 \text{ Pa bar}^{-1})} = \boxed{5.5 \times 10^{-8} \text{ m}}$$

$$(c) \quad \lambda = \frac{5.50 \times 10^{-3} \text{ m Pa}}{(1.0 \text{ Torr}) \times (1.013 \times 10^5 \text{ Pa atm}^{-1} / 760 \text{ Torr atm}^{-1})} = \boxed{4.1 \times 10^{-5} \text{ m}}$$

E21.7(b) The fraction F of molecules in the speed range from 200 to 250 m s⁻¹ is

$$F = \int_{200 \text{ m s}^{-1}}^{250 \text{ m s}^{-1}} f(v) dv$$

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

$$\begin{aligned} F &\approx 4\pi \left(\frac{44.0 \times 10^{-3} \text{ kg mol}^{-1}}{2\pi (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})} \right)^{3/2} \times (225 \text{ m s}^{-1})^2 \\ &\quad \times \exp \left(\frac{-(44.0 \times 10^{-3} \text{ kg mol}^{-1}) \times (225 \text{ m s}^{-1})^2}{2 (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})} \right) \times (50 \text{ m s}^{-1}), \\ &\quad \boxed{F \approx 9.6 \times 10^{-2}} \end{aligned}$$

COMMENT. The approximation we have employed, taking $f(v)$ to be nearly constant over a narrow range of speeds, might not be accurate enough, for that range of speeds includes about 10 percent of the molecules. You may wish to do the integration without this approximation (a considerably more complicated process) to see how much difference there is.

E21.8(b) The number of collisions is

$$\begin{aligned} N &= Z_W A t = \frac{p A t}{(2\pi m k T)^{1/2}} \\ &= \frac{(111 \text{ Pa}) \times (3.5 \times 10^{-3} \text{ m}) \times (4.0 \times 10^{-2} \text{ m}) \times (10 \text{ s})}{\{2\pi \times (4.00 \text{ u}) \times (1.66 \times 10^{-27} \text{ kg u}^{-1}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (1500 \text{ K})\}^{1/2}} \\ &= \boxed{5.3 \times 10^{21}} \end{aligned}$$

E21.9(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

$$\begin{aligned}\Delta m &= mN = mZ_W A t = \frac{mpAt}{(2\pi mkT)^{1/2}} = pAt \left(\frac{m}{2\pi kT} \right)^{1/2} = pAt \left(\frac{M}{2\pi RT} \right)^{1/2} \\ &= (0.224 \text{ Pa}) \times \pi \times \left(\frac{1}{2} \times 3.00 \times 10^{-3} \text{ m} \right)^2 \times (24.00 \text{ h}) \times (3600 \text{ s h}^{-1}) \\ &\quad \times \left\{ \frac{300 \times 10^{-3} \text{ kg mol}^{-1}}{2\pi \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (450 \text{ K})} \right\}^{1/2} \\ &= \boxed{4.98 \times 10^{-4} \text{ kg}}\end{aligned}$$

E21.10(b) The time dependence of the pressure of a gas effusing without replenishment is

$$p = p_0 e^{-t/\tau} \text{ where } \tau \propto \sqrt{m}$$

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

$$\frac{t_1}{t_2} = \left(\frac{M_1}{M_2} \right)^{1/2} \quad \text{and} \quad M_2 = M_1 \left(\frac{t_2}{t_1} \right)^2$$

$$\text{So } M_{\text{fluorocarbon}} = (28.01 \text{ g mol}^{-1}) \times \left(\frac{82.3 \text{ s}}{18.5 \text{ s}} \right)^2 = \boxed{554 \text{ g mol}^{-1}}$$

E21.11(b) The time dependence of the pressure of a gas effusion without replenishment is

$$p = p_0 e^{-t/\tau} \quad \text{so} \quad t = \tau \ln p_0/p$$

$$\begin{aligned}\text{where } \tau &= \frac{V}{A_0} \left(\frac{2\pi m}{kT} \right)^{1/2} = \frac{V}{A_0} \left(\frac{2\pi M}{RT} \right)^{1/2} \\ &= \left(\frac{22.0 \text{ m}^3}{\pi \times (0.50 \times 10^{-3} \text{ m})^2} \right) \times \left(\frac{2\pi \times (28.0 \times 10^{-3} \text{ kg mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293 \text{ K})} \right)^{1/2} = 2.4 \times 10^5 \text{ s}\end{aligned}$$

$$\text{so } t = (8.6 \times 10^5 \text{ s}) \ln \frac{122 \text{ kPa}}{105 \text{ kPa}} = \boxed{1.5 \times 10^4 \text{ s}}$$

E21.12(b) The flux is

$$J = -\kappa \frac{dT}{dz} = -\frac{1}{3} \lambda C_{V,m} \bar{c} [X] \frac{dT}{dz}$$

where the minus sign indicates flow toward lower temperature and

$$\lambda = \frac{1}{\sqrt{2}N\sigma}, \quad \bar{c} = \left(\frac{8kT}{\pi m}\right)^{1/2} = \left(\frac{8RT}{\pi M}\right)^{1/2}, \quad \text{and } [M] = n/V = N/N_A$$

$$\begin{aligned} \text{So } J &= -\frac{2C_{V,m}}{3\sigma N_A} \left(\frac{RT}{\pi M}\right)^{1/2} \frac{dT}{dz} \\ &= \left(\frac{2 \times (28.832 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}}{3 \times [0.27 \times (10^{-9} \text{ m})^2] \times (6.022 \times 10^{23} \text{ mol}^{-1})} \right) \\ &\quad \times \left(\frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (260 \text{ K})}{\pi \times (2.016 \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} \times (3.5 \text{ K m}^{-1}) \\ &= \boxed{0.17 \text{ J m}^{-2} \text{ s}^{-1}} \end{aligned}$$

E21.13(b) The thermal conductivity is

$$\begin{aligned} \kappa &= \frac{1}{3} \lambda C_{V,m} \bar{c} [X] = \frac{2C_{V,m}}{3\sigma N_A} \left(\frac{RT}{\pi M}\right)^{1/2} \quad \text{so } \sigma = \frac{2C_{V,m}}{3\kappa N_A} \left(\frac{RT}{\pi M}\right)^{1/2} \\ \kappa &= (0.240 \text{ mJ cm}^{-2} \text{ s}^{-1}) \times (\text{K cm}^{-1})^{-1} = 0.240 \times 10^{-1} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1} \\ \text{so } \sigma &= \left(\frac{2 \times (29.125 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}}{3 \times (0.240 \times 10^{-1} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}) \times (6.022 \times 10^{23} \text{ mol}^{-1})} \right) \\ &\quad \times \left(\frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{\pi \times (28.013 \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} \\ &= \boxed{1.61 \times 10^{-19} \text{ m}^2} \end{aligned}$$

E21.14(b) Assuming the space between sheets is filled with air, the flux is

$$\begin{aligned} J &= -k \frac{dT}{dz} = \left[(0.241 \times 10^{-3} \text{ J cm}^{-2} \text{ s}^{-1}) \times (\text{K cm}^{-1})^{-1} \right] \times \left(\frac{[50 - (-10) \text{ K}]}{10.0 \text{ cm}} \right) \\ &= 1.45 \times 10^{-3} \text{ J cm}^{-2} \text{ s}^{-1}. \end{aligned}$$

So the rate of energy transfer and energy loss is

$$JA = (1.45 \times 10^{-3} \text{ J cm}^{-2} \text{ s}^{-1}) \times (1.50 \text{ m}^2) \times (100 \text{ cm m}^{-1})^2 = \boxed{22 \text{ J s}^{-1}}$$

E21.15(b) The coefficient of viscosity is

$$\begin{aligned} \eta &= \frac{1}{3} \lambda m N \bar{c} = \frac{2}{3\sigma} \left(\frac{mkT}{\pi}\right)^{1/2} \quad \text{so } \sigma = \frac{2}{3\eta} \left(\frac{mkT}{\pi}\right)^{1/2} \\ \eta &= 1.66 \mu\text{P} = 166 \times 10^{-7} \text{ kg m}^{-1} \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned}\text{so } \sigma &= \left(\frac{2}{3 \times (166 \times 10^{-7} \text{ kg m}^{-1} \text{ s}^{-1})} \right) \\ &\times \left(\frac{(28.01 \times 10^{-3} \text{ kg mol}^{-1}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (273 \text{ K})}{\pi \times (6.022 \times 10^{23} \text{ mol}^{-1})} \right)^{1/2} \\ &= \boxed{3.00 \times 10^{-19} \text{ m}^2}\end{aligned}$$

E21.16(b) The rate of fluid flow through a tube is described by

$$\frac{dV}{dt} = \frac{(p_{\text{in}}^2 - p_{\text{out}}^2) \pi r^4}{16l\eta p_0} \quad \text{so} \quad p_{\text{in}} = \left(\frac{16l\eta p_0}{\pi r^4} \frac{dV}{dt} + p_{\text{out}}^2 \right)^{1/2}$$

Several of the parameters need to be converted to SI units

$$r = \frac{1}{2}(15 \times 10^{-3} \text{ m}) = 7.5 \times 10^{-3} \text{ m}$$

$$\text{and } \frac{dV}{dt} = 8.70 \text{ cm}^3 \times (10^{-2} \text{ m cm}^{-1})^3 \text{ s}^{-1} = 8.70 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}.$$

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

$$\begin{aligned}\eta(300 \text{ K}) &= \eta(293 \text{ K}) \times \left(\frac{300 \text{ K}}{293 \text{ K}} \right)^{1/2} = (176 \times 10^{-7} \text{ kg m}^{-1} \text{ s}^{-1}) \times \left(\frac{300}{293} \right)^{1/2} \\ &= 1.78 \times 10^{-7} \text{ kg m}^{-1} \text{ s}^{-1} \\ p_{\text{in}} &= \left\{ \left(\frac{16(10.5 \text{ m}) \times (178 \times 10^{-7} \text{ kg m}^{-1} \text{ s}^{-1}) \times (1.00 \times 10^5 \text{ Pa})}{\pi \times (7.5 \times 10^{-3} \text{ m})^4} \right) \right. \\ &\quad \times (8.70 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}) + (1.00 \times 10^5 \text{ Pa})^2 \left. \right\}^{1/2} \\ &= \boxed{1.00 \times 10^5 \text{ Pa}}\end{aligned}$$

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!

E21.17(b) The coefficient of viscosity is

$$\begin{aligned}\eta &= \frac{1}{3} \lambda m N \bar{c} = \frac{2}{3\sigma} \left(\frac{mkT}{\pi} \right)^{1/2} \\ &= \left(\frac{2}{3[0.88 \times (10^{-9} \text{ m})^2]} \right) \times \left(\frac{(78.12 \times 10^{-3} \text{ kg mol}^{-1}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) T}{\pi \times (6.022 \times 10^{23} \text{ mol}^{-1})} \right)^{1/2} \\ &= 5.72 \times 10^{-7} \times (T/\text{K})^{1/2} \text{ kg m}^{-1} \text{ s}^{-1}\end{aligned}$$

$$(a) \text{ At } 273 \text{ K} \quad \eta = (5.72 \times 10^{-7}) \times (273)^{1/2} \text{ kg m}^{-1} \text{ s}^{-1} = \boxed{0.95 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}}$$

$$(b) \text{ At } 298 \text{ K} \quad \eta = (5.72 \times 10^{-7}) \times (298)^{1/2} \text{ kg m}^{-1} \text{ s}^{-1} = \boxed{0.99 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}}$$

$$(c) \text{ At } 1000 \text{ K} \quad \eta = (5.72 \times 10^{-7}) \times (1000)^{1/2} \text{ kg m}^{-1} \text{ s}^{-1} = \boxed{1.81 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}}$$

E21.18(b) The thermal conductivity is

$$k = \frac{1}{3} \lambda C_{V,m} \bar{c} [X] = \frac{2C_{V,m}}{3\sigma N_A} \left(\frac{RT}{\pi M} \right)^{1/2}$$

$$(a) \quad \kappa = \left(\frac{2 \times [(20.786 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}]}{3 [0.24 \times (10^{-9} \text{ m})^2] \times (6.022 \times 10^{23} \text{ mol}^{-1})} \right) \\ \times \left(\frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{\pi (20.18 \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} \\ = \boxed{0.0114 \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}}$$

The flux is

$$J = -\kappa \frac{dT}{dz} = (0.0114 \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}) \times \left(\frac{(305 - 295) \text{ K}}{0.15 \text{ m}} \right) = 0.76 \text{ J m}^{-2} \text{ s}^{-1}$$

so the rate of energy loss is

$$JA = (0.76 \text{ J m}^{-2} \text{ s}^{-1}) \times (0.15 \text{ m})^2 = \boxed{0.017 \text{ J s}^{-1}}$$

$$(b) \quad \kappa = \left(\frac{2 \times [(29.125 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}]}{3 [0.43 \times (10^{-9} \text{ m})^2] \times (6.022 \times 10^{23} \text{ mol}^{-1})} \right) \\ \times \left(\frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{\pi (28.013 \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} \\ = \boxed{9.0 \times 10^{-3} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}}$$

The flux is

$$J = -\kappa \frac{dT}{dz} = (9.0 \times 10^{-3} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}) \times \left(\frac{(305 - 295) \text{ K}}{0.15 \text{ m}} \right) = 0.60 \text{ J m}^{-2} \text{ s}^{-1}$$

so the rate of energy loss is

$$JA = (0.60 \text{ J m}^{-2} \text{ s}^{-1}) \times (0.15 \text{ m})^2 = \boxed{0.014 \text{ J s}^{-1}}$$

E21.19(b) The rate of fluid flow through a tube is described by

$$\frac{dV}{dt} = \frac{(p_{\text{in}}^2 - p_{\text{out}}^2) \pi r^4}{16\eta \rho_0}$$

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

$$\frac{t_1}{t_2} = \frac{\eta_1}{\eta_2} \text{ so } \eta_2 = \frac{\eta_1 t_2}{t_1}$$

$$\eta_{\text{CFC}} = \frac{(208 \mu\text{P}) \times (18.0 \text{ s})}{72.0 \text{ s}} = \boxed{52.0 \mu\text{P}} = 52.0 \times 10^{-7} \text{ kg m}^{-1} \text{ s}^{-1}$$

The coefficient of viscosity is

$$\eta = \frac{1}{3} \lambda m N \bar{c} = \left(\frac{2}{3\sigma} \right) \times \left(\frac{mkT}{\pi} \right)^{1/2} = \left(\frac{2}{3\pi d^2} \right) \times \left(\frac{mkT}{\pi} \right)^{1/2}$$

so the molecular diameter is

$$\begin{aligned} d &= \left(\frac{2}{3\pi\eta} \right)^{1/2} \times \left(\frac{mkT}{\pi} \right)^{1/4} \\ &= \left(\frac{2}{3\pi (52.0 \times 10^{-7} \text{ kg m}^{-1} \text{ s}^{-1})} \right)^{1/2} \\ &\quad \times \left(\frac{(200 \times 10^{-3} \text{ kg mol}^{-1}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}{\pi \times (6.022 \times 10^{23} \text{ mol}^{-1})} \right)^{1/4} \\ &= 9.23 \times 10^{-10} \text{ m} = \boxed{923 \text{ pm}} \end{aligned}$$

E21.20(b)

$$\begin{aligned} \kappa &= \frac{1}{3} \lambda C_{V,m} \bar{c} [X] = \frac{2C_{V,m}}{3\sigma N_A} \left(\frac{RT}{\pi M} \right)^{1/2} \\ &= \left(\frac{2 \times (29.125 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}}{3 [0.43 \times (10^{-9} \text{ m})^2]} \right) \times \left(\frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{\pi \times (28.013 \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} \\ &= \boxed{9.0 \times 10^{-3} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}} \end{aligned}$$

E21.21(b) The diffusion constant is

$$\begin{aligned} D &= \frac{1}{3} \lambda \bar{c} = \frac{2(RT)^{3/2}}{3\sigma p N_A (\pi M)^{1/2}} \\ &= \frac{2 [(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})]^{3/2}}{3 [0.43 \times (10^{-9} \text{ m})^2] p (6.022 \times 10^{23} \text{ mol}^{-1}) \times \{\pi (28.013 \times 10^{-3} \text{ kg mol}^{-1})\}^{1/2}} \\ &= \frac{1.07 \text{ m}^2 \text{ s}^{-1}}{p/\text{Pa}} \end{aligned}$$

The flux due to diffusion is

$$J = -D \frac{d[X]}{dx} = -D \frac{d}{dx} \left(\frac{n}{V} \right) = - \left(\frac{D}{RT} \right) \frac{dp}{dx}$$

where the minus sign indicates flow from high pressure to low. So for a pressure gradient of 0.10 atm cm^{-1}

$$J = \left(\frac{D/(\text{m}^2 \text{ s}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} \right) \times (0.20 \times 10^5 \text{ Pa m}^{-1})$$

$$= (8.1 \text{ mol m}^{-2} \text{ s}^{-1}) \times (D/(\text{m}^2 \text{ s}^{-1}))$$

$$(a) \quad D = \frac{1.07 \text{ m}^2 \text{ s}^{-1}}{10.0} = \boxed{0.107 \text{ m}^2 \text{ s}^{-1}}$$

$$\text{and } J = (8.1 \text{ mol m}^{-2} \text{ s}^{-1}) \times (0.107) = \boxed{0.87 \text{ mol m}^{-2} \text{ s}^{-1}}$$

$$(b) \quad D = \frac{1.07 \text{ m}^2 \text{ s}^{-1}}{100 \times 10^3} = \boxed{1.07 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}}$$

$$\text{and } J = (8.1 \text{ mol m}^{-2} \text{ s}^{-1}) \times (1.07 \times 10^{-5}) = \boxed{8.7 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}}$$

$$(c) \quad D = \frac{1.07 \text{ m}^2 \text{ s}^{-1}}{15.0 \times 10^6} = \boxed{7.13 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}}$$

$$\text{and } J = (8.1 \text{ mol m}^{-2} \text{ s}^{-1}) \times (7.13 \times 10^{-8}) = \boxed{5.8 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}}$$

E21.22(b) Molar ionic conductivity is related to mobility by

$$\lambda = zuF = (1) \times (4.24 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}) \times (96485 \text{ C mol}^{-1})$$

$$= \boxed{4.09 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}}$$

E21.23(b) The drift speed is given by

$$s = uE = \frac{u\Delta\phi}{l} = \frac{(4.01 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}) \times (12.0 \text{ V})}{1.00 \times 10^{-2} \text{ m}} = \boxed{4.81 \times 10^{-5} \text{ m s}^{-1}}$$

E21.24(b) The limiting transport number for 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 $10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$.)

E21.25(b) The limiting molar conductivity of a dissolved salt is the sum of that of its ions, so

$$\Lambda_m^\circ(\text{MgI}_2) = \lambda(\text{Mg}^{2+}) + 2\lambda(\text{I}^-) = \Lambda_m^\circ(\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2) + 2\Lambda_m^\circ(\text{NaI}) - 2\Lambda_m^\circ(\text{NaC}_2\text{H}_3\text{O}_2)$$

$$= (18.78 + 2(12.69) - 2(9.10)) \text{ mS m}^2 \text{ mol}^{-1} = \boxed{25.96 \text{ mS m}^2 \text{ mol}^{-1}}$$

E21.26(b) Molar ionic conductivity is related to mobility by

$$\lambda = z\mu F \quad \text{so} \quad u = \frac{\lambda}{zF}$$

$$\text{F}^- : u = \frac{5.54 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}}{(1) \times (96485 \text{ C mol}^{-1})} = \boxed{5.74 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}}$$

$$\text{Cl}^- : u = \frac{7.635 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}}{(1) \times (96485 \text{ C mol}^{-1})} = \boxed{7.913 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}}$$

$$\text{Br}^- : u = \frac{7.81 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}}{(1) \times (96485 \text{ C mol}^{-1})} = \boxed{8.09 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}}$$

E21.27(b) The diffusion constant is related to the mobility by

$$D = \frac{uRT}{zF} = \frac{(4.24 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{(1) \times (96485 \text{ C mol}^{-1})} = \boxed{1.09 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}}$$

E21.28(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

$$t = \frac{\langle r^2 \rangle}{6D} = \frac{(1.0 \times 10^{-2} \text{ m})^2}{6(4.05 \times 10^{-9} \text{ m}^2 \text{ s}^{-1})} = \boxed{4.1 \times 10^3 \text{ s}}$$

E21.29(b) The diffusion constant is related to the viscosity of the medium and the size of the diffusing molecule as follows

$$D = \frac{kT}{6\pi\eta a} \quad \text{so} \quad a = \frac{kT}{6\pi\eta D} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}{6\pi (1.00 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}) \times (1.055 \times 10^{-9} \text{ m}^2 \text{ s}^{-1})}$$

$$a = 2.07 \times 10^{-10} \text{ m} = \boxed{207 \text{ pm}}$$

E21.30(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

$$D = \frac{kT}{6\pi\eta a} = \frac{kT}{3\pi\eta\lambda} \quad \text{so} \quad \lambda = \frac{kT}{3\pi\eta D}$$

$$\text{and } \tau = \frac{(kT)^2}{18 (\pi \eta)^2 D^3} = \frac{[(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})]^2}{18 [\pi (0.387 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})]^2 \times (3.17 \times 10^{-9} \text{ m}^2 \text{ s}^{-1})^3}$$

$$= \boxed{200 \times 10^{-11} \text{ s}} = 20 \text{ ps}$$

E21.31(b) The mean square displacement is (from Exercise 21.28(b))

$$\langle r^2 \rangle = 6Dt \quad \text{so} \quad t = \frac{\langle r^2 \rangle}{6D} = \frac{(1.0 \times 10^{-6} \text{ m})^2}{6 (1.0 \times 10^{-11} \text{ m}^2 \text{ s}^{-1})} = \boxed{1.7 \times 10^{-2} \text{ s}}$$

Solutions to problems

Solutions to numerical problems

P21.2 For discrete rather than continuous variables the equation analogous to the equation for obtaining \bar{c} (Example 21.1) is $\langle v_x \rangle = \sum_i v_{i,x} (N_i/N) = (1/N) \sum_i N_i v_{i,x}$ with (N_i/N) the analogue of $f(v)$

$$N = 40 + 62 + 53 + 12 + 2 + 38 + 59 + 60 + 2 = 328$$

$$\begin{aligned} \text{(a)} \quad \langle v_x \rangle &= \frac{1}{328} \{40 \times 80 + 62 \times 85 + \cdots + 2 \times 100 + 38 \times (-80) \\ &\quad + 59 \times (-85) + \cdots + 2 \times (-100)\} \text{ km h}^{-1} \\ &= \boxed{2.8 \text{ km h}^{-1}} \text{ east} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \langle |v_x| \rangle &= \frac{1}{328} \{40 \times 80 + 62 \times 85 + \cdots + 2 \times 100 + 38 \times 80 \\ &\quad + 59 \times 85 + \cdots + 2 \times 100\} \text{ km h}^{-1} \\ &= \boxed{86 \text{ km h}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{(c)} \quad \langle v_x^2 \rangle &= \frac{1}{328} \{40 \times 80^2 + 62 \times 85^2 + \cdots + 2 \times 100^2\} (\text{km h}^{-1})^2 = 7430 (\text{km h}^{-1})^2 \\ \sqrt{\langle v_x^2 \rangle} &= \boxed{86 \text{ km h}^{-1}} \quad \left[\text{that } \sqrt{\langle v_x^2 \rangle} = \langle |v_x| \rangle \text{ in this case is coincidental.} \right] \end{aligned}$$

P21.4 $\kappa = \frac{1}{3} \lambda \bar{c} C_{V,m} [A] \quad [21.23]$

$$\bar{c} = \left(\frac{8kT}{\pi m} \right)^{1/2} \quad [21.7] \propto T^{1/2}$$

$$\text{Hence, } \kappa \propto T^{1/2} C_{V,m}, \text{ so } \frac{\kappa'}{\kappa} = \left(\frac{T'}{T} \right)^{1/2} \times \left(\frac{C'_{V,m}}{C_{V,m}} \right)$$

$$\text{At } 300 \text{ K, } C_{V,m} \approx \frac{3}{2}R + R = \frac{5}{2}R \quad \text{At } 10 \text{ K, } C_{V,m} \approx \frac{3}{2}R \text{ [rotation not excited]}$$

$$\text{Therefore, } \frac{\kappa'}{\kappa} = \left(\frac{300}{10} \right)^{1/2} \times \left(\frac{5}{3} \right) = \boxed{9.1}$$

P21.6 Radioactive decay follows first-order kinetics (Chapter 22); hence the two contributions to the rate of change of the number of helium atoms are

$$\frac{dN}{dt} = k_r[\text{Bk}] \text{ (radioactive decay)} \quad \frac{dN}{dt} = -Z_W[A] \quad [\text{Problem 21.5}]$$

Therefore, the total rate of change is

$$\frac{dN}{dt} = k_r[\text{Bk}] - Z_W A \text{ with } Z_W = \frac{p}{(2\pi mkT)^{1/2}}$$

$$[\text{Bk}] = [\text{Bk}]_0 e^{-k_r t} \text{ and } p = \frac{nRT}{V} = \frac{nN_A kT}{V} = \frac{NkT}{V}$$

Therefore, the pressure of helium inside the container obeys

$$\frac{dp}{dt} = \frac{kT}{V} \frac{dN}{dt} = \frac{kk_r T}{V} [\text{Bk}]_0 e^{-k_r t} - \frac{(pAkT/V)}{(2\pi mkT)^{1/2}}$$

If we write $a = \frac{kk_r T[\text{Bk}]_0}{V}$, $b = \left(\frac{A}{V}\right) \times \left(\frac{kT}{2\pi m}\right)^{1/2}$, the rate equation becomes

$$\frac{dp}{dt} = ae^{-k_r t} - bp, \quad p = 0 \text{ at } t = 0$$

which is a first-order linear differential equation with the solution

$$p = \left(\frac{a}{k_r - b}\right) \times (e^{-bt} - e^{-k_r t})$$

Since $[\text{Bk}] = \frac{1}{2}[\text{Bk}]_0$ when $t = 4.4$ h, it follows from the radioactive decay law ($[\text{Bk}] = [\text{Bk}]_0 e^{-k_r t}$) that (Chapter 22)

$$k_r = \frac{\ln 2}{(4.4) \times (3600 \text{ s})} = 4.4 \times 10^{-5} \text{ s}^{-1}$$

We also know that $[\text{Bk}]_0 = \left(\frac{1.0 \times 10^{-3} \text{ g}}{244 \text{ g mol}^{-1}}\right) \times (6.022 \times 10^{23} \text{ mol}^{-1}) = 2.5 \times 10^{18}$

$$\begin{aligned} \text{Then, } a &= \frac{kk_r T[\text{Bk}]_0}{V} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (4.4 \times 10^{-5} \text{ s}^{-1}) \times (298 \text{ K}) \times (2.5 \times 10^{18})}{1.0 \times 10^{-6} \text{ m}^3} \\ &= 0.45 \text{ Pa s}^{-1} \end{aligned}$$

$$\text{and } b = \left(\frac{\pi \times (2.0 \times 10^{-6} \text{ m})^2}{1.0 \times 10^{-6} \text{ m}^3}\right) \times \left(\frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}{(2\pi) \times (4.0) \times (1.6605 \times 10^{-27} \text{ kg})}\right)^{1/2} = 3.9 \times 10^{-3} \text{ s}^{-1}$$

$$\begin{aligned} \text{Hence, } p &= \left(\frac{0.45 \text{ Pa s}^{-1}}{[(4.4 \times 10^{-5}) - (3.9 \times 10^{-3})] \text{ s}^{-1}}\right) \times (e^{-3.9 \times 10^{-3}(t/s)} - e^{-4.4 \times 10^{-5}(t/s)}) \\ &= (120 \text{ Pa}) \times (e^{-4.4 \times 10^{-5}(t/s)} - e^{-3.9 \times 10^{-3}(t/s)}) \end{aligned}$$

$$(a) \quad t = 1 \text{ h}, \quad p = (120 \text{ Pa}) \times (e^{-0.16} - e^{-14}) = \boxed{100 \text{ Pa}}$$

$$(b) \quad t = 10 \text{ h}, \quad p = (120 \text{ Pa}) \times (e^{-1.6} - e^{140}) = \boxed{24 \text{ Pa}}$$

$$\text{P21.8} \quad \kappa \propto \frac{1}{R} \text{ [21.27, and the discussion above 21.27]}$$

Because both solutions are aqueous their conductivities include a contribution of 76 mS m^{-1} from the water. Therefore,

$$\frac{\kappa(\text{acid soln})}{\kappa(\text{KCl soln})} = \frac{\kappa(\text{acid}) + \kappa(\text{water})}{\kappa(\text{KCl}) + \kappa(\text{water})} = \frac{R(\text{KCl soln})}{R(\text{acid soln})} = \frac{33.21 \Omega}{300.0 \Omega}$$

$$\text{Hence, } \kappa(\text{acid}) = \{\kappa(\text{KCl}) + \kappa(\text{water})\} \times \left(\frac{33.21}{300.0}\right) - \kappa(\text{water}) = 53 \text{ mS m}^{-1}$$

$$\Lambda_m = \frac{\kappa}{c} = \frac{53 \text{ mS m}^{-1}}{1.00 \times 10^5 \text{ mol m}^{-3}} = \boxed{5.3 \times 10^{-4} \text{ mS m}^2 \text{ mol}^{-1}}$$

$$\text{P21.10} \quad c = \frac{\kappa}{\Lambda_m} \text{ [21.28]} \approx \frac{\kappa}{\Lambda_m^\circ} \text{ [} c \text{ small, conductivity of water allowed for in the data]}$$

$$c \approx \frac{1.887 \times 10^{-6} \text{ S cm}^{-1}}{138.3 \text{ S cm}^2 \text{ mol}^{-1}} \text{ [Exercise 21.25(a)]}$$

$$\approx 1.36 \times 10^{-8} \text{ mol cm}^{-3} = \text{solubility} = \boxed{1.36 \times 10^{-5} \text{ M}}$$

$$\text{P21.12} \quad t(\text{H}^+) = \frac{u(\text{H}^+)}{u(\text{H}^+) + u(\text{Cl}^-)} \text{ [21.49b]} = \frac{3.623}{3.623 + 0.791} = \boxed{0.82}$$

When a third ion is present we use

$$t(\text{H}^+) = \frac{I(\text{H}^+)}{I(\text{H}^+) + I(\text{Na}^+) + I(\text{Cl}^-)} \text{ [21.47]}$$

For each I , $I = z u v c F A E = \text{constant} \times c u$. Hence, when NaCl is added

$$\begin{aligned} t(\text{H}^+) &= \frac{c(\text{H}^+) u(\text{H}^+)}{c(\text{H}^+) u(\text{H}^+) + c(\text{Na}^+) u(\text{Na}^+) + c(\text{Cl}^-) u(\text{Cl}^-)} \\ &= \frac{(1.0 \times 10^{-3}) \times (3.623)}{(1.0 \times 10^{-3}) \times (3.623) + (1.0) \times (0.519) + (1.001) \times (0.791)} = \boxed{0.0028} \end{aligned}$$

$$\text{P21.14} \quad t_+ = \left(\frac{z c A F}{I}\right) \times \left(\frac{x}{\Delta t}\right) \text{ [Problem 21.13]}$$

The density of the solution is 0.682 g cm^{-3} ; the concentration c is related to the molality m by

$$c/(\text{mol dm}^{-3}) = \rho/(\text{kg dm}^{-3}) \times m/(\text{mol kg}^{-1})$$

which holds for dilute solutions such as these.

$$A = \pi r^2 = \pi \times (2.073 \times 10^{-3} \text{ m})^2 = 1.350 \times 10^{-5} \text{ m}^2$$

$$\begin{aligned}\frac{czAF}{I\Delta t} &= \frac{(1.350 \times 10^{-5} \text{ m}^2) \times (9.6485 \times 10^4 \text{ C mol}^{-1})}{(5.000 \times 10^{-3} \text{ A}) \times (2500 \text{ s})} \times c = (0.1042 \text{ m}^2 \text{ mol}^{-1}) \times c \\ &= (0.1042 \text{ m}^2 \text{ mol}^{-1}) \times \rho \times m = (0.1042 \text{ m}^2 \text{ mol}^{-1}) \times (682 \text{ kg m}^{-3}) \times m \\ &= (71.06 \text{ kg m}^{-1} \text{ mol}^{-1}) \times m = (0.07106 \text{ kg mm}^{-1} \text{ mol}^{-1}) \times m\end{aligned}$$

$$\text{and so } t_+ = (0.07106 \text{ kg mm}^{-1} \text{ mol}^{-1}) \times x \times m$$

$$\text{In the first solution } t_+ = (0.07106 \text{ kg mm}^{-1} \text{ mol}^{-1}) \times (286.9 \text{ mm}) \times (0.01365 \text{ mol kg}^{-1}) = \boxed{0.278}$$

$$\text{In the second solution } t_+ = (0.07106 \text{ kg mm}^{-1} \text{ mol}^{-1}) \times (92.03 \text{ mm}) \times (0.04255 \text{ mol kg}^{-1}) = \boxed{0.278}$$

Therefore, $t(\text{H}^+) = 0.28$, a value much less than in pure water where $t(\text{H}^+) = 0.63$. Hence, the mobility is much less relative to its counter ion, NH_2^- .

P21.16

$$D = \frac{uRT}{zF} [21.63] \quad \text{and} \quad a = \frac{ze}{6\pi\eta u} [21.43]$$

$$D = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K}) \times u}{9.6485 \times 10^4 \text{ C mol}^{-1}} = 2.569 \times 10^{-2} \text{ V} \times u$$

$$\text{so } D/(\text{cm}^2 \text{ s}^{-1}) = (2.569 \times 10^{-2}) \times u/(\text{cm}^2 \text{ s}^{-1} \text{ V}^{-1})$$

$$\begin{aligned}a &= \frac{1.602 \times 10^{-19} \text{ C}}{(6\pi) \times (0.891 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}) \times u} \\ &= \frac{9.54 \times 10^{-18} \text{ C kg}^{-1} \text{ ms}}{u} = \frac{9.54 \times 10^{-18} \text{ V}^{-1} \text{ m}^3 \text{ s}^{-1}}{u} \quad (1 \text{ J} = 1 \text{ C V}, 1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2})\end{aligned}$$

$$\text{and so } a/m = \frac{9.54 \times 10^{-14}}{u/\text{cm}^2 \text{ s}^{-1} \text{ V}^{-1}}$$

$$\text{and therefore } a/\text{pm} = \frac{9.54 \times 10^{-2}}{u/\text{cm}^2 \text{ s}^{-1} \text{ V}^{-1}}$$

We can now draw up the following table using data from Table 21.6

	Li^+	Na^+	K^+	Rb^+
$10^4 u/(\text{cm}^2 \text{ s}^{-1} \text{ V}^{-1})$	4.01	5.19	7.62	7.92
$10^5 D/\text{cm}^2$	1.03	1.33	1.96	2.04
a/pm	238	184	125	120

The ionic radii themselves (i.e. their crystallographic radii) are

	Li^+	Na^+	K^+	Rb^+
r_+/pm	59	102	138	149

and it would seem that K^+ and Rb^+ have effective hydrodynamic radii that are smaller than their ionic radii. The effective hydrodynamic and ionic volumes of Li^+ and Na^+ are $(4\pi/3)\pi a^3$ and $(4\pi/3)\pi r_+^3$ respectively, and so the volumes occupied by hydrating water molecules are

$$(a) \quad Li^+ \Delta V = (4\pi/3) \times (212^3 - 59^3) \times 10^{-36} m^3 = 5.56 \times 10^{-29} m^3$$

$$(b) \quad Na^+ \Delta V = (4\pi/3) \times (164^3 - 102^3) \times 10^{-36} m^3 = 2.16 \times 10^{-29} m^3$$

The volume occupied by a single H_2O molecule is approximately $(4\pi/3) \times (150 pm)^3 = 1.4 \times 10^{-29} m^3$.

