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.
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Contents

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 $T \to T_c$. 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.

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

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

not 2.0 bar.

(b) The van der Waals equation is

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

$$\text{so } p = \frac{(8.31 \times 10^{-2}\text{ dm}^3\text{ bar K}^{-1}\text{mol}^{-1}) \times (30 + 273)\text{ K}}{(1.53\text{ dm}^3/0.62\bar{6}\text{ mol}) - 3.20 \times 10^{-2}\text{ dm}^3\text{ mol}^{-1}}$$

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

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

$$pV = nRT$$

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

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 $p = p_{ex} + \rho gh$ [1.3] as the pressure at the top of the straw and p as the atmospheric pressure on the liquid, the pressure difference is

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

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

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

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

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

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

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

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.

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

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

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

Draw up the following table

p/atm	$(pV_m/T)/(\text{dm}^3\,\text{atm K}^{-1}\text{mol}^{-1})$	$(\rho/p)/(\text{dm}^{-3}\text{atm}^{-1})$
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

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

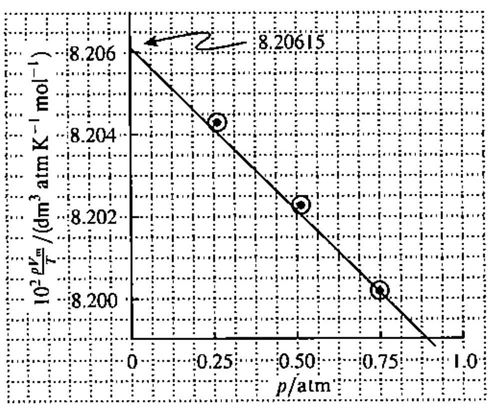


Figure 1.1(a)

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

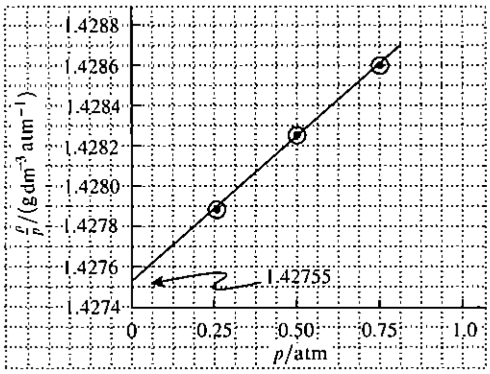


Figure 1.1(b)

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

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

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

The number of atoms per molecule is

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

suggesting a formula of $\boxed{P_4}$

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.

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

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

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

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)

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

$$= 1.11\bar{5} \times 10^{-2}\,\text{mol}, \quad p_{Ne} = 8.87\,\text{kPa}, \quad T = 300\,\text{K}$$

$$V = \frac{(1.11\bar{5} \times 10^{-2}\,\text{mol}) \times (8.314\,\text{dm}^3\,\text{kPa K}^{-1}\,\text{mol}^{-1}) \times 300\,\text{K})}{8.87\,\text{kPa}} = 3.13\bar{7}\,\text{dm}^3$$

$$= \boxed{3.14\,\text{dm}^3}$$

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

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

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

$$p = \frac{nRT}{V}[1.8] = \frac{(3.54\bar{8} \times 10^{-2}\,\text{mol}) \times (8.314\,\text{dm}^3\ \text{kPa K}^{-1}\,\text{mol}^{-1}) \times (300\ \text{K})}{3.13\bar{7}\,\text{dm}^3}$$

$$= \boxed{28.2\,\text{kPa}}$$

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

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

$$\rho = \frac{33.5\,\text{mg}}{250\,\text{cm}^3} = 0.134\bar{0}\,\text{g dm}^{-3}, \quad p = 152\,\text{Torr}, \quad T = 298\,\text{K}$$

$$M = \frac{(0.134\bar{0}\,\text{g dm}^{-3}) \times (62.36\,\text{dm}^3\,\text{Torr K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})}{152\,\text{Torr}} = \boxed{16.14\,\text{g mol}^{-1}}$$

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.

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

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

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

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

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

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

$T =$ (i) 273.15 K; (ii) 500 K

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

(i) $$p = \frac{(1.0\,\text{mol}) \times (8.206 \times 10^{-2}\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (273.15\,\text{K})}{22.414\,\text{dm}^3}$$

$$= \boxed{1.0\,\text{atm}}$$

(ii) $$p = \frac{(1.0\,\text{mol}) \times (8.206 \times 10^{-2}\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (500\,\text{K})}{0.150\,\text{dm}^3}$$

$$= \boxed{270\,\text{atm}}\ \text{(2 significant figures)}$$

(b) From Table (1.6) for H_2S

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

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

(i) $$p = \frac{(1.0\,\text{mol}) \times (8.206 \times 10^{-2}\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (273.15\,\text{K})}{22.414\,\text{dm}^3 - (1.0\,\text{mol}) \times (4.34 \times 10^{-2}\,\text{dm}^3\,\text{mol}^{-1})}$$

$$- \frac{(4.484\,\text{dm}^6\,\text{atm}\,\text{mol}^{-1}) \times (1.0\,\text{mol})^2}{(22.414\,\text{dm}^3)^2}$$

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

(ii) $$p = \frac{(1.0\,\text{mol}) \times (8.206 \times 10^{-2}\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (500\,\text{K})}{0.150\,\text{dm}^3 - (1.0\,\text{mol}) \times (4.34 \times 10^{-2}\,\text{dm}^3\,\text{mol}^{-1})}$$

$$- \frac{(4.484\,\text{dm}^6\text{atm}\,\text{mol}^{-1}) \times (1.0\,\text{mol})^2}{(0.150\,\text{dm}^3)^2}$$

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

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

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

Therefore,

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

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

$b = 0.0436$ dm^3 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 = $\boxed{1.12}$ $\boxed{\text{Repulsive}}$ forces dominate.

(b) The molar volume is

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

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

E1.16(b) **(a)**

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

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

(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

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

$$= (3.183 \times 10^{-2} + 0.120\bar{8})\,\text{dm}^3\,\text{mol}^{-1} = 0.152\bar{6}\,\text{dm}^3\text{mol}^{-1}$$

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

$$\frac{ab}{p} = \frac{(1.360\,\text{dm}^6\,\text{atm}\,\text{mol}^{-2}) \times (3.183 \times 10^{-2}\text{dm}^3\,\text{mol}^{-1})}{(200\,\text{bar}) \times (1.013\,\text{atm}\,\text{bar}^{-1})} = 2.13\bar{7} \times 10^{-4}(\text{dm}^3\,\text{mol}^{-1})^3$$

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

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

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

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

$$V_m = \frac{ZRT}{p} = \frac{(0.86) \times (0.08206\,\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}) \times (300\,\mathrm{K})}{20\,\mathrm{atm}} = 1.0\overline{59}\,\mathrm{dm^3\,mol^{-1}}$$

(a) Then, $V = nV_m = (8.2 \times 10^{-3}\,\mathrm{mol}) \times (1.0\overline{59}\,\mathrm{dm^3\,mol^{-1}}) = 8.7 \times 10^{-3}\,\mathrm{dm^3} = \boxed{8.7\,\mathrm{cm^3}}$

(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,

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

$$= (1.0\overline{59}\,\mathrm{dm^3\,mol^{-1}}) \times (0.86 - 1) = \boxed{-0.15\,\mathrm{dm^3mol^{-1}}}$$

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

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

Similarly, $x_H = \boxed{0.37}$

(b) According to the perfect gas law

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

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

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

(c) The partial pressures are

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

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

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

$$V_c = 3b$$

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

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

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

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

The critical pressure is

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

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

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

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

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

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

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 $\lim_{V_m\to\infty} \mathrm{d}Z/(\mathrm{d}(1/V_m))$ vanishes. According to the van der Waals equation

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

$$\text{so} \quad \frac{\mathrm{d}Z}{\mathrm{d}(1/V_m)} = \left(\frac{\mathrm{d}Z}{\mathrm{d}V_m}\right)\times\left(\frac{\mathrm{d}V_m}{\mathrm{d}(1/V_m)}\right)$$

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

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

In the limit of large molar volume, we have

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

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

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

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

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

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

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

The corresponding states are

(a) For H_2S

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

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

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

(b) For CO_2

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

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

(c) For Ar

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

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

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

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

which can be solved for b

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

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

The compression factor is

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

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 $\boxed{p = \rho\frac{RT}{M}}$, 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.

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

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

p/Torr	91.74	188.98	277.3	452.8	639.3	760.0
$p/(10^4\,{\rm Pa})$	1.223	2.519	3.696	6.036	8.522	10.132
$\rho/({\rm kg\,m^{-3}})$	0.225	0.456	0.664	1.062	1.468	1.734
$(p/\rho)\,(10^4\,{\rm m^2\,s^{-2}})$	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 $5.40 \times 10^4\,{\rm m^2\,s^{-2}}$. Then

$$M = \frac{RT}{5.40 \times 10^{4}\,{\rm m^2\,s^{-2}}} = \frac{(8.314\,{\rm J\,K^{-1}\,mol^{-1}}) \times (298.15\,{\rm K})}{5.40 \times 10^{4}\,{\rm m^2\,s^{-2}}}$$

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

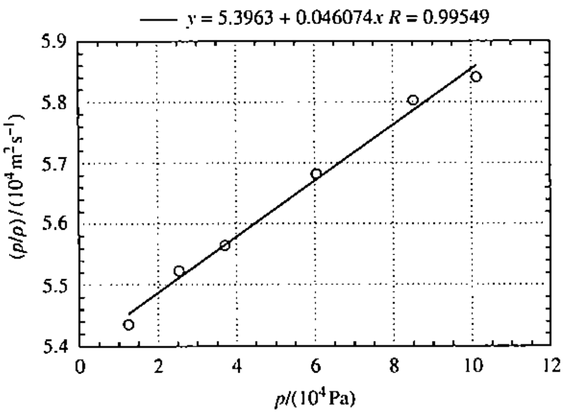


Figure 1.2

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

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

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

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

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

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

In experiment 1, $p = 423.22$ Torr, $p' = 327.10$ Torr; hence

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

In experiment 2, $p = 427.22$ Torr, $p' = 293.10$ 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 $\boxed{M \approx 102\text{ g mol}^{-1}}$. The molecules $\boxed{CH_2FCF_3}$ or $\boxed{CHF_2CHF_2}$ 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