Therefore, Li^+ has about four firmly attached H_2O molecules whereas Na^+ has only one to two (according to this analysis).

P21.18 This is essentially one-dimensional diffusion and therefore eqn 21.72 applies.

$$c = \frac{n_0 e^{-x^2/4Dt}}{A(\pi Dt)^{1/2}} \quad [21.72]$$

and we know that $n_0 = \left(\frac{10 g}{342 g mol^{-1}} \right) = 0.0292 mol$

$$A = \pi R^2 = 19.6 cm^2, \quad D = 5.21 \times 10^{-6} cm^2 s^{-1} \quad [Table 21.8]$$

$$\begin{aligned} A(\pi Dt)^{1/2} &= (19.6 cm^2) \times [(\pi) \times (5.21 \times 10^{-6} cm^2 s^{-1}) \times (t)]^{1/2} \\ &= 7.93 \times 10^{-2} cm^3 \times (t/s)^{1/2} \end{aligned}$$

$$\frac{x^2}{4Dt} = \frac{25 cm^2}{(4) \times (5.21 \times 10^{-6} cm^2 s^{-1}) \times t} = \frac{1.20 \times 10^6}{(t/s)}$$

$$\begin{aligned} \text{Therefore, } c &= \left(\frac{0.0292 mol \times 10^{22}}{(7.93 \times 10^{-2} cm^3) \times (t/s)^{1/2}} \right) \times e^{-1.20 \times 10^6 / (t/s)} \\ &= (369 M) \times \left(\frac{e^{-1.20 \times 10^6 / (t/s)}}{(t/s)^{1/2}} \right) \end{aligned}$$

$$(a) \quad t = 10 s, \quad c = (369 M) \times \left(\frac{e^{-1.2 \times 10^5}}{10^{1/2}} \right) \approx \boxed{0}$$

$$(b) \quad t = 1 yr = 3.16 \times 10^7 s, \quad c = (369 M) \times \left(\frac{e^{-0.038}}{(3.16 \times 10^7)^{1/2}} \right) = \boxed{0.063 M}$$

COMMENT. This problem illustrates the extreme slowness of diffusion through typical macroscopic distances; however, it is rapid enough through distances comparable to the dimensions of a cell. Compare to Problem 21.40.

P21.20 Kohlrausch's law states that the molar conductance of a strong electrolyte varies with the square root of concentration

$$\Lambda_m = \Lambda_m^\circ - Kc^{1/2}$$

Therefore a plot of Λ_m versus $c^{1/2}$ should be a straight line with y-intercept Λ_m° . The data and plot (Figure 21.1) are shown below

NaI			KI		
$c/(\text{mol dm}^{-3})$	$c^{1/2}$	$\Lambda_m/(\text{S cm}^2 \text{mol}^{-1})$	$c/(\text{mol dm}^{-3})$	$c^{1/2}$	$\Lambda_m/(\text{S cm}^2 \text{mol}^{-1})$
32.02	5.659	50.26	17.68	4.205	42.45
20.28	4.503	51.99	10.88	3.298	45.91
12.06	3.473	54.01	7.19	2.68	47.53
8.64	2.94	55.75	2.67	1.63	51.81
2.85	1.69	57.99	1.28	1.13	54.09
1.24	1.11	58.44	0.83	0.91	55.78
0.83	0.91	58.67	0.19	0.44	57.42

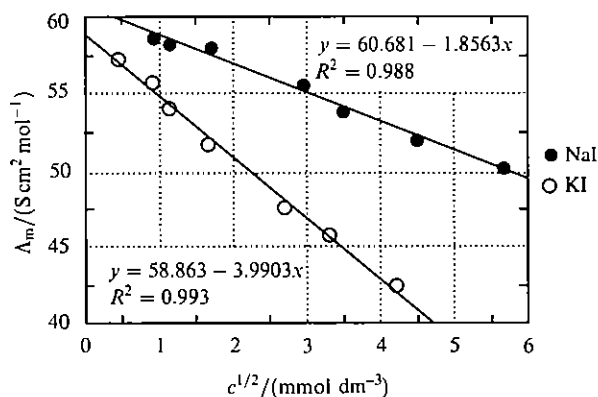


Figure 21.1

Thus $\Lambda_m^\circ(\text{NaI}) = 60.7 \text{ S cm}^2 \text{mol}^{-1}$ and $\Lambda_m^\circ(\text{KI}) = 58.9 \text{ S cm}^2 \text{mol}^{-1}$

Since these two electrolytes have a common anion, the difference in conductances is due to the cations

$$\lambda^\circ(\text{Na}^+) - \lambda^\circ(\text{K}^+) = \Lambda_m^\circ(\text{NaI}) - \Lambda_m^\circ(\text{KI}) = 1.8 \text{ S cm}^2 \text{mol}^{-1}$$

The analogous quantities in water are

$$\Lambda_m^\circ(\text{NaI}) = \lambda(\text{Na}^+) + \lambda(\text{I}^-) = (73.50 + 76.8) \text{ S cm}^2 \text{mol}^{-1} = 126.9 \text{ S cm}^2 \text{mol}^{-1}$$

$$\Lambda_m^\circ(\text{KI}) = \lambda(\text{K}^+) + \lambda(\text{I}^-) = (73.50 + 76.8) \text{ S cm}^2 \text{mol}^{-1} = 150.3 \text{ S cm}^2 \text{mol}^{-1}$$

$$\lambda^\circ(\text{Na}^+) - \lambda^\circ(\text{K}^+) = (50.10 - 73.50) \text{ S cm}^2 \text{mol}^{-1} = -23.4 \text{ S cm}^2 \text{mol}^{-1}$$

The ions are considerably more mobile in water than in this solvent. Also, the differences between Na^+ and K^+ are minimized and even inverted compared to water.

- P21.22** The diffusion constant of an ion in solution is related to the mobility of the ion and to its radius in separate relations

$$D = \frac{uRT}{zF} = \frac{kT}{6\pi\eta a} \quad \text{so} \quad a = \frac{zFk}{6\pi\eta uR} = \frac{ze}{6\pi\eta u}$$

$$a = \frac{(1) \times (1.602 \times 10^{-19} \text{ C})}{6\pi (0.93 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}) \times (1.1 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1})} = 8.3 \times 10^{-10} \text{ m} = \boxed{8.30 \text{ pm}}$$

Solutions to theoretical problems

- P21.24** We proceed as in Section 21.1(a) except that, instead of taking a product of three one-dimensional distributions in order to get the three-dimensional distribution, we make a product of two one-dimensional distributions.

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

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

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

The mean speed is determined as $\bar{c} = \int_0^\infty v f(v) dv = \int_0^\infty m/(kT) v^2 e^{-mv^2/2kT} dv$.

Using standard integrals this evaluates to $\boxed{\bar{c} = (\pi kT/2m)^{1/2} = (\pi RT/2M)^{1/2}}$.

COMMENT. The two-dimensional gas serves as a model of the motion of molecules of surfaces. See Chapter 24.

- P21.26** Rewriting eqn 21.4 with $(M/R) = (m/k)$

$$f(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT}$$

The proportion of molecules with speeds less than c is

$$P = \int_0^c f(v) dv = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^c v^2 e^{-mv^2/2kT} dv$$

Defining $a \equiv \frac{m}{2kT}$

$$P = 4\pi \left(\frac{a}{\pi}\right)^{3/2} \int_0^c v^2 e^{-av^2} dv = -4\pi \left(\frac{a}{\pi}\right)^{3/2} \frac{d}{da} \int_0^c e^{-av^2} dv$$

Defining $x^2 \equiv av^2$, $dv = a^{-1/2} dx$

$$\begin{aligned} P &= -4\pi \left(\frac{a}{\pi}\right)^{3/2} \frac{d}{da} \left\{ \frac{1}{a^{1/2}} \int_0^{ca^{1/2}} e^{-x^2} dx \right\} \\ &= -4\pi \left(\frac{a}{\pi}\right)^{3/2} \left\{ -\frac{1}{2} \left(\frac{1}{a}\right)^{3/2} \int_0^{ca^{1/2}} e^{-x^2} dx + \left(\frac{1}{a}\right)^{1/2} \frac{d}{da} \int_0^{ca^{1/2}} e^{-x^2} dx \right\} \end{aligned}$$

Then we use $\int_0^{ca^{1/2}} e^{-x^2} dx = \left(\pi^{1/2}/2\right) \operatorname{erf}(ca^{1/2})$

$$\frac{d}{da} \int_0^{ca^{1/2}} e^{-x^2} dx = \left(\frac{dca^{1/2}}{da}\right) \times (e^{-c^2a}) = \frac{1}{2} \left(\frac{c}{a^{1/2}}\right) e^{-c^2a}$$

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

Substituting and cancelling we obtain $P = \operatorname{erf}(ca^{1/2}) - (2ca^{1/2}/\pi^{1/2}) e^{-c^2a}$

Now, $c = (3kT/m)^{1/2}$, so $ca^{1/2} = (3kT/m)^{1/2} \times (m/2kT)^{1/2} = (3/2)^{1/2}$, and

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

Therefore (b) 61 percent of the molecules have a speed less than the root mean square speed and (a) 39 percent have a speed greater than the root mean square speed. (c) For the proportions in terms of the mean speed \bar{c} , replace c by $\bar{c} = (8kT/\pi m)^{1/2} = (8/3\pi)^{1/2} c$, so $\bar{c}a^{1/2} = 2/\pi^{1/2}$.

Then $P = \operatorname{erf}(\bar{c}a^{1/2}) - (2\bar{c}a^{1/2}/\pi^{1/2}) \times (e^{-\bar{c}^2a}) = \operatorname{erf}(2/\pi^{1/2}) - (4/\pi)e^{-4/\pi} = 0.889 - 0.356 = \boxed{0.533}$

That is, 53 percent of the molecules have a speed less than the mean, and 47 percent have a speed greater than the mean.

P21.28 An effusion oven has constant volume, fixed temperature, and effusion hole of area A . Gas escapes through the hole, which makes the effusion rate negative.

$$-\frac{dN}{dt} = Z_w A = \frac{pA N_A}{(2\pi MRT)^{1/2}} \quad [21.16]$$

For a perfect gas, $pV = nRT = NRT/N_A$ and, therefore, $N = N_A pV/RT$.

Differentiation gives $\frac{dN}{dt} = \frac{N_A V}{RT} \frac{dp}{dt}$. Substitution into the first equation yields:

$$\frac{N_A V}{RT} \frac{dp}{dt} = -\frac{pAN_A}{(2\pi MRT)^{1/2}}$$

$$\frac{dp}{dt} = -\left(\frac{RT}{2\pi M}\right)^{1/2} \frac{A}{V} p = -\frac{p}{\tau} \quad \text{where the time constant is } \tau = \left(\frac{2\pi M}{RT}\right)^{1/2} \frac{V}{A}$$

$$\frac{dp}{p} = -\frac{dt}{\tau}$$

$$\int_{p_0}^p \frac{dp}{p} = -\frac{1}{\tau} \int_0^t dt$$

$$\ln\left(\frac{p}{p_0}\right) = -\frac{t}{\tau} \quad \text{or} \quad p = p_0 e^{-t/\tau}$$

When $t = t_{1/2}$, $p = (1/2)p_0$. Substitution into the above equation gives

$$\ln\left(\frac{p_0}{2p_0}\right) = -\frac{t_{1/2}}{\tau} \quad \text{or} \quad t_{1/2} = \tau \ln(2) = \left(\frac{2\pi M}{RT}\right)^{1/2} \frac{V}{A} \ln(2)$$

The final equation indicates that the half-life for effusive loss is independent of p_0 . Furthermore, the half-life increases with both the V/A and $M^{1/2}$ factors. It decreases with the factor $T^{-1/2}$.

P21.30

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad [21.68] \quad \text{with } c = \frac{n_0 e^{-x^2/4Dt}}{A(\pi Dt)^{1/2}} \quad [21.72]$$

$$\text{or } c = \frac{a}{t^{1/2}} e^{-bx^2/t}$$

$$\text{then } \frac{\partial c}{\partial t} = -\left(\frac{1}{2}\right) \times \left(\frac{a}{t^{3/2}}\right) e^{-bx^2/t} + \left(\frac{a}{t^{1/2}}\right) \times \left(\frac{bx^2}{t^2}\right) e^{-bx^2/t} = -\frac{c}{2t} + \frac{bx^2}{t^2} c$$

$$\frac{\partial c}{\partial x} = \left(\frac{a}{t^{1/2}}\right) \times \left(\frac{-2bx}{t}\right) e^{-bx^2/t}$$

$$\frac{\partial^2 c}{\partial x^2} = -\left(\frac{2b}{t}\right) \times \left(\frac{a}{t^{1/2}}\right) e^{-bx^2/t} + \left(\frac{a}{t^{1/2}}\right) \times \left(\frac{2bx}{t}\right)^2 e^{-bx^2/t} = -\left(\frac{2b}{t}\right) c + \left(\frac{2bx}{t}\right)^2 c$$

$$= -\left(\frac{1}{2Dt}\right) c + \left(\frac{bx^2}{Dt^2}\right) c$$

$$= \frac{1}{D} \frac{\partial c}{\partial t} \text{ as required}$$

Initially the material is concentrated at $x = 0$. Note that $c = 0$ for $x > 0$ when $t = 0$ on account of the very strong exponential factor ($e^{-bx^2/t} \rightarrow 0$ more strongly than $1/t^{1/2} \rightarrow \infty$)

When $x = 0$, $e^{-x^2/4Dt} = 1$. We confirm the correct behavior by noting that $\langle x \rangle = 0$ and $\langle x^2 \rangle = 0$ at $t = 0$ [21.82], and so all the material must be at $x = 0$ at $t = 0$.

P21.32 Draw up the following table based on the third and last equations of *Justification 21.11*

N	4	6	8	10	20	30	40	60	100
$P(6\lambda)_{\text{Exact}}$	0	0.016	0.0313	0.0439	0.0739	0.0806	0.0807	0.0763	0.0666
$P(6\lambda)_{\text{Approx.}}$	0.004	0.162	0.0297	0.0417	0.0725	0.0799	0.0804	0.0763	0.0666

The points are plotted in Figure 21.2.

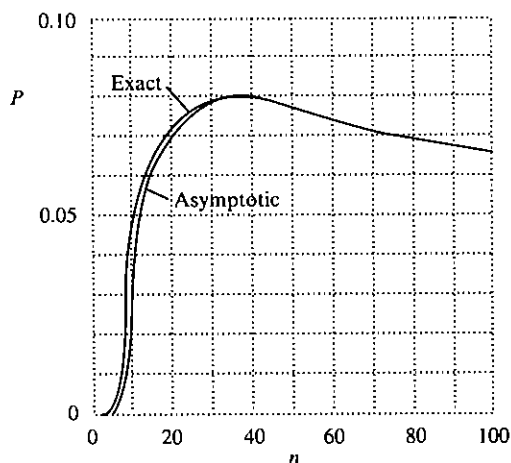


Figure 21.2

The discrepancy is less than 0.1 percent when $N > 60$

P21.34 $AB \rightleftharpoons A^+ + B^-$; $\gamma_{AB} \simeq 1$, because AB interacts weakly with ions.

$$K = \frac{a_{A^+} a_{B^-}}{a_{AB}} = \left(\frac{\gamma_{A^+} \gamma_{B^-}}{\gamma_{AB}} \right) \times \left(\frac{c_{A^+} c_{B^-}}{c_{AB}} \right)$$

$$K = \gamma_{\pm}^2 \left[\frac{(\alpha c)(\alpha c)}{(1 - \alpha)c} \right] = \gamma_{\pm}^2 \left(\frac{\alpha^2 c}{1 - \alpha} \right) \quad \text{or} \quad \frac{\gamma_{\pm}^2 c}{K} = \frac{1 - \alpha}{\alpha^2}$$

$$\Lambda_m = \frac{\kappa}{c} = \frac{(\lambda_+ + \lambda_-)c_{\text{ion}}}{c} = \frac{(\lambda_+ + \lambda_-)\alpha c}{c} = (\lambda_+ + \lambda_-)\alpha$$

Let $\Lambda_m^\circ = \lambda_+ + \lambda_-$ be the molar conductivity when the solution is infinitely dilute and $\alpha = 1$ (eqn 21.30). Then, $\alpha = \Lambda_m / (\lambda_+ + \lambda_-) = \Lambda_m / \Lambda_m^\circ$. Substitution into equilibrium expression gives:

$$K = \gamma_{\pm}^2 c \left(\frac{\Lambda_m}{\Lambda_m^\circ} \right)^2 \left(\frac{1}{1 - \frac{\Lambda_m}{\Lambda_m^\circ}} \right)$$

$$1 - \frac{\Lambda_m}{\Lambda_m^\circ} = \left(\frac{\Lambda_m}{\Lambda_m^\circ} \right)^2 \frac{\gamma_{\pm}^2 c}{K} = \left(\frac{\Lambda_m}{\Lambda_m^\circ} \right)^2 \left(\frac{1 - \alpha}{\alpha^2} \right)$$

Division by Λ_m gives:

$$\frac{1}{\Lambda_m} - \frac{1}{\Lambda_m^\circ} = \left(\frac{1-\alpha}{\alpha^2} \right) \frac{\Lambda_m}{(\Lambda_m^\circ)^2}$$

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^\circ} + \left(\frac{1-\alpha}{\alpha^2} \right) \frac{\Lambda_m}{(\Lambda_m^\circ)^2}$$

Solutions to application

P21.36 The diffusion coefficient for a perfect gas is

$$D = \frac{1}{3} \lambda \bar{c} \quad \text{where } \lambda = (2^{1/2} \sigma \mathcal{N})^{-1} \quad \text{where } \mathcal{N} \text{ is number density.}$$

The mean speed is

$$\bar{c} = \left(\frac{8kT}{\pi m} \right)^{1/2} = \left(\frac{8(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (10^4 \text{ K})}{\pi (1 \text{ u}) \times (1.66 \times 10^{-27} \text{ kg u}^{-1})} \right)^{1/2} = 1.46 \times 10^4 \text{ m s}^{-1}$$

$$\text{So } D = \frac{\bar{c}}{3\sigma \mathcal{N} 2^{1/2}} = \frac{1.46 \times 10^4 \text{ m s}^{-1}}{3(0.21 \times 10^{-18} \text{ m}^2) \times (1 \times (10^{-2} \text{ m})^{-3}) 2^{1/2}} = \boxed{1.6 \times 10^{16} \text{ m}^2 \text{ s}^{-1}}$$

The thermal conductivity is

$$\kappa = \frac{\bar{c} C_{V,m}}{3\sigma N_A 2^{1/2}} = \frac{(1.46 \times 10^4 \text{ m s}^{-1}) \times (20.784 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}}{3(0.21 \times 10^{-18} \text{ m}^2) \times (6.022 \times 10^{23} \text{ mol}^{-1}) 2^{1/2}}$$

$$k = \boxed{0.34 \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1}}$$

COMMENT. The validity of these calculations is in doubt because the kinetic theory of gases assumes the Maxwell-Boltzmann distribution, essentially an equilibrium distribution. In such a dilute medium, the timescales on which particles exchange energy by collision make an assumption of equilibrium unwarranted. It is especially dubious considering that atoms are more likely to interact with photons from stellar radiation than with other atoms.

P21.38 Concentration of ^1H nuclei, $[^1\text{H}] = \frac{n_{\text{H}}}{V} = \frac{(\text{mass percentage}) \times (\text{density})}{100(\text{molar mass})}$

$$= \frac{0.36(158 \text{ g cm}^{-3})}{1.0 \text{ g mol}^{-1}}$$

$$= 57 \text{ mol cm}^{-3}$$

Concentration ^4He nuclei, $[^4\text{He}] = \frac{n_{\text{He}}}{V} = \frac{(\text{mass percentage}) \times (\text{density})}{100(\text{molar mass})}$

$$= \frac{0.64(158 \text{ g cm}^{-3})}{4.0 \text{ g mol}^{-1}}$$

$$= 25 \text{ mol cm}^{-3}$$

$$\text{Concentration of } e^- = [^1\text{H}] + 2[^4\text{He}] = (57 + 2 \times 25) \text{ mol cm}^{-3} = 107 \text{ mol cm}^{-3}$$

Total concentration of gaseous particles = $(57 + 25 + 107) \text{ mol cm}^{-3} = 189 \text{ mol cm}^{-3}$

$$r_{\text{H nucleus}} = (1.4 \times 10^{-13} \text{ cm})(1)^{1/3} = 1.4 \times 10^{-13} \text{ cm}$$

$$r_{\text{He nucleus}} = (1.4 \times 10^{-13} \text{ cm})(4)^{1/3} = 2.2 \times 10^{-13} \text{ cm}$$

- (a) The excluded volume of a nuclear collisional pair is estimated to be equal to the volume of the dashed sphere in Figure 21.3. The excluded volume of a single nucleus is 1/2 of this.

$$b \approx (N_A) \times \left(\frac{1}{2}\right) \times \left[\frac{4\pi}{3}(2r)^3\right] = \frac{16\pi}{3} N_A r^3$$

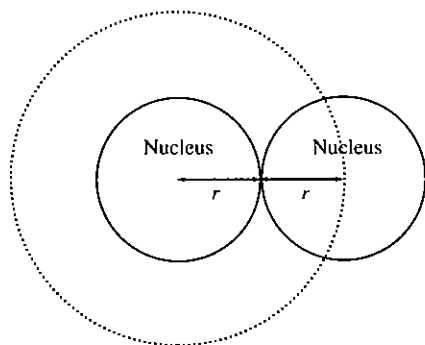


Figure 21.3

In this problem we have a mixture of hydrogen and helium nuclei so let us take r to equal the weighted average of hydrogen and helium radii. This is, of course, a very simple estimate. Then

$$r \approx 0.36(1.4 \times 10^{-13} \text{ cm}) + 0.64(2.2 \times 10^{-13} \text{ cm})$$

$$r \approx 1.9 \times 10^{-13} \text{ cm}$$

$$b \approx \frac{16\pi}{3} (6.022 \times 10^{23} \text{ mol}^{-1}) \times (1.9 \times 10^{-13} \text{ cm})^3$$

$$b \approx 7.1 \times 10^{-14} \text{ cm}^3 \text{ mol}^{-1}$$

$$b(\text{per cm}^3) \approx 82 \text{ mol} \times 7.1 \times 10^{-14} \text{ cm}^3 \text{ mol}^{-1}$$

$$\approx 5.8 \times 10^{-12} \text{ cm}^3$$

This b is extraordinarily small compared to 1 cm^3 , so we may treat the nuclei as points within any macroscopic volume. In the sense that the nuclei act as volumeless points, the perfect gas law would seem to be applicable. However, our analysis has not included details of the internuclear forces and these may be appreciably larger than the hard-sphere model estimate.

- (b) $T_{\text{perfect}} = \frac{pV}{nR}$, where n = total number of moles of gaseous particles including the number of moles of electrons

$$= \frac{p}{\left(\frac{n}{V}\right) R}$$

$$= \frac{(2.5 \times 10^{11} \text{ atm}) \times (1 \text{ dm}^3 / 10^3 \text{ cm}^3)}{(189 \text{ mol cm}^{-3}) \times (0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1})} = 1.6 \times 10^7 \text{ K} = T_{\text{perfect}}$$

$$\begin{aligned}
 \text{(c)} \quad T_{\text{vanderWaals}} &= \frac{V_m - b}{R} \left(p + \frac{a}{V_m^2} \right) \\
 &= \frac{p(V_m - b)}{R} \text{ assuming } \alpha \approx 0 \\
 &= \frac{p}{R} \left(\frac{V}{n} - b \right) = \frac{p}{R} \left\{ \left(\frac{1}{\frac{n_{\text{total}}}{V}} \right) - b \right\} \\
 &= \left(\frac{2.5 \times 10^{11} \text{ atm}}{0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}} \right) \\
 &\quad \times \left\{ \frac{1}{189 \text{ mol cm}^{-3}} - 7.1 \times 10^{-14} \text{ cm}^3 \text{ mol}^{-1} \right\} \\
 &= T_{\text{perfect}} - \frac{(7.1 \times 10^{-14} \text{ cm}^3 \text{ mol}^{-1}) \times (2.5 \times 10^{11} \text{ atm})}{(0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1})}
 \end{aligned}$$

where the last term is negligible. Therefore

$$T_{\text{vanderWaals}} = T_{\text{perfect}}$$

P21.40 The mean square displacement is (from Exercise 21.28(b))

$$\langle r^2 \rangle = 6Dt \quad \text{so} \quad t = \frac{\langle r^2 \rangle}{6D} = \frac{(1.0 \times 10^{-6} \text{ m})^2}{6(1.0 \times 10^{-11} \text{ m}^2 \text{ s}^{-1})} = \boxed{1.7 \times 10^{-2} \text{ s}}$$

22

The rates of chemical reactions

Answers to discussion questions

D22.2 No solution.

D22.4 The overall reaction order is the sum of the powers of the concentrations of all of the substances appearing in the *experimental* rate law for the reaction (eqn 22.7); hence, it is the sum of the individual orders (exponents) associated with a given reactant (or product). Reaction order is an experimentally determined, *not theoretical*, quantity, although theory may attempt to predict it. *Molecularity* is the number of reactant molecules participating in an elementary reaction. This concept has meaning only for an elementary reaction, but reaction order applies to any reaction. In general, reaction order bears no necessary relation to the stoichiometry of the reaction, with the exception of elementary reactions, where the order of the reaction corresponds to the number of molecules participating in the reaction; that is, to its molecularity. Thus for an elementary reaction, overall order and molecularity are the same and are determined by the stoichiometry.

D22.6 The steady-state approximation is the assumption that the rate of change of the concentrations of intermediates in consecutive chemical reactions is negligibly small. It is a good approximation when at least one of the reaction steps involving the intermediate is very fast, that is, has a large rate constant relative to other steps. See Section 22.7(b). A pre-equilibrium approximation is similar in that it is a good approximation when the rate of formation of the intermediate from the reactants and the rate of its reversible decay back to the reactants are both very fast in comparison to the rate of formation of the product from the intermediate. This results in the intermediate being in approximate equilibrium with the reactants over relatively long time periods (though short compared to the overall time scale of the reaction). Hence the concentration of the intermediate remains approximately constant over the time period that the equilibrium can be considered to be maintained. This allows one to relate the rate constants and concentrations to each other through a constant (the pre-equilibrium constant). See Section 22.7(e).

D22.8 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

$$E_a = RT^2 \left(\frac{d \ln k}{dT} \right) \quad [22.30]$$

This definition reduces to the earlier one (as the slope of a straight line) for a temperature-independent activation energy. However, this latter definition is more general, because it allows E_a to be obtained from the slope (at the temperature of interest) of a plot of $\ln k$ against $1/T$ even if the Arrhenius plot is not a straight line. Non-Arrhenius behavior is sometimes a sign that quantum mechanical tunnelling is playing a significant role in the reaction.

- D22.10** The expression $k = k_a k_b [A] / (k_b + k'_a [A])$ for the effective rate constant of a unimolecular reaction $A \rightarrow P$ is based on the validity of the assumption of the existence of the pre-equilibrium $A + A \xrightleftharpoons[k'_a]{k_a} A^* + A$. 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

$$\frac{1}{k} = \frac{k'_a}{k_a k_b} + \frac{1}{k_a [A]}$$

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.

Solutions to exercises

E22.1(b) $\nu = -\frac{d[A]}{dt} = -\frac{1}{3} \frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{1}{2} \frac{d[D]}{dt} = 1.00 \text{ mol dm}^{-3} \text{ s}^{-1}$, so

Rate of consumption of A = $1.0 \text{ mol dm}^{-3} \text{ s}^{-1}$

Rate of consumption of B = $3.0 \text{ mol dm}^{-3} \text{ s}^{-1}$

Rate of formation of C = $1.0 \text{ mol dm}^{-3} \text{ s}^{-1}$

Rate of formation of D = $2.0 \text{ mol dm}^{-3} \text{ s}^{-1}$

E22.2(b) Rate of consumption of B = $-\frac{d[B]}{dt} = 1.00 \text{ mol dm}^{-3} \text{ s}^{-1}$

Rate of reaction = $-\frac{1}{3} \frac{d[B]}{dt} = 0.33 \text{ mol dm}^{-3} \text{ s}^{-1} = \frac{d[C]}{dt} = \frac{1}{2} \frac{d[D]}{dt} = -\frac{d[A]}{dt}$

Rate of formation of C = $0.33 \text{ mol dm}^{-3} \text{ s}^{-1}$

Rate of formation of D = $0.66 \text{ mol dm}^{-3} \text{ s}^{-1}$

Rate of consumption of A = $0.33 \text{ mol dm}^{-3} \text{ s}^{-1}$

E22.3(b) The dimensions of k are

$$\frac{\text{dim of } \nu}{(\text{dim of } [A]) \times (\text{dim of } [B])^2} = \frac{\text{amount} \times \text{length}^{-3} \times \text{time}^{-1}}{(\text{amount} \times \text{length}^{-3})^3} \\ = \text{length}^6 \times \text{amount}^{-2} \times \text{time}^{-1}$$

In mol, dm, s units, the units of k are $\boxed{\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}}$

(a) $\nu = -\frac{d[A]}{dt} = k[A][B]^2$ so $\boxed{\frac{d[A]}{dt} = -k[A][B]^2}$

(b) $\nu = \frac{d[C]}{dt}$ so $\boxed{\frac{d[C]}{dt} = -k[A][B]^2}$

E22.4(b) The dimensions of k are

$$\frac{\text{dim of } \nu}{\text{dim of } [A] \times \text{dim of } [B] \times (\text{dim of } [C])^{-1}} = \frac{\text{amount} \times \text{length}^{-3} \times \text{time}^{-1}}{\text{amount} \times \text{length}^{-3}} = \text{time}^{-1}$$

The units of k are $\boxed{\text{s}^{-1}}$

$$\nu = \frac{d[C]}{dt} = \boxed{k[A][B][C]^{-1}}$$

E22.5(b) The rate law is

$$\nu = k[A]^a \propto p^a = \{p_0(1-f)\}^a$$

where a is the reaction order, and f the fraction reacted (so that $1-f$ is the fraction remaining). Thus

$$\frac{\nu_1}{\nu_2} = \frac{\{p_0(1-f_1)\}^a}{\{p_0(1-f_2)\}^a} = \left(\frac{1-f_1}{1-f_2}\right)^a \quad \text{and} \quad a = \frac{\ln(\nu_1/\nu_2)}{\ln\left(\frac{1-f_1}{1-f_2}\right)} = \frac{\ln(9.71/7.67)}{\ln\left(\frac{1-0.100}{1-0.200}\right)} = \boxed{2.00}$$

E22.6(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 22.3. 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 $\boxed{0}$.

E22.7(b) The rate law is

$$\nu = -\frac{1}{2} \frac{d[A]}{dt} = k[A]$$

The half-life formula in eqn 22.13 is based on the assumption that

$$-\frac{d[A]}{dt} = k[A].$$

That is, it would be accurate to take the half-life from the table and say

$$t_{1/2} = \frac{\ln 2}{k'}$$

where $k' = 2k$. Thus

$$t_{1/2} = \frac{\ln 2}{2(2.78 \times 10^{-7} \text{ s}^{-1})} = \boxed{1.80 \times 10^6 \text{ s}}$$

Likewise, we modify the integrated rate law (eqn 22.12b), noting that pressure is proportional to concentration:

$$p = p_0 e^{-2kt}$$

(a) Therefore, after 10 h, we have

$$p = (32.1 \text{ kPa}) \exp[-2 \times (2.78 \times 10^{-7} \text{ s}^{-1}) \times (3.6 \times 10^4 \text{ s})] = \boxed{31.5 \text{ kPa}}$$

(b) After 50 h,

$$p = (32.1 \text{ kPa}) \exp[-2 \times (2.78 \times 10^{-7} \text{ s}^{-1}) \times (1.8 \times 10^5 \text{ s})] = \boxed{29.0 \text{ kPa}}$$

E22.8(b) From Table 22.3, we see that for $A + 2B \rightarrow P$ the integrated rate law is

$$kt = \frac{1}{[B]_0 - 2[A]_0} \ln \left[\frac{[A]_0([B]_0 - 2[P])}{([A]_0 - [P])[B]_0} \right]$$

(a) Substituting the data after solving for k

$$\begin{aligned} k &= \frac{1}{(3.6 \times 10^3 \text{ s}) \times (0.080 - 2 \times 0.075) \times (\text{mol dm}^{-3})} \times \ln \left[\frac{(0.075 \times (0.080 - 0.060))}{(0.075 - 0.030) \times 0.080} \right] \\ &= \boxed{3.47 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}} \end{aligned}$$

(b) The half-life in terms of A is the time when $[A] = [A]_0/2 = [P]$, so

$$t_{1/2}(A) = \frac{1}{k([B]_0 - 2[A]_0)} \ln \left[\frac{[A]_0([B]_0 - (2[A]_0/2))}{([A]_0[B]_0/2)} \right]$$

which reduces to

$$\begin{aligned} t_{1/2}(A) &= \frac{1}{k([B]_0 - 2[A]_0)} \ln \left(2 - \frac{2[A]_0}{[B]_0} \right) \\ &= \frac{1}{(3.47 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \times (-0.070 \text{ mol dm}^{-3})} \times \ln \left(2 - \frac{0.150}{0.080} \right) \\ &= 8561 \text{ s} = \boxed{2.4 \text{ h}} \end{aligned}$$

The half-life in terms of B is the time when $[B] = [B]_0/2$ and $[P] = [B]_0/4$:

$$t_{1/2}(B) = \frac{1}{k([B]_0 - 2[A]_0)} \ln \left[\frac{[A]_0 \left([B]_0 - \frac{[B]_0}{2} \right)}{\left([A]_0 - \frac{[B]_0}{4} \right) [B]_0} \right]$$

which reduces to

$$\begin{aligned} t_{1/2}(B) &= \frac{1}{k([B]_0 - 2[A]_0)} \ln \left(\frac{[A]_0/2}{[A]_0 - [B]_0/4} \right) \\ &= \frac{1}{(3.47 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \times (-0.070 \text{ mol dm}^{-3})} \times \ln \left(\frac{0.075/2}{0.075 - (0.080/4)} \right) \\ &= 1576 \text{ s} = \boxed{0.44 \text{ h}} \end{aligned}$$

E22.9(b) (a) The dimensions of a second-order constant are

$$\frac{\text{dim of } \nu}{(\text{dim of } [A])^2} = \frac{\text{amount} \times \text{length}^{-3} \times \text{time}^{-1}}{(\text{amount} \times \text{length}^{-3})^2} = \text{length}^3 \times \text{amount}^{-1} \times \text{time}^{-1}$$

In molecule, m, s units, the units of k are $\boxed{\text{m}^3 \text{ molecule}^{-1} \text{ s}^{-1}}$

The dimensions of a third-order rate constant are

$$\frac{\text{dim of } \nu}{(\text{dim of } [A])^3} = \frac{\text{amount} \times \text{length}^{-3} \times \text{time}^{-1}}{(\text{amount} \times \text{length}^{-3})^3} = \text{length}^6 \times \text{amount}^{-2} \times \text{time}^{-1}$$

In molecule, m, s units, the units of k are $\boxed{\text{m}^6 \text{ molecule}^{-2} \text{ s}^{-1}}$

COMMENT. Technically, "molecule" is not a unit, so a number of molecules is simply a number of individual objects, that is, a pure number. In the chemical kinetics literature, it is common to see rate constants given in molecular units reported in units of $\text{m}^3 \text{ s}^{-1}$, $\text{m}^6 \text{ s}^{-1}$, $\text{cm}^3 \text{ s}^{-1}$, etc.

(b) The dimensions of a second-order rate constant in pressure units are

$$\frac{\text{dim of } \nu}{(\text{dim of } p)^2} = \frac{\text{pressure} \times \text{time}^{-1}}{(\text{pressure})^2} = \text{pressure}^{-1} \times \text{time}^{-1}$$

In SI units, the pressure unit is $\text{N m}^{-2} = \text{Pa}$, so the units of k are $\boxed{\text{Pa}^{-1} \text{ s}^{-1}}$

The dimensions of a third-order rate constant in pressure units are

$$\frac{\text{dim of } \nu}{(\text{dim of } p)^3} = \frac{\text{pressure} \times \text{time}^{-1}}{(\text{pressure})^3} = \text{pressure}^{-2} \times \text{time}^{-1}$$

In SI pressure units, the units of k are $\boxed{\text{Pa}^{-2} \text{ s}^{-1}}$.

E22.10(b) The integrated rate law is

$$kt = \frac{1}{[B]_0 - 2[A]_0} \ln \frac{[A]_0([B]_0 - 2[C])}{([A]_0 - [C])[B]_0} \quad [\text{Table 22.3}]$$

Solving for [C] yields, after some rearranging

$$[C] = \frac{[A]_0[B]_0(\exp[kt([B]_0 - 2[A]_0)] - 1)}{[B]_0 \exp[kt([B]_0 - 2[A]_0)] - 2[A]_0}$$

$$\text{so } \frac{[C]}{\text{mol dm}^{-3}} = \frac{(0.025) \times (0.150) \times (e^{0.21 \times (0.100) \times t/s} - 1)}{(0.150) \times e^{0.21 \times (0.100) \times t/s} - 2 \times (0.025)} = \frac{(3.75 \times 10^{-3}) \times (e^{0.021 \times t/s} - 1)}{(0.150) \times e^{0.021 \times t/s} - (0.050)}$$

$$(a) \quad [C] = \frac{(3.75 \times 10^{-3}) \times (e^{0.21} - 1)}{(0.150) \times e^{0.21} - (0.050)} \text{ mol dm}^{-3} = \boxed{6.5 \times 10^{-3} \text{ mol dm}^{-3}}$$

$$(b) \quad [C] = \frac{(3.75 \times 10^{-3}) \times (e^{12.6} - 1)}{(0.150) \times e^{12.6} - (0.050)} \text{ mol dm}^{-3} = \boxed{0.025 \text{ mol dm}^{-3}}$$

E22.11(b) The rate law is

$$v = -\frac{1}{2} \frac{d[A]}{dt} = k[A]^3$$

which integrates to

$$2kt = \frac{1}{2} \left(\frac{1}{[A]^2} - \frac{1}{[A]_0^2} \right) \quad \text{so} \quad t = \frac{1}{4k} \left(\frac{1}{[A]^2} - \frac{1}{[A]_0^2} \right),$$

$$t = \left(\frac{1}{4(3.50 \times 10^{-4} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1})} \right) \times \left(\frac{1}{(0.021 \text{ mol dm}^{-3})^2} - \frac{1}{(0.077 \text{ mol dm}^{-3})^2} \right) \\ = \boxed{1.5 \times 10^6 \text{ s}}$$

E22.12(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 $[A] = [A]_0/3$,

$$\text{so } -kt_{1/3} = \frac{(\frac{1}{3}[A]_0)^{1-n} - [A]_0^{1-n}}{1-n} = \frac{[A]_0^{1-n}[(\frac{1}{3})^{1-n} - 1]}{1-n}$$

$$\text{and } t_{1/3} = \boxed{\frac{3^{n-1} - 1}{k(n-1)} [A]_0^{1-n}}$$

E22.13(b) The equilibrium constant of the reaction is the ratio of rate constants of the forward and reverse reactions:

$$K = \frac{k_f}{k_r} \quad \text{so} \quad k_f = Kk_r.$$

The relaxation time for the temperature jump is (Example 22.4):

$$\tau = \{k_f + k_r([B] + [C])\}^{-1} \quad \text{so} \quad k_f = \tau^{-1} - k_r([B] + [C])$$

Setting these two expressions for k_r equal yields

$$Kk_r = \tau^{-1} - k_r([B] + [C]) \quad \text{so} \quad k_r = \frac{1}{\tau(K + [B] + [C])}$$

Hence

$$\begin{aligned} k_r &= \frac{1}{(3.0 \times 10^{-6} \text{ s}) \times (2.0 \times 10^{-16} + 2.0 \times 10^{-4} + 2.0 \times 10^{-4}) \text{ mol dm}^{-3}} \\ &= \boxed{8.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}} \end{aligned}$$

$$\text{and } k_r = (2.0 \times 10^{-16} \text{ mol dm}^{-3}) \times (8.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = \boxed{1.7 \times 10^{-7} \text{ s}^{-1}}$$

E22.14(b) The rate constant is given by

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad [22.31]$$

so at 24 °C it is

$$1.70 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = A \exp\left(\frac{-E_a}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times [(24 + 273) \text{ K}]}\right)$$

and at 37 °C it is

$$2.01 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = A \exp\left(\frac{-E_a}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times [(37 + 273) \text{ K}]}\right)$$

Dividing the two rate constants yields

$$\frac{1.70 \times 10^{-2}}{2.01 \times 10^{-2}} = \exp\left[\left(\frac{-E_a}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{297 \text{ K}} - \frac{1}{310 \text{ K}}\right)\right]$$

$$\text{so } \ln\left(\frac{1.70 \times 10^{-2}}{2.01 \times 10^{-2}}\right) = \left(\frac{-E_a}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{297 \text{ K}} - \frac{1}{310 \text{ K}}\right)$$

$$\text{and } E_a = -\left(\frac{1}{297 \text{ K}} - \frac{1}{310 \text{ K}}\right)^{-1} \ln\left(\frac{1.70 \times 10^{-2}}{2.01 \times 10^{-2}}\right) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$= 9.9 \times 10^3 \text{ J mol}^{-1} = \boxed{9.9 \text{ kJ mol}^{-1}}$$

With the activation energy in hand, the prefactor can be computed from either rate constant value

$$\begin{aligned} A &= k \exp\left(\frac{E_a}{RT}\right) = (1.70 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \times \exp\left(\frac{9.9 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (297 \text{ K})}\right) \\ &= \boxed{0.94 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}} \end{aligned}$$

E22.15(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

$$\frac{k_T}{k_H} = e^{-\lambda}, \quad \text{where } \lambda = \left(\frac{\hbar k_f^{1/2}}{2k_B T}\right) \times \left(\frac{1}{\mu_{CH}^{1/2}} - \frac{1}{\mu_{CD}^{1/2}}\right) \quad [22.53 \text{ with } \hbar c \tilde{\nu} = \hbar \omega = \hbar(k/\mu)^{1/2}]$$

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

$$\begin{aligned}\lambda &\approx \frac{(1.0546 \times 10^{-34} \text{ J s}) \times (450 \text{ N m}^{-1})^{1/2}}{2 \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})} \\ &\quad \times \left(\frac{1}{(1 \text{ u})^{1/2}} - \frac{1}{(3 \text{ u})^{1/2}} \right) \times (1.66 \times 10^{-27} \text{ kg u}^{-1})^{-1/2} \\ &\approx 2.8\end{aligned}$$

$$\text{so } \frac{k_{\text{T}}}{k_{\text{H}}} \approx e^{-2.8} = \boxed{0.06 \approx 1/16}$$

- (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 rather widely depending on the size of the whole molecule, but in no case will they be terribly different for the two isotopes. Take ^{12}CO , for example:

$$\mu_{16} = \frac{(16.0 \text{ u}) \times (12.0 \text{ u})}{(16.0 + 12.0) \text{ u}} = 6.86 \text{ u} \quad \text{and} \quad \mu_{18} = \frac{(18.0 \text{ u}) \times (12.0 \text{ u})}{(18.0 + 12.0) \text{ u}} = 7.20 \text{ u}$$

$$\begin{aligned}\lambda &= \frac{(1.0546 \times 10^{-34} \text{ J s}) \times (1750 \text{ N m}^{-1})^{1/2}}{2 \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})} \\ &\quad \times \left(\frac{1}{(6.86 \text{ u})^{1/2}} - \frac{1}{(7.20 \text{ u})^{1/2}} \right) \times (1.66 \times 10^{-27} \text{ kg u}^{-1})^{-1/2} \\ &= 0.12\end{aligned}$$

$$\text{so } \frac{k_{18}}{k_{16}} = e^{-0.12} = \boxed{0.89}$$

At the other extreme, the O atoms could be attached to heavy fragments such that the effective mass of the relevant vibration approximates the mass of the oxygen isotope. That is, $\mu_{16} \approx 16 \text{ u}$ and $\mu_{18} \approx 18 \text{ u}$

$$\text{so } \lambda \approx 0.19 \quad \text{so } \frac{k_{18}}{k_{16}} = e^{-0.19} = \boxed{0.83}$$

E22.16(b) $\frac{1}{k} = \frac{k'_a}{k_a k_b} + \frac{1}{k_a p_A}$ [analogous to 22.67]

Therefore, for two different pressures we have

$$\frac{1}{k} - \frac{1}{k'} = \frac{1}{k_a} \left(\frac{1}{p} - \frac{1}{p'} \right),$$

$$\begin{aligned}\text{so } k_a &= \left(\frac{1}{p} - \frac{1}{p'} \right) \left(\frac{1}{k} - \frac{1}{k'} \right)^{-1} \\ &= \left(\frac{1}{1.09 \times 10^3 \text{ Pa}} - \frac{1}{25 \text{ Pa}} \right) \times \left(\frac{1}{1.7 \times 10^{-3} \text{ s}^{-1}} - \frac{1}{2.2 \times 10^{-4} \text{ s}^{-1}} \right)^{-1} \\ &= \boxed{9.9 \times 10^{-6} \text{ s}^{-1} \text{ Pa}^{-1}} = \boxed{9.9 \text{ s}^{-1} \text{ MPa}^{-1}}\end{aligned}$$

Solutions to problems

Solutions to numerical problems

P22.2 The procedure is that described in solution to Problem 22.1. 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 22.12b:

$$\ln \left(\frac{[A]}{[A]_0} \right) = -kt$$

As in Example 22.3 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 ($A = (\text{CH}_3)_3\text{CBr}$)

t/h	0	3.15	6.20	10.00	18.30	30.80
$[A]/(10^{-2}\text{mol dm}^{-3})$	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
$\left(\frac{1}{[A]} \right) / (\text{dm}^3 \text{mol}^{-1})$	9.62	11.16	12.89	15.65	28.3	48.3

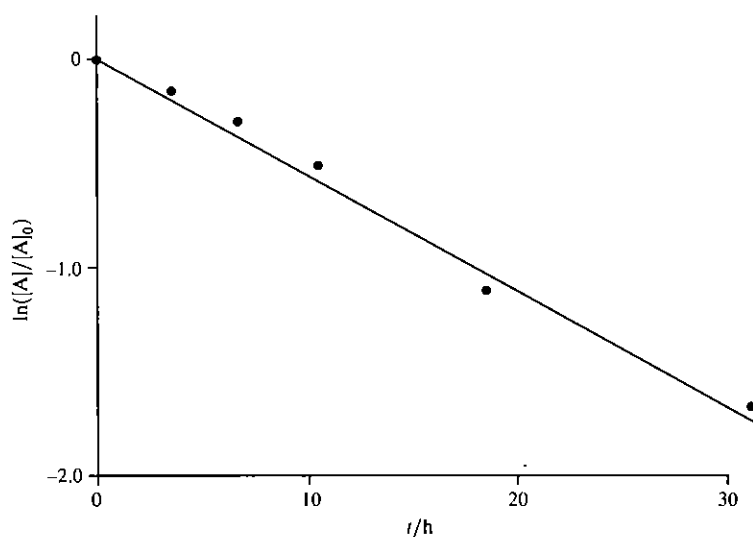


Figure 22.1

The data are plotted in Figure 22.1. The fit to a straight line is only fair, but the deviations look more like experimental scatter than systematic curvature. The correlation coefficient is 0.996. If we try to fit the data to eqn 22.15b, which corresponds to a second-order reaction, the fit is not as good; that correlation coefficient is 0.985. Thus we conclude that the reaction is most likely first-order. A non-integer order, neither first nor second, is also possible.

The rate constant k is the negative of the slope of the first-order plot:

$$k = 0.0542 \text{ h}^{-1} = \boxed{1.51 \times 10^{-5} \text{ s}^{-1}}$$

At 43.8 h

$$\ln \left(\frac{[A]}{[A]_0} \right) = -(0.0542 \text{ h}^{-1}) \times (43.8 \text{ h}) = -2.359$$

$$[A] = (10.39 \times 10^{-2} \text{ mol dm}^{-3}) \times e^{-2.359} = \boxed{9.82 \times 10^{-3} \text{ mol dm}^{-3}}$$

P22.4

Examination of the data shows that the half-life remains constant at about 2 minutes. Therefore, the reaction is **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.

$$\ln \left(\frac{[A]}{[A]_0} \right) = -kt \quad [22.12b, A = \text{N}_2\text{O}_5]$$

Solving for k ,

$$k = \frac{\ln ([A]_0/[A])}{t}$$

At $t = 1.00 \text{ min}$, $[A] = 0.705 \text{ mol dm}^{-3}$ and

$$k = \frac{\ln (1.000/0.705)}{1.00 \text{ min}} = 0.350 \text{ min}^{-1} = 5.83 \times 10^{-3} \text{ s}^{-1}$$

At $t = 3.00 \text{ min}$, $[A] = 0.399 \text{ mol dm}^{-3}$ and

$$k = \frac{\ln (1.000/0.349)}{3.00 \text{ min}} = 0.351 \text{ min}^{-1} = 5.85 \times 10^{-3} \text{ s}^{-1}$$

Values of k may be determined in a similar manner at all other times. The average value of k obtained is $\boxed{5.84 \times 10^{-3} \text{ s}^{-1}}$. The constancy of k , which varies only between 5.83 and $5.85 \times 10^{-3} \text{ s}^{-1}$ confirms that the reaction is **first order**. A linear regression of $\ln[A]$ against t yields the same result. The half-life is (eqn 22.13)

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{5.84 \times 10^{-3} \text{ s}^{-1}} = 118.7 \text{ s} = \boxed{1.98 \text{ min}}$$

P22.6

Since both reactions are first-order, we have

$$-\frac{d[A]}{dt} = k_1[A] + k_2[A] = (k_1 + k_2)[A]$$

so $[A] = [A]_0 e^{-(k_1+k_2)t}$ [22.12b with $k = k_1 + k_2$]

We are interested in the yield of ketene, CH_2CO ; call it K:

$$\frac{d[\text{K}]}{dt} = k_2[\text{A}] = k_2[\text{A}]_0 e^{-(k_1+k_2)t}$$

Integrating yields

$$\int_0^{[\text{K}]} d[\text{K}] = k_2[\text{A}]_0 \int_0^t e^{-(k_1+k_2)t'} dt'$$

$$[\text{K}] = \frac{k_2[\text{A}]_0}{k_1 + k_2} (1 - e^{-(k_1+k_2)t}) = \frac{k_2}{k_1 + k_2} ([\text{A}]_0 - [\text{A}])$$

The percent yield is the amount of K produced compared to complete conversion; since the stoichiometry of reaction (2) is one-to-one, we can write:

$$\% \text{ yield} = \frac{[\text{K}]}{[\text{A}]_0} \times 100\% = \frac{k_2}{k_1 + k_2} (1 - e^{-(k_1+k_2)t}) \times 100\%,$$

which has its maximum value when the reaction reaches completion

$$\max \% \text{ yield} = \frac{k_2}{k_1 + k_2} \times 100\% = \frac{4.65 \text{ s}^{-1}}{(3.74 + 4.65) \text{ s}^{-1}} \times 100\% = \boxed{55.4\%}$$

COMMENT. If we are interested in yield of the desired product (ketene) compared to the products of side reactions (products of reaction 1), it makes sense to define the conversion ratio, the ratio of desired product formed to starting material *reacted*, namely

$$\frac{[\text{K}]}{[\text{A}]_0 - [\text{A}]}$$

which works out in this case to be independent of time

$$\frac{[\text{K}]}{[\text{A}]_0 - [\text{A}]} = \frac{k_2}{k_1 + k_2}$$

If a substance reacts by parallel processes of the same order, then the ratio of the amounts of products will be constant and independent of the extent of the reaction, no matter what the order.

Question. Can you demonstrate the truth of the statement made in the above comment?

P22.8

The stoichiometry of the reaction relates product and reaction concentrations as follows:

$$[\text{A}] = [\text{A}]_0 - 2[\text{B}]$$

When the reaction goes to completion, $[\text{B}] = [\text{A}]_0/2$; hence $[\text{A}]_0 = 0.624 \text{ mol dm}^{-3}$. We can therefore tabulate $[\text{A}]$, and examine its half-life. 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 (in Figure 22.2), using

$$\ln \frac{[\text{A}]_0}{[\text{A}]} = k_A t$$

which follows from

$$\frac{d[A]}{dt} = -k_A[A]$$

t/s	0	600	1200	1800	2400
$[B]/(\text{mol dm}^{-3})$	0	0.089	0.153	0.200	0.230
$[A]/(\text{mol dm}^{-3})$	0.624	0.446	0.318	0.224	0.164
$\ln \frac{[A]_0}{[A]}$	0	0.34	0.67	1.02	1.34

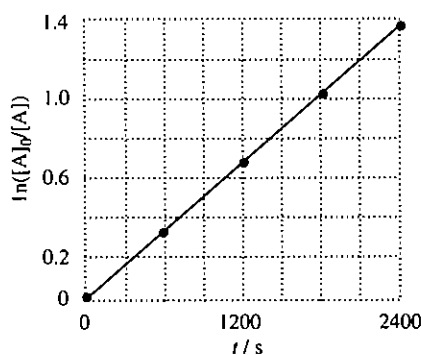


Figure 22.2

The points lie on a straight line, which confirms **first-order** kinetics. Since the slope of the line is 5.6×10^{-4} , we conclude that $k_A = 5.6 \times 10^{-4} \text{ s}^{-1}$. To express the rate law in the form $v = k[A]$ we note that

$$v = -\frac{1}{2} \frac{d[A]}{dt} = -\left(\frac{1}{2}\right) \times (-k_A[A]) = \frac{1}{2} k_A[A]$$

and hence $k = \frac{1}{2} k_A = \boxed{2.8 \times 10^{-4} \text{ s}^{-1}}$

P22.10 If the reaction is first-order the concentrations obey

$$\ln \left(\frac{[A]}{[A]_0} \right) = -kt \quad [22.12b]$$

and, since pressures and concentrations of gases are proportional, the pressures should obey

$$\ln \frac{p_0}{p} = kt$$

and $\frac{1}{t} \ln \frac{p_0}{p}$ should be a constant. We test this by drawing up the following table

p_0/Torr	200	200	400	400	600	600
t/s	100	200	100	200	100	200
p/Torr	186	173	373	347	559	520
$10^4 \left(\frac{1}{t/s} \right) \ln \frac{p_0}{p}$	7.3	7.3	7.0	7.1	7.1	7.2

The values in the last row of the table are virtually constant, and so (in the pressure range spanned by the data) the reaction has **first-order kinetics** with $k = 7.2 \times 10^{-4} \text{ s}^{-1}$

P22.12 Using spreadsheet software to evaluate eqn 22.40, one can draw up a plot like that in Figure 22.3. 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 $k_2 = 1 \text{ s}^{-1}$ for all curves and k_1 varies. The thickest curve, labeled 10, corresponds to $k_2 = 10 \text{ s}^{-1}$, 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 **steady-state approximation**, which becomes more and more valid as consumption of the intermediate becomes fast compared with its formation.

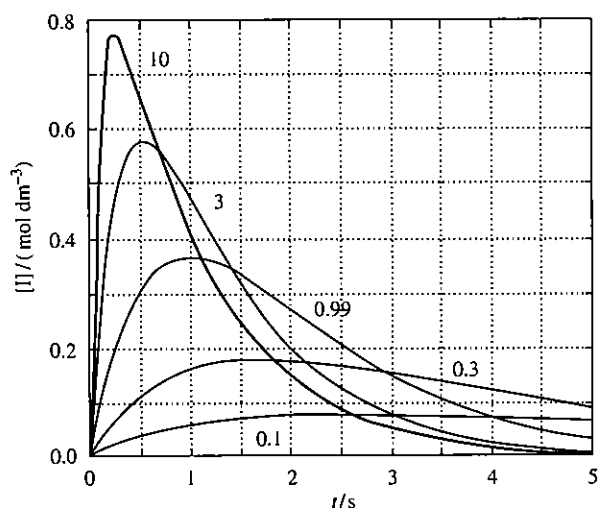


Figure 22.3

P22.14 (a) First, find an expression for the relaxation time, using Example 22.4 as a model:

$$\frac{d[A]}{dt} = -2k_a[A]^2 + 2k_b[A_2]$$

Rewrite the expression in terms of a difference from equilibrium values, $[A] = [A]_{\text{eq}} + x$:

$$\begin{aligned} \frac{d[A]}{dt} &= \frac{d([A]_{\text{eq}} + x)}{dt} = \frac{dx}{dt} = -2k_a([A]_{\text{eq}} + x)^2 + 2k_b([A_2]_{\text{eq}} - \frac{1}{2}x) \\ \frac{dx}{dt} &= -2k_a[A]_{\text{eq}}^2 - 4k_a[A]_{\text{eq}}x - 2k_ax^2 + 2k_b[A_2]_{\text{eq}} - k_bx \approx -(4k_a[A]_{\text{eq}} + k_b)x \end{aligned}$$

Neglect powers of x greater than x^1 , and use the fact that at equilibrium the forward and reverse rates are equal:

$$k_a[A]_{\text{eq}}^2 = k_b[A_2]_{\text{eq}}$$

to obtain

$$\frac{dx}{dt} \approx -(4k_a[A]_{\text{eq}} + k_b)x \quad \text{so} \quad \frac{1}{\tau} \approx 4k_a[A]_{\text{eq}} + k_b$$

To get the desired expression, square the reciprocal relaxation time,

$$\frac{1}{\tau^2} \approx 16k_a^2[A]_{\text{eq}}^2 + 8k_a k_b[A]_{\text{eq}} + k_b^2 \quad (*)$$

introduce $[A]_{\text{tot}} = [A]_{\text{eq}} + 2[A_2]_{\text{eq}}$ into the middle term,

$$\begin{aligned} \frac{1}{\tau^2} &\approx 16k_a^2[A]_{\text{eq}}^2 + 8k_a k_b([A]_{\text{tot}} - 2[A_2]_{\text{eq}}) + k_b^2 \\ &\approx 16k_a^2[A]_{\text{eq}}^2 + 8k_a k_b[A]_{\text{tot}} - 16k_a k_b[A_2]_{\text{eq}} + k_b^2 = \boxed{8k_a k_b[A]_{\text{tot}} + k_b^2} \end{aligned}$$

and use the equilibrium condition again to see that the remaining equilibrium concentrations cancel each other.

COMMENT. Introducing $[A]_{\text{tot}}$ into just one term of eqn * above is a permissible step, but not a very systematic one. It is worth trying because of the resemblance between eqn * and the desired expression: we would be finished if we could get $[A]_{\text{tot}}$ into the middle term and somehow get the first term to disappear! A more systematic but messier approach would be to express $[A]_{\text{eq}}$ in terms of the desired $[A]_{\text{tot}}$ by using the equilibrium condition and $[A]_{\text{tot}} = [A]_{\text{eq}} + 2[A_2]_{\text{eq}}$: solve both of those equations for $[A_2]_{\text{eq}}$, set the two resulting expressions equal to each other, solve for $[A]_{\text{eq}}$ in terms of the desired $[A]_{\text{tot}}$, and substitute **that** expression for $[A]_{\text{eq}}$ everywhere in eqn *.

(b) Plot $\frac{1}{\tau^2}$ vs. $[A]_{\text{tot}}$. The resulting curve should be a straight line whose y-intercept is k_b^2 and whose slope is $8k_a k_b$.

(c) Draw up the following table:

$[A]_{\text{tot}}/(\text{mol dm}^{-3})$	0.500	0.352	0.251	0.151	0.101
τ/ns	2.3	2.7	3.3	4.0	5.3
$1/(\tau/\text{ns})^2$	0.189	0.137	0.092	0.062	0.036

The plot is shown in Figure 22.4.

The y-intercept is 0.0003 ns^{-2} and the slope is $0.38 \text{ ns}^{-2} \text{ dm}^3 \text{ mol}^{-1}$, so

$$k_b = \{3 \times 10^{-4} \times (10^{-9} \text{ s})^{-2}\}^{1/2} = (3 \times 10^{14} \text{ s}^{-2})^{1/2} = \boxed{1.7 \times 10^7 \text{ s}^{-1}}$$

$$\text{and } k_a = \frac{0.38 \times (10^{-9} \text{ s})^{-2} \text{ dm}^3 \text{ mol}^{-1}}{8 \times (1.7 \times 10^7 \text{ s}^{-1})} = \boxed{2.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

$$K = \frac{k_a/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}{k_b/\text{s}^{-1}} = \frac{2.7 \times 10^9}{1.7 \times 10^7} = \boxed{1.6 \times 10^2}$$

COMMENT. The data define a good straight line, as the correlation coefficient $R^2 = 0.996$ shows. That straight line appears to go through the origin, but the best-fit equation gives a small non-zero y-intercept. Inspection of the plot shows that several of the data points lie about as far from the fit line as the y-intercept does from zero. This suggests that y-intercept has a fairly high relative uncertainty, and so do the rate constants.

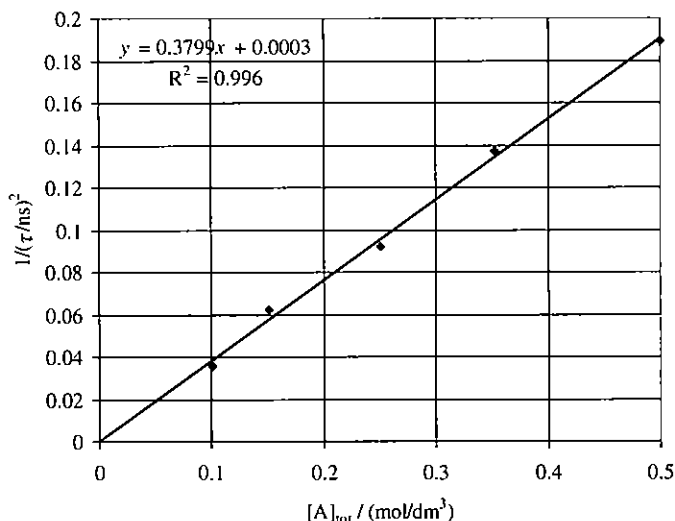


Figure 22.4

P22.16 Apply the equation derived in P22.5 to the rate constant data in pairs

$$E_a = \frac{-R \ln(k/k')}{((1/T) - (1/T'))}$$

T/K	300.3	300.3	341.2
T'/K	341.2	392.2	392.2
$10^{-7} k/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	1.44	1.44	3.03
$10^{-7} k'/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	3.03	6.9	6.9
$E_a/(\text{kJ mol}^{-1})$	15.5	16.7	18.0

The mean is 16.7 kJ mol^{-1} . Compute A from each rate constant, using the mean E_a and $A = ke^{E_a/RT}$.

T/K	300.3	341.2	392.2
$10^{-7} k/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	1.44	3.03	6.9
E_a/RT	6.69	5.89	5.12
$10^{-10} A/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	1.16	1.10	1.16

The mean is $1.14 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

P22.18 The relation between the equilibrium constant and the rate constants is obtained from

$$\Delta_r G^\ominus = -RT \ln K = \Delta_r H^\ominus - T \Delta_r S^\ominus \quad \text{and} \quad K = \frac{k}{k'}$$

$$\text{So } K = \frac{k}{k'} = \exp\left(\frac{-\Delta_r H^\ominus}{RT}\right) \exp\left(\frac{\Delta_r S^\ominus}{R}\right) = \left(\frac{A}{A'}\right) \exp\left(\frac{E'_a - E_a}{RT}\right)$$

Setting the temperature-dependent parts equal yields

$$\Delta_r H^\circ = E_a - E'_a = [-4.2 - (53.3)] \text{ kJ mol}^{-1} = -57.5 \text{ kJ mol}^{-1}$$

Setting the temperature-independent parts equal yields

$$\exp\left(\frac{\Delta_r S^\circ}{R}\right) = \left(\frac{A}{A'}\right)$$

$$\text{so } \Delta_r S^\circ = R \ln\left(\frac{A}{A'}\right) = (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln\left(\frac{1.0 \times 10^9}{1.4 \times 10^{11}}\right) = -41.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

The thermodynamic quantities of the reaction are related to standard molar quantities

$$\Delta_r H^\circ = \Delta_f H^\circ(\text{C}_2\text{H}_6) + \Delta_f H^\circ(\text{Br}) - \Delta_f H^\circ(\text{C}_2\text{H}_5) - \Delta_f H^\circ(\text{HBr})$$

$$\text{so } \Delta_f H^\circ(\text{C}_2\text{H}_5) = \Delta_f H^\circ(\text{C}_2\text{H}_6) + \Delta_f H^\circ(\text{Br}) - \Delta_f H^\circ(\text{HBr}) - \Delta_r H^\circ$$

$$\text{and } \Delta_f H^\circ(\text{C}_2\text{H}_5) = [(-84.68) + 111.88 - (-36.40) - (-57.5)] \text{ kJ mol}^{-1} = \boxed{121.2 \text{ kJ mol}^{-1}}$$

Similarly

$$S_m^\circ(\text{C}_2\text{H}_5) = [229.60 + 175.02 - 198.70 - (-41.1)] \text{ J mol}^{-1} \text{ K}^{-1} = \boxed{247.0 \text{ J K}^{-1} \text{ mol}^{-1}}$$

Finally

$$\begin{aligned} \Delta_r G^\circ(\text{C}_2\text{H}_5) &= [-32.82 + 82.396 - (-53.45)] \text{ kJ mol}^{-1} - \Delta_r G^\circ \\ &= 103.03 \text{ kJ mol}^{-1} - \Delta_r G^\circ \end{aligned}$$

but

$$\begin{aligned} \Delta_r G^\circ &= \Delta_r H^\circ - T \Delta_r S^\circ = -57.5 \text{ kJ mol}^{-1} - (298 \text{ K}) \times (-41.1 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \\ &= -45.3 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{so } \Delta_r G^\circ(\text{C}_2\text{H}_5) = [103.03 - (-45.3)] \text{ kJ mol}^{-1} = \boxed{148.3 \text{ kJ mol}^{-1}}$$

Solutions to theoretical problems

P22.20 We assume a pre-equilibrium (as the initial step is fast), and write

$$K = \frac{[\text{A}]^2}{[\text{A}_2]}, \quad \text{implying that } [\text{A}] = K^{1/2}[\text{A}_2]^{1/2}$$

The rate-determining step then gives

$$v = \frac{d[\text{P}]}{dt} = k_2[\text{A}][\text{B}] = \boxed{k_2 K^{1/2} [\text{A}_2]^{1/2} [\text{B}]} = k_{\text{eff}} [\text{A}_2]^{1/2} [\text{B}]$$

where $k_{\text{eff}} = k_2 K^{1/2}$.

P22.22
$$v = \frac{d[P]}{dt} = k[A][B]$$

Let the initial concentrations be $[A]_0 = A_0$, $[B]_0 = B_0$, and $[P]_0 = 0$. Then, when P is formed in concentration x , the concentration of A changes to $A_0 - 2x$ and that of B changes to $B_0 - 3x$. Therefore

$$\begin{aligned}\frac{d[P]}{dt} &= \frac{dx}{dt} = k(A_0 - 2x)(B_0 - 3x) \quad \text{with } x = 0 \text{ at } t = 0. \\ \int_0^t k \, dt &= \int_0^x \frac{dx}{(A_0 - 2x)(B_0 - 3x)} \\ &= \int_0^x \left(\frac{6}{2B_0 - 3A_0} \right) \times \left(\frac{1}{3(A_0 - 2x)} - \frac{1}{2(B_0 - 3x)} \right) dx \\ &= \left(\frac{-1}{2B_0 - 3A_0} \right) \times \left(\int_0^x \frac{dx}{x - (1/2)A_0} - \int_0^x \frac{dx}{x - (1/3)B_0} \right) \\ kt &= \left(\frac{-1}{(2B_0 - 3A_0)} \right) \times \left[\ln \left(\frac{x - \frac{1}{2}A_0}{-\frac{1}{2}A_0} \right) - \ln \left(\frac{x - \frac{1}{3}B_0}{-\frac{1}{3}B_0} \right) \right] \\ &= \left(\frac{-1}{2B_0 - 3A_0} \right) \ln \left(\frac{(2x - A_0)B_0}{A_0(3x - B_0)} \right) \\ &= \boxed{\left(\frac{1}{(3A_0 - 2B_0)} \right) \ln \left(\frac{(2x - A_0)B_0}{A_0(3x - B_0)} \right)}\end{aligned}$$

P22.24 The rate equations are

$$\begin{aligned}\frac{d[A]}{dt} &= -k_a[A] + k'_a[B] \\ \frac{d[B]}{dt} &= k_a[A] - k'_a[B] - k_b[B] + k'_b[C] \\ \frac{d[C]}{dt} &= k_b[B] - k'_b[C]\end{aligned}$$

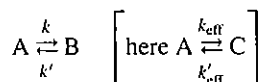
These equations are a set of coupled differential equations and, though it is not immediately apparent, they do admit of an analytical general solution. However, we are looking for specific circumstances under which the mechanism reduces to the second form given. Since the reaction involves an intermediate, let us explore the result of applying the steady-state approximation to it. Then

$$\frac{d[B]}{dt} = k_a[A] - k'_a[B] - k_b[B] + k'_b[C] = 0$$

$$\text{and } [B] = \frac{k_a[A] + k'_b[C]}{k'_a + k_b}$$

$$\text{Therefore, } \frac{d[A]}{dt} = -\frac{k_a k_b}{k'_a + k_b}[A] + \frac{k'_a k'_b}{k'_a + k_b}[C]$$

This rate expression may be compared to that given in the text [Section 22.4] for the mechanism



$$\text{Hence, } k_{\text{eff}} = \frac{k_a k_b}{k'_a + k_b} \quad k'_{\text{eff}} = \frac{k'_a k'_b}{k'_a + k_b}$$

$$\text{The solutions are } [A] = \left(\frac{k'_{\text{eff}} + k_{\text{eff}} e^{-(k'_{\text{eff}} + k_{\text{eff}})t}}{k'_{\text{eff}} + k_{\text{eff}}} \right) \times [A]_0 \quad [22.23]$$

$$\text{and } [C] = [A]_0 - [A]$$

Thus, the conditions under which the first mechanism given reduces to the second are the conditions under which the steady-state approximation holds, namely, when B can be treated as a steady-state intermediate.

P22.26 Let the forward rates be written as

$$r_1 = k_1[A], \quad r_2 = k_2[B], \quad r_3 = k_3[C]$$

and the reverse rates as

$$r'_1 = k'_1[B], \quad r'_2 = k'_2[C], \quad r'_3 = k'_3[D]$$

The net rates are then

$$R_1 = k_1[A] - k'_1[B], \quad R_2 = k_2[B] - k'_2[C], \quad R_3 = k_3[C] - k'_3[D]$$

But $[A] = [A]_0$ and $[D] = 0$, so that the steady-state equations for the net rates of the individual steps are

$$k_1[A]_0 - k'_1[B] = k_2[B] - k'_2[C] = k_3[C]$$

From the second of these equations we find

$$[C] = \frac{k_2[B]}{k'_2 + k_3}$$

After inserting this expression for $[C]$ into the first of the steady-state equations we obtain

$$[B] = \frac{k_1[A]_0 + k'_2[C]}{k'_1 + k_2} = \frac{k_1[A]_0 + k'_2 \left((k_2[B]) / (k'_2 + k_3) \right)}{k'_1 + k_2}$$

which yields, upon isolating $[B]$,

$$[B] = [A]_0 \times \frac{k_1}{k'_1 + k_2 - (k_2 k'_2 / (k'_2 + k_3))}$$

Thus, at the steady state

$$R_1 = R_2 = R_3 = [A]_0 k_1 \times \left(1 - \frac{k_1}{k'_1 + k_2 - \left(\frac{k_2 k'_2}{k'_2 + k_3} \right)} \right) = \boxed{\frac{k_1 k_2 k_3 [A]_0}{k'_1 k'_2 + k'_1 k_3 + k_2 k_3}}$$

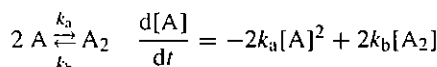
COMMENT. At steady state, not only are the net rates of reactions 1, 2, and 3 steady, but so are the concentrations [B] and [C]. That is,

$$\frac{d[B]}{dt} = k_1[A]_0 - (k'_1 + k_2)[B] + k'_2[C] \approx 0$$

$$\text{and } \frac{d[C]}{dt} = k_2[B] - (k'_2 + k_3)[C] \approx 0$$

In fact, another approach to solving the problem is to solve these equations for [B] and [C].