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

We can draw up the following table

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

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

$$p(H_2) = x(H_2)p = \boxed{0}$$

$$p(N_2) = x(N_2)p = (0.20 \times (1.66\,\text{atm})) = \boxed{0.33\,\text{atm}}$$

$$p(NH_3) = x(NH_3)p = (0.80) \times (1.66\,\text{atm}) = \boxed{1.33\,\text{atm}}$$

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

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

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 $(1/V_m)$

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

$$Z = 1 + (-21.7 \times 10^{-3}\,\text{dm}^3\,\text{mol}^{-1}) \times \left(\frac{100\,\text{atm}}{(0.0821\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\text{mol}^{-1}) \times (273\,\text{K})}\right)$$

$$+ (1.200 \times 10^{-3}\,\text{dm}^6\,\text{mol}^{-2}) \times \left(\frac{100\,\text{atm}}{(0.0821\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (273\,\text{K})}\right)^2$$

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

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

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

P1.10 Since $B'(T_B) = 0$ 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

$$T_c = \left(\frac{2}{3}\right) \times \left(\frac{12p_cb}{R}\right) = \left(\frac{8}{3}\right) \times \left(\frac{p_cV_c}{R}\right)$$

$$= \left(\frac{8}{3}\right) \times \left(\frac{(40\,\text{atm}) \times (160 \times 10^{-3}\,\text{dm}^3\,\text{mol}^{-1})}{8.206 \times 10^{-2}\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}}\right) = \boxed{21\bar{0}\,\text{K}}$$

$$v_{mol} = \frac{b}{N_A} = \left(\frac{1}{3}\right) \times \left(\frac{V_c}{N_A}\right) = \frac{160 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1}}{(3) \times (6.022 \times 10^{23}\,\text{mol}^{-1})} = 8.86 \times 10^{-29}\,\text{m}^3$$

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

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

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

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

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

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

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

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

Thus $Z < 1$ when attractive forces predominate, and $Z > 1$ 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.

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

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

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

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

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

Solving the middle equation for T_c, substitution of the result into the last equation, and solving for V_c yields the result: $V_c = 2b$ 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: $Z_c = p_cV_c/RT_c = 2e^{-2} = 0.2707$. This is significantly lower than the critical compression factor that is predicted by the van der Waals equation (eqn 1.21a): $Z_c(\text{vdW}) = p_cV_c/RT_c = 3/8 = 0.3750$. Experimental values for Z_c are summarized in Table 1.5 where it is seen that the Dieterici equation prediction is often better.

P1.18

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

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

whence $B'p + C'p^2 + \cdots = \dfrac{B}{V_m} + \dfrac{C}{V_m^2} + \cdots$

Now multiply through by V_m, replace pV_m by $RT\{1 + (B/V_m) + \cdots\}$, and equate coefficients of powers of $\dfrac{1}{V_m}$: $B'RT + \dfrac{BB'RT + C'R^2T^2}{V_m} + \cdots = B + \dfrac{C}{V_m} + \cdots$

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

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

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

Restricting the variations of T and p to those which leave V_m constant, that is $\mathrm{d}V_m = 0$, 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

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

Substituting

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

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

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

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

From the given equation of state

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

For $V_m = 10b$, $10b = b + V_m^o$ or $V_m^o = 9b$

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

P1.24 The virial equation is

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

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

(a) If we assume that the series may be truncated after the B term, then a plot of (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 $B = \boxed{-1.32 \times 10^{-2}\ \text{dm}^3\text{mol}^{-1}}$.

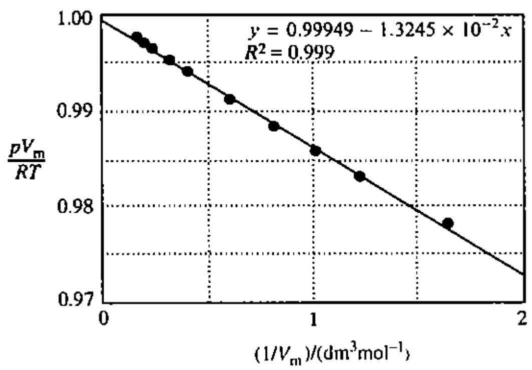


Figure 1.3

(**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

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

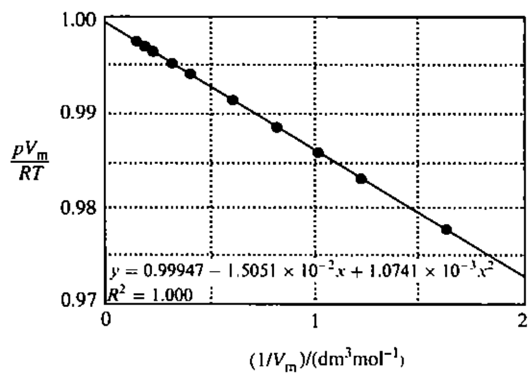


Figure 1.4

Solutions to applications

P1.26 The perfect gas law is

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

At mid-latitudes

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

In the ozone hole

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

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

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

(a) $$n = \frac{(1.0\,\text{atm}) \times (11\bar{3} \times 10^3\,\text{dm}^3)}{(8.206 \times 10^{-2}\,\text{dm}^3\,\text{atm K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})} = \boxed{4.6\bar{2} \times 10^3\,\text{mol}}$$

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

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

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

Therefore, the payload is $(13\bar{8}\,\text{kg}) - (9.3\bar{3}\,\text{kg}) = \boxed{1.3 \times 10^2\,\text{kg}}$

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

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

P1.30 Avogadro's principle states that equal volumes of gases 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) $$\frac{n(\text{CCl}_3\text{F})}{V} = \frac{(261 \times 10^{-12}) \times (1.0\,\text{atm})}{(0.08206\,\text{dm}^3\,\text{atm K}^{-1}\text{mol}^{-1}) \times (10 + 273)\,\text{K}} = \boxed{1.1 \times 10^{-11}\,\text{mol dm}^{-3}}$$

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

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

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

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 intergrated to give the total work

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

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

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

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

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

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

E2.3(b) For all cases $\Delta U = 0$, since the internal energy of a perfect gas depends only on temperature. (See *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) $\boxed{\Delta U = \Delta H = 0}$

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

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

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

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 $\boxed{w = 0}$. The heat flow is

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

$$= \boxed{3.28 \times 10^3\,\mathrm{J}}$$

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

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

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

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

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

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

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

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

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

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

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

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

E2.7(b) The reaction is

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$$

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

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

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

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

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

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

$$= \left[(20.17) \times (373 - 273) + \frac{1}{2}(0.4001) \times (373^2 - 273^2)\right]\mathrm{J} = \boxed{14.9 \times 10^3\ \mathrm{J}} = \Delta H$$

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

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

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

E2.9(b) For reversible adiabatic expansion

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

where

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

so the final temperature is

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

E2.10(b) Reversible adiabatic work is

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

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

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

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

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

E2.11(b) For reversible adiabatic expansion

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

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

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

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

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

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

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

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

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

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):

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

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

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

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

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

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

Find V_i from the perfect gas law:

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

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

Find the final temperature from the perfect gas law:

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

Adiabatic work is (eqn 2.27)

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

E2.16(b) At constant pressure

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

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

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

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

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

E2.17(b) The reaction is

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

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

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

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

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

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

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

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

E2.19(b) For anthracene the reaction is

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

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

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

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

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

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

When phenol is used the reaction is

$$C_6H_5OH(s) + \tfrac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$$

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

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

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

$$\Delta T = \frac{|q|}{C} = \frac{4.37\bar{5}\,\text{kJ}}{0.0683\,\text{kJ K}^{-1}} = \boxed{+64.1\,\text{K}}$$

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

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

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

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

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

E2.22(b) **(a)** reaction(3) = $(-2) \times$ reaction(1) + reaction(2) and $\Delta n_g = -1$

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

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

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

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

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

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

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.

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

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

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

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

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

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

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

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

Combining this expression with our original integral, we have

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

Now for the pieces

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

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

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

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

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

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

E2.26(b) The hydrogenation reaction is

(1) $C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g) \quad \Delta_r H^\ominus(T) = ?$

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

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

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

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

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

(a) Hence, at 298 K:

$$\Delta_r H^\ominus = \Delta_c H^\ominus(2) - \Delta_c H^\ominus(3) + \Delta_c H^\ominus(4)$$

$$= [(-285.83) - (-1411) + (-1300)]\,\mathrm{kJ\,mol^{-1}} = \boxed{-175\,\mathrm{kJ\,mol^{-1}}}$$

$$\Delta_r U^\ominus = \Delta_r H^\ominus - \Delta n_g RT \quad [2.21]; \quad \Delta n_g = -1$$

$$= -175\,\mathrm{kJ\,mol^{-1}} - (-1) \times (2.48\,\mathrm{kJ\,mol^{-1}}) = \boxed{-173\,\mathrm{kJ\,mol^{-1}}}$$

(b) At 348 K:

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

$$\Delta_r C_p = \sum_J \nu_J C_{p,\mathrm{m}}^\ominus(J)\ [2.37] = C_{p,\mathrm{m}}^\ominus(C_2H_4, g) - C_{p,\mathrm{m}}^\ominus(C_2H_2, g) - C_{p,\mathrm{m}}^\ominus(H_2, g)$$

$$= (43.56 - 43.93 - 28.82) \times 10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}} = -29.19 \times 10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}}$$

$$\Delta_r H^\ominus(348\,\mathrm{K}) = (-175\,\mathrm{kJ\,mol^{-1}}) - (29.19 \times 10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}}) \times (50\,\mathrm{K})$$

$$= \boxed{-176\,\mathrm{kJ\,mol^{-1}}}$$

E2.27(b) NaCl, $AgNO_3$, and $NaNO_3$ are strong electrolytes; therefore the net ionic equation is

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

$$\Delta_r H^\ominus = \Delta_f H^\ominus(AgCl) - \Delta_f H^\ominus(Ag^+) - \Delta_f H^\ominus(Cl^-)$$

$$= [(-127.07) - (105.58) - (-167.16)]\,\mathrm{kJ\,mol^{-1}} = \boxed{-65.49\,\mathrm{kJ\,mol^{-1}}}$$