P22.28



Define the deviation from equilibrium x by the following equations, which satisfy the law of mass conservation.

$$[A] = [A]_{eq} + 2x \quad \text{and} \quad [A_2] = [A_2]_{eq} - x$$

Then,

$$\frac{d([A]_{eq} + 2x)}{dt} = -2k_a([A]_{eq} + 2x)^2 + 2k_b([A_2]_{eq} - x)$$

$$\begin{aligned} \frac{dx}{dt} &= -k_a([A]_{eq} + 2x)^2 + k_b([A_2]_{eq} - x) = -k_a([A]_{eq}^2 + 4[A]_{eq}x + 4x^2) + k_b([A_2]_{eq} - x) \\ &= -\left\{ 4k_ax^2 + (k_b + 4k_a[A]_{eq})x + k_a[A]_{eq}^2 - k_b[A_2]_{eq} \right\} \\ &= -\left\{ (k_b + 4k_a[A]_{eq})x + k_a[A]_{eq}^2 - k_b[A_2]_{eq} \right\} \end{aligned}$$

In the last equation the term containing x^2 has been dropped because x will be small near equilibrium and the x^2 term will be negligibly small. The equation may now be rearranged and integrated using the following integration, which is found in standard mathematical handbooks.

$$\begin{aligned} \int \frac{dw}{aw + b} &= \frac{1}{a} \ln(aw + b) \\ \int \frac{dx}{(k_b + 4k_a[A]_{eq})x + k_a[A]_{eq}^2 - k_b[A_2]_{eq}} &= - \int dt + \text{constant} \\ \frac{1}{(k_b + 4k_a[A]_{eq})} \ln((k_b + 4k_a[A]_{eq})x + k_a[A]_{eq}^2 - k_b[A_2]_{eq}) &= -t + \text{constant} \\ \ln\left(\frac{y}{y_0}\right) &= -(k_b + 4k_a[A]_{eq})t \quad \text{where } y = (k_b + 4k_a[A]_{eq})x + k_a[A]_{eq}^2 - k_b[A_2]_{eq} \\ y &= y_0 e^{-(k_b + 4k_a[A]_{eq})t} \end{aligned}$$

Comparison of the above exponential to the decay equation $y = y_0 e^{-t/\tau}$ reveals that

$$\tau = \frac{1}{k_b + 4k_a[A]_{\text{eq}}}$$

Note that this equation can be used as an alternate derivation of the equation discussed in problem 22.14. The manipulations use the facts that $K = [A_2]_{\text{eq}}/[A]_{\text{eq}}^2 = k_a/k_b$ and $[A]_{\text{tot}} = [A]_{\text{eq}} + 2[A_2]_{\text{eq}}$ by conservation of mass, which can be used to show that

$$[A]_{\text{tot}} = [A]_{\text{eq}} + \frac{2k_a}{k_b}[A]_{\text{eq}}^2 \quad \text{or} \quad \frac{2k_a}{k_b}[A]_{\text{eq}}^2 + [A]_{\text{eq}} - [A]_{\text{tot}} = 0$$

This quadratic equation can be solved for $[A]_{\text{eq}}$.

$$[A]_{\text{eq}} = \frac{k_b}{4k_a} \left(\sqrt{1 + \frac{8k_a[A]_{\text{tot}}}{k_b}} - 1 \right)$$

Substitution of this equation into $\frac{1}{\tau^2} = (k_b + 4k_a[A]_{\text{eq}})^2$ and some algebraic manipulation yields the result of problem 22.14: $\frac{1}{\tau^2} = k_b^2 + 8k_a k_b [A]_{\text{tot}}$.

Solutions to applications

P22.30 The first-order half-life is related to the rate constant by eqn 22.13

$$t_{1/2} = \frac{\ln 2}{k} \quad \text{so} \quad k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{28.1 \text{ y}} = 2.47 \times 10^{-2} \text{ y}^{-1}$$

The integrated rate law tells us

$$[^{90}\text{Sr}] = [^{90}\text{Sr}]_0 e^{-kt} \quad \text{so} \quad m = m_0 e^{-kt}$$

where m is the mass of ^{90}Sr .

$$(a) \text{ After 18 y: } m = (1.00 \mu\text{g}) \times \exp[-(2.47 \times 10^{-2} \text{ y}^{-1}) \times (18 \text{ y})] = \boxed{0.642 \mu\text{g}}$$

$$(b) \text{ After 70 y: } m = (1.00 \mu\text{g}) \times \exp[-(2.47 \times 10^{-2} \text{ y}^{-1}) \times (70 \text{ y})] = \boxed{0.177 \mu\text{g}}$$

P22.32 (a) $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

The peak concentration of B, $[P]_n$, immediately after administration of the n^{th} dose, each of which have been administered at the time interval τ , is given by the sum:

$$[P]_n = [B]_0 + [B]_0 e^{-k_2 \tau} + [B]_0 e^{-2k_2 \tau} + \dots + [B]_0 e^{-(n-1)k_2 \tau} = [B]_0 \sum_{m=0}^{n-1} e^{-mk_2 \tau}$$

Conc. contribution of n^{th} dose
remainder of $(n-1)^{\text{th}}$ dose
remainder of $(n-2)^{\text{th}}$ dose
remainder of 1^{st} dose

The residual concentration of B, $[R]_n$, just before administration of the $(n + 1)^{\text{th}}$ dose results from the first-order elimination of $[P]_n$: $[R]_n = [P]_n e^{-k_2 \tau}$ [22.12 a, b],

$$[P]_{\infty} = \lim_{n \rightarrow \infty} [P]_n = [B]_0 \sum_{m=0}^{\infty} e^{-mk_2 \tau} = [B]_0 (1 + x + x^2 + \dots) \text{ where } x = e^{-k_2 \tau} < 1$$

This may be simplified using the Taylor series: $1 + x + x^2 + \dots = \frac{1}{1-x} = \frac{1}{1-e^{-k_2 \tau}}$ when $x < 1$

We conclude that $[P]_{\infty} = [B]_0 (1 - e^{-k_2 \tau})^{-1}$.

Furthermore, $[R]_n = [B]_0 e^{-k_2 \tau} \sum_{m=0}^{n-1} e^{-mk_2 \tau} = [B]_0 \sum_{m=1}^n e^{-mk_2 \tau}$.

$$[R]_{\infty} = [P]_{\infty} e^{-k_2 \tau} = \frac{[B]_0 e^{-k_2 \tau}}{1 - e^{-k_2 \tau}} = \frac{[B]_0}{e^{k_2 \tau} - 1} = [B]_0 (e^{k_2 \tau} - 1)^{-1}.$$

$$\begin{aligned} [P]_{\infty} - [R]_{\infty} &= [B]_0 \left\{ (1 - e^{-k_2 \tau})^{-1} - (e^{k_2 \tau} - 1)^{-1} \right\} \\ &= [B]_0 \left\{ (1 - e^{-k_2 \tau})^{-1} - e^{-k_2 \tau} (1 - e^{-k_2 \tau})^{-1} \right\} \\ &= [B]_0 \left\{ (1 - e^{-k_2 \tau}) (1 - e^{-k_2 \tau})^{-1} \right\} = [B]_0. \end{aligned}$$

(b) (i) Solving the equation $[P]_{\infty} = [B]_0 (1 - e^{-k_2 \tau})^{-1}$ for τ gives:

$$\begin{aligned} \frac{[B]_0}{[P]_{\infty}} &= 1 - e^{-k_2 \tau} \quad \text{or} \quad e^{-k_2 \tau} = 1 - \frac{[B]_0}{[P]_{\infty}} \quad \text{or} \quad -k_2 \tau = \ln \left(1 - \frac{[B]_0}{[P]_{\infty}} \right) \\ \tau &= -\frac{1}{k_2} \ln \left(1 - \frac{[B]_0}{[P]_{\infty}} \right) = -\frac{1}{0.0289 \text{ h}^{-1}} \ln \left(1 - \frac{1}{10} \right) = \boxed{3.65 \text{ h}} \end{aligned}$$

Figure 22.5(a) shows peak and residual drug concentrations against the number of administrations. Figure 22.5(b) shows the concentration variation with time. It clearly demonstrates the peak and residual concentration and the elimination decay between drug administrations.

(ii) By using the trace function of the plot, or by directly reading the graph, it is found that $[P]_n$ is 75% of the maximum value when $n = \boxed{13}$.

$$\begin{aligned} t_{75\% \max} &= (n - 1) \tau \\ &= (13 - 1)(3.65 \text{ h}) \\ &= 43.8 \text{ h} \end{aligned}$$

(iii) The magnitude of the variation $[P]_n - [R]_n$ may be reduced by reducing the drug dosage $[B]_0$. However, in order to avoid changing $[P]_{\infty}$ it becomes necessary to reduce τ .

(c) For first-order absorption and zero-order elimination of a single dose $[A]_0$:

$$\frac{d[A]}{dt} = k_1[A] \quad \text{and} \quad [A] = [A]_0 e^{-k_1 t} \quad [22.12a, b]$$

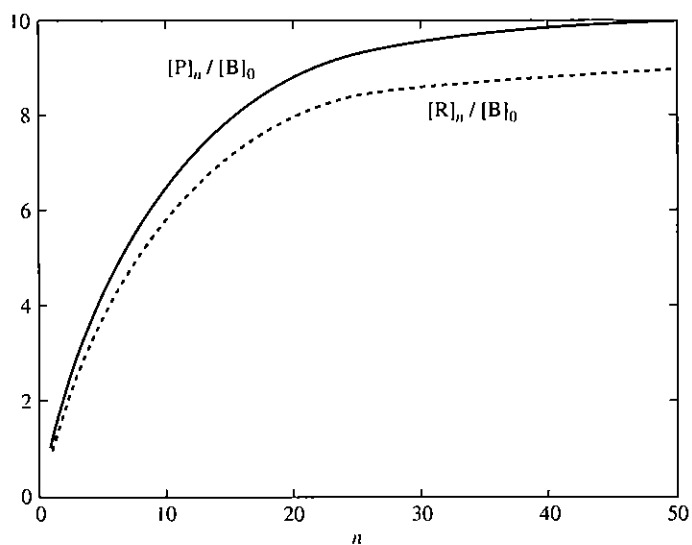


Figure 22.5(a)

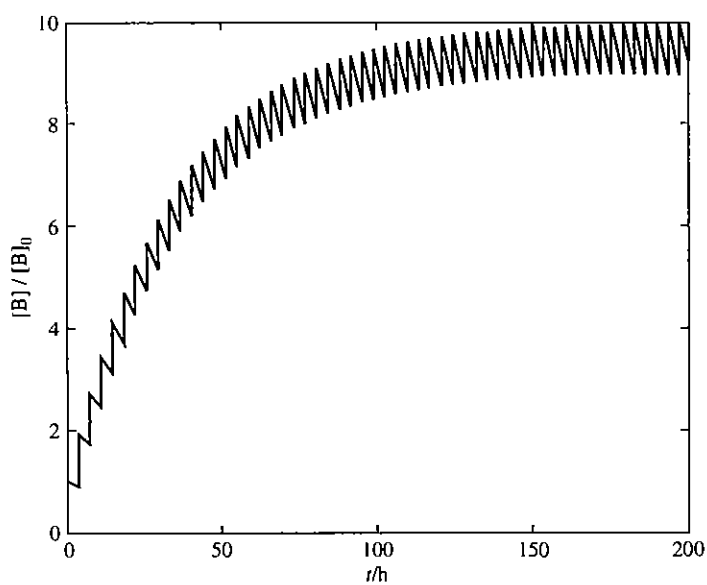


Figure 22.5(b)

$$\frac{d[B]}{dt} = k_1[A] - k_2 = k_1[A]_0 e^{-k_1 t} - k_2$$

$$\int_0^{[B]} d[B] = \int_0^t (k_1[A]_0 e^{-k_1 t} - k_2) dt = k_1[A]_0 \int_0^t e^{-k_1 t} dt - k_2 \int_0^t dt$$

$$\boxed{[B] = [A]_0 (1 - e^{-k_1 t}) - k_2 t}$$

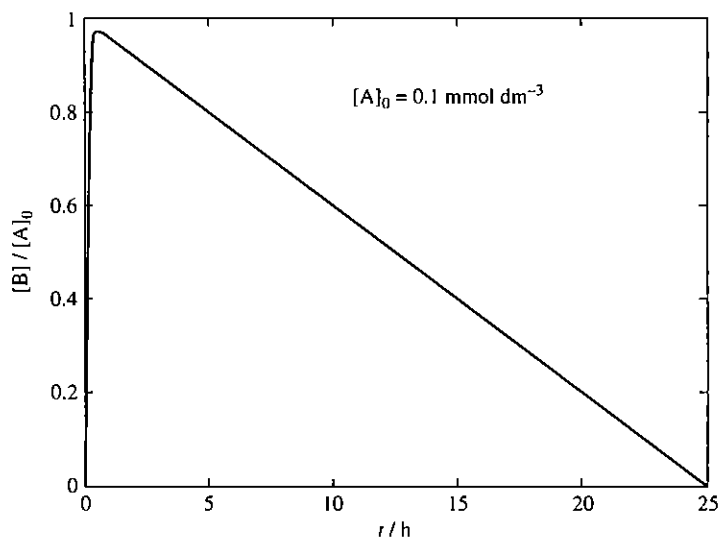


Figure 22.5(c)

The plot of $[B]/[A]_0$ (Figure 22.5(c)) shows rapid absorption of the drug into the blood followed by the slower, linear elimination that corresponds to zeroth-order elimination. Elimination occurs within 25 h with these rate constants.

- (d) Let $\{[B]_{\max}, t_{\max}\}$ be the maximum of a curve such as that shown above. To find formulas for this point, we must examine the curve at the point for which $d[B]/dt = 0$.

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t_{\max}} - k_2 = 0$$

$$e^{-k_1 t_{\max}} = \frac{k_2}{k_1[A]_0} \quad \text{or} \quad -k_1 t_{\max} = \ln\left(\frac{k_2}{k_1[A]_0}\right)$$

$$t_{\max} = \frac{1}{k_1} \ln\left(\frac{k_1[A]_0}{k_2}\right)$$

$$[B]_{\max} = [A]_0 \left(1 - e^{-k_1 t_{\max}}\right) - k_2 t_{\max} = [A]_0 \left(1 - e^{-k_1 \frac{1}{k_1} \ln\left(\frac{k_1[A]_0}{k_2}\right)}\right) - k_2 t_{\max}$$

$$= [A]_0 \left(1 - e^{\ln\left(\frac{k_2}{k_1[A]_0}\right)}\right) - k_2 t_{\max} = [A]_0 \left(1 - \frac{k_2}{k_1[A]_0}\right) - k_2 t_{\max}$$

$$[B]_{\max} = [A]_0 - \frac{k_2}{k_1} - k_2 t_{\max}$$

P22.34

Analysis of NMR lineshapes can be used to infer time scales of protein folding or unfolding steps. Protons (or other nuclei, for that matter) that have different chemical shifts in folded and unfolded proteins will yield a single peak if the time scale for interconversion (i.e. for folding or unfolding) is comparable to or less than the reciprocal of the two peaks' frequency difference. Monitoring the change from two peaks (indicating that a sample contains both folded and unfolded proteins, which might be observed at one temperature) to a broad single peak (indicating fast interconversion, which might be the case at a higher temperature) can allow the determination of the time constant for the conversion. One advantage of

NMR over vibrational or electronic spectroscopy is that the radiation used to probe the system is much less energetic, and therefore much less likely to alter the folding or unfolding process it is designed to investigate. The lineshape strategy cannot be used to investigate processes as fast as those accessible by electronic or vibrational spectroscopy. (cf. Example 15.2.)

P22.36 First, turn eqn 22.30 into an expression involving the functional forms given in the data:

$$\begin{aligned} E_a &= RT^2 \frac{d \ln k}{dT} = RT^2 \frac{d \ln k}{d(1/T)} \frac{d(1/T)}{dT} = -R \frac{d \ln k}{d(1/T)} = -R \ln(10) \frac{d \log k}{d(1/T)} \\ &= -R \ln(10) \frac{d}{d(1/T)} \left(11.75 - \frac{5488}{T/K} \right) = -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln(10) (-5488 \text{ K}) \\ &= \boxed{105 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\Delta_r G^\ominus = -RT \ln K = -RT \ln(10) \log K \text{ [section 7.2d for } \Delta_r G^\ominus]$$

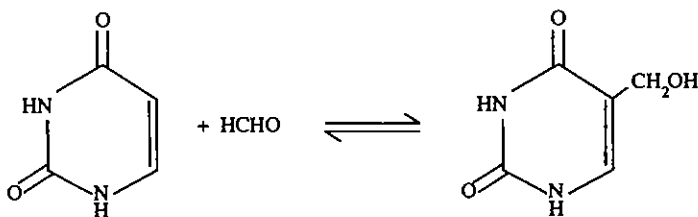
At 298.15 K

$$\Delta_r G^\ominus = -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K}) \ln(10) \left(-1.36 + \frac{1794}{298.15} \right)$$

$$\Delta_r G^\ominus = \boxed{-26.6 \text{ kJ mol}^{-1}}$$

$$\begin{aligned} \Delta_r H^\ominus &= -R \frac{d \ln(K)}{d(1/T)} \text{ [7.23b]} = -R \ln(10) \frac{d \log(K)}{d(1/T)} \\ &= -R \ln(10) \frac{d}{d(1/T)} \left(-1.36 + \frac{1794}{T/K} \right) = -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln(10) (1794 \text{ K}) \\ &= \boxed{-34.3 \text{ kJ mol}^{-1}} \end{aligned}$$

The reaction is



The equations for the rate constant k and the equilibrium constant K were obtained under conditions corresponding to the biological standard state ($\text{pH} = 7$, $p = 1$ bar; Section 7.2d). Thus the values of $\Delta_r G$ calculated from the equation for K are $\Delta_r G^\ominus$ values which can differ significantly from $\Delta_r G$ ($\text{pH} = 1$, $p = 1$ bar). Prebiotic conditions are more likely to be near $\text{pH} = 7$ than $\text{pH} = 1$ so we expect that the reaction will still be favorable ($K \gg 1$) thermodynamically.

Because $\Delta_r G = \Delta_r G^\ominus + RT \ln Q$ [7.11] and since we might expect $Q < 1$ in a prebiotic environment, $\Delta_r G < \Delta_r G^\ominus$. But, as shown in the calculation above, $\Delta_r G^\ominus$ is rather large and negative ($-26.6 \text{ kJ mol}^{-1}$), so we expect it will still be large and negative under the prebiotic conditions; hence the reaction will be spontaneous for these conditions. We expect that $\Delta_r H \approx \Delta_r H^\ominus$ because enthalpy changes largely reflect bond breakage and bond formation energies.

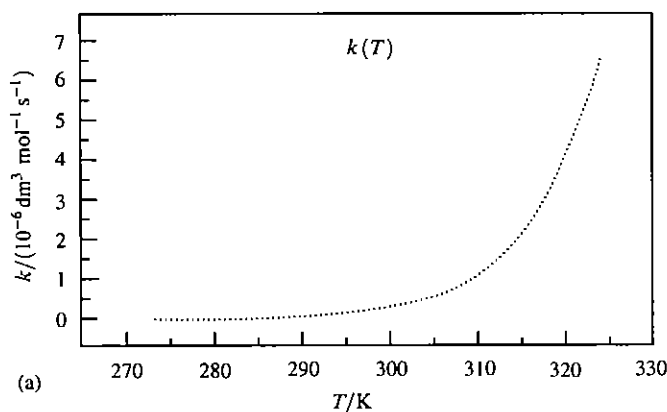


Figure 22.6(a)

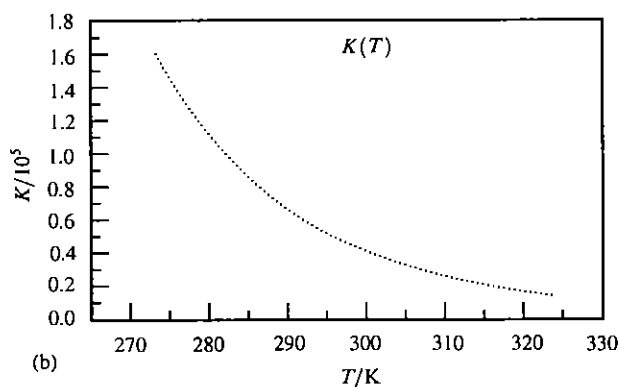


Figure 22.6(b)

A plot of the equation for the rate constant k is shown in Figure 22.6(a) and that for the equilibrium constant in Figure 22.6(b). From a kinetic point of view the reaction becomes more favorable at higher temperatures; from a thermodynamic point of view it becomes less favorable, but $K \gg 1$ at all temperatures.

P22.38 (a) The rate of reaction is

$$\begin{aligned}
 v &= k[\text{CH}_4][\text{OH}] \\
 &= (1.13 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \times \exp\left(\frac{-14.1 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (263 \text{ K})}\right) \\
 &\quad \times (4.0 \times 10^{-8} \text{ mol dm}^{-3}) \times (1.5 \times 10^{-15} \text{ mol dm}^{-3}) = \boxed{1.1 \times 10^{-16} \text{ mol dm}^{-3} \text{ s}^{-1}}
 \end{aligned}$$

(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.

$$\begin{aligned}
 m &= M\nu Vt = (0.01604 \text{ kg mol}^{-1}) \times (1.1 \times 10^{-16} \text{ mol dm}^{-3} \text{ s}^{-1}) \\
 &\quad \times (4 \times 10^{21} \text{ dm}^3) \times (365 \times 24 \times 3600 \text{ s}) \\
 &= \boxed{2.2 \times 10^{11} \text{ kg or 220 Tg}}
 \end{aligned}$$

P22.40 The initial rate is

$$\begin{aligned}
 v_0 &= (3.6 \times 10^6 \text{ dm}^9 \text{ mol}^{-3} \text{ s}^{-1}) \times (5 \times 10^{-4} \text{ mol dm}^{-3})^2 \times (10^{-4.5} \text{ mol dm}^{-3})^2 \\
 &= \boxed{9 \times 10^{-10} \text{ mol dm}^{-3} \text{ s}^{-1}}
 \end{aligned}$$

The half-life for a second-order reaction is

$$t_{1/2} = \frac{1}{k'[\text{HSO}_3^-]_0}$$

where k' is the rate constant in the expression

$$-\frac{d[\text{HSO}_3^-]}{dt} = k'[\text{HSO}_3^-]^2$$

Comparison to the given rate law and rate constant shows

$$\begin{aligned}
 k' &= 2k[\text{H}^+]^2 = 2(3.6 \times 10^6 \text{ dm}^9 \text{ mol}^{-3} \text{ s}^{-1}) \times (10^{-4.5} \text{ mol dm}^{-3})^2 \\
 &= 7.2 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}
 \end{aligned}$$

$$\text{and } t_{1/2} = \frac{1}{(7.2 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \times (5 \times 10^{-4} \text{ mol dm}^{-3})} = \boxed{2.8 \times 10^5 \text{ s} = 3 \text{ days}}$$

23

The kinetics of complex reactions

Answers to discussion questions

- D23.2** In the analysis of stepwise polymerization, the rate constant for the second-order condensation is assumed to be independent of the chain length and to remain constant throughout the reaction. It follows, then, that the degree of polymerization is given by

$$\langle n \rangle = 1 + kt[A]_0$$

Therefore, the average molar mass can be controlled by adjusting the initial concentration of monomer and the length of time that the polymerization is allowed to proceed.

Chain polymerization is a complicated radical chain mechanism involving initiation, propagation, and termination steps (see Section 23.4 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:

$$\langle n \rangle = 2k[M][I]^{-1/2},$$

where $k = (1/2)k_p(fk_i k_t)^{-1/2}$, 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.

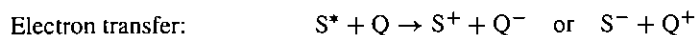
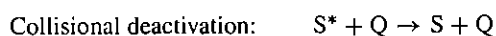
- D23.4** Refer to eqns 23.26 and 23.27, which are the analogues of the Michaelis–Menten and Lineweaver–Burk equations (23.21 and 23.22), as well as to Figure 23.13. There are three major modes of inhibition that give rise to distinctly different kinetic behavior (Figure 23.13). In competitive inhibition 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 23.13c shows the special case of $K_I = K'_I$ and $\alpha = \alpha'$, which results in intersection of the lines at the x -axis.

In all cases, the efficiency of the inhibitor may be obtained by determining K_M and v_{\max} from a control experiment with uninhibited enzyme and then repeating the experiment with a known concentration of inhibitor. From the slope and y -intercept of the Lineweaver–Burk plot for the inhibited enzyme (eqn 23.27), the mode of inhibition, the values of α or α' , and the values of K_I , or K'_I may be obtained.

D23.6 The 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 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 14.6e). 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.

Solutions to exercises

In the following exercises and problems, it is recommended that rate constants are labeled with the number of the step in the proposed reaction mechanism and that any reverse steps are labeled similarly but with a prime.

E23.1(b) The intermediates are NO and NO_3 and we apply the steady-state approximation to each of their concentrations

$$k_2 [NO_2] [NO_3] - k_3 [NO] [N_2O_5] = 0$$

$$k_1 [N_2O_5] - k'_1 [NO_2] [NO_3] - k_2 [NO_2] [NO_3] = 0$$

$$\text{Rate} = -\frac{1}{2} \frac{d[N_2O_5]}{dt}$$

$$\frac{d[N_2O_5]}{dt} = -k_1 [N_2O_5] + k'_1 [NO_2] [NO_3] - k_3 [NO] [N_2O_5]$$

From the steady-state equations

$$k_3 [\text{NO}] [\text{N}_2\text{O}_5] = k_2 [\text{NO}_2] [\text{NO}_3]$$

$$[\text{NO}_2] [\text{NO}_3] = \frac{k_1 [\text{N}_2\text{O}_5]}{k'_1 + k_2}$$

Substituting,

$$\frac{d[\text{N}_2\text{O}_5]}{dt} = -k_1 [\text{N}_2\text{O}_5] + \frac{k'_1 k_1}{k'_1 + k_2} [\text{N}_2\text{O}_5] - \frac{k_2 k_1}{k'_1 + k_2} [\text{N}_2\text{O}_5] = -\frac{2k_1 k_2}{k'_1 + k_2} [\text{N}_2\text{O}_5]$$

$$\text{Rate} = \frac{k_1 k_2}{k'_1 + k_2} [\text{N}_2\text{O}_5] = k [\text{N}_2\text{O}_5]$$

E23.2(b)
$$\frac{d[\text{R}]}{dt} = 2k_1 [\text{R}_2] - k_2 [\text{R}] [\text{R}_2] + k_3 [\text{R}'] - 2k_4 [\text{R}]^2$$

$$\frac{d[\text{R}']}{dt} = k_2 [\text{R}] [\text{R}_2] - k_3 [\text{R}']$$

Apply the steady-state approximation to both equations

$$2k_1 [\text{R}_2] - k_2 [\text{R}] [\text{R}_2] + k_3 [\text{R}'] - 2k_4 [\text{R}]^2 = 0$$

$$k_2 [\text{R}] [\text{R}_2] - k_3 [\text{R}'] = 0$$

The second solves to $[\text{R}'] = \frac{k_2}{k_3} [\text{R}] [\text{R}_2]$

and then the first solves to $[\text{R}] = \left(\frac{k_1}{k_4} [\text{R}_2] \right)^{1/2}$

Therefore,
$$\frac{d[\text{R}_2]}{dt} = -k_1 [\text{R}_2] - k_2 [\text{R}_2] [\text{R}] = k_1 [\text{R}_2] - k_2 \left(\frac{k_1}{k_4} \right)^{1/2} [\text{R}_2]^{3/2}$$

E23.3(b) (a) The figure suggests that a chain-branching explosion 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

$$\log(p/\text{Pa}) = 2.1 \quad \text{so} \quad p = 10^{2.1} \text{ Pa} = \boxed{1.3 \times 10^2 \text{ Pa}}$$

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

$$\log(p/\text{Pa}) = 4.5 \quad \text{so} \quad p = 10^{4.5} \text{ Pa} = \boxed{3 \times 10^4 \text{ Pa}}$$

E23.4(b) The rate of production of the product is

$$\frac{d[\text{BH}^+]}{dt} = k_2 [\text{HAH}^+] [\text{B}]$$

HAH^+ is an intermediate involved in a rapid pre-equilibrium

$$\frac{[\text{HAH}^+]}{[\text{HA}][\text{H}^+]} = \frac{k_1}{k'_1} \text{ so } [\text{HAH}^+] = \frac{k_1 [\text{HA}][\text{H}^+]}{k'_1}$$

and $\frac{d[\text{BH}^+]}{dt} = \boxed{\frac{k_1 k_2}{k'_1} [\text{HA}][\text{H}^+][\text{B}]}$

This rate law can be made independent of $[\text{H}^+]$ if the source of H^+ is the acid HA, for then H^+ is given by another equilibrium

$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = K_a = \frac{[\text{H}^+]^2}{[\text{HA}]} \text{ so } [\text{H}^+] = (K_a[\text{HA}])^{1/2}$$

and $\frac{d[\text{BH}^+]}{dt} = \boxed{\frac{k_1 k_2 K_a^{1/2}}{k'_1} [\text{HA}]^{3/2} [\text{B}]}$

E23.5(b) A_2 appears in the initiation step only.

$$\frac{d[\text{A}_2]}{dt} = -k_1 [\text{A}_2]$$

Consequently, the rate of consumption of $[\text{A}_2]$ is first order in A_2 and the rate is independent of intermediate concentrations.

E23.6(b) The maximum velocity is $k_b [\text{E}]_0$ and the velocity in general is

$$v = k [\text{E}]_0 = \frac{k_b [\text{S}][\text{E}]_0}{K_M + [\text{S}]} \text{ so } v_{\max} = k_b [\text{E}]_0 = \frac{K_M + [\text{S}]}{[\text{S}]} v$$

$$v_{\max} = \frac{(0.042 + 0.890) \text{ mol dm}^{-3}}{0.890 \text{ mol dm}^{-3}} (2.45 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}) = \boxed{2.57 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}}$$

E23.7(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 $1.77 \times 10^{-3} \text{ mol} / (1.2 \times 10^2 \text{ mol Einstein}^{-1}) = \boxed{1.5 \times 10^{-5} \text{ moles of photons}}$

E23.8(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).

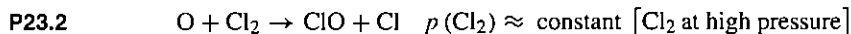
$$\Phi = \frac{n_A hc N_A}{(1 - f_{\text{trans}}) \lambda P t}$$

$$= \frac{(0.324 \text{ mol}) \times (6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1}) \times (6.022 \times 10^{23} \text{ mol}^{-1})}{(1 - 0.257) \times (320 \times 10^{-9} \text{ m}) \times (87.5 \text{ W}) \times (28.0 \text{ min}) \times (60 \text{ s min}^{-1})}$$

$$= \boxed{1.11}$$

Solutions to problems

Solutions to numerical problems



Therefore, the reaction is probably pseudo-first order, and

$$[\text{O}] \approx [\text{O}]_0 e^{-k't}$$

That being so, $\ln \frac{[\text{O}]_0}{[\text{O}]} = k't = k[\text{Cl}_2]t = k[\text{Cl}_2] \times \frac{d}{v}$

where $k' = [\text{Cl}_2]k$, 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
$\ln \frac{[\text{O}]_0}{[\text{O}]}$	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 Figure 23.1.

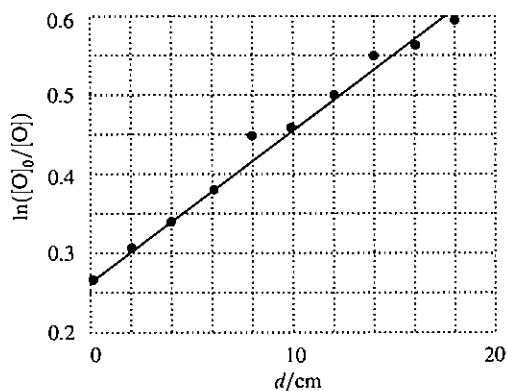


Figure 23.1

The slope is 0.0189, and so $\frac{k[\text{Cl}_2]}{v} = 0.0189 \text{ cm}^{-1}$.

$$\begin{aligned} \text{Therefore, } k &= \frac{(0.0189 \text{ cm}^{-1}) \times v}{[\text{Cl}_2]} \\ &= \frac{(0.0189 \text{ cm}^{-1}) \times (6.66 \times 10^2 \text{ cm s}^{-1})}{2.54 \times 10^{-7} \text{ mol dm}^{-3}} = \boxed{5.0 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}} \end{aligned}$$

(There is a very fast $\text{O} + \text{ClO} \rightarrow \text{Cl} + \text{O}_2$ reaction, and so the answer given here is actually twice the true value.)

P23.4

$\text{H}_2 \rightarrow 2\text{H}\cdot$	initiation,	$v = v_{\text{init}}$
$\text{H}\cdot + \text{O}_2 \rightarrow \cdot\text{OH} + \cdot\text{O}\cdot$	branching,	$v = k_1 [\text{H}\cdot] [\text{O}_2]$
$\cdot\text{O}\cdot + \text{H}_2 \rightarrow \cdot\text{OH} + \text{H}\cdot$	branching,	$v = k_2 [\cdot\text{O}\cdot] [\text{H}_2]$
$\text{H}\cdot + \text{O}_2 \rightarrow \text{HO}_2\cdot$	propagation,	$v = k_3 [\text{H}\cdot] [\text{O}_2]$
$\text{HO}_2\cdot + \text{H}_2 \rightarrow \text{H}_2\text{O} + \cdot\text{OH}$	propagation,	$v = k_4 [\text{HO}_2\cdot] [\text{H}_2]$
$\text{HO}_2\cdot + \text{wall} \rightarrow \text{destruction}$	termination,	$v = k_5 [\text{HO}_2\cdot]$
$\text{H}\cdot + \text{M} \rightarrow \text{destruction}$	termination,	$v = k_6 [\text{H}\cdot] [\text{M}]$

We identify the onset of explosion with the rapid increase in the concentration of radicals which we initially identify with $[\text{H}\cdot]$. 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.

$$\frac{d[\cdot\text{O}\cdot]}{dt} = k_1 [\text{H}\cdot] [\text{O}_2] - k_2 [\cdot\text{O}\cdot] [\text{H}_2] \approx 0$$

$$[\cdot\text{O}\cdot]_{\text{ss}} \approx \frac{k_1 [\text{H}\cdot] [\text{O}_2]}{k_2 [\text{H}_2]}$$

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 $[\text{H}\cdot]$. No explosion is possible according to this mechanism, or at least no exponential growth of $[\text{H}\cdot]$ is observed.

Let us try a second approach for which the concentration of radicals is identified with $[\cdot\text{O}\cdot]$.

$$v_{\text{rad}} = k_1 [\text{H}\cdot] [\text{O}_2] - k_2 [\cdot\text{O}\cdot] [\text{H}_2]$$

Using the steady-state approximation to describe $[\text{H}\cdot]$, we find that

$$\begin{aligned} [\text{H}\cdot]_{\text{ss}} &= \frac{v_{\text{init}} + k_2 [\text{H}_2] [\cdot\text{O}\cdot]}{(k_1 + k_3) [\text{O}_2] + k_6 [\text{M}]} \\ v_{\text{rad}} &= \frac{v_{\text{init}} k_1 [\text{O}_2]}{(k_1 + k_3) [\text{O}_2] + k_6 [\text{M}]} + \left\{ \frac{k_1 k_2 [\text{H}_2] [\text{O}_2]}{(k_1 + k_3) [\text{O}_2] + k_6 [\text{M}]} - k_2 [\text{H}_2] \right\} [\cdot\text{O}\cdot] \end{aligned}$$

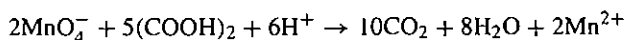
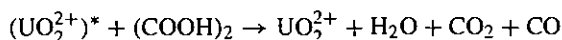
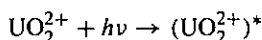
This has the form

$$v_{\text{rad}} = \frac{d[\cdot\text{O}\cdot]}{dt} = C_1 + \{C_2 - C_3\} [\cdot\text{O}\cdot]$$

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 $k_1 [\text{O}_2] / ((k_1 + k_3) [\text{O}_2] + k_6 [\text{M}]) > 1$. But this is not possible. So no exponential growth of $[\cdot\text{O}\cdot]$ 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 $\cdot\text{O}$. It is, however, unlikely that the steady-state approximation can be applied to explosive reactions, and this is where the analysis breaks down.

P23.6



17.0 cm³ of 0.212 M KMnO₄ is equivalent to

$$\frac{5}{2} \times (17.0 \text{ cm}^3) \times (0.212 \text{ mol dm}^{-3}) = 9.01 \times 10^{-3} \text{ mol } (\text{COOH})_2$$

The initial sample contained 5.232 g (COOH)₂, corresponding to

$$\frac{5.232 \text{ g}}{90.04 \text{ g mol}^{-1}} = 5.81 \times 10^{-2} \text{ mol } (\text{COOH})_2$$

Therefore, $(5.81 \times 10^{-2} \text{ mol}) - (9.01 \times 10^{-3} \text{ mol}) = 4.91 \times 10^{-2} \text{ mol}$ of the acid has been consumed. A quantum efficiency 0.53 implies that the amount of photons absorbed must have been

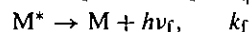
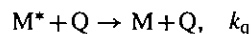
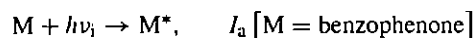
$$\frac{4.91 \times 10^{-2} \text{ mol}}{0.53} = 9.3 \times 10^{-2} \text{ mol}$$

Since the exposure was for 300 s, the rate of incidence of photons was

$$\frac{9.3 \times 10^{-2} \text{ mol}}{300 \text{ s}} = 3.1 \times 10^{-4} \text{ mol s}^{-1}$$

Since 1 mol photons = 1 einstein, the incident rate is $3.1 \times 10^{-4} \text{ einstein s}^{-1}$ or $1.9 \times 10^{20} \text{ s}^{-1}$

P23.8



$$\frac{d[\text{M}^*]}{dt} = I_a - k_f[\text{M}^*] - k_q[\text{Q}][\text{M}^*] \approx 0 \text{ [steady state]}$$

$$\text{and hence } [\text{M}^*] = \frac{I_a}{k_f + k_q[\text{Q}]}$$

$$\text{Then } I_f = k_f[\text{M}^*] = \frac{k_f I_a}{k_f + k_q[\text{Q}]}$$

$$\text{and so } \frac{1}{I_f} = \frac{1}{I_a} + \frac{k_q[\text{Q}]}{k_f I_a}$$

If the exciting light is extinguished, $[\text{M}^*]$, 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 $[\text{Q}]$, and then use k_f to determine k_q .

We draw up the following table

$10^3 [Q]/M$	1	5	10
$1/I_f$	2.4	4.0	6.3

The points are plotted in Figure 23.2.

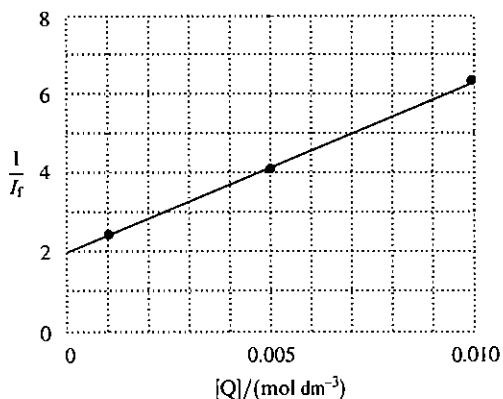


Figure 23.2

The intercept lies at 2.0, and so $I_a = 1/2.0 = 0.50$. The slope is 430, and so

$$\frac{k_q}{k_f I_a} = 430 \text{ dm}^3 \text{ mol}^{-1}$$

Then, since $I_a = 0.50$ and $k_f = \frac{\ln 2}{t_{1/2}}$,

$$k_q = (0.50) \times (430 \text{ dm}^3 \text{ mol}^{-1}) \times \left(\frac{\ln 2}{29 \times 10^{-6} \text{ s}} \right) = \boxed{5.1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

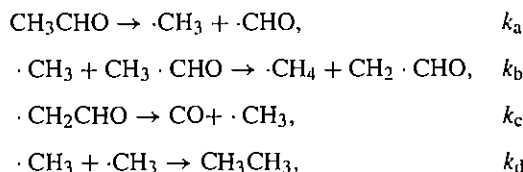
P23.10

$$E_T = \frac{R_0^6}{R_0^6 + R^6} \quad \text{or} \quad \frac{1}{E_T} = 1 + (R/R_0)^6 \quad [23.38]$$

Since a plot of E_T^{-1} values against R^6 (Figure 23.3) appears to be linear with an intercept equal to 1, we conclude that eqn 23.38 adequately describes the data. Solving eqn 23.38 for R_0 gives $R_0 = R(E_T^{-1} - 1)^{1/6}$. R_0 may be evaluated by taking the mean of experimental data in this expression. The two data points at lowest R must be excluded from the mean as they are highly uncertain. $R_0 = 3.52 \text{ nm}$ with a standard deviation of 0.173 nm .

Solutions to theoretical problems

P23.12



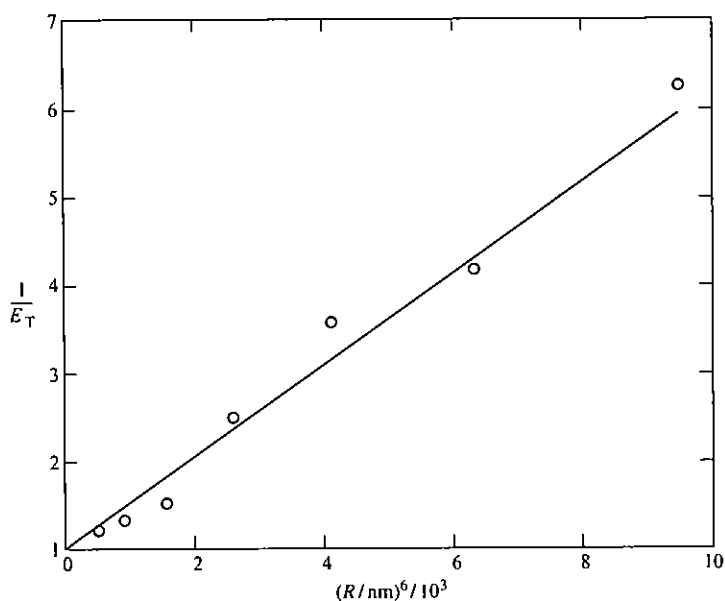


Figure 23.3

$$\frac{d[\text{CH}_4]}{dt} = -k_b [\text{CH}_3] [\text{CH}_3\text{CHO}]$$

$$\frac{d[\text{CH}_3\text{CHO}]}{dt} = -k_a [\text{CH}_3\text{CHO}] - k_b [\text{CH}_3\text{CHO}] [\text{CH}_3]$$

$$\frac{d[\text{CH}_3]}{dt} = k_a [\text{CH}_3\text{CHO}] - k_b [\text{CH}_3\text{CHO}] [\text{CH}_3] + k_c [\text{CH}_2\text{CHO}] - 2k_d [\text{CH}_3]^2 = 0$$

$$\frac{d[\text{CH}_2\text{CHO}]}{dt} = k_b [\text{CH}_3] [\text{CH}_3\text{CHO}] - k_c [\text{CH}_2\text{CHO}] = 0$$

Adding the last two equations gives

$$k_a [\text{CH}_3\text{CHO}] - 2k_d [\text{CH}_3]^2 = 0, \quad \text{or} \quad [\text{CH}_3] = \left(\frac{k_a}{2k_d} \right)^{1/2} [\text{CH}_3\text{CHO}]^{1/2}$$

Therefore

$$\frac{d[\text{CH}_4]}{dt} = k_b \left(\frac{k_a}{2k_d} \right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

$$\frac{d[\text{CH}_3\text{CHO}]}{dt} = -k_a [\text{CH}_3\text{CHO}] - k_b \left(\frac{k_a}{2k_d} \right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

Note that, to lowest order in k_a ,

$$\frac{d[\text{CH}_3\text{CHO}]}{dt} \approx -k_b \left(\frac{k_a}{2k_d} \right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

and the reaction is three-halves order in CH_3CHO .

P23.14 (a) $\overline{M}_n^3 = M^3 \sum_n n^3 P_n = M^3 (1-p) \sum_n n^3 p^{n-1}$ [$P_n = p^{n-1} (1-p)$, Problem 23.13]

$$= M^3 (1-p) \frac{d}{dp} \sum_n n^2 p^n = M^3 (1-p) \frac{d}{dp} p \frac{d}{dp} p \frac{d}{dp} \sum_n p^n$$

$$= M^3 (1-p) \frac{d}{dp} p \frac{d}{dp} p \frac{d}{dp} (1-p)^{-1} = \frac{M^3 (1+4p+p^2)}{(1-p)^3}$$

$$\overline{M}_n^2 = \frac{M^2 (1+p)}{(1-p)^2} \text{ [Problem 23.13]}$$

Therefore, $\frac{\overline{M}_n^3}{\overline{M}_n^2} = \boxed{\frac{M(1+4p+p^2)}{1-p^2}}$

(b) $\langle n \rangle = \frac{1}{1-p}$ [23.8], so $p = 1 - \frac{1}{\langle n \rangle}$

$$\frac{\overline{M}_n^3}{\overline{M}_n^2} = \boxed{(6\langle n \rangle^2 - 6\langle n \rangle + 1)\langle n \rangle}$$

P23.16 $\frac{d[A]}{dt} = -k[A]^2[OH] = -k[A]^3$ because $[A] = [OH]$.

$$\frac{d[A]}{[A]^3} = -k dt \quad \text{and} \quad \int_{[A]_0}^{[A]} \frac{d[A]}{[A]^3} = -k \int_0^t dt = -kt$$

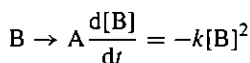
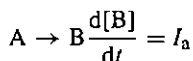
Since $\int \frac{dx}{x^3} = \frac{-1}{2x^2}$, the equation becomes

$$\frac{1}{[A]^2} - \frac{1}{[A]_0^2} = 2kt \quad \text{or} \quad [A] = [A]_0 (1 + 2kt[A]_0)^{-1/2}$$

By eqn 23.8a the degree of polymerization, $\langle n \rangle$, is given by

$$\langle n \rangle = \frac{[A]_0}{[A]} = \boxed{(1 + 2kt[A]_0)^{1/2}}$$

P23.18

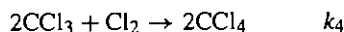
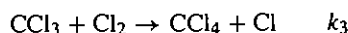
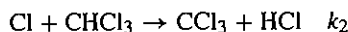
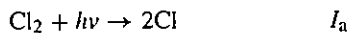


In the photostationary state $I_a - k[B]^2 = 0$. Hence,

$$[B] = \left(\frac{I_a}{k} \right)^{1/2} \propto [A]^{1/2} \quad [\text{because } I \propto [A]]$$

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.

P23.20



$$(i) \quad \frac{d[\text{CCl}_4]}{dt} = 2k_4 [\text{CCl}_3]^2 [\text{Cl}_2] + k_3 [\text{CCl}_3] [\text{Cl}_2]$$

$$(ii) \quad \frac{d[\text{CCl}_3]}{dt} = k_2 [\text{Cl}] [\text{CHCl}_3] - k_3 [\text{CCl}_3] [\text{Cl}_2] - 2k_4 [\text{CCl}_3]^2 [\text{Cl}_2] = 0$$

$$(iii) \quad \frac{d[\text{Cl}]}{dt} = 2I_a - k_2 [\text{Cl}] [\text{CHCl}_3] + k_3 [\text{CCl}_3] [\text{Cl}_2] = 0$$

$$(iv) \quad \frac{d[\text{Cl}_2]}{dt} = -I_a - k_3 [\text{CCl}_3] [\text{Cl}_2] - k_4 [\text{CCl}_3]^2 [\text{Cl}_2]$$

Therefore, $I_a = k_4 [\text{CCl}_3]^2 [\text{Cl}_2] [(ii) + (iii)]$

which implies that

$$[\text{CCl}_3] = \left(\frac{1}{k_4} \right)^{1/2} \left(\frac{I_a}{[\text{Cl}_2]} \right)^{1/2}$$

Then, with (i),

$$\frac{d[\text{CCl}_4]}{dt} = 2I_a + \frac{k_3 I_a^{1/2} [\text{Cl}]^{1/2}}{k_4^{1/2}}$$

When the pressure of chlorine is high, and the initiation rate is slow (in the sense that the lowest powers of I_a dominate), the second term dominates the first, giving

$$\frac{d[\text{CCl}_4]}{dt} = \frac{k_3 I_a^{1/2}}{k_4^{1/2}} [\text{Cl}_2]^{1/2} = \boxed{k I_a^{1/2} [\text{Cl}_2]^{1/2}}$$

with $k = k_3/k_4^{1/2}$. It seems necessary to suppose that $\text{Cl} + \text{Cl}$ recombination (which needs a third body) is unimportant.

Solutions to applications

P23.22

The rate equation is

$$\frac{dN}{dt} = bN - dN$$

which has the solution

$$\boxed{N(t) = N_0 e^{(b-d)t} = N_0 e^{kt}}$$

A least squares fit to the above data gives

$$N_0 = 0.484 \times 10^9 \approx 0.5 \times 10^9$$

$$k = 9.19 \times 10^{-3} \text{ y}^{-1}$$

$$R^2 = (\text{coefficient of determination}) = 0.983$$

$$\text{Standard error of estimate} = 0.130 \times 10^9$$

Thus, this model of population growth for the planet as a whole fits the data fairly well.

COMMENT. Despite the fact that the Malthusian model seems to fit the (admittedly crude) population data it has been much criticized. An alternative rate equation that takes into account the carrying capacity K of the planet is due to Verhulst (1836). This rate equation is

$$\frac{dN}{dt} = kN \left(1 - \frac{N}{K} \right)$$

Question. Does the Verhulst model fit our limited data any better?

P23.24 We draw up the table below, which includes data rows required for a Lineweaver–Burk plot ($1/v$ against $1/[S]_0$). The linear regression fit is found for the plot. See Figure 23.4

$[\text{ATP}]/(\mu\text{mol dm}^{-3})$	0.60	0.80	1.4	2.0	3.0
$v/(\mu\text{mol dm}^{-3} \text{ s}^{-1})$	0.81	0.97	1.30	1.47	1.69
$1/[\text{ATP}]/(\mu\text{mol dm}^{-3})$	1.67	1.25	0.714	0.500	0.333
$1/v/(\mu\text{mol dm}^{-3} \text{ s}^{-1})$	1.23	1.03	0.769	0.680	0.592

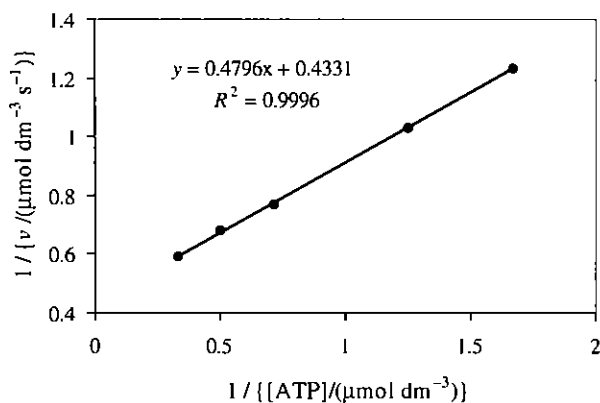


Figure 23.4

$$1/v_{\max} = \text{intercept [23.22]}$$

$$v_{\max} = 1/\text{intercept} = 1/(0.433 \mu\text{mol dm}^{-3} \text{ s}^{-1}) = \boxed{2.31 \mu\text{mol dm}^{-3} \text{ s}^{-1}}$$

$$k_b = v_{\max} / [E]_0 \text{ [23.20b]} = (2.31 \mu\text{mol dm}^{-3} \text{ s}^{-1}) / (0.020 \mu\text{mol dm}^{-3}) = \boxed{115 \text{ s}^{-1}}$$

$$k_{\text{cat}} = k_b \text{ [23.23]} = \boxed{115 \text{ s}^{-1}}$$

$$K_M = v_{\max} \times \text{slope [23.22]} = (2.31 \mu\text{mol dm}^{-3} \text{ s}^{-1}) \times (0.480 \text{ s}) = \boxed{1.11 \mu\text{mol dm}^{-3}}$$

$$\varepsilon = k_{\text{cat}} / K_M \text{ [23.24]} = (115 \text{ s}^{-1}) / (1.11 \mu\text{mol dm}^{-3}) = \boxed{104 \text{ dm}^3 \mu\text{mol}^{-1} \text{ s}^{-1}}$$

P23.26 (a) The dissociation equilibrium may be rearranged to give the following relationships.

$$\begin{aligned} [\text{E}^-] &= K_{\text{E,a}}[\text{EH}]/[\text{H}^+] & [\text{EH}_2^+] &= [\text{EH}][\text{H}^+]/K_{\text{E,b}} \\ [\text{ES}^-] &= K_{\text{ES,a}}[\text{ESH}]/[\text{H}^+] & [\text{ESH}_2] &= [\text{ESH}][\text{H}^+]/K_{\text{ES,b}} \end{aligned}$$

Mass balance provides an equation for [EH].

$$\begin{aligned} [\text{E}]_0 &= [\text{E}^-] + [\text{EH}] + [\text{EH}_2^+] + [\text{ES}^-] + [\text{ESH}] + [\text{ESH}_2] \\ &= \frac{K_{\text{E,a}}[\text{EH}]}{[\text{H}^+]} + [\text{EH}] + \frac{[\text{EH}][\text{H}^+]}{K_{\text{E,b}}} + \frac{K_{\text{ES,a}}[\text{ESH}]}{[\text{H}^+]} + [\text{ESH}] + \frac{[\text{ESH}][\text{H}^+]}{K_{\text{ES,b}}} \\ [\text{EH}] &= \frac{[\text{E}]_0 - \{1 + ([\text{H}^+]/K_{\text{ES,b}}) + (K_{\text{ES,a}}/[\text{H}^+])\} [\text{ESH}]}{1 + ([\text{H}^+]/K_{\text{E,b}}) + (K_{\text{E,a}}/[\text{H}^+])} \\ &= \frac{[\text{E}]_0 - c_1[\text{ESH}]}{c_2} \end{aligned}$$

The steady-state approximation provides an equation for [ESH],

$$\begin{aligned} \frac{d[\text{ESH}]}{dt} &= k_a[\text{EH}][\text{S}] - k'_a[\text{ESH}] - k_b[\text{ESH}] = 0 \\ [\text{ESH}] &= \frac{k_a}{k'_a + k_b} [\text{EH}][\text{S}] = k_{\text{M}}^{-1} [\text{EH}][\text{S}] \\ &= k_{\text{M}}^{-1} [\text{S}] \left\{ \frac{[\text{E}]_0 - c_1[\text{ESH}]}{c_2} \right\} \\ [\text{ESH}] &= \frac{K_{\text{M}}^{-1} [\text{S}][\text{E}]_0/c_2}{1 + (k_{\text{M}}^{-1} [\text{S}]c_1/c_2)} = \frac{[\text{E}]_0/c_1}{1 + (k_{\text{M}}(c_2/c_1)/[\text{S}])} \end{aligned}$$

The rate law becomes:

$$\begin{aligned} v &= d[\text{P}]/dt = k_b[\text{ESH}] \\ v &= \frac{v'_{\text{max}}}{1 + k'_{\text{M}}/[\text{S}]} \end{aligned}$$

$$\text{where } v'_{\text{max}} = \frac{k_b[\text{E}]_0}{\{1 + ([\text{H}^+]/K_{\text{ES,b}}) + (K_{\text{ES,a}}/[\text{H}^+])\}}$$

$$K'_{\text{M}} = \left\{ \frac{1 + ([\text{H}^+]/K_{\text{E,b}}) + (K_{\text{E,a}}/[\text{H}^+])}{1 + ([\text{H}^+]/K_{\text{ES,b}}) + (K_{\text{ES,a}}/[\text{H}^+])} \right\}$$

(b) $v_{\text{max}} = 1.0 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$

$$K_{\text{ES,b}} = 1.0 \times 10^{-6} \text{ mol dm}^{-3}$$

$$K_{\text{ES,a}} = 1.0 \times 10^{-8} \text{ mol dm}^{-3}$$

The graph (Figure 23.5a) indicates a maximum value of v'_{max} at pH = 7.0 for this set of equilibrium and kinetic constants. A formula for the pH of the maximum can be derived by finding the point at

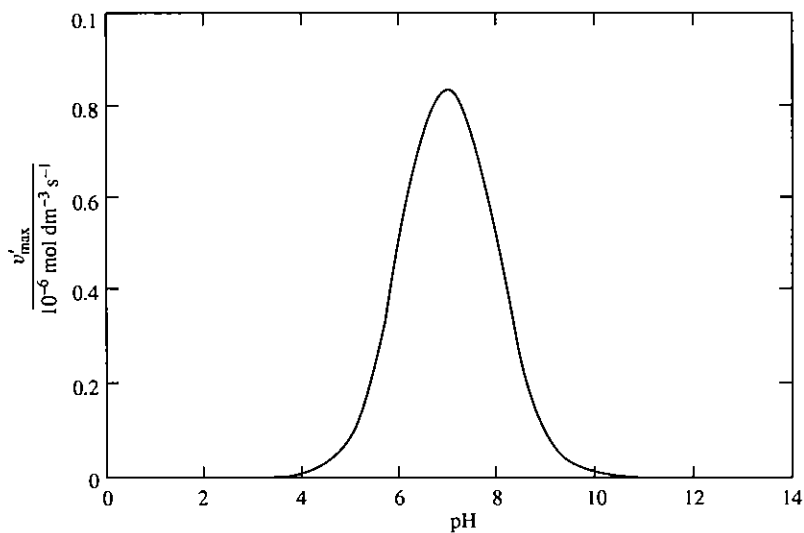


Figure 23.5(a)

which $\frac{dv'_{\max}}{d[H^+]} = 0$. This gives:

$$[H^+]_{\max} = (K_{ES,a} K_{ES,b})^{1/2}$$

$$\begin{aligned} \text{Inserting constants, } [H^+]_{\max} &= \sqrt{(1.0 \times 10^{-8} \text{ mol dm}^{-3})(1.0 \times 10^{-6} \text{ mol dm}^{-3})} \\ &= 1.0 \times 10^{-7} \text{ mol dm}^{-3} \end{aligned}$$

which corresponds to pH = 7.0

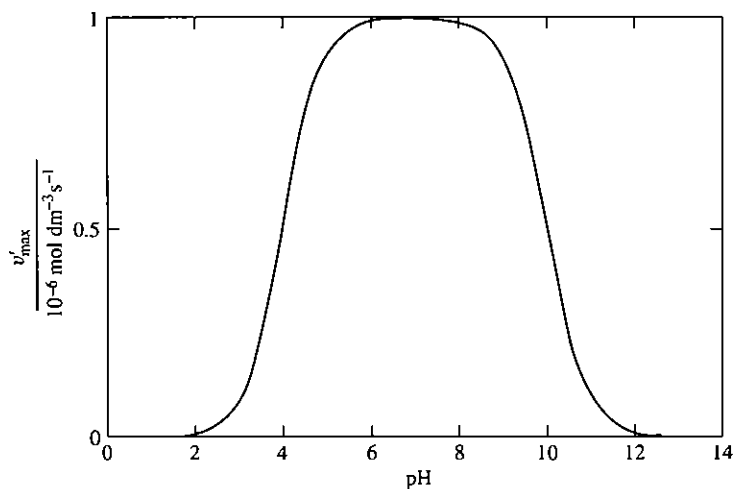


Figure 23.5(b)

$$(c) \quad v_{\max} = 1.0 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$K_{\text{ES},b} = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$$

$$K_{\text{ES},a} = 1.0 \times 10^{-10} \text{ mol dm}^{-3}$$

The constants of part (c) give a much broader curve (Figure 23.5b) than do the constants of part (b). This reflects the behavior of the term $1 + [\text{H}^+]/K_{\text{ES},b} + K_{\text{ES},a}/[\text{H}^+]$ in the denominator of the v'_{\max} expression. When $K_{\text{ES},b}$ is relatively large, large $[\text{H}^+]$ values (low pH) cause growth in the values of v'_{\max} . However, when $K_{\text{ES},a}$ is relatively small, very small $[\text{H}^+]$ values (high pH) cause a decline in the v'_{\max} values.

P23.28 The description of the progress of infectious diseases can be represented by the mechanism



Only the first step is autocatalytic as indicated in the first rate expression. If the three rate equations are added

$$\frac{dS}{dt} + \frac{dI}{dt} + \frac{dR}{dt} = 0$$

and, hence there is no change with time of the total population, that is

$$S(t) + I(t) + R(t) = N$$

Whether the infection spreads or dies out is determined by

$$\frac{dI}{dt} = rSI - aI$$

At $t = 0$, $I = I(0) = I_0$. Since the process is autocatalytic $I(0) \neq 0$.

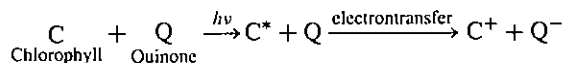
$$\left(\frac{dI}{dt} \right)_{t=0} = I_0 (rS_0 - a)$$

If $a > rS_0 \left(\frac{dI}{dt} \right)_{t=0} < 0$, and the infection dies out. If $a < rS_0 \left(\frac{dI}{dt} \right)_{t=0} > 0$ and the infection spreads (an epidemic). Thus

$$\boxed{\frac{a}{r} < S_0} \quad [\text{infection spreads}]$$

$$\boxed{\frac{a}{r} > S_0} \quad [\text{infection dies out}]$$

P23.30



Direct electron transfer from the ground state of C is not spontaneous. It is spontaneous from the excited state. The difference between the ΔG 's of the two processes is given by the expression:

$$\Delta(\Delta G) = \Delta G_{\text{C}^*} - \Delta G_{\text{C}} \approx U_{\text{C}} - U_{\text{C}^*} \approx -(U_{\text{LUMO}} - U_{\text{HOMO}})$$

where U_{LUMO} and U_{HOMO} are energies of the LUMO and HOMO of chlorophyll. Since $\Delta\Delta G < 0$, we see that electron transfer is exergonic and spontaneous when the electron is transferred from the excited state of chlorophyll.

- P23.32** 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

$$A = -\log T = \epsilon cl \quad \text{so} \quad 1 - T = 1 - 10^{-\epsilon cl}$$

$$1 - T = 1 - 10^{-(260 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) \times (8 \times 10^{-9} \text{ mol dm}^{-3}) \times (10^5 \text{ cm})} = 0.38$$

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

$$\begin{aligned} \nu &= \phi (1 - T) F = (0.94) \times (0.38) \times \frac{(1 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}) \times (1000 \text{ cm}^3 \text{ dm}^{-3})}{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (10^5 \text{ cm})} \\ &= \boxed{5.9 \times 10^{-13} \text{ mol dm}^{-3} \text{ s}^{-1}} \end{aligned}$$

- P23.34** The rate of reaction for this reaction is

$$\nu = k[\text{Cl}][\text{O}_3]$$

$$\begin{aligned} \text{(a)} \quad \nu &= (1.7 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \exp(-260 \text{ K}/220 \text{ K}) \times (5 \times 10^{-17} \text{ mol dm}^{-3}) \\ &\quad \times (8 \times 10^{-9} \text{ mol dm}^{-3}) \\ &= \boxed{2.1 \times 10^{-15} \text{ mol dm}^{-3} \text{ s}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \nu &= (1.7 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \exp(-260 \text{ K}/270 \text{ K}) \times (3 \times 10^{-15} \text{ mol dm}^{-3}) \\ &\quad \times (8 \times 10^{-11} \text{ mol dm}^{-3}) \\ &= \boxed{1.6 \times 10^{-15} \text{ mol dm}^{-3} \text{ s}^{-1}} \end{aligned}$$

24

Molecular reaction dynamics

Answers to discussion questions

- D24.2** A reaction in solution can be regarded as the outcome of two stages: one is the encounter of two reactant species; this is followed by their reaction in the second stage, if they acquire their activation energy. If the rate-determining step is the 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 $A + B \rightarrow P$ that obeys the second-order rate law $v = k_2[A][B]$, in the diffusion-controlled regime,

$$k_2 = 4\pi R^* D N_A$$

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.

- D24.4** 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–Hückel 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

$$\log k = \log k^\circ + 2A z_A z_B I^{1/2}$$

- D24.6** Refer to Figures 24.21 and 24.22 of the text. The first of these figures shows an attractive potential energy surface, the second, a repulsive surface.

(a) Consider Figure 24.21. 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 (Figure 24.22). 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.

D24.8 Donor (D) and acceptor (A) must collide before they can react. Consequently, the rate of their reaction in solution is initially determined by the rate of diffusion of the reacting species. After D and A have arrived at the critical reaction distance r^* (comparable to r , the edge-to-edge distance), the rate constant for electron transfer is a function of two factors. See Sections 24.11(a) and (b) and eqn 24.81. The first is the tunneling rate of the electron through an energy barrier that is a function of the ionization energies of the complexes DA and D^+A^- . The second is the Gibbs energy of activation.

Effective transfer can occur only when the electronic energies in the two complexes match. The electronic energies are a function of the internuclear separations in DA and D^+A^- as illustrated in Figures 24.27 and 24.28; therefore, the distance between D and A plays a critical role in determining the rate of electron transfer. The tunneling rate is determined by the matrix element of the coupling term in the Hamiltonian which exhibits an exponential dependence on the negative of r , as given by eqn 24.80.

Further Information 24.1 shows how the Gibbs energy of activation is related to the reorganization energy associated with molecular rearrangements which include the relative reorientation of the D and A molecules and the relative reorientation of the solvent molecules surrounding DA.

Solutions to exercises

E24.1(b) The collision frequency is

$$\begin{aligned}
 z &= \frac{2^{1/2} \sigma \langle \bar{c} \rangle p}{kT} \quad \text{where } \sigma = \pi d^2 = 4\pi r^2 \text{ and } \langle \bar{c} \rangle = \left(\frac{8RT}{\pi M} \right)^{1/2} \\
 \text{so } z &= \frac{2^{1/2} p (4\pi r^2) \left(\frac{8RT}{\pi M} \right)^{1/2}}{kT} = \frac{16pN_A r^2 \pi^{1/2}}{(RTM)^{1/2}} \\
 &= \frac{16 \times (100 \times 10^3 \text{ Pa}) \times (6.022 \times 10^{23} \text{ mol}^{-1}) \times (180 \times 10^{-12} \text{ m})^2 \times (\pi)^{1/2}}{[(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (28.01 \times 10^{-3} \text{ kg mol}^{-1})]^{1/2}} \\
 &= \boxed{6.64 \times 10^9 \text{ s}^{-1}}
 \end{aligned}$$

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 percent increase in z and Z_{AA} due to a 10 K increase in temperature is $\boxed{1.6 \text{ percent}}$, same as Exercise 24.1(a).

E24.2(b) The appropriate fraction is given by

$$f = \exp\left(\frac{-E_a}{RT}\right)$$

The values in question are

$$\begin{aligned} \text{(a)} \quad \text{(i)} \quad f &= \exp\left(\frac{-15 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}\right) = \boxed{2.4 \times 10^{-3}} \\ \text{(ii)} \quad f &= \exp\left(\frac{-15 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (800 \text{ K})}\right) = \boxed{0.10} \\ \text{(b)} \quad \text{(i)} \quad f &= \exp\left(\frac{-150 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}\right) = \boxed{7.7 \times 10^{-27}} \\ \text{(ii)} \quad f &= \exp\left(\frac{-150 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (800 \text{ K})}\right) = \boxed{1.6 \times 10^{-10}} \end{aligned}$$

E24.3(b) A straightforward approach would be to compute $f = \exp(-E_a/RT)$ at the new temperature and compare it to that at the old temperature. An approximate approach would be to note that f changes from $f_0 = \exp(-E_a/RT)$ to $f = \exp(-E_a/RT(1+x))$, where x is the fractional increase in the temperature. If x is small, the exponent changes from $-E_a/RT$ to approximately $(-E_a/RT)(1-x)$ and f changes from $\exp(-E_a/RT)$ to $\exp(-E_a(1-x)/RT) = \exp(-E_a/RT) [\exp(-E_a/RT)]^{-x} = f_0 f_0^{-x}$. Thus the new Boltzmann factor is the old one times a factor of f_0^{-x} . The factor of increase is

$$\begin{aligned} \text{(a)} \quad \text{(i)} \quad f_0^{-x} &= (2.4 \times 10^{-3})^{-10/300} = \boxed{1.2} \\ \text{(ii)} \quad f_0^{-x} &= (0.10)^{-10/800} = \boxed{1.03} \\ \text{(b)} \quad \text{(i)} \quad f_0^{-x} &= (7.7 \times 10^{-27})^{-10/300} = \boxed{7.4} \\ \text{(ii)} \quad f_0^{-x} &= (1.6 \times 10^{-10})^{-10/800} = \boxed{1.3} \end{aligned}$$

E24.4(b) The reaction rate is given by

$$\nu = P\sigma \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} N_A \exp(-E_a/RT) [D_2][Br_2]$$

so, in the absence of any estimate of the reaction probability P , the rate constant is

$$\begin{aligned}
 k &= \sigma \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} N_A \exp(-E_a/RT) \\
 &= [0.30 \times (10^{-9} \text{ m})^2] \times \left(\frac{8(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (450 \text{ K})}{\pi(3.930 \text{ u}) \times (1.66 \times 10^{-27} \text{ kg u}^{-1})} \right)^{1/2} \\
 &\quad \times (6.022 \times 10^{23} \text{ mol}^{-1}) \exp \left(\frac{-200 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (450 \text{ K})} \right) \\
 &= 1.71 \times 10^{-15} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} = \boxed{1.7 \times 10^{12} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}
 \end{aligned}$$

E24.5(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

$$k_d = \boxed{3.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

E24.6(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

$$k_d = \frac{8RT}{3\eta} = \frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{3 \times (27 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})} = \boxed{2.4 \times 10^5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

E24.7(b) The diffusion-controlled rate constant is

$$k_d = \frac{8RT}{3\eta} = \frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{3 \times (0.601 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})} = \boxed{1.10 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

In more common units, $k_d = \boxed{1.10 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$

The recombination reaction has a rate of

$$v = k_d[A][B] \quad \text{with } [A] = [B]$$

so the half-life is given by

$$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{(1.10 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \times (1.8 \times 10^{-3} \text{ mol dm}^{-3})} = \boxed{5.05 \times 10^{-8} \text{ s}}$$

E24.8(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

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

$$\text{Now } \sigma_{AB} = \pi d_{AB}^2 = \pi \left[\frac{1}{2}(d_A + d_B) \right]^2 = \frac{1}{4}(\sigma_{AA}^{1/2} + \sigma_{BB}^{1/2})^2$$

$$\begin{aligned} \text{so } P &= \frac{\sigma^*}{\frac{1}{4}(\sigma_{AA}^{1/2} + \sigma_{BB}^{1/2})^2} \\ &= \frac{8.7 \times 10^{-22} \text{ m}^2}{\frac{1}{4}[(0.88)^{1/2} + (0.40)^{1/2}]^2 \times 10^{-9} \text{ m}^2} = \boxed{1.41 \times 10^{-3}} \end{aligned}$$

E24.9(b) The diffusion-controlled rate constant is

$$k_d = \frac{8RT}{3\eta} = \frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293 \text{ K})}{3 \times (1.27 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})} = 5.12 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

In more common units, $k_d = 5.12 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

The recombination reaction has a rate of

$$\begin{aligned} \nu &= k_d[A][B] = (5.12 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \times (0.200 \text{ mol dm}^{-3}) \times (0.150 \text{ mol dm}^{-3}) \\ &= \boxed{1.54 \times 10^8 \text{ mol dm}^{-3} \text{ s}^{-1}} \end{aligned}$$

E24.10(b) The enthalpy of activation for a reaction in solution is

$$\begin{aligned} \Delta^\ddagger H &= E_a - RT = (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (6134 \text{ K}) - (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \\ &= 4.852 \times 10^4 \text{ J mol}^{-1} = \boxed{48.52 \text{ kJ mol}^{-1}} \end{aligned}$$

The entropy of activation is

$$\begin{aligned} \Delta^\ddagger S &= R \left(\ln \frac{A}{B} - 1 \right) \quad \text{where } B = \frac{kRT^2}{hp^\ominus} \\ B &= \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})^2}{(6.626 \times 10^{-34} \text{ J s}) \times (1.00 \times 10^5 \text{ Pa})} \\ &= 1.54 \times 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} \text{so } \Delta^\ddagger S &= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left(\ln \frac{8.72 \times 10^{12} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}{(1000 \text{ dm}^3 \text{ m}^{-3}) \times (1.54 \times 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1})} - 1 \right) \\ &= \boxed{-32.2 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

COMMENT. In this connection, the enthalpy of activation is often referred to as "energy" of activation.