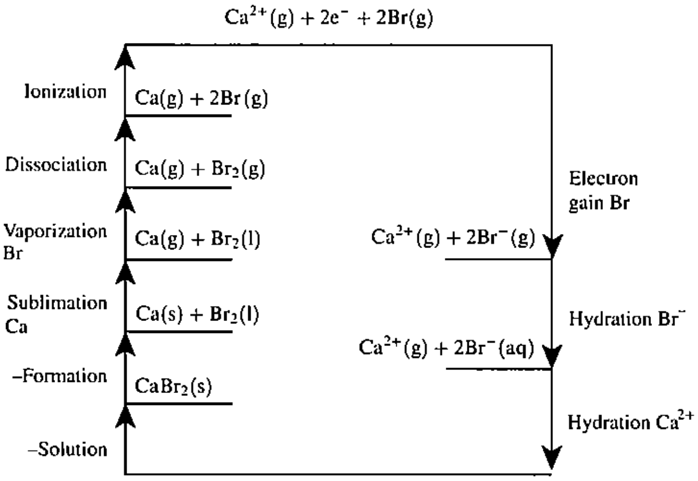


Figure 2.1

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

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

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

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

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

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

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

For an isothermal expansion $\mathrm{d}T = 0$; hence

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

$$\Delta U_{\mathrm{m}} = \int_{V_{\mathrm{m,1}}}^{V_{\mathrm{m,2}}} \mathrm{d}U_{\mathrm{m}} = \int_{V_{\mathrm{m,1}}}^{V_{\mathrm{m,2}}} \frac{a}{V_{\mathrm{m}}^2}\,\mathrm{d}V_{\mathrm{m}} = a\int_{1.00\,\mathrm{dm^3\,mol^{-1}}}^{22.1\,\mathrm{dm^3\,mol^{-1}}} \frac{\mathrm{d}V_{\mathrm{m}}}{V_{\mathrm{m}}^2} = -\frac{a}{V_{\mathrm{m}}}\bigg|_{1.00\,\mathrm{dm^3\,mol^{-1}}}^{22.1\,\mathrm{dm^3\,mol^{-1}}}$$

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

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

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

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

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

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

Hence,

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

Thus

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

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

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

E2.31(b) The expansion coefficient is

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

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

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

E2.32(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

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

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

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

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

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

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

Solutions to problems

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

Solutions to numerical problems

P2.2 $$w = -p_{\mathrm{ex}}\Delta V\ [2.8] \qquad V_\mathrm{f} = \frac{nRT}{p_{\mathrm{ex}}} \gg V_\mathrm{i}; \quad \text{so} \quad \Delta V \approx V_\mathrm{f}$$

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

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

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

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

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

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

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

From the data,

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

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

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

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

Therefore,

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

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

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

$$\Delta(pV) = nRTB\Delta\left(\frac{1}{V_\text{m}}\right) = nRTB\left(\frac{1}{V_{\text{m,f}}} - \frac{1}{V_{\text{m,i}}}\right), \quad \text{as } \Delta T = 0$$

$$= (21\overline{7}\,\text{J}) \times (6.3\overline{4} \times 10^{-2}) = 13.\overline{8}\,\text{J}$$

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

P2.6

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

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

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

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

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

and, after substitution

$$w \approx -nRT\ln\left(\frac{V_2}{V_1}\right) + n^2bRT\left(\frac{1}{V_2} - \frac{1}{V_1}\right) - n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

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

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

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)

$$w_0 = -nRT\ln\left(\frac{V_\text{f}}{V_\text{i}}\right) = (-1.0\,\text{mol}^{-1}) \times (8.314\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K}) \times \ln\left(\frac{2.0\,\text{dm}^3}{1.0\,\text{dm}^3}\right)$$

$$w_0 = -1.7\overline{2} \times 10^3\,\text{J} = \boxed{-1.7\,\text{kJ}}$$

(b)

$$w = w_0 - (1.0\,\text{mol})^2 \times [0 - (5.11 \times 10^{-2}\,\text{dm}^3\,\text{mol}^{-1}) \times (8.314\,\text{J}\,\text{K}^{-1}\text{mol}^{-1}) \times (298\,\text{K})]$$

$$\times\left(\frac{1}{2.0\,\text{dm}^3} - \frac{1}{1.0\,\text{dm}^3}\right) = (-1.7\overline{2} \times 10^3\,\text{J}) - (63\,\text{J}) = -1.7\overline{8} \times 10^3\,\text{J} = \boxed{-1.8\,\text{kJ}}$$

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

$$w = w_0 + 2.1\,\text{dm}^3\,\text{atm}$$

$$= (-1.7\bar{2} \times 10^3\,\text{J}) + (2.1\,\text{dm}^3\text{atm}) \times \left(\frac{1\,\text{m}}{10\,\text{dm}}\right)^3 \times \left(\frac{1.01 \times 10^5\,\text{Pa}}{1\,\text{atm}}\right)$$

$$= (-1.7\bar{2} \times 10^3\,\text{J}) + (0.21 \times 10^3\,\text{J}) = \boxed{-1.5\,\text{kJ}}$$

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

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

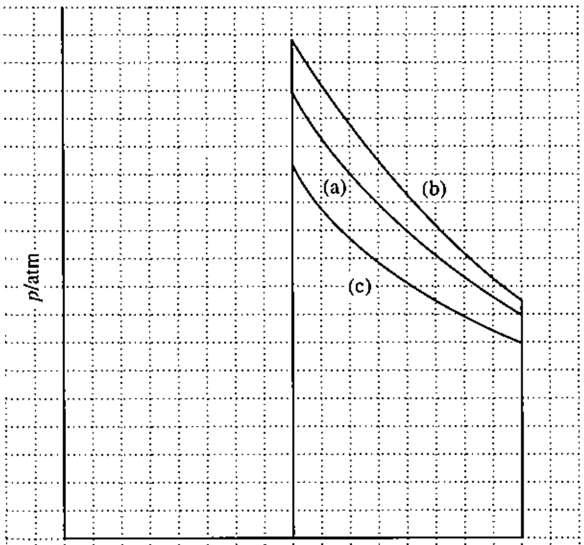


Figure 2.2

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

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

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

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

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

The combustion reaction for D-ribose is

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

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

	$\Delta H/(\text{kJ mol}^{-1})$
$5CO_2(g) + 5H_2O(l) \rightarrow C_5H_{10}O_5(s) + 5O_2(g)$	2130
$5C(s) + 5O_2(g) \rightarrow 5CO_2(g)$	$5 \times (-393.51)$
$5H_2(g) + \frac{5}{2}O_2(g) \rightarrow 5H_2O(l)$	$5 \times (-285.83)$
$5C(s) + 5H_2(g) + \frac{5}{2}O_2(g) \rightarrow C_5H_{10}O_5(s)$	-1267

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

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

Species	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_8H_{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

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

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

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

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

$R = 1.000$

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

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

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

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

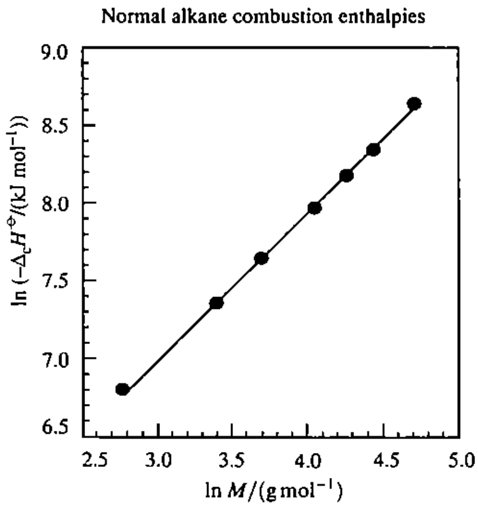


Figure 2.3

Percent error of prediction = $\boxed{2.17 \text{ percent}}$

P2.12

$$H_3O^+(aq) + NaCH_3COO \cdot 3H_2O(s) \to Na^+(aq) + CH_3COOH(aq) + 4H_2O(l)$$

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

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:

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

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

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

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

P2.14 We must relate the formation of $DyCl_3$

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

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

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

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

$$= \boxed{-994.30\,\text{kJ mol}^{-1}}$$

P2.16 **(a)** $\Delta_r H^\ominus = \Delta_f H^\ominus(SiH_3OH) - \Delta_f H^\ominus(SiH_4) - \frac{1}{2}\Delta_f H^\ominus(O_2)$

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

(b) $\Delta_r H^\ominus = \Delta_f H^\ominus(SiH_2O) - \Delta_f H^\ominus(H_2O) - \Delta_f H^\ominus(SiH_4) - \Delta_f H^\ominus(O_2)$

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

(c) $\Delta_r H^\ominus = \Delta_f H^\ominus(SiH_2O) - \Delta_f H^\ominus(SiH_3OH) - \Delta_f H^\ominus(H_2)$

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

P2.18

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

$$\left(\frac{\partial H_m}{\partial p}\right)_T = -\mu C_{p,m}\,[2.53] = -\left(\frac{2a}{RT} - b\right)$$

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

$$= -0.248\overline{3}\,\text{dm}^3\,\text{mol}^{-1}$$

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

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

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

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

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

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

Solutions to theoretical problems

P2.20 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) $$\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial}{\partial y}(2xy) = 2x \quad \text{and} \quad \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial}{\partial x}(x^2+6y) = 2x$$

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

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

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

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

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

P2.22 $$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

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

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

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

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

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

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

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

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

P2.26 **(a)** $V = V(p,T)$; hence, $\mathrm{d}V = \boxed{\left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p + \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T}$

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

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

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

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

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

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

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

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

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

P2.28 $$w = -\int_{V_1}^{V_2} p\mathrm{d}V = -nRT\int_{V_1}^{V_2} \frac{\mathrm{d}V}{V-nb} + n^2a\int_{V_1}^{V_2}\frac{\mathrm{d}V}{V^2}$$

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

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

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

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

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

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

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

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

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

P2.30 $$\mu \equiv \left(\frac{\partial T}{\partial p}\right)_H \quad [2.51]$$

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

$$\mu = -\frac{(\partial H_m/\partial p)_T}{C_{p,m}} \quad [2.53]$$

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

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

$$\left(\frac{\partial U_m}{\partial V_m}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T = \pi_T = \frac{a}{V_m^2} \quad \text{[Exercise 2.30]}$$

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

$$\left[\frac{\partial(pV_{\mathrm{m}})}{\partial p}\right]_T \approx b - \frac{a}{RT}, \quad \left(\frac{\partial V_{\mathrm{m}}}{\partial p}\right)_T \approx -\frac{RT}{p^2}$$

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

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, $(pV_{\mathrm{m}})^2 = (RT)^2$.

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

P2.32

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

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

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

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

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

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

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

Alternatively, from the definitions of α and κ_T above

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

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

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

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

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

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.

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

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

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

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

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

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

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

P2.36

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

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

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.)

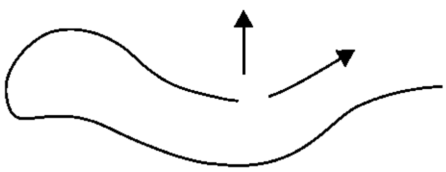


Figure 2.4

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

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

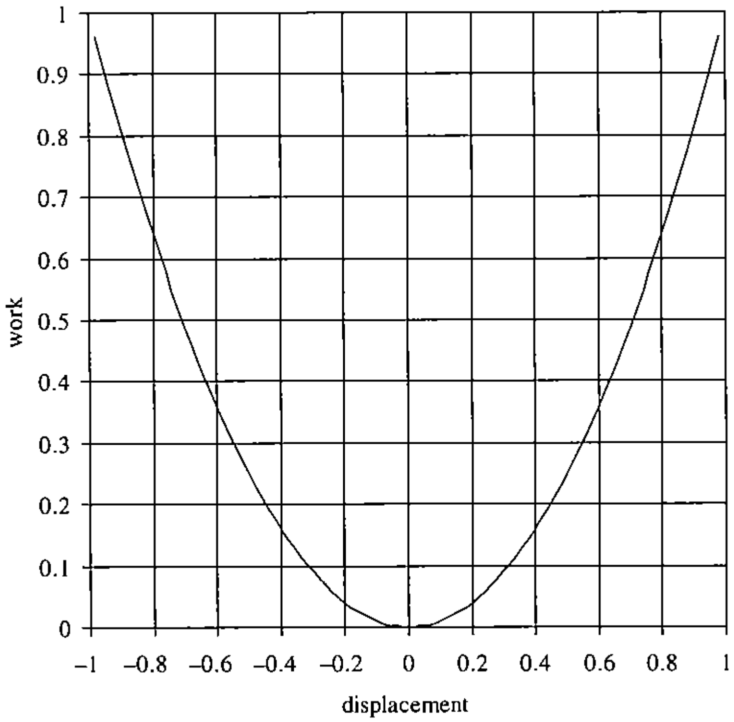


Figure 2.5

(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

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

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

(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 $dw = -F\,dx = \dfrac{kT}{2l} \ln\left(\dfrac{1+\nu}{1-\nu}\right) dx = \dfrac{kNT}{2} \ln\left(\dfrac{1+\nu}{1-\nu}\right) d\nu$

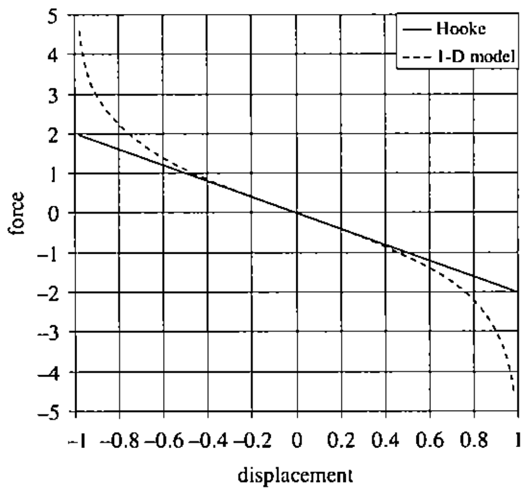


Figure 2.6

This integrates to

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

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

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

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

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

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

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

$$|F| = \frac{kT}{2l}\ln\left(\frac{1+\nu}{1-\nu}\right) = \frac{kT}{2l}[\ln(1+\nu) - \ln(1-\nu)]$$
$$\approx \frac{kT}{2l}[\nu - (-\nu)] = \frac{\nu kT}{l} = \frac{nkT}{Nl} = \frac{xkT}{Nl^2}$$

(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*.

$$C_{p,\mathrm{m}}(\mathrm{H_2O,l}) = 75.3\ \mathrm{J\,K^{-1}\,mol^{-1}} \qquad \Delta_{\mathrm{vap}}H^{\ominus}(\mathrm{H_2O}) = 44.0\ \mathrm{kJ\,mol^{-1}}$$

$$n(\mathrm{H_2O}) = \frac{65\ \mathrm{kg}}{0.018\ \mathrm{kg\,mol^{-1}}} = 3.6\times10^3\ \mathrm{mol}$$

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

$$\Delta T = \frac{\Delta H}{nC_{p,\mathrm{m}}} = \frac{1.0\times10^4\ \mathrm{kJ}}{(3.6\times10^3\ \mathrm{mol})\times(0.0753\ \mathrm{kJ\,K^{-1}\,mol^{-1}})} = \boxed{+37\ \mathrm{K}}$$

From $\Delta H = n\Delta_{\mathrm{vap}}H^{\ominus} = \dfrac{m}{M}\Delta_{\mathrm{vap}}H^{\ominus}$

$$m = \frac{M\times\Delta H}{\Delta_{\mathrm{vap}}H^{\ominus}} = \frac{(0.018\ \mathrm{kg\,mol^{-1}})\times(1.0\times10^4\ \mathrm{kJ})}{44.0\ \mathrm{kJ\,mol^{-1}}} = \boxed{4.09\ \mathrm{kg}}$$

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) $q_V = -n\Delta_{\mathrm{c}}U^{\ominus}$; hence

(i) The complete aerobic oxidation is

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

Since there is no change in the number of moles of gas, $\Delta_{\mathrm{r}}H = \Delta_{\mathrm{r}}U$ [2.21] and

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

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

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

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

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

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

$= \boxed{-127\bar{4}\ \mathrm{kJ\,mol^{-1}}}$

(b) The anaerobic glycolysis to lactic acid is

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

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

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

P2.44 The three possible fates of the radical are

(a) $tert\text{-}C_4H_9 \rightarrow sec\text{-}C_4H_9$
(b) $tert\text{-}C_4H_9 \rightarrow C_3H_6 + CH_3$
(c) $tert\text{-}C_4H_9 \rightarrow C_2H_4 + C_2H_5$

The three corresponding enthalpy changes are

(a) $\Delta_r H^\ominus = \Delta_f H^\ominus(sec\text{-}C_4H_9) - \Delta_f H^\ominus(tert\text{-}C_4H_9) = (67.5 - 51.3) \text{ kJ mol}^{-1}$
$$= \boxed{16.2 \text{ kJ mol}^{-1}}$$

(b) $\Delta_r H^\ominus = \Delta_f H^\ominus(C_3H_6) + \Delta_f H^\ominus(CH_3) - \Delta_f H^\ominus(tert\text{-}C_4H_9)$
$$= (20.42 + 145.49 - 51.3) \text{ kJ mol}^{-1} = \boxed{1146 \text{ kJ mol}^{-1}}$$

(c) $\Delta_r H^\ominus = \Delta_f H^\ominus(C_2H_4) + \Delta_f H^\ominus(C_2H_5) - \Delta_f H^\ominus(tert\text{-}C_4H_9)$
$$= (52.26 + 121.0 - 51.3) \text{ kJ mol}^{-1} = \boxed{122.0 \text{ kJ mol}^{-1}}$$

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

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

(b) The Joule–Thomson coefficient is defined as

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

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

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

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.

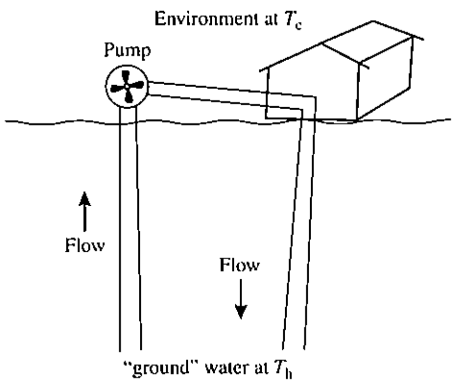


Figure 3.1 C_V and C_p are the temperature dependent heat capacities of water

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?

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

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

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

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

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

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

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

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

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

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

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

This expression satisfies the second law ($\Delta S_{\mathrm{tot}} > 0$) only when $T_{\mathrm{h}} > T_{\mathrm{c}}$. 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 $T_{\mathrm{h}} > T_{\mathrm{c}}$, 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.

$$E_{\mathrm{rev}} = 1 - \frac{T_{\mathrm{c}}}{T_{\mathrm{h}}}$$

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

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

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

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

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

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

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

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

where A is defined as $U - TS$.