E24.11(b) The Gibbs energy of activation is related to the rate constant by

$$k_2 = B \exp\left(\frac{-\Delta^\ddagger G}{RT}\right) \quad \text{where } B = \frac{kRT^2}{hp^\ominus} \quad \text{so } \Delta^\ddagger G = -RT \ln \frac{k_2}{B}$$

$$\begin{aligned} k_2 &= (6.45 \times 10^{13} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) e^{-(5375 \text{ K})/(298 \text{ K})} = 9.47 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\ &= 947 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \end{aligned}$$

Using the value of B computed in Exercise 27.13(b), we obtain

$$\begin{aligned} \Delta^\ddagger G &= -(8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln\left(\frac{947 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}{1.54 \times 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}\right) \\ &= \boxed{46.8 \text{ kJ mol}^{-1}} \end{aligned}$$

E24.12(b) The entropy of activation for a bimolecular reaction in the gas phase is

$$\begin{aligned} \Delta^\ddagger S &= R \left(\ln \frac{A}{B} - 2 \right) \quad \text{where } B = \frac{kRT^2}{hp^\ominus} \\ B &= \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times [(55 + 273) \text{ K}]^2}{(6.626 \times 10^{-34} \text{ J s}) \times (1.00 \times 10^5 \text{ Pa})} \\ &= 1.86 \times 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \end{aligned}$$

The rate constant is

$$\begin{aligned} k_2 &= A \exp\left(\frac{-E_a}{RT}\right) \quad \text{so } A = k_2 \exp\left(\frac{E_a}{RT}\right) \\ A &= (0.23 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}) \times \exp\left(\frac{49.6 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (328 \text{ K})}\right) \\ &= 1.8 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} \text{and } \Delta^\ddagger S &= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left(\ln \left(\frac{1.8 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}{1.86 \times 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}} \right) - 2 \right) \\ &= \boxed{-93 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

E24.13(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

$$A = 4 \times (6.022 \times 10^{23} \text{ mol}^{-1}) \times \left(\frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (500 \text{ K})}{\pi \times (78 \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} \times (0.68 \times 10^{-18} \text{ m}^2)$$

$$= 2.13 \times 10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$B = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (500 \text{ K})^2}{(6.626 \times 10^{-34} \text{ J s}) \times (1.00 \times 10^5 \text{ Pa})}$$

$$= 4.33 \times 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$\text{and } \Delta^\ddagger S = (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left(\ln \left(\frac{2.13 \times 10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}{4.33 \times 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}} \right) - 2 \right)$$

$$= \boxed{-80.0 \text{ J K}^{-1} \text{ mol}^{-1}}$$

E24.14(b) (a) The entropy of activation for a unimolecular gas-phase reaction is

$$\Delta^\ddagger S = R \left(\ln \frac{A}{B} - 1 \right) \quad \text{where } B = 1.54 \times 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ [See Exercise 24.14(a)]}$$

$$\text{so } \Delta^\ddagger S = (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\times \left(\ln \left(\frac{2.3 \times 10^{13} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}{(1000 \text{ dm}^3 \text{ m}^{-3}) \times (1.54 \times 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1})} \right) - 1 \right)$$

$$= \boxed{-24.1 \text{ J K}^{-1} \text{ mol}^{-1}}$$

(b) The enthalpy of activation is

$$\Delta^\ddagger H = E_a - RT = 30.0 \times 10^3 \text{ J mol}^{-1} - (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})$$

$$= 27.5 \times 10^3 \text{ J mol}^{-1} = \boxed{27.5 \text{ kJ mol}^{-1}}$$

(c) The Gibbs energy of activation is

$$\Delta^\ddagger G = \Delta^\ddagger H - T \Delta^\ddagger S = 27.5 \text{ kJ mol}^{-1} - (298 \text{ K}) \times (-24.1 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})$$

$$= \boxed{34.7 \text{ kJ mol}^{-1}}$$

E24.15(b) The dependence of a rate constant on ionic strength is given by

$$\log k_2 = \log k_2^\circ + 2A z_A z_B I^{1/2}$$

At infinite dilution, $I = 0$ and $k_2 = k_2^\circ$, so we must find

$$\begin{aligned}\log k_2^\circ &= \log k_2 - 2A z_A z_B I^{1/2} = \log(1.55) - 2 \times (0.509) \times (+1) \times (+1) \times (0.0241)^{1/2} \\ &= 0.0323 \quad \text{and} \quad \boxed{k_2^\circ = 1.08 \text{ dm}^6 \text{ mol}^{-2} \text{ min}^{-1}}\end{aligned}$$

E24.16(b) Equation 24.84 holds for a donor-acceptor pair separated by a constant distance, assuming that the reorganization energy is constant:

$$\ln k_{\text{et}} = -\frac{(\Delta_r G^\ominus)^2}{4\lambda RT} - \frac{\Delta_r G^\ominus}{2RT} + \text{constant},$$

or equivalently

$$\ln k_{\text{et}} = -\frac{(\Delta_r G^\ominus)^2}{4\lambda kT} - \frac{\Delta_r G^\ominus}{2kT} + \text{constant},$$

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 equations (eqn 24.84 applied to the two sets) in two unknowns: λ and the constant.

$$\ln k_{\text{et},1} + \frac{(\Delta_r G_1^\ominus)^2}{4\lambda kT} + \frac{\Delta_r G_1^\ominus}{2kT} = \text{constant} = \ln k_{\text{et},2} + \frac{(\Delta_r G_2^\ominus)^2}{4\lambda kT} + \frac{\Delta_r G_2^\ominus}{2kT},$$

$$\text{so } \frac{(\Delta_r G_1^\ominus)^2 - (\Delta_r G_2^\ominus)^2}{\Delta\lambda kT} = \ln \frac{k_{\text{et},2}}{k_{\text{et},1}} + \frac{\Delta_r G_2^\ominus - \Delta_r G_1^\ominus}{2kT}$$

$$\text{and } \lambda = \frac{(\Delta_r G_1^\ominus)^2 - (\Delta_r G_2^\ominus)^2}{4 \left(kT \ln(k_{\text{et},2}/k_{\text{et},1}) + (\Delta_r G_2^\ominus - \Delta_r G_1^\ominus)/2 \right)}$$

$$\lambda = \frac{(-0.665 \text{ eV})^2 - (-0.975 \text{ eV})^2}{4(1.381 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K}) \ln \frac{3.33 \times 10^6}{2.02 \times 10^5} - 2(0.975 - 0.665) \text{ eV}} = \boxed{1.53 \text{ eV}}$$

If we knew the activation Gibbs energy, we could use eqn 24.81 to compute $\langle H_{\text{DA}} \rangle$ from either rate constant, and we *can* compute the activation Gibbs energy from eqn 24.82:

$$\Delta^\ddagger G = \frac{(\Delta_r G^\ominus + \lambda)^2}{4\lambda} = \frac{[(-0.665 + 1.53 \text{ eV})]^2}{4(1.53 \text{ eV})} = 0.122 \text{ eV}.$$

$$\text{Now } k_{\text{et}} = \frac{2 \langle H_{\text{DA}} \rangle^2}{h} \left(\frac{\pi^3}{4\lambda kT} \right)^{1/2} \exp \left(\frac{-\Delta^\ddagger G}{kT} \right)$$

$$\begin{aligned}
 \text{so } \langle H_{\text{DA}} \rangle &= \left(\frac{h k_{\text{ct}}}{2} \right)^{1/2} \left(\frac{4 \lambda k T}{\pi^3} \right)^{1/4} \exp \left(\frac{\Delta^\ddagger G}{2 k T} \right), \\
 \langle H_{\text{DA}} \rangle &= \left(\frac{(6.626 \times 10^{-34} \text{ J s})(2.02 \times 10^5 \text{ s}^{-1})}{2} \right)^{1/2} \\
 &\quad \times \left(\frac{4(1.53 \bar{\text{I}} \text{ eV})(1.602 \times 10^{-19} \text{ J eV}^{-1})(1.381 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}{\pi^3} \right)^{1/4} \\
 &\quad \times \exp \left(\frac{(0.122 \text{ eV})(1.602 \times 10^{-19} \text{ J eV}^{-1})}{2(1.381 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})} \right) = \boxed{9.39 \times 10^{-24} \text{ J}}
 \end{aligned}$$

E24.17(b) Equation 24.83 applies. In Exercise 24.17(a), we found the parameter β to equal 12 nm^{-1} , so:

$$\ln k_{\text{ct}}/\text{s}^{-1} = -\beta r + \text{constant} \quad \text{so} \quad \text{constant} = \ln k_{\text{ct}}/\text{s}^{-1} + \beta r,$$

and $\text{constant} = \ln 2.02 \times 10^5 + (12 \text{ nm}^{-1})(1.11 \text{ nm}) = 25$.

Taking the exponential of eqn 24.83 yields:

$$k_{\text{ct}} = e^{-\beta r + \text{constant}} \text{s}^{-1} = e^{-(12/\text{nm})(1.48 \text{ nm}) + 25} \text{s}^{-1} = \boxed{1.4 \times 10^3 \text{ s}^{-1}}.$$

Solutions to problems

Solutions to numerical problems

P24.2 Draw up the following table as the basis of an Arrhenius plot

T/K	600	700	800	1000
$10^3 \text{ K}/T$	1.67	1.43	1.25	1.00
$k/(\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	4.6×10^2	9.7×10^3	1.3×10^5	3.1×10^6
$\ln(k/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	6.13	9.18	11.8	14.9

The points are plotted in Figure 24.1.

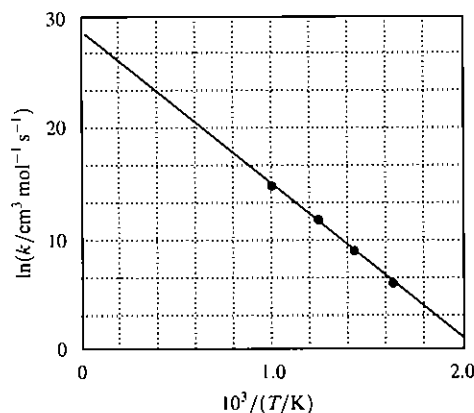


Figure 24.1

The least-squares intercept is at 28.3, which implies that

$$A/(\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = e^{28.3} = 2.0 \times 10^{12}$$

$$\text{From } A = N_A \sigma^* \left(\frac{8kT}{\pi\mu} \right)^{1/2} \quad [\text{Exercise 24.13(a)}]$$

$$\begin{aligned} \sigma^* &= \frac{A_{\text{exptl}}}{N_A (8kT/\pi\mu)^{1/2}} \quad \text{with } \mu = \frac{1}{2}m(\text{NO}_2) \\ &= \left(\frac{A_{\text{exptl}}}{4N_A} \right) \left(\frac{\pi m}{kT} \right)^{1/2} = \left(\frac{2.0 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}{(4) \times (6.022 \times 10^{23} \text{ mol}^{-1})} \right) \\ &\quad \times \left(\frac{(\pi) \times (46 \text{ u}) \times (1.6605 \times 10^{-27} \text{ kg u}^{-1})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (750 \text{ K})} \right)^{1/2} \\ &= 4.0 \times 10^{-21} \text{ m}^2 \quad \text{or} \quad \boxed{4.0 \times 10^{-3} \text{ nm}^2} \end{aligned}$$

$$P = \frac{\sigma^*}{\sigma} = \frac{4.0 \times 10^{-3} \text{ nm}^2}{0.60 \text{ nm}^2} = \boxed{0.007}$$

P24.4 Draw up the following table for an Arrhenius Plot

$\theta/^\circ\text{C}$	-24.82	-20.73	-17.02	-13.00	-8.95
T/K	248.33	252.42	256.13	260.15	264.20
$10^3/(T/\text{K})$	4.027	3.962	3.904	3.844	3.785
$\ln(k/\text{s}^{-1})$	-9.01	-8.37	-7.73	-7.07	-6.55

The points are plotted in Figure 24.2.

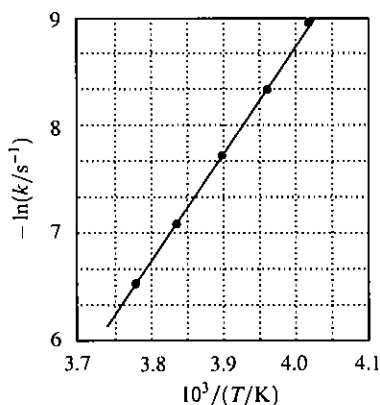


Figure 24.2

A least-squares fit of the data yields the intercept $+32.6$ at $1/T = 0$ and slope $-10.33 \times 10^3 \text{ K}$. The former implies that $\ln(A/\text{s}^{-1}) = 32.6$, and hence that $A = 1.4 \times 10^{14} \text{ s}^{-1}$. The slope yields $E_a/R = 10.33 \times 10^3 \text{ K}$, and hence $E_a = \boxed{85.9 \text{ kJ mol}^{-1}}$

In solution $\Delta^\ddagger H = E_a - RT$, so at -20°C

$$\begin{aligned}\Delta^\ddagger H &= (85.9 \text{ kJ mol}^{-1}) - (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (253 \text{ K}) \\ &= \boxed{83.8 \text{ kJ mol}^{-1}}\end{aligned}$$

We assume that the reaction is first-order for which, by analogy to Section 24.4

$$K^\ddagger = K = \frac{kT}{h\nu} \bar{K}^\ddagger$$

$$\text{and } k_1 = k^\ddagger K^\ddagger = \nu \times \frac{kT}{h\nu} \times \bar{K}^\ddagger$$

$$\text{with } \Delta^\ddagger G = -RT \ln \bar{K}^\ddagger$$

$$\text{Therefore, } k_1 = A e^{-E_a/RT} = \frac{kT}{h} e^{-\Delta^\ddagger G/RT} = \frac{kT}{h} e^{\Delta^\ddagger S/R} e^{-\Delta^\ddagger H/RT}$$

and hence we can identify $\Delta^\ddagger S$ by writing

$$k_1 = \frac{kT}{h} e^{\Delta^\ddagger S/R} e^{-E_a/RT} = A e^{-E_a/RT}$$

and hence obtain

$$\begin{aligned}\Delta^\ddagger S &= R \left[\ln \left(\frac{hA}{kT} \right) - 1 \right] \\ &= 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times \left[\ln \left(\frac{(6.626 \times 10^{-34} \text{ J s}) \times (1.4 \times 10^{14} \text{ s}^{-1})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (253 \text{ K})} \right) - 1 \right] \\ &= \boxed{+19.1 \text{ J K}^{-1} \text{ mol}^{-1}}\end{aligned}$$

$$\text{Therefore, } \Delta^\ddagger G = \Delta^\ddagger H - T\Delta^\ddagger S = 83.8 \text{ kJ mol}^{-1} - 253 \text{ K} \times 19.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= \boxed{+79.0 \text{ kJ mol}^{-1}}$$

P24.6 Figure 24.3 shows that $\log k$ is proportional to the ionic strength for neutral molecules.

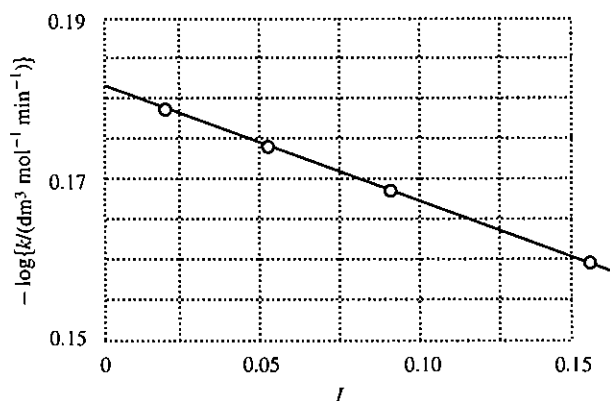


Figure 24.3

From the graph, the intercept at $I = 0$ is -0.182 , so

$$k^\circ = 0.658 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$$

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 24.69.

P24.8

Both approaches involve plots of $\log k$ versus $\log \gamma$, where γ is the activity coefficient. The limiting law has $\log \gamma$ proportional to $I^{1/2}$ (where I is ionic strength), so a plot of $\log k$ versus $I^{1/2}$ should give a straight line whose y -intercept is $\log k^\circ$ and whose slope is $2A z_A z_B$, where z_A and z_B are charges involved in the activated complex. The extended Debye–Hückel law has $\log \gamma$ proportional to $[I^{1/2}/(1 + B I^{1/2})]$, so it requires plotting $\log k$ versus $[I^{1/2}/(1 + B I^{1/2})]$, and it also has a slope of $2A z_A z_B$ and a y -intercept of $\log k^\circ$. The ionic strength in a 2 : 1 electrolyte solution is three times the molar concentration. The transformed data and plot (Figure 24.4) follow

$[\text{Na}_2\text{SO}_4] / (\text{mol kg}^{-1})$	0.2	0.15	0.1	0.05	0.025	0.0125	0.005
$k / (\text{dm}^{3/2} \text{ mol}^{-1} \text{ s}^{-1})$	0.462	0.430	0.390	0.321	0.283	0.252	0.224
$I^{1/2}$	0.775	0.671	0.548	0.387	0.274	0.194	0.122
$I^{1/2}/(1 + B I^{1/2})$	0.436	0.401	0.354	0.279	0.215	0.162	0.109
$\log k$	-0.335	-0.367	-0.409	-0.493	-0.548	-0.599	-0.650

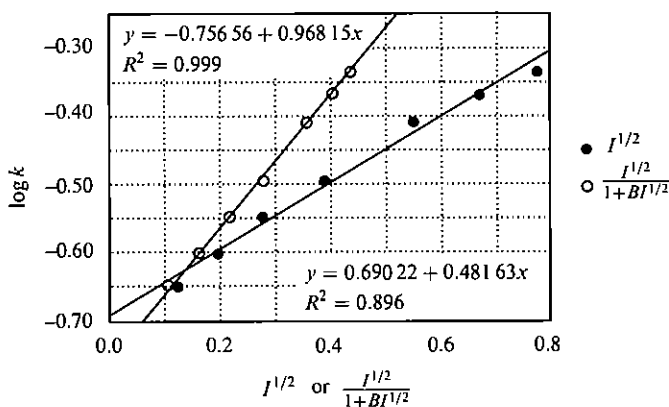


Figure 24.4

The line based on the limiting law appears curved. The zero-ionic-strength rate constant based on it is

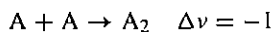
$$k^\circ = 10^{-0.690} \text{ dm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1} = 0.204 \text{ dm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1}$$

The slope is positive, so the complex must overcome repulsive interactions. The product of charges, however, works out to be 0.5, not easily interpretable in terms of charge numbers. The line based on the extended law appears straighter and has a better correlation coefficient. The zero-ionic-strength rate constant based on it is

$$k^\circ = 10^{-0.757} \text{ dm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1} = 0.175 \text{ dm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1}$$

The product of charges works out to be 0.9, nearly 1, interpretable in terms of
 a complex of two univalent ions of the same sign

P24.10



$$\begin{aligned} \Delta^\ddagger S &= R \left(\ln \left[\frac{A}{(kT/h) \times (RT/p^\ominus)} \right] + 2 \right) \quad [24.63] \\ &= -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &\quad \times \left[\ln \left[\frac{4.07 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} (m^3/10^3 \text{ dm}^3)}{\frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (300 \text{ K})^2 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})}{(6.626 \times 10^{-34} \text{ J s}) \times (1.013 \times 10^5 \text{ Pa})}} \right] + 2 \right] \\ &= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times [\ln(2.631 \times 10^{-9}) + 2] \end{aligned}$$

$$\Delta^\ddagger S = -148 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \Delta^\ddagger H &= E_a - 2RT = 65.43 \text{ kJ mol}^{-1} - 2 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K}) \\ &\quad \times \left(\frac{10^{-3} \text{ kJ}}{\text{J}} \right) \quad [24.60, 24.61] \end{aligned}$$

$$\Delta^\ddagger H = 60.44 \text{ kJ mol}^{-1}$$

$$\Delta^\ddagger H = \Delta^\ddagger U + \Delta^\ddagger(pV)$$

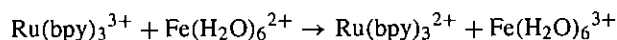
$$\begin{aligned} \Delta^\ddagger U &= \Delta^\ddagger H - \Delta^\ddagger(pV) = \Delta^\ddagger H - \Delta\nu RT \\ &= (60.44 \text{ kJ mol}^{-1}) - (-1) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K}) \times \left(\frac{10^{-3} \text{ kJ}}{\text{J}} \right) \end{aligned}$$

$$\Delta^\ddagger U = 62.9 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta^\ddagger G &= \Delta^\ddagger H - T\Delta^\ddagger S = 60.44 \text{ kJ mol}^{-1} - (300 \text{ K}) \times (-148 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &\quad \times \left(\frac{10^{-3} \text{ kJ}}{\text{J}} \right) \quad [24.59] \end{aligned}$$

$$\Delta^\ddagger G = 104.8 \text{ kJ mol}^{-1}$$

P24.12 Estimate the bimolecular rate constant k_{12} for the reaction



by using the approximate Marcus cross-relation:

$$k_{12} \approx (k_{11}k_{22}K)^{1/2}.$$

The standard cell potential for the reaction is:

$$E^{\circ} = E_{\text{red}}^{\circ}(\text{Ru}(\text{bpy})_3^{3+}) - E_{\text{red}}^{\circ}(\text{Fe}(\text{H}_2\text{O})_6^{3+}) = (1.26 - 0.77) \text{ V} = 0.49 \text{ V}$$

The equilibrium constant is:

$$K = \exp\left(\frac{\nu F E^{\circ}}{R T}\right) = \exp\left(\frac{(1)(96485 \text{ C mol}^{-1} \text{ s}^{-1})(0.49 \text{ V})}{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}\right) = 1.9 \times 10^8$$

The rate constant is approximately:

$$k_{12} \approx [(4.0 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})(4.2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})(1.9 \times 10^8)]^{1/2},$$

$$k_{12} \approx \boxed{5.6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

Solutions to theoretical problems

- P24.14** 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 24.40 by writing

$$z^2 = \frac{kx^2}{4D}, \quad \tau = kt, \quad j = \left(\frac{A}{n_0}\right) \left(\frac{\pi D}{k}\right)^{1/2} [\text{J}]^*$$

Then evaluate

$$j = \int_0^{\tau} \left(\frac{1}{\tau}\right)^{1/2} e^{-z^2/\tau} e^{-\tau} d\tau + \left(\frac{1}{\tau}\right)^{1/2} e^{-z^2/\tau} e^{-\tau}$$

for various values of k .

P24.16
$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]\gamma_{\text{HA}}} \gamma_{\pm}^2 \approx \frac{[\text{H}^+][\text{A}^-]\gamma_{\pm}^2}{[\text{HA}]}$$

Therefore,
$$[\text{H}^+] = \frac{[\text{HA}]K_a}{[\text{A}^-]\gamma_{\pm}^2}$$

and
$$\log[\text{H}^+] = \log K_a + \log \frac{[\text{HA}]}{[\text{A}^-]} - 2 \log \gamma_{\pm} = \log K_a + \log \frac{[\text{HA}]}{[\text{A}^-]} + 2A I^{1/2}$$

Write $v = k_2[\text{H}^+][\text{B}]$

then

$$\begin{aligned} \log v &= \log(k_2[\text{B}]) + \log[\text{H}^+] \\ &= \log(k_2[\text{B}]) + \log \frac{[\text{HA}]}{[\text{A}^-]} + 2A I^{1/2} + \log K_a \\ &= \log v^{\circ} + 2A I^{1/2}, \quad v^{\circ} = k_2 \frac{[\text{B}][\text{HA}]K_a}{[\text{A}^-]} \end{aligned}$$

That is, the logarithm of the rate should depend linearly on the square root of the ionic strength,

$$\boxed{\log v \propto I^{1/2}}$$

P24.18

$$k_1 = \frac{kT}{h} \times \frac{q^\ddagger}{q} e^{-\beta \Delta E} \text{ [Problem 24.17]}$$

$$q^\ddagger = q_z^{\ddagger V} q_y^{\ddagger V} q_x^R \approx \left(\frac{kT}{h\nu^\ddagger} \right)^2 q^R$$

$$q^R \approx \frac{1.027}{\sigma} \times \frac{(T/K)^{3/2}}{(B/\text{cm}^{-1})^{3/2}} \text{ [Table 20.4, } A = B = C] \approx 80$$

$$q = q_z^V q_y^V q_x^V \approx \left(\frac{kT}{h\nu} \right)^3$$

Therefore, $k_1 \approx 80 \times \frac{\nu^\ddagger}{\nu^3} e^{-\beta \Delta E_0} \approx 80 \times 5.4 \times 10^4 \text{ s}^{-1}$ [Problem 24.15] $= 4 \times 10^6 \text{ s}^{-1}$

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 $\nu^\ddagger = \frac{1}{2}\nu$.

P24.20

It follows that, since \mathcal{N}_S and l are the same for the two experiments,

$$\frac{\sigma(\text{CH}_2\text{F}_2)}{\sigma(\text{Ar})} = \frac{\ln 0.6}{\ln 0.9} \text{ [Problem 24.17]} = \boxed{5}$$

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 .

P24.22

We use the Eyring equation (combining eqns 24.53 and 24.51) to compute the bimolecular rate constant

$$k_2 = k \frac{kT}{h} \left(\frac{RT}{p^\ominus} \right) \frac{N_A \bar{q}_{\text{C}^\ddagger}^\ominus}{q_{\text{H}}^\ominus q_{\text{D}_2}^\ominus} \exp\left(\frac{-\Delta E_0}{RT}\right) \approx \frac{(RT)^2 \bar{q}_{\text{C}^\ddagger}^\ominus}{h p^\ominus q_{\text{H}}^\ominus q_{\text{D}_2}^\ominus} \exp\left(\frac{-\Delta E_0}{RT}\right)$$

We are to consider a variety of activated complexes, but the reactants, (H and D_2) and their partition functions do not change. Consider them first. The partition function of H is solely translational:

$$q_{\text{H}}^\ominus = \frac{RT}{p^\ominus \Lambda_{\text{D}_2}^3} \text{ and } \Lambda_{\text{H}} = \left(\frac{h^2}{2\pi k T m_{\text{H}}} \right)^{1/2} \text{ so } q_{\text{H}}^\ominus = \frac{RT(2\pi k T m_{\text{H}})^{3/2}}{p^\ominus h^3}$$

We have neglected the spin degeneracy of H, which will cancel with the spin degeneracy of the activated complex. The partition function of D_2 has a rotational term as well.

$$q_{\text{D}_2}^\ominus = \frac{RT}{p^\ominus \Lambda_{\text{D}_2}^3} \times \frac{kT}{\sigma h c B_{\text{D}_2}} = \frac{RkT^2(2\pi k T m_{\text{D}_2})^{3/2}}{2p^\ominus h^4 c B_{\text{D}_2}}$$

We have neglected the vibrational partition function of D_2 , which is very close to unity at the temperature in question. The symmetry number σ is 2 for a homonuclear diatomic, and the rotational constant is 30.44 cm^{-1} . Now, the partition function of the activated complex will have a translational piece that is the same regardless of the model:

$$\bar{q}_{\text{C}^\ddagger}^\ominus = q_{\text{C}^\ddagger, \text{trans}}^\ominus \times q_{\text{C}^\ddagger, \text{rot}}^\ominus \times \bar{q}_{\text{C}^\ddagger, \text{vib}}^\ominus$$

$$\text{where } q_{\text{C}^\ddagger, \text{trans}}^\ominus = \frac{RT(2\pi k T m_{\text{HD}_2})^{3/2}}{p^\ominus h^3}$$

Let us aggregate the model-independent factors into a single term, F where:

$$F = \frac{(RT)^2 q_{C^\ddagger, \text{trans}}^\ominus}{h p^\ominus q_H^\ominus q_{D_2}^\ominus} \exp\left(\frac{-\Delta E_0}{RT}\right) = \frac{2h^3 c B_{D_2} m_{HD_2}^{3/2}}{kT (2\pi m_H m_{D_2} kT)^{3/2}} \exp\left(\frac{-\Delta E_0}{RT}\right)$$

$$F = h^3 c B_{D_2} \left(\frac{5^3}{2m_H^3 (4)^3 \pi^3 T^3 k^5} \right)^{1/2} \exp\left(\frac{-\Delta E_0}{RT}\right) = 2.71 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

where we have taken $m_{HD_2} = 5m_H$ and $m_{D_2} = 4m_H$.

Now $\kappa_2 = F \times q_{C^\ddagger, \text{rot}} \times \bar{q}_{C^\ddagger, \text{vib}}$. The number of vibrational modes in the activated complex is $3 \times 3 - 6 = 3$ for a nonlinear complex, one more for a linear complex; however, in either case, one mode is the reaction coordinate, and is removed from the partition function. Therefore, assuming all real vibrations to have the same wavenumber $\tilde{\nu}$

$$\bar{q}_{C^\ddagger} = q_{\text{mode}}^2 (\text{nonlinear}) \text{ or } q_{\text{mode}}^3 (\text{linear})$$

where

$$q_{\text{mode}} = \left[1 - \exp\left(\frac{-hc\tilde{\nu}}{kT}\right) \right]^{-1} = 1.028$$

if the vibrational wavenumbers are 1000 cm^{-1} . The rotational partition function is

$$q_{C^\ddagger, \text{rot}} = \frac{kT}{\sigma hcB} (\text{linear}) \text{ or } \frac{1}{\sigma} \left(\frac{\kappa T}{hc} \right)^{3/2} \left(\frac{\pi}{ABC} \right)^{1/2} (\text{nonlinear})$$

where the rotational constants are related to moments of inertia by

$$B = \frac{h}{4\pi cI} \text{ where } I = \sum mr^2$$

and r is the distance from an atom to a rotational axis.

(a) The first model for the activated complex is triangular, with two equal sides of

$$s = 1.30(74 \text{ pm}) = 96 \text{ pm}$$

and a base of

$$b = 1.20(74 \text{ pm}) = 89 \text{ pm}$$

The moment of inertia about the axis of the altitude of the triangle (z-axis) is

$$I_1 = 2m_D(b/2)^2 = m_H b^2 \text{ so } A = \frac{h}{4\pi c m_H b^2} = 21.2 \text{ cm}^{-1}$$

To find the other moments of inertia, we need to find the center of mass. Clearly it is in the plane of the molecule and on the z-axis; the center of mass is the position z at which

$$\sum_i m_i(z_i - z) = 0 = 2(2m_H)(0 - z) + m_H(H - z)$$

where H is the height of the triangle,

$$H = [s^2 - (b/2)^2]^{1/2} = 85 \text{ pm}$$

so the center of mass is

$$z = H/5$$

The moment of inertia about the axis in the plane of the triangle perpendicular to the altitude is

$$I_2 = 2(2m_{\text{H}})(H/5)^2 + m_{\text{H}}(4H/5)^2 = (4m_{\text{H}}/5)H^2$$

$$\text{so } B = \frac{\hbar}{4\pi c(4m_{\text{H}}/5)H^2} = 28.3 \text{ cm}^{-1}$$

The distance from the center of mass to the D atoms is

$$r_D = [(H/5)^2 + (b/2)^2]^{1/2} = 48 \text{ pm}$$

and the moment of inertia about the axis perpendicular to the plane of the triangle is

$$I_3 = 2(2m_{\text{H}})r_D^2 + m_{\text{H}}(4H/5)^2 = 2(2m_{\text{H}})[(H/5)^2 + (b/2)^2] + m_{\text{H}}(4H/5)^2$$

$$I_3 = (4m_{\text{H}}/5)(s^2 + b^2)$$

$$\text{so } C = \frac{\hbar}{4\pi c(4m_{\text{H}}/5)(s^2 + b^2)} = 12.2 \text{ cm}^{-1}. \text{ The rotational partition function is:}$$

$$q_{\text{C}^\ddagger, \text{rot}} = \frac{1}{s} \left(\frac{kT}{hc} \right)^{3/2} \left(\frac{\pi}{ABC} \right)^{1/2} = 47.7$$

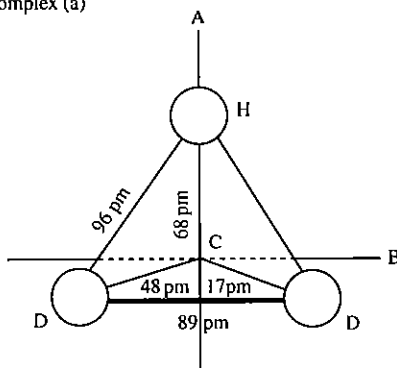
(The symmetry number σ is 2 for this model.) The vibrational partition function is

$$\bar{q}_{\text{C}^\ddagger, \text{vib}} = q_{\text{mode}}^2 = 1.057$$

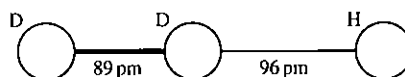
So the rate constant is:

$$k_2 = F \times q_{\text{C}^\ddagger, \text{rot}} \times \bar{q}_{\text{C}^\ddagger, \text{vib}} = \boxed{1.37 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

complex (a)



complex (b)



- (b) To compute the moment of inertia, we need the center of mass. Let the terminal D atom be at $x = 0$, the central D atom at $x = b$, and the H atom at $x = b + s$. The center of mass is the position X at which

$$\sum_i m_i(x_i - X) = 0 = 2m_H(0 - X) + 2m_H(b - X) + m_H(s + b - X)$$

$$5X = 3b + s \text{ so } x = (3b + s)/5$$

The moment of inertia is

$$I = \sum_i m_i(x_i - X)^2 = 2m_H X^2 + 2m_H(b - X)^2 + m_H(s + b - X)^2$$

$$= 3.97 \times 10^{-47} \text{ m kg}^2$$

and $B = \frac{h}{4\pi cI} = 7.06 \text{ cm}^{-1}$. The rotational partition function is

$$q_{C^\ddagger, \text{rot}} = \frac{kT}{\sigma hcB} = 39.4$$

(The symmetry number σ is 1 for this model.) The vibrational partition function is

$$\bar{q}_{C^\ddagger, \text{vib}} = q_{\text{mode}}^3 = 1.09$$

So the rate constant is

$$k_2 = F \times q_{C^\ddagger, \text{rot}} \times \bar{q}_{C^\ddagger, \text{vib}} = \boxed{1.16 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

- (c) Both models are already pretty good, coming within a factor of 3 to 4 of the experimental result, and neither model has much room for improvement. Consider how to try to change either model to reduce the rate constant toward the experimental value. The factor F is model-independent. The factor $\bar{q}_{C^\ddagger, \text{vib}}$ is nearly at its minimum possible value, 1, so stiffening the vibrational modes will have almost no effect. Only the factor $q_{C^\ddagger, \text{rot}}$ is amenable to lowering, and even that not by much. It would be decreased if the rotational constants were increased, which means decreasing the moments of inertia and the bond lengths. Reducing the lengths s and b in the models to the equilibrium bond length of H_2 would only drop k_2 to 6.5×10^5 (model a) or 6.9×10^5 (model b) $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, even with a stiffening of vibrations. Reducing the HD distance in model a to 80% of the H_2 bond length does produce a rate constant of $4.2 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (assuming stiff vibrations of 2000 cm^{-1}); such a model is not intermediate in structure between reactants and products, though. It appears that the rate constant is rather insensitive to the geometry of the complex.