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

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

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 $\pi_T = a/V_{\text{m}}^2$ 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

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

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

Solutions to exercises

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

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

(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

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

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

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

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

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

For the first step

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

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

and for the second

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$T_f = \tfrac{1}{2}(200\,°\text{C} + 25\,°\text{C}) = 112.\bar{5}\,°\text{C}$$

The heat capacity of each block is

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

so ΔH (individual) $= mC_s\Delta T = 1.00 \times 10^3\,\text{g} \times 0.449\,\text{J K}^{-1}\,\text{g}^{-1} \times (\pm 87.\bar{5}\,\text{K}) = \pm 39\,\text{kJ}$

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

$$\Delta S = mC_s \ln\left(\frac{T_f}{T_i}\right);\ 200\,°\text{C} = 473.2\,\text{K};\ 25\,°\text{C} = 298.2\,\text{K};\ 112.\bar{5}\,°\text{C} = 385.\bar{7}\,\text{K}$$

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

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

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

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

(b) $$w = -p_{\text{ex}}\Delta V = -(1.5\,\text{atm}) \times \left(\frac{1.01 \times 10^5\,\text{Pa}}{\text{atm}}\right) \times (100.0\,\text{cm}^2) \times (15\,\text{cm}) \times \left(\frac{1\,\text{m}^3}{10^6\,\text{cm}^3}\right)$$

$$= -22\overline{7.2}\,\text{J} = \boxed{-230\,\text{J}}$$

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

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

$$\Delta T = \frac{\Delta U}{nC_{V,\text{m}}} = \frac{-22\overline{7.2}\,\text{J}}{(1.5\,\text{mol}) \times (28.8\,\text{J K}^{-1}\,\text{mol}^{-1})}$$

$$= \boxed{-5.3\,\text{K}}$$

(e) 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:

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

$$T_f = 288.\overline{15}\,\text{K} - 5.26\,\text{K} = 282.\bar{9}\,\text{K}$$

$$V_i = \frac{nRT}{p_i} = \frac{(1.5\,\text{mol}) \times (8.206 \times 10^{-2}\,\text{dm}^3\,\text{atm K}^{-1}\,\text{mol}^{-1}) \times (288.\bar{2}\,\text{K})}{9.0\,\text{atm}}$$

$$= 3.9\overline{42}\,\text{dm}^3$$

$$V_f = 3.9\overline{42}\ \mathrm{dm^3} + (100\ \mathrm{cm^2}) \times (15\ \mathrm{cm}) \times \left(\frac{1\ \mathrm{dm^3}}{1000\ \mathrm{cm^3}}\right)$$

$$= 3.9\overline{42}\ \mathrm{dm^3} + 1.5\ \mathrm{dm^3} = 5.4\overline{4}\ \mathrm{dm^3}$$

$$\Delta S = (1.5\ \mathrm{mol}) \times \left\{(28.8\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{282.\overline{9}}{288.\overline{2}}\right) + (8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{5.4\overline{4}}{3.9\overline{42}}\right)\right\}$$

$$= 1.5\ \mathrm{mol}(-0.534\overline{6}\ \mathrm{J\,K^{-1}\,mol^{-1}} + 2.67\overline{8}\ \mathrm{J\,K^{-1}\,mol^{-1}}) = \boxed{3.2\ \mathrm{J\,K^{-1}}}$$

E3.7(b) (a) $\Delta_{\mathrm{vap}}S = \dfrac{\Delta_{\mathrm{vap}}H}{T_b} = \dfrac{35.27 \times 10^3\ \mathrm{J\,mol^{-1}}}{(64.1 + 273.15)\ \mathrm{K}} = +104.5\overline{8}\ \mathrm{J\,K^{-1}} = \boxed{104.6\ \mathrm{J\,K^{-1}}}$

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

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

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

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

(b) $\Delta_r S^\ominus = 12S_m^\ominus(\mathrm{CO_2, g}) + 11S_m^\ominus(\mathrm{H_2O, l}) - S_m^\ominus(\mathrm{C_{12}H_{22}O_{11}, s}) - 12S_m^\ominus(\mathrm{O_2, g})$

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

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

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

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

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

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

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

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

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

(b) $\Delta_r G^\ominus = 12\Delta_f G^\ominus(\mathrm{CO_2, g}) + 11\Delta_f G^\ominus(\mathrm{H_2O, l}) - \Delta_f G^\ominus(\mathrm{C_{12}H_{22}O_{11}, s}) - 12\Delta_f G^\ominus(\mathrm{O_2, g})$

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

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

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

E3.11(b) $CO(g) + CH_3OH(l) \rightarrow CH_3COOH(l)$

$$\Delta_r H^\ominus = \sum_{\text{Products}} \nu\Delta_f H^\ominus - \sum_{\text{Reactants}} \nu\Delta_f H^\ominus \ [2.32]$$

$$= -484.5\,\text{kJ mol}^{-1} - (-238.66\,\text{kJ mol}^{-1}) - (-110.53\,\text{kJ mol}^{-1})$$

$$= -135.3\bar{1}\,\text{kJ mol}^{-1}$$

$$\Delta_r S^\ominus = \sum_{\text{Products}} \nu S_m^\ominus - \sum_{\text{Reactants}} \nu S_m^\ominus \ [3.21]$$

$$= 159.8\,\text{J K}^{-1}\,\text{mol}^{-1} - 126.8\,\text{J K}^{-1}\,\text{mol}^{-1} - 197.67\,\text{J K}^{-1}\,\text{mol}^{-1}$$

$$= -164.6\bar{7}\,\text{J K}^{-1}\,\text{mol}^{-1}$$

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$$

$$= -135.3\bar{1}\,\text{kJ mol}^{-1} - (298\,\text{K}) \times (-164.6\bar{7}\,\text{J K}^{-1}\,\text{mol}^{-1})$$

$$= -135.3\bar{1}\,\text{kJ mol}^{-1} + 49.07\bar{2}\,\text{kJ mol}^{-1} = \boxed{-86.2\,\text{kJ mol}^{-1}}$$

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

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

The combustion reaction is

$$CO(NH_2)_2(s) + \tfrac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l) + N_2(g)$$

$$\Delta_c H = \Delta_f H^\ominus(CO_2, g) + 2\Delta_f H^\ominus(H_2O, l) - \Delta_f H^\ominus(CO(NH_2)_2, s)$$

$$\Delta_f H^\ominus(CO(NH_2)_2, s) = \Delta_f H^\ominus(CO_2, g) + 2\Delta_f H^\ominus(H_2O, l) - \Delta_c H(CO(NH_2)_2, s)$$

$$= -393.51\,\text{kJ mol}^{-1} + (2) \times (-285.83\,\text{kJ mol}^{-1}) - (-632\,\text{kJ mol}^{-1})$$

$$= -333.17\,\text{kJ mol}^{-1}$$

$$\Delta_f S^\ominus = S_m^\ominus(CO(NH_2)_2, s) - S_m^\ominus(C, gr) - \tfrac{1}{2}S_m^\ominus(O_2, g) - S_m^\ominus(N_2, g) - 2S_m^\ominus(H_2, g)$$

$$= 104.60\,\text{J K}^{-1}\,\text{mol}^{-1} - 5.740\,\text{J K}^{-1}\,\text{mol}^{-1} - \tfrac{1}{2}(205.138\,\text{J K}^{-1}\,\text{mol}^{-1})$$

$$- 191.61\,\text{J K}^{-1}\,\text{mol}^{-1} - 2(130.684\,\text{J K}^{-1}\,\text{mol}^{-1})$$

$$= -456.68\bar{7}\,\text{J K}^{-1}\,\text{mol}^{-1}$$

$$\Delta_f G^\ominus = \Delta_f H^\ominus - T\Delta_f S^\ominus$$

$$= -333.1\bar{7}\,\text{kJ mol}^{-1} - (298\,\text{K}) \times (-456.68\bar{7}\,\text{J K}^{-1}\,\text{mol}^{-1})$$

$$= -333.1\bar{7}\,\text{kJ mol}^{-1} + 136.\overline{093}\,\text{kJ mol}^{-1}$$

$$= \boxed{-197\,\text{kJ mol}^{-1}}$$

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

$= 3.0\overline{29}\,\text{J K}^{-1} = \boxed{3.0\,\text{J K}^{-1}}$

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

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

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

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

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

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

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

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

E3.14(b) $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

$$\Delta_r G^\ominus = 3\Delta_f G^\ominus(CO_2, g) + 4\Delta_f G^\ominus(H_2O, l) - \Delta_f G^\ominus(C_3H_8, g) - 0$$

$$= 3(-394.36\,\text{kJ mol}^{-1}) + 4(-237.13\,\text{kJ mol}^{-1}) - 1(-23.49\,\text{kJ mol}^{-1})$$

$$= -2108.11\,\text{kJ mol}^{-1}$$

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

$$|q_{c,\min}| = |q_h| - |w_{\max}|$$

$$= 1.0\,\text{kJ} - 0.50\,\text{kJ}$$

$$= \boxed{0.5\,\text{kJ}}$$

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]

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

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 $\left(\frac{\partial G_i}{\partial T}\right)_p = -S_i$

$$\Delta S = S_f - S_i = -\left(\frac{\partial G_f}{\partial T}\right)_p + \left(\frac{\partial G_i}{\partial T}\right)_p = -\left(\frac{\partial (G_f - G_i)}{\partial T}\right)_p$$

$$= -\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\frac{\partial}{\partial T}\left(-73.1\,\text{J} + 42.8\,\text{J} \times \frac{T}{\text{K}}\right)$$

$$= \boxed{-42.8\,\text{J K}^{-1}}$$

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).

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

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.

$$\begin{aligned}
\Delta G &= \int_{100\,\mathrm{kPa}}^{100\,\mathrm{MPa}} \frac{m}{\rho}(1 - \kappa_T p)\,dp \\
&= \frac{m}{\rho}\left(\int_{100\,\mathrm{kPa}}^{100\,\mathrm{MPa}} dp - \kappa_T \int_{100\,\mathrm{kPa}}^{100\,\mathrm{MPa}} p\,dp\right) \\
&= \frac{m}{\rho}\left(p\Big|_{100\,\mathrm{kPa}}^{100\,\mathrm{MPa}} - \frac{1}{2}\kappa_T p^2\Big|_{100\,\mathrm{kPa}}^{100\,\mathrm{MPa}}\right) \\
&= \frac{25\,\mathrm{g}}{0.791\,\mathrm{g\,cm^{-3}}}\left(9.99 \times 10^7\,\mathrm{Pa} - \frac{1}{2}(1.26 \times 10^{-9}\,\mathrm{Pa}^{-1}) \times (1.00 \times 10^{16}\,\mathrm{Pa}^2)\right) \\
&= 31.\bar{6}\,\mathrm{cm}^3 \times \left(\frac{1\,\mathrm{m}}{100\,\mathrm{cm}}\right)^3 \times 9.36 \times 10^7\,\mathrm{Pa} \\
&= 2.9\bar{6} \times 10^3\,\mathrm{J} = \boxed{3.0\,\mathrm{kJ}}
\end{aligned}$$

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

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

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

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

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

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

E3.21(b) $\Delta G = nV_\mathrm{m}\Delta p$ [3.55] $= V\Delta p$

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

E3.22(b) $$\Delta G_\mathrm{m} = RT\ln\left(\frac{p_\mathrm{f}}{p_\mathrm{i}}\right) = (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (500\,\mathrm{K}) \times \ln\left(\frac{100.0\,\mathrm{kPa}}{50.0\,\mathrm{kPa}}\right) = \boxed{+2.88\,\mathrm{kJ\,mol^{-1}}}$$