Solutions to applications

- P24.24** (a) The rate constant of a diffusion-limited reaction is

$$k = \frac{8RT}{3\eta} = \frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (10^3 \text{ dm}^3 \text{ m}^{-3})}{3 \times (1.06 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})}$$

$$= \boxed{6.23 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

(b) The rate constant is related to the diffusion constants and reaction distance by

$$k = 4\pi R^* D N_A \quad \text{so} \quad R^* = \frac{k}{4\pi D N_A}$$

$$= \frac{(2.77 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \times (10^{-3} \text{ m}^{-3} \text{ dm}^{-3})}{4\pi \times (1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}) \times (6.022 \times 10^{23} \text{ mol}^{-1})}$$

$$R^* = \boxed{3.7 \times 10^{-10} \text{ m or } 0.37 \text{ nm}}$$

P24.26 For a series of reactions with a fixed edge-to-edge distance and reorganization energy, the log of the rate constant depends quadratically on the reaction free-energy; eqn 24.84 applies: $\ln k_{\text{et}} = -((\Delta_r G^\ominus)^2 / 4\lambda kT) - (\Delta_r G^\ominus / 2kT) + \text{constant}$,

where we have replaced RT by kT since the energies are given in molecular rather than molar units.

Draw up the following table:

$\Delta_r G^\ominus / \text{eV}$	$K_{\text{et}} / (10^6 \text{ s}^{-1})$	$\ln K_{\text{et}} / \text{s}^{-1}$
-0.665	0.657	13.4
-0.705	1.52	14.2
-0.745	1.12	13.9
-0.975	8.99	16.0
-1.015	5.76	15.6
-1.055	10.1	16.1

and plot $\ln k_{\text{et}}$ vs. $\Delta_r G^\ominus$ (see Figure 24.5)

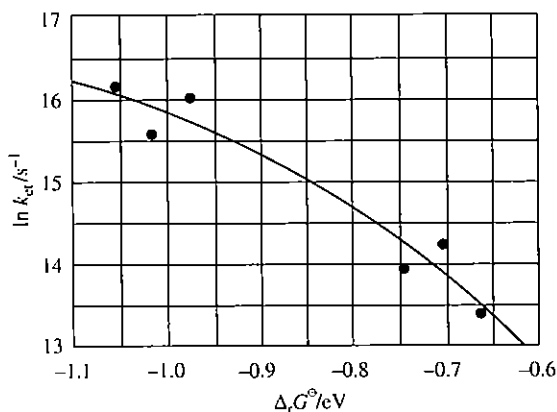


Figure 24.5

The least squares quadratic fit equation is:

$$\ln k_{\text{et}} / \text{s}^{-1} = 3.23 - 21.1(\Delta_r G^\ominus / \text{eV}) - 8.48 - (\Delta_r G^\ominus / \text{eV})^{-2} \quad r^2 = 0.938$$

The coefficient of the quadratic term is:

$$-\frac{1}{4\lambda kt} = -\frac{8.48}{\text{eV}^2},$$

$$\text{so } \lambda = \frac{(\text{eV})^2}{4(8.48)kT} = \frac{(1.602 \times 10^{-19} \text{ J eV}^{-1})(\text{eV})^2}{2(8.48)(1.381 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})},$$

$$\boxed{\lambda = 2.30 \text{ eV}}$$

As a check on the reliability of the fit, note that according to eqn 24.84, the coefficient of the linear term is:

$$\frac{1}{2kT} = -\frac{21.1}{\text{eV}},$$

$$\text{so } T = \frac{\text{eV}}{2k(21.1)} = \frac{(1.602 \times 10^{-19} \text{ J eV}^{-1})\text{eV}}{2(1.381 \times 10^{-23} \text{ J K}^{-1})(21.1)} = \boxed{275 \text{ K}},$$

which differs by about 8% from the stated temperature of 298 K.

- P24.28** The theoretical treatment of section 24.11 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 24.81, namely increasing rate with increasing temperature. Below 130 K, the temperature dependent terms in eqn 24.81 are replaced by Frank-Condon factors; that is, temperature-dependent terms are replaced by temperature-independent wavefunction overlap integrals.

25 Processes at solid surfaces

Answers to discussion questions

- D25.2** (a) AES can provide a depth profile or fingerprint of the sample, since the Auger spectrum is characteristic of the material present. Information about the atoms present and their bonding can be obtained. The technique is limited to a depth of about 100 nm.
- EELS and HREELS can detect very tiny amounts of adsorbate. The incident beam can induce vibrational excitations in the adsorbate that is characteristic of the species and its environment.
- RAIRS resolves the problem of the opacity of surfaces to infrared or visible radiation but the spectral bands observed are typically very weak.
- SERS resolves the problem of weak spectral observed in RAIRS. It generally gives a greatly enhanced resonance Raman intensity. The disadvantages are that it provides only a weak enhancement for flat single crystal surfaces and the technique works well only for certain metals.
- SEXAFS can provide nearest neighbor distributions, giving the number and interatomic distances of surface atoms
- SHG provides information about adsorption and surface coverage and rapid surface changes.
- UPS can provide detailed information about the chemisorption process, surface composition, and the oxidation state of atoms. It can distinguish between chemical absorption and physical adsorption.
- XPS is similar to UPS in the information revealed.
- See the references listed under *Further reading* for more information about these modern techniques for probing the properties of surfaces.
- (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: 25.5(b); LEED: 25.2(e); MBRS: 25.7(c); MBS: 25.2(f); SAM: 25.2(c); SEM: 28.2(h); and STM: 25.5(b).

D25.4

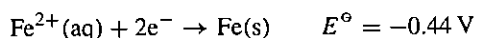
$$R_{eq} = R_{max} \left(\frac{a_0 K}{a_0 K + 1} \right)$$

Taking the inverse of the above equation and multiplication by a_0 gives:

$$\frac{a_0}{R_{eq}} = \frac{1}{R_{max} K} + \frac{a_0}{R_{max}}$$

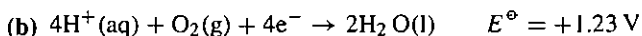
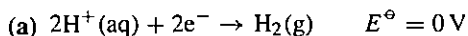
This working equation predicts that a plot of a_0/R_{eq} against a_0 should be linear if the model is applicable to the experimental data. The slope of a linear regression fit to the data gives the value of $1/R_{max}$ or $R_{max} = 1/\text{slope}$. Likewise, the regression intercept equals $1/R_{max} K$ or $K = \text{slope}/\text{intercept}$.

- D25.6** Heterogeneous catalysis on a solid surface requires the reacting molecules or fragments to encounter each other by adsorption on the surface. Therefore, the rate of the catalysed reaction is determined by the sticking probabilities of the species on the surface as described by Figure 25.28 of the text.
- D25.8** (a) There are three models of the structure of the electrical double layer. The Helmholtz model, the Gouy–Chapman model, and the Stern model. We will describe the Stern model which is a combination of the first two and illustrates most of the structural features associated with the double layer. The electrode surface is a rigid plane of, say, excess positive charge. Next to it is a plane of negatively charged ions with their solvating molecules, called the outer Helmholtz layer. Adjoining this region is a diffuse layer with perhaps only a slight excess of negative charge. This region fades away into the bulk neutral solution. At another level of sophistication, an inner Helmholtz plane is added, see Section 25.8(a) for a brief description of this layer.
- (b) The electrical double layer is present near the electrode surface whether or not current is flowing in the cell. The Nernst diffusion layer is invoked to explain polarization effects near a working electrode and is a region of linear variation in concentration between the bulk solution and outer Helmholtz plane. It is typically 0.1–0.5 mm in thickness without stirring or convection, but can be reduced to 0.001 mm with such agitation. The electrical double layer is unaffected by hydrodynamic flow and is typically about 1 nm in thickness.
- D25.10** 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 25.45 and 25.46). As the potential difference approaches E° (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° (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° (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° (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 $(59 \text{ mV})/n$ 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 $(59 \text{ mV})/n$ 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.
- D25.12** 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 that occurs in the presence of water and oxygen, is revealed by comparing the standard potentials of the metal reduction, such as

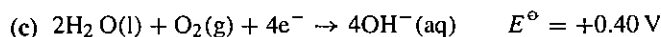


with the values for one of the following half-reactions

In acidic solution



In basic solution:



Because all three redox couples have standard potentials more positive than $E^\circ(Fe^{2+}/Fe)$, 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

$$E(a) = E^\circ(a) + (RT/F) \ln a(H^+) = -(0.059 \text{ V}) \text{ pH}$$

$$E(b) = E^\circ(b) + (RT/F) \ln a(H^+) = 1.23 \text{ V} - (0.059 \text{ V}) \text{ pH}$$

These expressions let us judge at what pH the iron will have a tendency to oxidize (see Chapter 7). 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 $10^{-14} \text{ A cm}^{-2}$, whereas for (a) it is $10^{-6} \text{ A cm}^{-2}$. The latter therefore dominates kinetically, and iron corrodes by hydrogen evolution in acidic solution. For corrosion reactions with similar exchange current densities, eqn 25.66 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 25.66 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 V , which is more negative than that of the iron couple, the corrosion of zinc is thermodynamically favored 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 V). The magnesium acts as a sacrificial anode, supplying its own electrons to the iron and becoming oxidized to Mg^{2+} in the process.

Solutions to exercises

E25.1(b) The number of collisions of gas molecules per unit surface area is

$$Z_w = \frac{N_A p}{(2\pi MRT)^{1/2}}$$

(a) For N_2

$$\begin{aligned} \text{(i)} \quad Z_W &= \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (10.0 \text{ Pa})}{(2\pi \times (28.013 \times 10^{-3} \text{ kg mol}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}))^{1/2}} \\ &= 2.88 \times 10^{23} \text{ m}^{-2} \text{ s}^{-1} \\ &= \boxed{2.88 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{(ii)} \quad Z_W &= \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (0.150 \times 10^{-6} \text{ Torr}) \times (1.01 \times 10^5 \text{ Pa}/760 \text{ Torr})}{(2\pi \times (28.013 \times 10^{-3} \text{ kg mol}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}))^{1/2}} \\ &= 5.75 \times 10^{17} \text{ m}^{-2} \text{ s}^{-1} \\ &= \boxed{5.75 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}} \end{aligned}$$

(b) For methane

$$\begin{aligned} \text{(i)} \quad Z_W &= \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (10.0 \text{ Pa})}{(2\pi \times (16.04 \times 10^{-3} \text{ kg mol}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}))^{1/2}} \\ &= 3.81 \times 10^{23} \text{ m}^{-2} \text{ s}^{-1} \\ &= \boxed{3.81 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{(ii)} \quad Z_W &= \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (0.150 \times 10^{-6} \text{ Torr}) \times (1.01 \times 10^5 \text{ Pa}/760 \text{ Torr})}{(2\pi \times (16.04 \times 10^{-3} \text{ kg mol}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}))^{1/2}} \\ &= 7.60 \times 10^{17} \text{ m}^{-2} \text{ s}^{-1} \\ &= \boxed{7.60 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}} \end{aligned}$$

E25.2(b) The number of collisions of gas molecules per unit surface area is

$$\begin{aligned} Z_W &= \frac{N_A p}{(2\pi MRT)^{1/2}} \quad \text{so} \quad p = \frac{Z_W A (2\pi MRT)^{1/2}}{N_A A} \\ p &= \frac{(5.00 \times 10^{19} \text{ s}^{-1})}{(6.022 \times 10^{23} \text{ mol}^{-1}) \times \pi \times (1/2 \times 2.0 \times 10^{-3} \text{ m})^2} \\ &\quad \times (2\pi \times (28.013 \times 10^{-3} \text{ kg mol}^{-1}) \times (8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \times (525 \text{ K}))^{1/2} \\ &= \boxed{7.3 \times 10^2 \text{ Pa}} \end{aligned}$$

E25.3(b) The number of collisions of gas molecules per unit surface area is

$$Z_W = \frac{N_A p}{(2\pi M RT)^{1/2}}$$

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

$$A = c^2 \quad \text{and} \quad \text{rate} = Z_W A = \frac{N_A p c^2}{(2\pi M RT)^{1/2}}$$

where c is the length of the unit cell. So

$$\begin{aligned}\text{rate} &= \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (24 \text{ Pa}) \times (145 \times 10^{-12} \text{ m})^2}{(2\pi \times (4.003 \times 10^{-3} \text{ kg mol}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (100 \text{ K}))^{1/2}} \\ &= \boxed{6.6 \times 10^4 \text{ s}^{-1}}\end{aligned}$$

E25.4(b) The number of CO molecules adsorbed on the catalyst is

$$\begin{aligned}N = nN_A &= \frac{pVN_A}{RT} = \frac{(1.00 \text{ atm}) \times (4.25 \times 10^{-3} \text{ dm}^3) \times (6.022 \times 10^{23} \text{ mol}^{-1})}{(0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})} \\ &= 1.14 \times 10^{20}\end{aligned}$$

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

$$A = Na = (1.14 \times 10^{20}) \times (0.165 \times 10^{-18} \text{ m}^2) = \boxed{18.8 \text{ m}^2}$$

E25.5(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}

$$\begin{aligned}\frac{V_1/V_{\text{mon}}}{p_1(1 - V_1/V_{\text{mon}})} &= \frac{V_2/V_{\text{mon}}}{p_2(1 - V_2/V_{\text{mon}})} \quad \text{so} \quad \frac{p_1(V_{\text{mon}} - V_1)}{V_1} = \frac{p_2(V_{\text{mon}} - V_2)}{V_2} \\ V_{\text{mon}} &= \frac{p_1 - p_2}{p_1/V_1 - p_2/V_2} = \frac{(52.4 - 104) \text{ kPa}}{(52.4/1.60 - 104/2.73) \text{ kPa cm}^{-3}} = \boxed{9.7 \text{ cm}^3}\end{aligned}$$

E25.6(b) The mean lifetime of a chemisorbed molecule is comparable to its half-life:

$$t_{1/2} = \tau_0 \exp\left(\frac{E_d}{RT}\right) \approx (10^{-14} \text{ s}) \exp\left(\frac{155 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (500 \text{ K})}\right) = \boxed{200 \text{ s}}$$

E25.7(b) The desorption rate constant is related to the half-life by

$$t = (\ln 2)/k_d \quad \text{so} \quad k_d = (\ln 2)/t$$

The desorption rate constant is related to its Arrhenius parameters by

$$k_d = A \exp\left(\frac{-E_d}{RT}\right) \quad \text{so} \quad \ln k_d = \ln A - \frac{E_d}{RT}$$

$$\text{and } E_d = \frac{(\ln k_1 - \ln k_2)R}{T_2^{-1} - T_1^{-1}} = \frac{(\ln 1.35 - \ln 1) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})}{(600 \text{ K})^{-1} - (1000 \text{ K})^{-1}}$$

$$E_d = \boxed{3.7 \times 10^3 \text{ J mol}^{-1}}$$

E25.8(b) The Langmuir isotherm is

$$\theta = \frac{Kp}{1 + Kp} \text{ so } p = \frac{\theta}{K(1 - \theta)}$$

$$(a) \quad p = \frac{0.20}{(0.777 \text{ kPa}^{-1}) \times (1 - 0.20)} = \boxed{0.32 \text{ kPa}}$$

$$(b) \quad p = \frac{0.75}{(0.777 \text{ kPa}^{-1}) \times (1 - 0.75)} = \boxed{3.9 \text{ kPa}}$$

E25.9(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}

$$\frac{m_1/m_{\text{mon}}}{p_1(1 - m_1/m_{\text{mon}})} = \frac{m_2/m_{\text{mon}}}{p_2(1 - m_2/m_{\text{mon}})} \text{ so } \frac{p_1(m_{\text{mon}} - m_1)}{m_1} = \frac{p_2(m_{\text{mon}} - m_2)}{m_2}$$

$$m_{\text{mon}} = \frac{p_1 - p_2}{p_1/m_1 - p_2/m_2} = \frac{(36.0 - 4.0) \text{ kPa}}{(36.0/0.63 - 4.0/0.21) \text{ kPa mg}^{-1}} = 0.84 \text{ mg}$$

$$\text{So } \theta_1 = 0.63/0.84 = \boxed{0.75} \text{ and } \theta_2 = 0.21/0.84 = \boxed{0.25}$$

E25.10(b) The mean lifetime of a chemisorbed molecule is comparable to its half-life

$$t_{1/2} = \tau_0 \exp\left(\frac{E_d}{RT}\right)$$

$$(a) \quad \text{At } 400 \text{ K: } t_{1/2} = (0.12 \times 10^{-12} \text{ s}) \exp\left(\frac{20 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K})}\right) \\ = \boxed{4.9 \times 10^{-11} \text{ s}}$$

$$\text{At } 800 \text{ K: } t_{1/2} = (0.12 \times 10^{-12} \text{ s}) \exp\left(\frac{20 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (800 \text{ K})}\right) \\ = \boxed{2.4 \times 10^{-12} \text{ s}}$$

$$(b) \quad \text{At } 400 \text{ K: } t_{1/2} = (0.12 \times 10^{-12} \text{ s}) \exp\left(\frac{200 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K})}\right) \\ = \boxed{1.6 \times 10^{13} \text{ s}}$$

$$\text{At } 800 \text{ K: } t_{1/2} = (0.12 \times 10^{-12} \text{ s}) \exp\left(\frac{200 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (800 \text{ K})}\right) \\ = \boxed{1.4 \text{ s}}$$

E25.11(b) The Langmuir isotherm is

$$\theta = \frac{Kp}{1 + Kp} \quad \text{so} \quad p = \frac{\theta}{K(1 - \theta)}$$

For constant fractional adsorption

$$pK = \text{constant} \quad \text{so} \quad p_1 K_1 = p_2 K_2 \quad \text{and} \quad p_2 = p_1 \frac{K_1}{K_2}$$

$$\text{But } K \propto \exp\left(\frac{-\Delta_{\text{ad}}H^\ominus}{RT}\right) \quad \text{so} \quad \frac{K_1}{K_2} = \exp\left(\frac{-\Delta_{\text{ad}}H^\ominus}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)$$

$$\begin{aligned} p_2 &= p_1 \exp\left(\frac{-\Delta_{\text{ad}}H^\ominus}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right) \\ &= (8.86 \text{ kPa}) \times \exp\left(\left(\frac{-12.2 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{298 \text{ K}} - \frac{1}{318 \text{ K}}\right)\right) = \boxed{6.50 \text{ kPa}} \end{aligned}$$

E25.12(b) The Langmuir isotherm would be

$$(a) \quad \theta = \frac{Kp}{1 + Kp}$$

$$(b) \quad \theta = \frac{(Kp)^{1/2}}{1 + (Kp)^{1/2}}$$

$$(c) \quad \theta = \frac{(Kp)^{1/3}}{1 + (Kp)^{1/3}}$$

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.

E25.13(b) The Langmuir isotherm is

$$\theta = \frac{Kp}{1 + Kp} \quad \text{so} \quad p = \frac{\theta}{K(1 - \theta)}$$

For constant fractional adsorption

$$pK = \text{constant} \quad \text{so} \quad p_1 K_1 = p_2 K_2 \quad \text{and} \quad \frac{p_2}{p_1} = \frac{K_1}{K_2}$$

$$\text{But } K \propto \exp\left(\frac{-\Delta_{\text{ad}}H^\ominus}{RT}\right) \quad \text{so} \quad \frac{p_2}{p_1} = \exp\left(\frac{-\Delta_{\text{ad}}H^\ominus}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)$$

$$\text{and } \Delta_{\text{ad}}H^\ominus = R \left(\frac{1}{T_1} - \frac{1}{T_2}\right)^{-1} \ln \frac{p_1}{p_2},$$

$$\begin{aligned} \Delta_{\text{ad}}H^\ominus &= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left(\frac{1}{180 \text{ K}} - \frac{1}{240 \text{ K}}\right)^{-1} \times \left(\ln \frac{350 \text{ kPa}}{1.02 \times 10^3 \text{ kPa}}\right) \\ &= -6.40 \times 10^4 \text{ J mol}^{-1} = \boxed{-6.40 \text{ kJ mol}^{-1}} \end{aligned}$$

E25.14(b) The time required for a given quantity of gas to desorb is related to the activation energy for desorption by

$$t \propto \exp\left(\frac{E_d}{RT}\right) \quad \text{so} \quad \frac{t_1}{t_2} = \exp\left(\frac{E_d}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)$$

$$\text{and } E_d = R \left(\frac{1}{T_1} - \frac{1}{T_2}\right)^{-1} \ln \frac{t_1}{t_2}$$

$$\begin{aligned} E_d &= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left(\frac{1}{873 \text{ K}} - \frac{1}{1012 \text{ K}}\right)^{-1} \times \left(\ln \frac{1856 \text{ s}}{8.44 \text{ s}}\right) \\ &= \boxed{2.85 \times 10^5 \text{ J mol}^{-1}} \end{aligned}$$

(a) The same desorption at 298 K would take

$$t = (1856 \text{ s}) \times \exp\left(\left(\frac{2.85 \times 10^5 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{298 \text{ K}} - \frac{1}{873 \text{ K}}\right)\right) = \boxed{1.48 \times 10^{36} \text{ s}}$$

(b) The same desorption at 1500 K would take

$$\begin{aligned} t &= (8.44 \text{ s}) \times \exp\left(\left(\frac{2.85 \times 10^5 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{1500 \text{ K}} - \frac{1}{1012 \text{ K}}\right)\right) \\ &= \boxed{1.38 \times 10^{-4} \text{ s}} \end{aligned}$$

E25.15(b) Disregarding signs, the electric field is the gradient of the electrical potential

$$\varepsilon = \frac{d\Delta\phi}{dx} \approx \frac{\Delta\phi}{d} = \frac{\sigma}{\varepsilon} = \frac{\sigma}{\varepsilon_r \varepsilon_0} = \frac{0.12 \text{ C m}^{-2}}{(48) \times (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1})} = \boxed{2.8 \times 10^8 \text{ V m}^{-1}}$$

E25.16(b) In the high overpotential limit

$$j = j_0 e^{(1-\alpha)f\eta} \quad \text{so} \quad \frac{j_1}{j_2} = e^{(1-\alpha)f(\eta_1 - \eta_2)} \quad \text{where} \quad f = \frac{F}{RT} = \frac{1}{25.69 \text{ mV}}$$

The overpotential η_2 is

$$\begin{aligned} \eta_2 &= \eta_1 + \frac{1}{f(1-\alpha)} \ln \frac{j_2}{j_1} = 105 \text{ mV} + \left(\frac{25.69 \text{ mV}}{1 - 0.42}\right) \times \ln \left(\frac{72 \text{ mA cm}^{-2}}{17.0 \text{ mA cm}^{-2}}\right) \\ &= \boxed{167 \text{ mV}} \end{aligned}$$

E25.17(b) In the high overpotential limit

$$\begin{aligned} j &= j_0 e^{(1-\alpha)f\eta} \quad \text{so} \quad j_0 = j e^{(\alpha-1)f\eta} \\ j_0 &= (17.0 \text{ mA cm}^{-2}) \times e^{[(0.42-1) \times (105 \text{ mV}) / (25.69 \text{ mV})]} = \boxed{1.6 \text{ mA cm}^{-2}} \end{aligned}$$

E25.18(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

$$j_2 = (1.22 \text{ mA cm}^{-2}) \times e^{[(1-0.50) \times (0.60 \text{ V} - 0.50 \text{ V}) / (0.02569 \text{ V})]} = \boxed{8.5 \text{ mA cm}^{-2}}$$

Note: the exercise says the data refer to the same material and at the same temperature as the previous Exercise (25.18(a)), yet the results for the current density at the same overpotential differ by a factor of over 5!

E25.19(b) (a) The Butler–Volmer equation gives

$$\begin{aligned} j &= j_0(e^{(1-\alpha)f\eta} - e^{-\alpha f\eta}) \\ &= (2.5 \times 10^{-3} \text{ A cm}^{-2}) \times \left(e^{[(1-0.58) \times (0.30 \text{ V}) / (0.02569 \text{ V})]} - e^{-[(0.58) \times (0.30 \text{ V}) / (0.02569 \text{ V})]} \right) \\ &= \boxed{0.34 \text{ A cm}^{-2}} \end{aligned}$$

(b) According to the Tafel equation

$$\begin{aligned} j &= j_0 e^{(1-\alpha)f\eta} \\ &= (2.5 \times 10^{-3} \text{ A cm}^{-2}) e^{[(1-0.58) \times (0.30 \text{ V}) / (0.02569 \text{ V})]} = \boxed{0.34 \text{ A cm}^{-2}} \end{aligned}$$

The validity of the Tafel equation improves as the overpotential increases.

E25.20(b) The limiting current density is

$$j_{\text{lim}} = \frac{zFDc}{\delta}$$

but the diffusivity is related to the ionic conductivity (Chapter 21)

$$D = \frac{\lambda RT}{z^2 F^2} \quad \text{so} \quad j_{\text{lim}} = \frac{c\lambda}{\delta z f}$$

$$\begin{aligned} j_{\text{lim}} &= \frac{(1.5 \text{ mol m}^{-3}) \times (10.60 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}) \times (0.02569 \text{ V})}{(0.32 \times 10^{-3} \text{ m}) \times (+1)} \\ &= \boxed{1.3 \text{ A m}^{-2}} \end{aligned}$$

E25.21(b) For the iron electrode $E^\ominus = -0.44 \text{ V}$ (Table 7.2) and the Nernst equation for this electrode (section 7.7a) is

$$E = E^\ominus - \frac{RT}{\nu F} \ln \left(\frac{1}{[\text{Fe}^{2+}]} \right) \quad \nu = 2$$

Since the hydrogen overpotential is 0.60 V evolution of H_2 will begin when the potential of the Fe electrode reaches -0.60 V . Thus

$$-0.60 \text{ V} = -0.44 \text{ V} + \frac{0.02569 \text{ V}}{2} \ln [\text{Fe}^{2+}]$$

$$\ln[\text{Fe}^{2+}] = \frac{-0.16 \text{ V}}{0.0128 \text{ V}} = -12.5$$

$$[\text{Fe}^{2+}] = \boxed{4 \times 10^{-6} \text{ mol dm}^{-3}}$$

COMMENT. Essentially all Fe^{2+} has been removed by deposition before evolution of H_2 begins

E25.22(b) The zero-current potential of the electrode is given by the Nernst equation

$$E = E^\ominus - \frac{RT}{\nu F} \ln Q = E^\ominus - \frac{1}{f} \ln \frac{a(\text{Fe}^{2+})}{a(\text{Fe}^{3+})} = 0.77 \text{ V} - \frac{1}{f} \ln \frac{a(\text{Fe}^{2+})}{a(\text{Fe}^{3+})}$$

The Butler–Volmer equation gives

$$j = j_0(e^{(1-\alpha)f\eta} - e^{-\alpha f\eta}) = j_0(e^{(0.42)f\eta} - e^{-0.58f\eta})$$

where η is the overpotential, defined as the working potential E' minus the zero-current potential E .

$$\eta = E' - 0.77 \text{ V} + \frac{1}{f} \ln \frac{a(\text{Fe}^{2+})}{a(\text{Fe}^{3+})} = E' - 0.77 \text{ V} + \frac{1}{f} \ln r,$$

where r is the ratio of activities; so

$$j = j_0(e^{(0.42)E'/f} e^{[(0.42) \times (-0.77 \text{ V}) / (0.02569 \text{ V})]} r^{0.42} - e^{(-0.58)E'/f} e^{[(-0.58) \times (-0.77 \text{ V}) / (0.02569 \text{ V})]} r^{-0.58})$$

Specializing to the condition that the ions have equal activities yields

$$j = \boxed{(2.5 \text{ mA cm}^{-2}) \times [(e^{(0.42)E'/f} \times (3.4 \times 10^{-6}) - e^{(-0.58)E'/f} \times (3.55 \times 10^7))]}$$

E25.23(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 25.22(b)

$$j = j_0(e^{(0.50)E'/f} e^{-(0.50)E^\ominus/f} r^{0.50} - e^{(-0.50)E'/f} e^{(0.50)E^\ominus/f} r^{-0.50}) \\ = 2j_0 \sinh\left[\frac{1}{2}f E' - \frac{1}{2}f E^\ominus + \frac{1}{2} \ln r\right],$$

so, if the working potential is set at 0.50 V, then

$$j = 2j_0 \sinh\left[\frac{1}{2}(0.91 \text{ V}) / (0.02569 \text{ V}) + \frac{1}{2} \ln r\right]$$

$$j/j_0 = 2 \sinh\left(8.48 + \frac{1}{2} \ln r\right)$$

$$\text{At } r = 0.1 : j/j_0 = 2 \sinh\left(8.48 + \frac{1}{2} \ln 0.10\right) = 1.5 \times 10^3 \text{ mA cm}^{-2} = \boxed{1.5 \text{ A cm}^{-2}}$$

$$\text{At } r = 1 : j/j_0 = 2 \sinh(8.48 + 0.0) = 4.8 \times 10^3 \text{ mA cm}^{-2} = \boxed{4.8 \text{ A cm}^{-2}}$$

$$\text{At } r = 10 : j/j_0 = 2 \sinh\left(8.48 + \frac{1}{2} \ln 10\right) = 1.5 \times 10^4 \text{ mA cm}^{-2} = \boxed{15 \text{ A cm}^{-2}}$$

E25.24(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

$$j = j_0(e^{(1-\alpha)f\eta} - e^{-\alpha f\eta})$$

This cannot be solved analytically for η , but in the high-overpotential limit it reduces to the Tafel equation

$$j = j_0 e^{(1-\alpha)f\eta} \quad \text{so} \quad \eta = \frac{1}{(1-\alpha)f} \ln \frac{j}{j_0} = \frac{0.02569 \text{ V}}{1-0.75} \ln \frac{15 \text{ mA cm}^{-2}}{4.0 \times 10^{-2} \text{ mA cm}^{-2}}$$

$$\eta = \boxed{0.61 \text{ V}}$$

This is a sufficiently large overpotential to justify use of the Tafel equation.

E25.25(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, $\text{H}_2|\text{H}^+$ 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 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

$$f = Na = (2.5 \times 10^{14} \text{ s}^{-1} \text{ cm}^{-2}) \times (260 \times 10^{-10} \text{ cm})^2 = \boxed{0.17 \text{ s}^{-1}}$$

E25.26(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

$$\eta = \frac{j}{f j_0} \quad \text{so} \quad R = \frac{1}{f j_0 A}$$

$$(a) R = \frac{0.02569 \text{ V}}{(5.0 \times 10^{-12} \text{ A cm}^{-2}) \times (1.0 \text{ cm}^2)} = 5.1 \times 10^9 \Omega = \boxed{5.1 \text{ G}\Omega}$$

$$(b) R = \frac{0.02569 \text{ V}}{(2.5 \times 10^{-3} \text{ A cm}^{-2}) \times (1.0 \text{ cm}^2)} = \boxed{10 \Omega}$$

E25.27(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 .

E25.28(b) As was noted in Exercise 25.18(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.

E25.29(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)

$$j = (0.79 \text{ mA cm}^{-2}) \times e^{-(0.5) \times (-0.76 \text{ V}) / (0.02569 \text{ V})} = 2.1 \times 10^9 \text{ mA cm}^{-2}$$

much too large to allow deposition. (That is, H_2 would begin being evolved, and fast, long before Zn began to deposit.)

E25.30(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

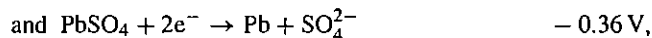
$$j = j_0 e^{-\alpha f \eta}$$

At the standard potential for reduction of Fe^{2+} (-0.44 V)

$$j = (1 \times 10^{-6} \text{ A cm}^{-2}) \times e^{-(0.5) \times (-0.44 \text{ V}) / (0.02569 \text{ V})} = 5.2 \times 10^{-3} \text{ A cm}^{-2}$$

a bit too large to allow deposition. (That is, H_2 would begin being evolved at a moderate rate before Fe began to deposit.)

E25.31(b) The lead acid battery half-cells are



for a total of $E^\ominus = 2.03 \text{ V}$. Power is

$$P = IV = (100 \times 10^{-3} \text{ A}) \times (2.03 \text{ V}) = 0.203 \text{ W}$$

if the cell were operating at its zero-current potential yet producing 100mA.

E25.32(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 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

$$\begin{aligned} \text{rate} &= \frac{jM}{2e\rho N_A} = \frac{(2.0 \text{ A m}^{-2}) \times (65.39 \times 10^{-3} \text{ kg mol}^{-1})}{2(1.602 \times 10^{-19} \text{ C}) \times (7133 \text{ kg m}^{-3}) \times (6.022 \times 10^{23} \text{ mol}^{-1})} \\ &= 9.5 \times 10^{-11} \text{ m s}^{-1} \\ &= (9.5 \times 10^{-11} \text{ m s}^{-1}) \times (10^3 \text{ mm m}^{-1}) \times (3600 \times 24 \times 365 \text{ y}^{-1}) \\ &= 3.0 \text{ mm y}^{-1} \end{aligned}$$

Solutions to problems

Solutions to numerical problems

P25.2

$$\begin{aligned} Z_W &= \frac{p}{(2\pi mkT)^{1/2}} \quad [25.1a] \\ &= \frac{p/\text{Pa}}{[(2\pi) \times (32.0) \times (1.6605 \times 10^{-27} \text{ kg}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) (300 \text{ K})]^{1/2}} \\ &= (2.69 \times 10^{22} \text{ m}^{-2} \text{ s}^{-1}) \times p/\text{Pa} = (2.69 \times 10^{18} \text{ cm}^{-2} \text{ s}^{-1}) \times p/\text{Pa} \end{aligned}$$

(a) At 100 kPa, $Z_W = 2.69 \times 10^{23} \text{ cm}^{-2} \text{ s}^{-1}$

(b) At 1.000 Pa, $Z_W = 2.69 \times 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$

The nearest neighbor in titanium is 291 pm, so the number of atoms per cm^2 is approximately 1.4×10^{15} (the precise value depends on the details of the packing, which is hcp, and the identity of the surface). The number of collisions per exposed atom is therefore $Z_W/(1.4 \times 10^{15} \text{ cm}^{-2})$.

(a) When $p = 100 \text{ kPa}$, $Z_{\text{atom}} = 2.0 \times 10^8 \text{ s}^{-1}$

(b) When $p = 1.000 \text{ Pa}$, $Z_{\text{atom}} = 2.0 \times 10^3 \text{ s}^{-1}$

P25.4 We follow Example 25.1 and draw up the following table (with pressures converted to Torr)

p/Torr	0.19	0.97	1.90	4.05	7.50	11.95
$(p/V)/(\text{Torr cm}^{-3})$	4.52	5.95	8.60	12.6	18.3	25.4

p/V is plotted against p in Figure 25.1.

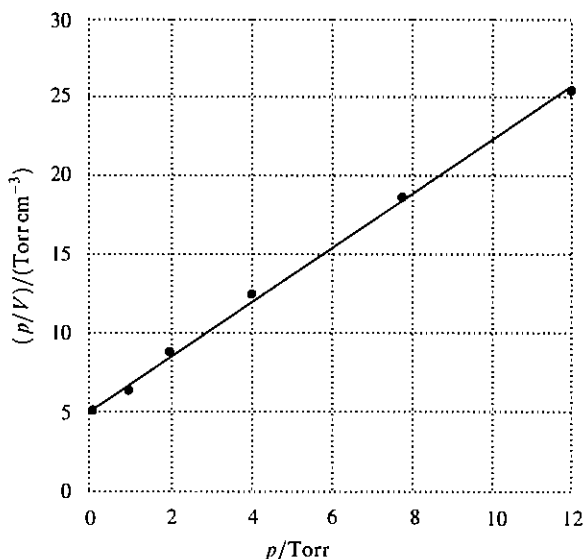


Figure 25.1

The low-pressure points fall on a straight line with intercept 4.7 and slope 1.8. It follows that $1/V_{\infty} = 1.8 \text{ Torr cm}^{-3}/\text{Torr} = 1.8 \text{ cm}^{-3}$, or $V_{\infty} = 0.57 \text{ cm}^3$ and $1/KV_{\infty} = 4.7 \text{ Torr cm}^{-3}$. Therefore,

$$K = \frac{1}{(4.7 \text{ Torr cm}^{-3}) \times (0.57 \text{ cm}^3)} = \boxed{0.37 \text{ Torr}^{-1}} = \boxed{0.0028 \text{ Pa}^{-1}}$$

COMMENT. It is unlikely that low-pressure data can be used to obtain an accurate value of the volume corresponding to complete coverage. See Problem 25.6 for adsorption data at higher pressures.

P25.6 We assume that the data fit the Langmuir isotherm; to confirm this we plot p/V against p and expect a straight line [Example 25.1]. We draw up the following table

p/atm	0.050	0.100	0.150	0.200	0.250
$p/V/(10^{-2} \text{ atm cm}^{-3})$	4.1	7.52	11.5	14.7	17.9

The data are plotted in Figure 25.2.

They fit closely to a straight line with slope 0.720 dm^{-3} . Hence

$$V_{\infty} = \boxed{1.39 \text{ cm}^{-3}} = 1.39 \times 10^{-3} \text{ dm}^{-3} \approx V_{\text{mon}}$$

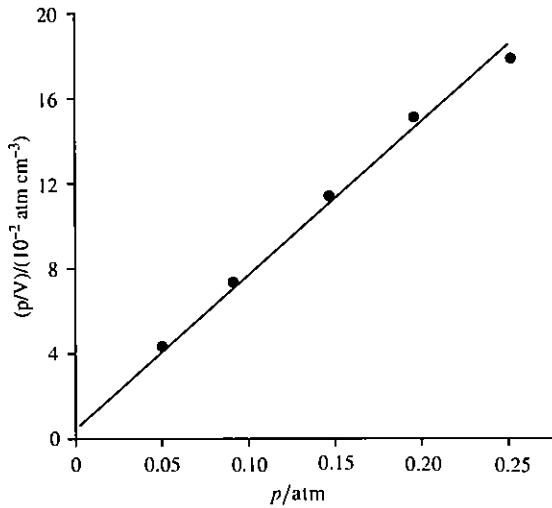


Figure 25.2

The number of H_2 molecules corresponding to this volume is

$$N_{\text{H}_2} = \frac{pVN_A}{RT} = \frac{(1.00 \text{ atm}) \times (1.39 \times 10^{-3} \text{ dm}^3) \times (6.02 \times 10^{23} \text{ mol}^{-1})}{(0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})} = 3.73 \times 10^{19}$$

The area occupied is the number of molecules times the area per molecule. The area per molecule can be estimated from the density of the liquid

$$\begin{aligned} A &= \pi \left(\frac{3V}{4\pi} \right)^{2/3} \left[V = \text{volume of molecule} = \frac{M}{\rho N_A} \right] \\ &= \pi \left(\frac{3M}{4\pi \rho N_A} \right)^{2/3} = \pi \left(\frac{3 \times (2.02 \text{ g mol}^{-1})}{4\pi \times (0.0708 \text{ g cm}^{-3}) \times (6.02 \times 10^{23} \text{ mol}^{-1})} \right)^{2/3} \\ &= 1.58 \times 10^{-15} \text{ cm}^2 \end{aligned}$$

$$\text{Area occupied} = (3.73 \times 10^{19}) \times (1.58 \times 10^{-15} \text{ cm}^2) = (5.9 \times 10^4 \text{ cm}^2) = \boxed{5.9 \text{ m}^2}$$

COMMENT. The value for V_∞ calculated here may be compared to the value obtained in Problem 25.4. The agreement is not good and illustrates the point that these kinds of calculations provide only rough value surface areas.

P25.8 We assume that the Langmuir isotherm applies.

$$\theta = \frac{Kp}{1 + Kp} \quad [25.4] \quad \text{and} \quad 1 - \theta = \frac{1}{1 + Kp}$$

For a strongly adsorbed species, $Kp \gg 1$ and $1 - \theta = 1/Kp$. Since the reaction rate is proportional to the pressure of ammonia and the fraction of sites left uncovered by the strongly adsorbed hydrogen product, we can write

$$\frac{dp_{\text{NH}_3}}{dt} = -k_c p_{\text{NH}_3} (1 - \theta) \approx - \boxed{\frac{k_c p_{\text{NH}_3}}{K p_{\text{H}_2}}}$$

To solve the rate law, we write

$$p_{\text{H}_2} = \frac{3}{2} \{p_{0\text{NH}_3} - p_{\text{NH}_3}\} \left[\text{NH}_3 \rightarrow \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \right]$$

from which it follows that, with $p = p_{\text{NH}_3}$

$$\frac{-dp}{dt} = \frac{kp}{p_0 - p}, \quad k = \frac{2k_c}{3K}$$

This equation integrates as follows

$$\int_{p_0}^p \left(1 - \frac{p_0}{p} \right) dp = k \int_0^t dt$$

$$\text{or } \boxed{\frac{p - p_0}{t} = k + \frac{p_0}{t} \ln \frac{p}{p_0}}$$

We write $F' = (p_0/t) \ln (p/p_0)$, $G = (p - p_0)/t$

and obtain $G = k + F' = p_0 F$

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 (with pressures converted to Torr)

t/s	0	30	60	100	160	200	250
p/Torr	100	88	84	80	77	74	72
$G/(\text{Torr s}^{-1})$		-0.40	-0.27	-0.20	-0.14	-0.13	-0.11
$F'/(\text{Torr s}^{-1})$		-0.43	-0.29	-0.22	-0.16	-0.15	-0.13
$(G - F')/(\text{Torr s}^{-1})$		0.03	0.02	0.02	0.02	0.02	0.02

Thus, the data fit the rate law, and we find $\boxed{k = 0.02 \text{ Torr s}^{-1}} = \boxed{0.05 \text{ kPa s}^{-1}}$.

P25.10 Application of the van't Hoff equation [25.7] to adsorption equilibria yields

$$\left(\frac{\partial \ln K}{\partial T} \right)_\theta = \frac{-\Delta_{\text{ad}} H^\ominus}{RT^2} \quad \text{or} \quad \left(\frac{\partial \ln K}{\partial (1/T)} \right)_\theta = \frac{-\Delta_{\text{ad}} H^\ominus}{R}$$

Hence, a plot (Figure 25.3) of $\ln K$ against $1/T$ should be a straight line with slope $-\Delta_{\text{ad}} H^\ominus/R$. The transformed data and plot follow

T/K	28.3	298	308	318
$10^{-11} K$	2.642	2.078	1.286	1.085
$1000 \text{ K}/T$	3.53	3.36	3.25	3.14
$\ln K$	26.30	26.06	25.58	25.41

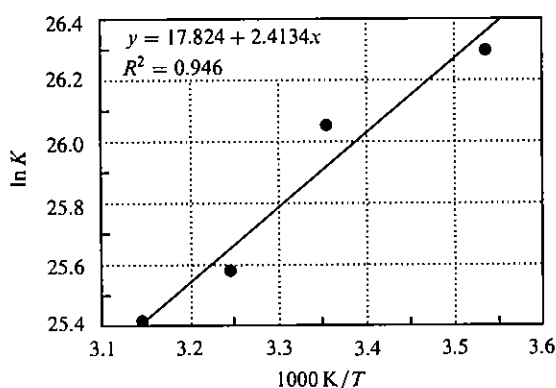


Figure 25.3

The plot is not the straightest of lines. Still, we can extract

$$\begin{aligned}
 -\Delta_{\text{ad}}H^{\ominus} &= -(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \times (2.41 \times 10^3 \text{ K}) \\
 &= -20.0 \times 10^3 \text{ J mol}^{-1} = \boxed{-20.1 \text{ kJ mol}^{-1}}
 \end{aligned}$$

The Gibbs energy for absorption is

$$\begin{aligned}
 -\Delta_{\text{ad}}G^{\ominus} &= -\Delta_{\text{ad}}H^{\ominus} - T\Delta_{\text{ad}}S^{\ominus} = -20.1 \text{ kJ mol}^{-1} - (298 \text{ K}) \times (0.146 \text{ kJ mol}^{-1} \text{ K}^{-1}) \\
 &= \boxed{63.6 \text{ kJ mol}^{-1}}
 \end{aligned}$$

P25.12 For the Langmuir adsorption isotherm we must alter eqn 25.4 so that it describes adsorption from solution. This can be done with the transforms

$p \rightarrow$ concentration, c

$V \rightarrow$ amount adsorbed per gram adsorbent, s

Langmuir isotherm and regression analysis:

$$\frac{c}{s} = \frac{c}{s_{\infty}} + \frac{1}{Ks_{\infty}}$$

$$\frac{1}{s_{\infty}} = 0.163 \text{ g mmol}^{-1}, \text{ standard deviation} = 0.017 \text{ g mmol}^{-1}$$

$$\frac{1}{Ks_{\infty}} = 35.6 (\text{mmol dm}^{-3}) \times (\text{g mmol}^{-1}),$$

$$\text{standard deviation} = 5.9 (\text{mmol dm}^{-3}) \times (\text{g mmol}^{-1})$$

$$\boxed{R (\text{Langmuir}) = 0.973}$$

$$K = \frac{0.163 \text{ g mmol}^{-1}}{35.6 (\text{mmol dm}^{-3}) \times (\text{g mmol}^{-1})} = 0.0046 \text{ dm}^3 \text{ mmol}^{-1}$$

Freundlich isotherm and regression analysis:

$$s = c_1 c^{1/c_2}$$

$$c_1 = 0.139, \quad \text{standard deviation} = 0.012$$

$$\frac{1}{c_2} = 0.539, \quad \text{standard deviation} = 0.003$$

$$R (\text{Freundlich}) = 0.99994$$

Temkin isotherm and regression analysis:

$$s = c_1 \ln(c_2 c)$$

$$c_1 = 1.08, \quad \text{standard deviation} = 0.14$$

$$c_2 = 0.074, \quad \text{standard deviation} = 0.023$$

$$R (\text{Temkin}) = 0.9590$$

The correlation coefficients and standard deviations indicate that the **Freundlich isotherm** provides the best fit of the data.

P25.14 $E = E^\ominus + (RT/zF) \ln a(M^+)$

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 $a(\text{Sn}^{2+}) \approx 2.2a(\text{Pb}^{2+})$

P25.16 $E' = E - IR_s - \frac{2RT}{zF} \ln g(I) \quad [25.64a]$

$$g = \frac{(I/Aj)^{2z}}{[(1 - (I/Aj_{\text{lim,L}})) \times (1 - (I/Aj_{\text{lim,R}}))]}^{1/2}$$

with $j_{\text{lim}} = cRT\lambda/zF\delta \quad [25.57b] = a\lambda$

$$R_s = \frac{l}{\kappa A} = \frac{l}{cA\Lambda_m} \quad \text{with } \Lambda_m = \lambda_+ + \lambda_-$$

Therefore, $E' = E - \frac{lI}{cA\Lambda_m} - \frac{2RT}{zF} \ln g(I)$

$$\text{with } g(I) = \frac{(I^2/A^2 j_{\text{LOjRO}})^z}{[1 - (I/Aa_L\lambda_{L+})]^{1/2} [1 - (I/Aa_R\lambda_{R+})]^{1/2}}$$

with $a_L = RTc_L/z_L F\delta_L$ and $a_R = RTc_R/z_R F\delta_R$

For the cell $\text{Zn}|\text{ZnSO}_4(\text{aq})||\text{CuSO}_4(\text{aq})|\text{Cu}$, $l = 5 \text{ cm}$, $A = 5 \text{ cm}^2$, $c(\text{M}_L^+) = c(\text{M}_R^+) = 1 \text{ mol dm}^{-3}$, $z_L = z_R = 2$, $\lambda_{L+} = 107 \text{ S cm}^2 \text{ mol}^{-1}$, $\lambda_{R+} = 106 \text{ S cm}^2 \text{ mol}^{-1} \approx \lambda_{L+}$, $\lambda_- = \lambda_{\text{SO}_4^{2-}} = 160 \text{ S cm}^2 \text{ mol}^{-1}$. $\Lambda_m \approx (107 + 160) \text{ S cm}^2 \text{ mol}^{-1} = 267 \text{ S cm}^2 \text{ mol}^{-1}$ for both electrolyte solutions. We take $\delta \approx 0.25 \text{ mm}$ [25.57b] and $j_{\text{LO}} \approx j_{\text{RO}} \approx 1 \text{ mA cm}^{-2}$. We can also take

$$E^\ominus(a \approx 1) = E^\ominus(\text{Cu}, \text{Cu}^{2+}) - E^\ominus(\text{Zn}, \text{Zn}^{2+}) = [0.34 - (-0.76)] \text{ V} = 1.10 \text{ V}$$

$$R_s = \frac{5 \text{ cm}}{(1 \text{ M}) \times (267 \text{ S cm}^2 \text{ mol}^{-1}) \times (5 \text{ cm}^2)} = 3.8 \Omega$$

$$j_{\text{lim}} = j_{\text{lim}}^+ = \frac{1}{2} \times \left(\frac{(0.0257 \text{ V}) \times (107 \text{ S cm}^2 \text{ mol}^{-1}) \times (1 \text{ M})}{0.25 \times 10^{-3} \text{ m}} \right) \approx 5.5 \times 10^{-2} \text{ S V cm}^{-2}$$

$$= 5.5 \times 10^{-2} \text{ A cm}^{-2}$$

If follows that

$$E'/\text{V} = (1.10) - 3.75(I/A) - (0.0257) \ln \left(\frac{(I/5 \times 10^{-3} \text{ A})^4}{1 - 3.6(I/A)} \right)$$

$$= (1.10) - 3.75(I/A) - (0.0257) \ln \left(\frac{1.6 \times 10^9 (I/A)^4}{1 - 3.6(I/A)} \right)$$

This function is plotted in Figure 25.4.

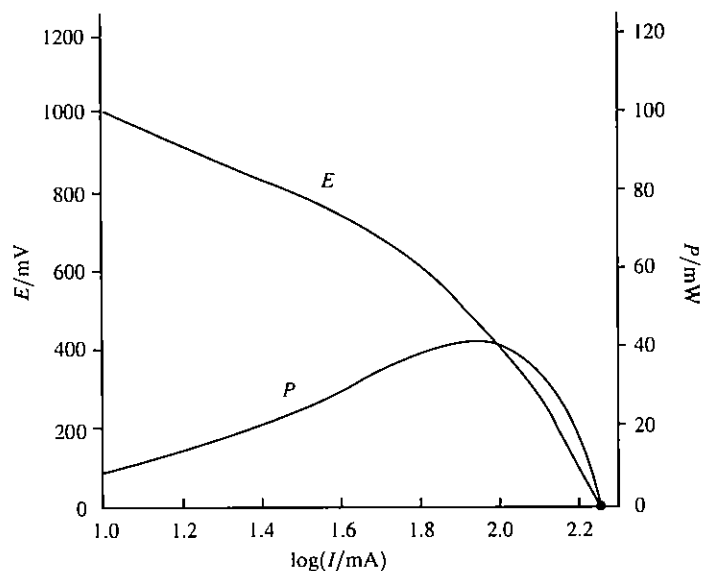


Figure 25.4

The power is

$$P = IE'$$

$$\text{and so } P/W = 1.10(I/A) - 3.75(I/A)^2 - 0.0257(I/A) \ln \left(\frac{1.6 \times 10^9 (I/A)^4}{1 - 3.6(I/A)} \right)$$

This function is also plotted in Figure 25.4. Maximum power is delivered at about **87 mA** and 0.46 V and is about 40 mW.

P25.18 $\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$ $\nu = 2$; $E^\ominus = -0.447$

$$\begin{aligned}
 \text{(a)} \quad E_0 &= E^\ominus - \frac{RT}{\nu F} \ln Q \quad [7.29] \\
 &= E^\ominus - \frac{RT}{\nu F} \frac{1}{\text{Fe}^{2+}} \quad \text{assuming } \gamma_{\text{Fe}^{2+}} = 1 \\
 &= -0.447 \text{ V} - \frac{25.693 \times 10^{-3} \text{ V}}{2} \ln \left(\frac{1 \text{ mol dm}^{-3}}{1.70 \times 10^{-6} \text{ mol dm}^{-3}} \right) \\
 \boxed{E_0} &= -0.618 \text{ V} \\
 \eta &= E' - E_0 \quad [25.39]
 \end{aligned}$$

 η values are reported in the table below.

$$\begin{aligned}
 \text{(b)} \quad j &= \frac{\nu F}{A} \frac{dn_{\text{Fe}}}{dt} = \frac{2 (96485 \text{ C mol}^{-1})}{9.1 \text{ cm}^2} \frac{dn_{\text{Fe}}}{dt} \\
 j &= j_0 \left(e^{(1-\alpha)fn} - e^{-\alpha fn} \right) = j_0 e^{-\alpha fn} (e^{fn} - 1) \\
 &= -j_c (e^{fn} - 1) \quad [25.40, 25.41] \\
 j_c &= \frac{-j}{e^{fn} - 1}
 \end{aligned}$$

 j_c values are reported in the following table

dn_{Fe}/dt ($10^{-12} \text{ mol s}^{-1}$)	$-E'/\text{mV}$	$-\eta/\text{mV}$	$j/(\mu\text{A cm}^{-12})$	$j_c/(\mu\text{A cm}^{-12})$
1.47	702	84	0.0312	0.0324
2.18	727	109	0.0462	0.0469
3.11	752	134	0.0659	0.0663
7.26	812	194	0.154	0.154

$$\begin{aligned}
 \text{(c)} \quad j_c &= j_0 e^{-\alpha fn} \quad [25.40] \\
 \ln j_c &= \ln j_0 - \alpha fn
 \end{aligned}$$

Performing a linear regression analysis of the $\ln j_c$ versus η data, we find

$$\begin{aligned}
 \ln j_0 &= 4.608, & \text{standard deviation} &= 0.015 \\
 \alpha f &= 0.0413 \text{ mV}, & \text{standard deviation} &= 0.00011
 \end{aligned}$$

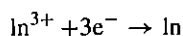
$$\boxed{R = 0.99994}$$

The correlation coefficient and the standard deviation indicate that the plot provides an excellent description of the data

$$\begin{aligned}
 j_0 &= e^{4.608} \quad \text{or} \quad j_0 = 0.00997 \mu\text{A cm}^{-2} \\
 \alpha &= \frac{0.01413}{f} = (0.01413 \text{ mV}^{-1}) \times (26.693 \text{ mV})
 \end{aligned}$$

$$\boxed{\alpha = 0.363}$$

P25.20 This problem differs somewhat from the simpler one-electron transfers considered in the text. In place of $\text{Ox} + e^- \rightarrow \text{Red}$ we have here



namely, a three-electron transfer. Therefore eqns 25.33a, 25.33b, and all subsequent equations including the Butler–Volmer equation [25.41] and the Tafel equations [25.44–25.46] need to be modified by including the factor z (in this case 3) in the equation. Thus, in the place of eqn 25.33b, we have

$$\Delta^\ddagger G_c = \Delta^\ddagger G_c(0) + z\alpha F \Delta\phi$$

and in place of eqns 25.45 and 25.47

$$\begin{aligned} \ln j &= \ln j_0 + z(1 - \alpha)f\eta & \text{anode} \\ \ln(-j) &= \ln j_0 - z\alpha f\eta & \text{cathode} \end{aligned}$$

We draw up the following table

$j/(\text{A m}^{-2})$	$-E/\text{V}$	η/V	$\ln(j/\text{A m}^{-2})$
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 Figure 25.5)

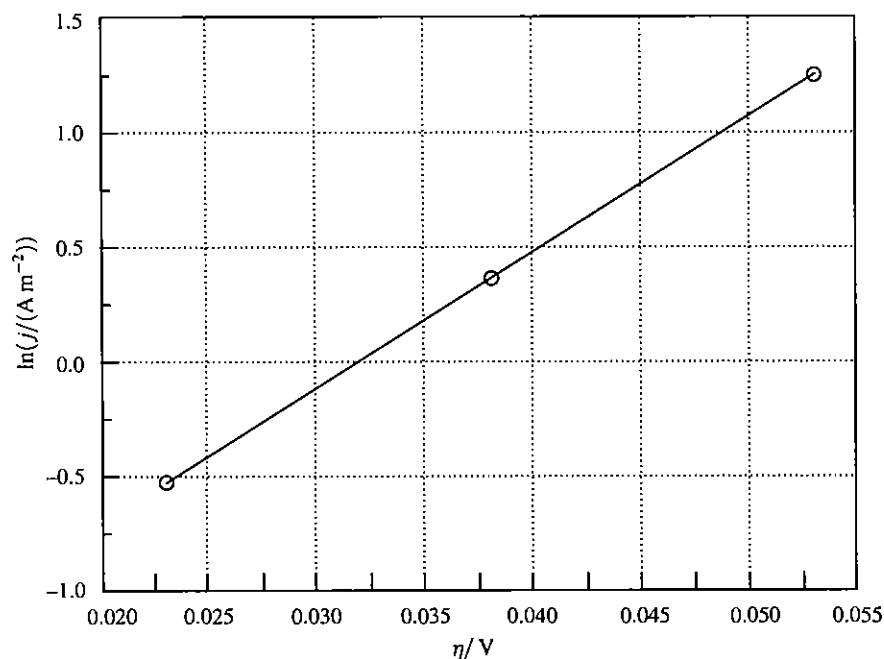


Figure 25.5

$$z(1 - \alpha)f = 59.42 \text{ V}^{-1}, \quad \text{standard deviation} = 0.0154$$

$$\ln j_0 = -1.894, \quad \text{standard deviation} = 0.0006$$

$$R = 1 \text{ (almost exact)}$$

Thus, although there are only three data points, the fit to the Tafel equation is almost exact. Solving for α from $z(1 - \alpha)f = 59.42 \text{ V}^{-1}$, we obtain

$$\begin{aligned} \alpha &= 1 - \frac{59.42 \text{ V}^{-1}}{3f} = 1 - \left(\frac{59.42 \text{ V}^{-1}}{3} \right) \times (0.025262 \text{ V}) \\ &= 0.4996 = \boxed{0.50} \end{aligned}$$

which matches the usual value of α exactly.

$$j_0 = e^{-1.894} = \boxed{0.150 \text{ A m}^{-2}}$$

The cathodic current density is obtained from

$$\begin{aligned} \ln(-j_c) &= \ln j_0 - z\alpha f \eta \quad \eta = 0.023 \text{ V at } -E/V = 0.365 \\ &= -1.894 - (3 \times 0.4996 \times 0.023)/(0.025262) \\ &= -3.259 \end{aligned}$$

$$-j_c = e^{-3.259} = 0.0384 \text{ A m}^{-2}$$

$$-j_c = \boxed{0.0384 \text{ A m}^{-2}}$$

P25.22 At large positive values of the overpotential the current density is anodic.

$$j = j_0 \left[e^{(1-\alpha)f\eta} - e^{-\alpha f\eta} \right] \quad [25.41]$$

$$\approx j_0 e^{(1-\alpha)f\eta} = j_a \quad [25.40]$$

$$\ln j = \ln j_0 + (1 - \alpha)f\eta$$

Performing a linear regression analysis of $\ln j$ against η , we find

$$\ln(j_0/(\text{mA m}^{-2})) = -10.826, \quad \text{standard deviation} = 0.287$$

$$(1 - \alpha)f = 19.550 \text{ V}^{-1}, \quad \text{standard deviation} = 0.355$$

$$\boxed{R = 0.99901}$$

$$j_0 = e^{-10.826} \text{ mA m}^{-2} = \boxed{2.00 \times 10^{-5} \text{ mA m}^{-2}}$$

$$\alpha = 1 - \frac{19.550 \text{ V}^{-1}}{f} = 1 - \frac{19.550 \text{ V}^{-1}}{(0.025693 \text{ V})^{-1}}$$

$$\boxed{\alpha = 0.498}$$

The linear regression explains 99.90 percent of the variation in a $\ln j$ against η plot and standard deviations are low. There are no deviations from the Tafel equation/plot.

Solutions to theoretical problems

P25.24 A general change in the Gibbs function of a one-component system with a surface is

$$dG = -S dT + V dp + \gamma d\sigma + \mu dn$$

Let $G = G(g) + G(\sigma)$ and $n = n(g) + n(\sigma)$; then

$$dG(g) = -S(g) dT + V(g) dp + \mu(g) dn(g)$$

$$dG(\sigma) = -S(\sigma) dT + \gamma d\sigma + \mu(\sigma) dn(\sigma)$$

At equilibrium, $\mu(\sigma) = \mu(g) = \mu$. At constant temperature, $dG(\sigma) = \gamma d\sigma + \mu dn(\sigma)$. Since dG is an exact differential, this expression integrates to

$$G(\sigma) = \gamma\sigma + \mu n(\sigma)$$

Therefore, $dG(\sigma) = \sigma d\gamma + \gamma d\sigma + \mu dn(\sigma) + n(\sigma) d\mu$

But since $dG(\sigma) = \gamma d\sigma + \mu dn(\sigma)$ we conclude that $\sigma d\gamma + n(\sigma) d\mu = 0$

Since $d\mu = RT d \ln p$, this relation is equivalent to

$$n(\sigma) = -\frac{\sigma d\gamma}{d\mu} = -\left(\frac{\sigma}{RT}\right) \times \left(\frac{d\gamma}{d \ln p}\right)$$

Now express $n(\sigma)$ as an adsorbed volume using

$$n(\sigma) = \frac{p^\ominus V_a}{RT^\ominus}$$

and express $d\gamma$ as a kind of chemical potential through

$$d\mu' = \frac{RT^\ominus}{p^\ominus} d\gamma$$

evaluated at a standard temperature and pressure (T^\ominus and p^\ominus), then

$$\boxed{-\left(\frac{\sigma}{RT}\right) \times \left(\frac{d\mu'}{d \ln p}\right) = V_a}$$

P25.26

$$\theta = \frac{Kp}{1 + Kp}, \quad \theta = \frac{V}{V_\infty}$$

$$p = \frac{\theta}{K(1 - \theta)} = \frac{V}{K(V_\infty - V)}$$

$$\frac{dp}{dV} = \frac{1}{K(V_\infty - V)} + \frac{V}{K(V_\infty - V)^2} = \frac{V_\infty}{K(V_\infty - V)^2}$$

$$\begin{aligned} d\mu' &= -\left(\frac{RT}{\sigma}\right) V d \ln p = \frac{-RT}{p\sigma} V dp \\ &= -\left(\frac{RT}{\sigma}\right) \left(\frac{K(V_\infty - V)}{V}\right) V \left(\frac{V_\infty}{K(V_\infty - V)^2}\right) dV \\ &= -\left(\frac{RT}{\sigma}\right) \left(\frac{V_\infty dV}{V_\infty - V}\right) \end{aligned}$$

Therefore, we can adopt any of several forms,

$$d\mu' = -\frac{((RT/\sigma)V_\infty)}{V_\infty - V}dV = -\frac{(RT/\sigma)}{1 - \theta}dV = -\frac{(RTV_\infty/\sigma)}{1 - \theta}d\theta = \boxed{\left(\frac{RTV_\infty}{\sigma}\right)d\ln(1 - \theta)}$$

P25.28

$$j = j_0[e^{(1-\alpha)f\eta} - e^{-\alpha f\eta}] \quad [25.41]$$

$$= j_0 \left\{ 1 + (1 - \alpha)\eta f + \frac{1}{2}(1 - \alpha)^2\eta^2 f^2 + \cdots - 1 + \alpha f\eta - \frac{1}{2}\alpha^2\eta^2 f^2 + \cdots \right\}$$

$$= j_0 \left\{ \eta f + \frac{1}{2}(\eta f)^2(1 - 2\alpha) + \cdots \right\}$$

$$\langle j \rangle = j_0 \left\{ \langle \eta \rangle f + \frac{1}{2}(1 - 2\alpha)f^2 \langle \eta^2 \rangle + \cdots \right\}$$

$$\langle \eta \rangle = 0, \text{ because } \frac{\omega}{2\pi} \int_0^{2\pi/\omega} \cos \omega t \, dt = 0 \quad \left[\frac{2\pi}{\omega} \text{ is the period} \right]$$

$$\langle \eta^2 \rangle = \frac{1}{2}\eta_0^2, \text{ because } \frac{\omega}{2\pi} \int_0^{2\pi/\omega} \cos^2 \omega t \, dt = \frac{1}{2}$$

$$\text{Therefore, } \boxed{\langle j \rangle = \frac{1}{4}(1 - 2\alpha)f^2 j_0 \eta_0^2}$$

and $\langle j \rangle = 0$ when $\alpha = \frac{1}{2}$. For the mean current,

$$\begin{aligned} \langle I \rangle &= \frac{1}{4}(1 - 2\alpha)f^2 j_0 S \eta_0^2 \\ &= \frac{1}{4} \times (1 - 0.76) \times \left(\frac{(7.90 \times 10^{-4} \text{ A cm}^{-2}) \times (1.0 \text{ cm}^2)}{(0.0257 \text{ V})^2} \right) \times (10 \text{ mV})^2 \\ &= \boxed{7.2 \mu\text{A}} \end{aligned}$$

P25.30

$$j = \left(\frac{cFD}{\delta} \right) \times (1 - e^{f\eta^c}) \quad [29.51; z = 1] = \boxed{j_L (1 - e^{F\eta^c/RT})}$$

The form of this expression is illustrated in Figure 25.6.

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 (Figure 25.6).

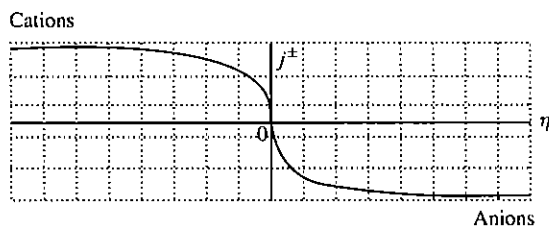


Figure 25.6

Solutions to applications

- P25.32** Equilibrium constants vary with temperature according to the van't Hoff equation [7.25] which can be written in the form

$$\frac{K_1}{K_2} = e^{-\left[(\Delta_{\text{ad}}H^\ominus/R)\left((1/T_1)-(1/T_2)\right)\right]}$$

or

$$\frac{K_1}{K_2} = \exp \left[\frac{160 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{673 \text{ K}} - \frac{1}{773 \text{ K}} \right) \right] = \boxed{40.4}$$

As measured by the equilibrium constant of absorption, NO is about 40 times more strongly absorbed at 500 °C than at 400 °C.

- P25.34** (a) $q_{\text{water}} = k(\text{RH})^{1/n}$

With a power law regression analysis we find

$$\boxed{k = 0.2289}, \text{ standard deviation} = 0.0068$$

$$1/n = 1.6182, \text{ standard deviation} = 0.0093; \boxed{n = 0.6180}$$

$$R = 0.999508$$

A linear regression analysis may be performed by transforming the equation to the following form by taking the logarithm of the Freundlich type equation

$$\ln q_{\text{water}} = \ln k + \frac{1}{n} \ln(\text{RH})$$

$$\ln k = -1.4746, \text{ standard deviation} = 0.0068; \boxed{k = 0.2289}$$

$$\frac{1}{n} = 1.6183, \text{ standard deviation} = 0.0093; \boxed{n = 0.6180}$$

$$R = 0.999508$$

The two methods give exactly the same result because the software package for performing the power law regression performs the transformation to linear form for you. Both methods are actually performing a linear regression.

The correlation coefficient indicates that 99.95 percent of the data variation is explained with the Freundlich type isotherm. The Freundlich fit hypothesis looks very good.

- (b) The Langmuir isotherm model describes adsorption sites that are independent and equivalent. This assumption seems to be valid for the VOC case in which molecules interact very weakly. However, water molecules interact much more strongly through forces such as hydrogen bonding and multilayers may readily form at the lower temperatures. The intermolecular forces of water apparently cause adsorption sites to become nonequivalent and dependent. In this particular case the Freundlich type isotherm becomes the better description.

(c) $r_{\text{VOC}} = 1 - q_{\text{water}} \quad \text{where } r_{\text{VOC}} \equiv q_{\text{VOC}}/q_{\text{VOC,RH}=0}$

$$r_{\text{VOC}} = 1 - k(\text{RH})^{1/n}$$

$$1 - r_{\text{VOC}} = k(\text{RH})^{1/n}$$

To determine the goodness-of-fit, k , and n we perform a power law regression fit of $1 - r_{\text{VOC}}$ against RH. Results are

$$k = 0.5227, \text{ standard deviation} = 0.0719$$

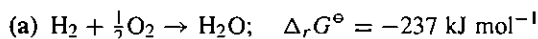
$$\frac{1}{n} = 1.3749, \text{ standard deviation} = 0.0601; n = 0.7273$$

$$R = 0.99620$$

Since 99.62 percent of the variation is explained by the regression, we conclude that the hypothesis that $r_{\text{VOC}} = 1 - q_{\text{water}}$ may be very useful. The values of R and n differ significantly from those of part (a). It may be that water is adsorbing to some portions of the surface and VOC to others.

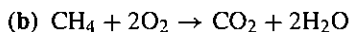
P25.36

$$E^{\ominus} = \frac{-\Delta_r G^{\ominus}}{\nu F}$$



Since $\nu = 2$,

$$E^{\ominus} = \frac{-(-237 \text{ kJ mol}^{-1})}{(2) \times (96.48 \text{ kC mol}^{-1})} = +1.23 \text{ V}$$



$$\begin{aligned} \Delta_r G^{\ominus} &= 2\Delta_f G^{\ominus}(\text{H}_2\text{O}) + \Delta_f G^{\ominus}(\text{CO}_2) - \Delta_f G^{\ominus}(\text{CH}_4) \\ &= [(2) \times (-237.1) + (-394.4) - (-50.7)] \text{ kJ mol}^{-1} = -817.9 \text{ kJ mol}^{-1} \end{aligned}$$

As written, the reaction corresponds to the transfer of eight electrons. It follows that, for the species in their standard states,

$$E^{\ominus} = \frac{-(-817.9 \text{ kJ mol}^{-1})}{(8) \times (96.48 \text{ kC mol}^{-1})} = +1.06 \text{ V}$$

P25.38

$$I_{\text{corr}} = \bar{A} \bar{j}_0 e^{fE/4} \quad [25.66]$$

with $E = -0.62 - (-0.94) \text{ V} = 0.32 \text{ V}$ [as in Problem 25.37]

$$I_{\text{corr}} \approx (0.25 \times 10^{-6} \text{ A}) \times (e^{0.32/4 \times 0.0257}) \approx 6 \mu\text{A}$$