Solutions to problems

Solutions to numerical problems

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

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

$$\Delta S_\mathrm{m} = (91.47\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{300\,\mathrm{K}}{273\,\mathrm{K}}\right) + (0.075\,\mathrm{J\,K^{-2}\,mol^{-1}}) \times (27\,\mathrm{K})$$

$$= \boxed{10.\bar{7}\,\mathrm{K^{-1}\,mol^{-1}}}$$

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

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

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

$$\Delta S_\mathrm{A} = (2.0\,\mathrm{mol}) \times (20\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln 3.00$$

$$+ (2.00\,\mathrm{mol}) \times (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{3.00\,\mathrm{dm^3}}{2.00\,\mathrm{dm^3}}\right)$$

$$= \boxed{50.7\,\mathrm{J\,K^{-1}}}$$

$$\Delta S_\mathrm{B} = nR\ln\left(\frac{V_\mathrm{B,f}}{V_\mathrm{B,i}}\right) = (2.00\,\mathrm{mol}) \times (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{1.00\,\mathrm{dm^3}}{2.00\,\mathrm{dm^3}}\right)$$

$$= \boxed{-11.5\,\mathrm{J\,K^{-1}}}$$

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

$$\Delta A_\mathrm{B} = -T_\mathrm{B}\Delta S_\mathrm{B} = -(300\mathrm{K})(-11.5\,\mathrm{J\,K^{-1}}) = 3.46 \times 10^3\,\mathrm{J} = \boxed{+3.46\,\mathrm{kJ}}$$

In Section A, we cannot compute $\Delta(TS)$, so we cannot compute ΔU. ΔA $\boxed{\text{is indeterminate}}$ in both magnitude and sign. We know that in a perfect gas, U depends only on temperature; moreover, $U(T)$ is an increasing function of T, for $\partial U/\partial T = C$ (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

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

ΔG_A is $\boxed{\text{indeterminate}}$ in both magnitude and sign.

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

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

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

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

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

P3.6

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

Path (*a*)

$$w = -nRT\ln\left(\frac{V_f}{V_i}\right)\ [3.13] = -nRT\ln\left(\frac{p_i}{p_f}\right)\ [\text{Boyle's law}]$$

$$= -(1.00\,\mathrm{mol}) \times (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (300\,\mathrm{K}) \times \ln\left(\frac{3.00\,\mathrm{atm}}{1.00\,\mathrm{atm}}\right) = -2.74 \times 10^3\,\mathrm{J}$$

$$= \boxed{-2.74\ \mathrm{kJ}}$$

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

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

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

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

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

Path (*b*)

$$w = -p_{\text{ex}}(V_{\text{f}} - V_{\text{i}}) = -p_{\text{ex}}\left(\frac{nRT}{p_{\text{f}}} - \frac{nRT}{p_{\text{i}}}\right) = -nRT\left(\frac{p_{\text{ex}}}{p_{\text{f}}} - \frac{p_{\text{ex}}}{p_{\text{i}}}\right)$$

$$= -(1.00\,\text{mol}) \times (8.314\,\text{J K}^{-1}) \times (300\,\text{K}) \times \left(\frac{1.00\,\text{atm}}{1.00\,\text{atm}} - \frac{1.00\,\text{atm}}{3.00\,\text{atm}}\right)$$

$$= -1.66 \times 10^3\,\text{J} = \boxed{-1.66\,\text{kJ}}$$

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

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

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

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

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

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

P3.8 ΔS depends on only the initial and final states, so we can use $\Delta S = nC_{p,\text{m}} \ln \dfrac{T_{\text{f}}}{T_{\text{i}}}$ [3.19]

Since $q = nC_{p,\text{m}}(T_{\text{f}} - T_{\text{i}})$, $T_{\text{f}} = T_{\text{i}} + \dfrac{q}{nC_{p,\text{m}}} = T_{\text{i}} + \dfrac{I^2Rt}{nC_{p,\text{m}}}$ $[q = ItV = I^2Rt]$

That is, $\Delta S = nC_{p,\text{m}} \ln\left(1 + \dfrac{I^2Rt}{nC_{p,\text{m}}T_{\text{i}}}\right)$

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

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

$$= (192\,\text{J K}^{-1}) \times (\ln 1.27) = \boxed{+45.4\ \text{J K}^{-1}}$$

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

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

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

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

so $\text{d}T = \left(\dfrac{\partial T}{\partial p}\right)_H \text{d}p + \left(\dfrac{\partial T}{\partial H}\right)_p \text{d}H$

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

$$dT = \left(\frac{\partial T}{\partial p}\right)_H dp = \mu\, dp$$

$$\Delta T = \int_{p_i}^{p_f} \mu\, dp = \mu \Delta p \quad [\mu \text{ is constant}]$$

$$= (0.21\,\text{K atm}^{-1}) \times (1.00\,\text{atm} - 100\,\text{atm}) = \boxed{-21\,\text{K}}$$

$$T_f = T_i + \Delta T = (373 - 21)\,\text{K} = 352\,\text{K}\ [\text{Mean}\ T = 363\,\text{K}]$$

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

Therefore, $dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \qquad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad [\text{Table 3.5}]$$

For $V_m = \frac{RT}{p}(1 + Bp)$

$$\left(\frac{\partial V_m}{\partial T}\right)_p = \frac{R}{p}(1 + Bp)$$

Then $dS_m = \frac{C_{p,m}}{T}\, dT - \frac{R}{p}(1 + Bp)\, dp$

or $\quad dS_m = \frac{C_{p,m}}{T}\, dT - \frac{R}{p} dp - RB\, dp$

Upon integration

$$\Delta S_m = \int_1^2 dS_m = C_{p,m} \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{p_2}{p_1}\right) - RB(p_2 - p_1)$$

$$= \frac{5}{2} R \ln\left(\frac{352}{373}\right) - R \ln\left(\frac{1}{100}\right) - R\left(-\frac{0.525\,\text{atm}^{-1}}{363}\right) \times (-99\,\text{atm})$$

$$= \boxed{+35.9\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

P3.12

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

$$\Delta_r H^\ominus(298\,\text{K}) = 1 \times \Delta_f H^\ominus(\text{CO, g}) + 1 \times \Delta_f H^\ominus(\text{H}_2\text{O, g}) - 1 \times \Delta_f H^\ominus(\text{CO}_2\text{, g})$$

$$= \{-110.53 - 241.82 - (-393.51)\}\,\text{kJ mol}^{-1} = \boxed{+41.16\,\text{kJ mol}^{-1}}$$

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

$$\Delta_r S^\ominus(298\,\text{K}) = 1 \times S_m^\ominus(\text{CO, g}) + 1 \times S_m^\ominus(\text{H}_2\text{O, g}) - 1 \times S_m^\ominus(\text{CO}_2\text{, g}) - 1 \times S_m^\ominus(\text{H}_2\text{, g})$$

$$= (197.67 + 188.83 - 213.74 - 130.684)\,\text{kJ mol}^{-1} = \boxed{+42.08\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

$$\Delta_r H^\ominus(398\,\text{K}) = \Delta_r H^\ominus(298\,\text{K}) + \int_{298\,\text{K}}^{398\,\text{K}} \Delta_r C_p\,\mathrm{d}T \text{ [2.36]}$$

$$= \Delta_r H^\ominus(298\,\text{K}) + \Delta_r C_p \Delta T \text{ [heat capacities constant]}$$

$$\Delta_r C_p = 1 \times C_{p,\text{m}}(\text{CO, g}) + 1 \times C_{p,\text{m}}(\text{H}_2\text{O, g}) - 1 \times C_{p,\text{m}}(\text{CO}_2\text{, g}) - 1 \times C_{p,\text{m}}(\text{H}_2\text{, g})$$

$$= (29.14 + 33.58 - 37.11 - 28.824)\,\text{J K}^{-1}\,\text{mol}^{-1} = -3.21\,\text{J K}^{-1}\,\text{mol}^{-1}$$

$$\Delta_r H^\ominus(398\,\text{K}) = (41.16\,\text{kJ mol}^{-1}) + (-3.21\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (100\,\text{K}) = \boxed{+40.84\,\text{kJ mol}^{-1}}$$

For each substance in the reaction

$$\Delta S_\text{m} = C_{p,\text{m}} \ln\left(\frac{T_\text{f}}{T_\text{i}}\right) = C_{p,\text{m}} \ln\left(\frac{398\,\text{K}}{298\,\text{K}}\right) \text{ [3.19]}$$

Thus

$$\Delta_r S^\ominus(398\,\text{K}) = \Delta_r S^\ominus(298\,\text{K}) + \sum_\text{products} \nu_\text{J} C_{p,\text{m}}(\text{J}) \ln\left(\frac{T_\text{f}}{T_\text{i}}\right) - \sum_\text{reactants} \nu_\text{J} C_{p,\text{m}}(\text{J}) \ln\left(\frac{T_\text{f}}{T_\text{i}}\right)$$

$$= \Delta_r S^\ominus(298\,\text{K}) + \Delta_r C_p \ln\left(\frac{398\,\text{K}}{298\,\text{K}}\right)$$

$$= (42.01\,\text{J K}^{-1}\,\text{mol}^{-1}) + (-3.21\,\text{J K}^{-1}\,\text{mol}^{-1}) \ln\left(\frac{398\,\text{K}}{298\,\text{K}}\right)$$

$$= (42.01 - 0.93)\,\text{J K}^{-1}\,\text{mol}^{-1} = \boxed{+41.08\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

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

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

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

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

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

$$H_\text{m}^\ominus(298\,\text{K}) - H_\text{m}^\ominus(0) = \int_0^{298\,\text{K}} C_{p,\text{m}}\,\mathrm{d}T = \boxed{34.4\,\text{kJ mol}^{-1}}$$

$$S_\text{m}(298\,\text{K}) = S_\text{m}(0) + \int_0^{298\,\text{K}} \frac{C_{p,\text{m}}}{T}\mathrm{d}T = S_\text{m}(0) + \boxed{243\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

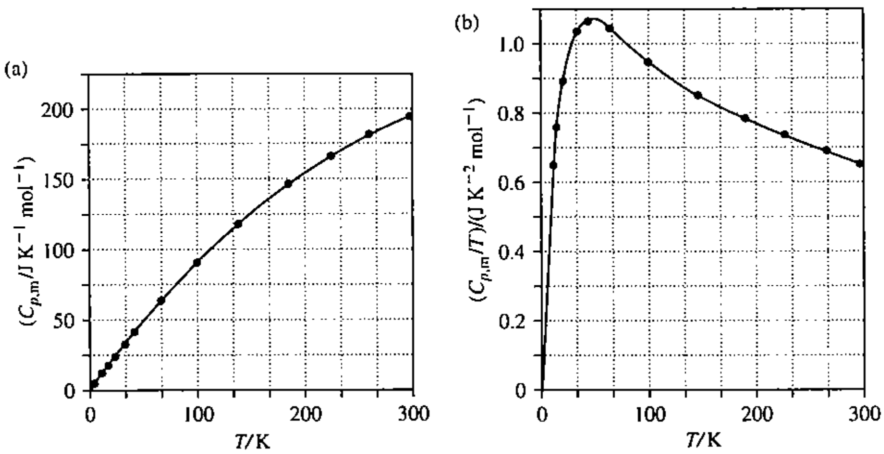


Figure 3.2

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

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = \left(\frac{\partial G_\mathrm{f}}{\partial T}\right)_p - \left(\frac{\partial G_\mathrm{i}}{\partial T}\right)_p$$

and $\Delta H = H_\mathrm{f} - H_\mathrm{i}$

Thus,

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

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

$$\Delta\left(\frac{\Delta_\mathrm{r}G^\ominus}{T}\right) = -\int_{T_\mathrm{c}}^{T}\frac{\Delta_\mathrm{r}H^\ominus\,\mathrm{d}T}{T^2}$$

$$\approx -\Delta_\mathrm{r}H^\ominus\int_{T_\mathrm{c}}^{T}\frac{\mathrm{d}T}{T^2} = \Delta_\mathrm{r}H^\ominus\left(\frac{1}{T}-\frac{1}{T_\mathrm{c}}\right) \quad [\Delta_\mathrm{r}H^\ominus \text{ assumed constant}]$$

Therefore, $\dfrac{\Delta_\mathrm{r}G^\ominus(T)}{T} - \dfrac{\Delta_\mathrm{r}G^\ominus(T_\mathrm{c})}{T_\mathrm{c}} \approx \Delta_\mathrm{r}H^\ominus\left(\dfrac{1}{T}-\dfrac{1}{T_\mathrm{c}}\right)$

$$\Delta_\mathrm{r}G^\ominus(T) = \frac{T}{T_\mathrm{c}}\Delta_\mathrm{r}G^\ominus(T_\mathrm{c}) + \left(1-\frac{T}{T_\mathrm{c}}\right)\Delta_\mathrm{r}H^\ominus(T_\mathrm{c})$$

and so

$$= \tau\Delta_\mathrm{r}G^\ominus(T_\mathrm{c}) + (1-\tau)\Delta_\mathrm{r}H^\ominus(T_\mathrm{c}) \text{ where } \tau = \frac{T}{T_\mathrm{c}}$$

For the reaction

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

$$\Delta_\mathrm{r}G^\ominus(T_\mathrm{c}) = 2\Delta_\mathrm{f}G^\ominus(CO_2, g) - 2\Delta_\mathrm{f}G^\ominus(CO, g)$$

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

$$\Delta_r H^\ominus(T_c) = 2\Delta_f H^\ominus(CO_2, g) - 2\Delta_f H^\ominus(CO, g)$$
$$= [2 \times (-393.51) - 2 \times (-110.53)]\, kJ\, mol^{-1} = -565.96\, kJ\, mol^{-1}$$

Therefore, since $\tau = 375/298.15 = 1.25\bar{8}$

$$\Delta_r G^\ominus(375\, K) = \{(1.25\bar{8}) \times (-514.38) + (1 - 1.25\bar{8}) \times (-565.96)\}\, kJ\, mol^{-1}$$
$$= \boxed{-501\, kJ\, mol^{-1}}$$

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
$10^3\left(\frac{Z-1}{p}\right)\Big/$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 atm × 0.73 = $\boxed{73\text{ atm}}$

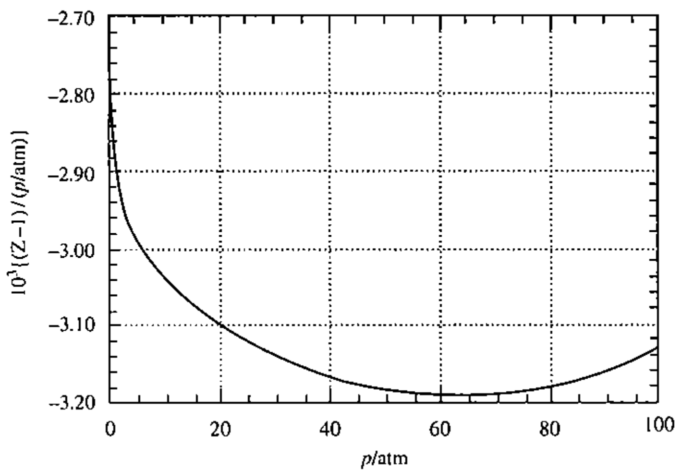


Figure 3.3

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 → 2, step 1; 2 → 3, step 2; 3 → 1, step 3).

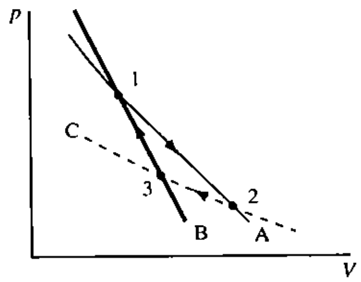


Figure 3.4

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

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

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

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

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

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

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

P3.22

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

which is the virial equation of state.

P3.24 We start from the fundamental relation

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V \text{ [3.43]}$$

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

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V$$

Comparing the two expressions, we see that

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

These relations are true in general and hence hold for the perfect gas. We can demonstrate this more explicitly for the perfect gas as follows. For the perfect gas at constant volume

$$\mathrm{d}U = C_V\,\mathrm{d}T$$

and

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

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

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

$$dU = dw = -p\,dV$$

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

P3.26 $$\alpha = \left(\frac{1}{V}\right) \times \left(\frac{\partial V}{\partial T}\right)_p \text{ [3.8]}; \qquad \kappa_T = -\left(\frac{1}{V}\right) \times \left(\frac{\partial V}{\partial p}\right)_T \text{ [3.14]}$$

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

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

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

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

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

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

First treat the numerator:

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

As for the denominator, at constant p

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

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]

$$-\left(\frac{\partial T}{\partial V}\right)_S = \frac{1}{\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial V}{\partial S}\right)_T} \text{ [Euler chain]} = \frac{\left(\frac{\partial S}{\partial V}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_V} \text{ [reciprocal]}$$

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

$$= \frac{-\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial U}{\partial S}\right)_V}{\left(\frac{\partial V}{\partial p}\right)_T\left(\frac{\partial U}{\partial T}\right)_V} \text{ [reciprocal identity, twice]} = \boxed{\frac{\alpha T}{\kappa_T C_V}}\left[\left(\frac{\partial U}{\partial S}\right)_V = T\right]$$

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

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

We will be able to identify some of these terms if we examine an expression for $\mathrm{d}H$ analogous to the fundamental equation [3.43]. From the definition of enthalpy, we have:

$$\mathrm{d}H = \mathrm{d}U + p\,\mathrm{d}V + V\,\mathrm{d}p = T\,\mathrm{d}S - p\,\mathrm{d}V\ [3.43] + p\,\mathrm{d}V + V\,\mathrm{d}p = T\,\mathrm{d}S + V\,\mathrm{d}p$$

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

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

Thus, $\left(\frac{\partial H}{\partial S}\right)_p = T$, $\left(\frac{\partial H}{\partial p}\right)_S = V$ [$\mathrm{d}H$ exact]

Substitution yields $\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V = \boxed{-T\left(\frac{\partial V}{\partial T}\right)_p + V}$ [Maxwell relation]

(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

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

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

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

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

which yields after algebraic manipulation

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

When $\frac{b}{V_m} \ll 1$, $\lambda \approx 1$ and

$$\frac{2na}{RTV} = \frac{2na}{RT} \times \frac{1}{V} \approx \frac{2na}{RT} \times \frac{p}{nRT} = \frac{2pa}{R^2T^2}$$

Therefore, $$\left(\frac{\partial H}{\partial p}\right)_T \approx \frac{nb - \left(\frac{2na}{RT}\right)}{1 - \left(\frac{2pa}{R^2T^2}\right)}$$

For argon, $a = 1.337\,\mathrm{dm^6\,atm\,mol^{-2}}$, $b = 3.20 \times 10^{-2}\,\mathrm{dm^3\,mol^{-1}}$,

$$\frac{2na}{RT} = \frac{(2) \times (1.0\,\mathrm{mol}) \times (1.337\,\mathrm{dm^6\,atm\,mol^{-2}})}{(8.206 \times 10^{-2}\,\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})} = 0.11\,\mathrm{dm^3}$$

$$\frac{2pa}{R^2T^2} = \frac{(2) \times (10.0\,\mathrm{atm}) \times (1.337\,\mathrm{dm^6\,atm\,mol^{-2}})}{[(8.206 \times 10^{-2}\,\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})]^2} = 0.045$$

Hence, $$\left(\frac{\partial H}{\partial p}\right)_T \approx \frac{\{(3.20 \times 10^{-2}) - (0.11)\}\,\mathrm{dm^3}}{1 - 0.045} = -0.0817\,\mathrm{dm^3} = \boxed{-8.3\,\mathrm{J\,atm^{-1}}}$$

$$\Delta H \approx \left(\frac{\partial H}{\partial p}\right)_T \Delta p \approx (-8.3\,\mathrm{J\,atm^{-1}}) \times (1\,\mathrm{atm}) = \boxed{-8\,\mathrm{J}}$$

P3.30
$$\mu_J = \left(\frac{\partial T}{\partial V}\right)_U \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\mu_J C_V = \left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial U}{\partial T}\right)_V = \frac{-1}{\left(\frac{\partial V}{\partial U}\right)_T} \text{ [Euler chain relation]}$$

$$= -\left(\frac{\partial U}{\partial V}\right)_T \text{ [reciprocal identity]} = p - T\left(\frac{\partial p}{\partial T}\right)_V \text{ [3.48]}$$

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

Therefore, $\boxed{\mu_J C_V = p - \dfrac{\alpha T}{\kappa_T}}$

P3.32
$$\kappa_S = -\left(\frac{1}{V}\right) \times \left(\frac{\partial V}{\partial p}\right)_S = -\frac{1}{V\left(\frac{\partial p}{\partial V}\right)_S}$$

The only constant-entropy changes of state for a perfect gas are reversible adiabatic changes, for which

$$pV^\gamma = \text{const}$$

Then, $\left(\dfrac{\partial p}{\partial V}\right)_S = \left(\dfrac{\partial}{\partial V}\dfrac{\text{const}}{V^\gamma}\right)_S = -\gamma \times \left(\dfrac{\text{const}}{V^{\gamma+1}}\right) = \dfrac{-\gamma p}{V}$

Therefore, $\kappa_S = \dfrac{-1}{V\left(\dfrac{-\gamma p}{V}\right)} = \dfrac{+1}{\gamma p}$

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

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

and hence

$$Z = 1 - \frac{a}{RTV_\text{m}}$$

Then substituting into eqn 3.60 we get

$$\ln\phi = \int_0^p \left(\frac{Z-1}{p}\right)\text{d}p = \int_0^p \frac{-a}{pRTV_\text{m}}\,\text{d}p$$

In order to perform this integration we must eliminate the variable V_m by solving for it in terms of p. Rewriting the expression for p in the form of a quadratic we have

$$V_\text{m}^2 - \frac{RT}{p}V_\text{m} + \frac{a}{p} = 0$$

The solution is

$$V_\text{m} = \frac{1}{2}\left(\frac{RT}{p} \pm \frac{1}{p}\sqrt{(RT)^2 - 4ap}\right)$$

Applying the approximation $(RT)^2 \gg 4ap$ we obtain

$$V_\text{m} = \frac{1}{2}\left(\frac{RT}{p} \pm \frac{RT}{p}\right)$$

Choosing the + sign we get

$$V_\text{m} = \frac{RT}{p} \text{ which is the perfect-gas volume.}$$

Then

$$\ln\phi = \int_0^p -\frac{a}{(RT)^2}\,\text{d}p = \boxed{-\frac{ap}{(RT)^2}}$$

For ammonia $a = 4.169\,\text{atm dm}^6\,\text{mol}^{-2}$

$$\ln\phi = -\frac{4.169\,\text{atm dm}^3\,\text{mol}^{-1} \times 10.00\,\text{atm}}{(0.08206\,\text{dm}^3\,\text{atm K}^{-1}\,\text{mol}^{-1} \times 298.15\,\text{K})^2} = -0.06965$$

$$\phi = 0.9237 = \frac{f}{p}$$

$$f = \phi p = 0.9237 \times 10.00\,\text{atm} = \boxed{9.237\,\text{atm}}$$

Solutions to applications

P3.36 Taking the hint, we have

$$\Delta_{\text{trs}}S^{\ominus}(25°\text{C}) = \Delta S_{\text{i}} + \Delta S_{\text{ii}} + \Delta S_{\text{iii}}.$$

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:

$$\Delta S_{\text{i}} = C_p \ln\left(\frac{T_{\text{f}}}{T_{\text{i}}}\right) = C_{p,\text{m}} \ln\left(\frac{348.7\,\text{K}}{298.2\,\text{K}}\right) \text{ [3.19]}$$

and $\quad \Delta S_{\text{iii}} = (C_{p,\text{m}} + 6.28\,\text{kJ K}^{-1}\,\text{mol}^{-1}) \ln\left(\dfrac{298.2\,\text{K}}{348.7\,\text{K}}\right)$

so $\quad \Delta S_{\text{i}} + \Delta S_{\text{iii}} = C_{p,\text{m}} \ln\left(\dfrac{348.7\,\text{K}}{298.2\,\text{K}}\right) + (C_{p,\text{m}} + 6.28\,\text{kJ K}^{-1}\,\text{mol}^{-1}) \ln\left(\dfrac{298.2\,\text{K}}{348.7\,\text{K}}\right)$

$$= (6.28\,\text{kJ K}^{-1}\,\text{mol}^{-1}) \ln\left(\frac{298.2\,\text{K}}{348.7\,\text{K}}\right) = -0.983\,\text{kJ K}^{-1}\,\text{mol}^{-1}$$

For the transition itself, use Trouton's rule (eqn 3.16):

$$\Delta S_{\text{ii}} = \frac{\Delta_{\text{trs}}H^{\ominus}}{T_{\text{trs}}} = \frac{509\,\text{kJ mol}^{-1}}{348.2\,\text{K}} = 1.46\bar{0}\,\text{kJ K}^{-1}\,\text{mol}^{-1}$$

Hence, $\Delta_{\text{trs}}S^{\ominus} = (1.46\bar{0} - 0.983)\,\text{kJ K}^{-1}\,\text{mol}^{-1} = 0.47\bar{7}\,\text{kJ K}^{-1}\,\text{mol}^{-1} = \boxed{47\bar{7}\,\text{J K}^{-1}\,\text{mol}^{-1}}$

P3.38 **(a)** At constant temperature,

$$\Delta_{\text{r}}G = \Delta_{\text{r}}H - T\Delta_{\text{r}}S \quad \text{so} \quad \Delta_{\text{r}}S = \frac{\Delta_{\text{r}}H - \Delta_{\text{r}}G}{T}$$

and $\Delta_{\text{r}}S = \dfrac{[-20 - (-31)]\,\text{kJ mol}^{-1}}{310\,\text{K}} = +0.035\,\text{kJ K}^{-1}\,\text{mol}^{-1} = \boxed{+35\,\text{J K}^{-1}\,\text{mol}^{-1}}$

(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

$$n = \frac{N}{N_A} = \frac{10^6\,\mathrm{s}^{-1}}{6.02 \times 10^{23}\,\mathrm{mol}^{-1}} = 1.6\bar{6} \times 10^{-18}\,\mathrm{mol\,s^{-1}}$$

and V is the volume of the cell

$$V = \tfrac{4}{3}\pi r^3 = \tfrac{4}{3}\pi(10 \times 10^{-6}\,\mathrm{m})^3 = 4.1\bar{9} \times 10^{-15}\,\mathrm{m}^3$$

Thus $P = \dfrac{|\Delta_r G| n}{V} = \dfrac{(31 \times 10^3\,\mathrm{J\,mol^{-1}}) \times (1.6\bar{6} \times 10^{-18}\,\mathrm{mol\,s^{-1}})}{4.1\bar{9} \times 10^{-15}\,\mathrm{m}^3} = \boxed{12\,\mathrm{W\,m^{-3}}}$

This is orders of magnitude less than the power density of a computer battery, which is about

$$P_{\text{battery}} = \frac{15\,\mathrm{W}}{100\,\mathrm{cm}^3} \times \left(\frac{100\,\mathrm{cm}}{1\,\mathrm{m}}\right)^3 = \boxed{1.5 \times 10^4\,\mathrm{W\,m^{-3}}}$$

(c) Simply make a ratio of the magnitudes of the free energies

$$\frac{14.2\,\mathrm{kJ\,(mol\,glutamine)^{-1}}}{31\,\mathrm{kJ\,(mol\,ATP)^{-1}}} = \boxed{0.46\frac{\mathrm{mol\,ATP}}{\mathrm{mol\,glutamine}}}$$

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

$$\Delta\left(\frac{\Delta_r G^\ominus}{T}\right) = \frac{\Delta_r H^\ominus}{T^2}\Delta T \quad \text{and} \quad \frac{\Delta_r G_2^\ominus}{T_2} = \frac{\Delta_r G_1^\ominus}{T_1} - \frac{\Delta_r H^\ominus}{T^2 \Delta T}$$

$$\text{so} \int \mathrm{d}\frac{\Delta_r G^\ominus}{T} = -\int \frac{\Delta_r H^\ominus \mathrm{d}T}{T^2} \quad \text{and} \quad \frac{\Delta_r G_{190}^\ominus}{T_{190}} = \frac{\Delta_r G_{220}^\ominus}{T_{220}} + \Delta_r H^\ominus\left(\frac{1}{T_{190}} - \frac{1}{T_{220}}\right)$$

$$\Delta_r G_{190}^\ominus = \Delta_r G_{220}^\ominus \frac{T_{190}}{T_{220}} + \Delta_r H^\ominus\left(1 - \frac{T_{190}}{T_{220}}\right)$$

For the monohydrate

$$\Delta_r G_{190}^\ominus = (46.2\,\mathrm{kJ\,mol^{-1}}) \times \left(\frac{190\,\mathrm{K}}{220\,\mathrm{K}}\right) + (127\,\mathrm{kJ\,mol^{-1}}) \times \left(1 - \frac{190\,\mathrm{K}}{220\,\mathrm{K}}\right),$$

$$\Delta_r G_{190}^\ominus = \boxed{57.2\,\mathrm{kJ\,mol^{-1}}}$$

For the dihydrate

$$\Delta_r G_{190}^\ominus = (69.4\,\mathrm{kJ\,mol^{-1}}) \times \left(\frac{190\,\mathrm{K}}{220\,\mathrm{K}}\right) + (188\,\mathrm{kJ\,mol^{-1}}) \times \left(1 - \frac{190\,\mathrm{K}}{220\,\mathrm{K}}\right),$$

$$\Delta_r G_{190}^\ominus = \boxed{85.6\,\mathrm{kJ\,mol^{-1}}}$$

For the trihydrate

$$\Delta_r G^{\ominus}_{190} = (93.2\,\mathrm{kJ\,mol^{-1}}) \times \left(\frac{190\,\mathrm{K}}{220\,\mathrm{K}}\right) + (237\,\mathrm{kJ\,mol^{-1}}) \times \left(1 - \frac{190\,\mathrm{K}}{220\,\mathrm{K}}\right),$$

$$\Delta_r G^{\ominus}_{190} = \boxed{112.8\,\mathrm{kJ\,mol^{-1}}}$$

P3.42 In effect, we are asked to compute the maximum work extractable from a gallon of octane, assuming that the internal combustion engine is a reversible heat engine operating between the specified temperatures, and to equate that quantity of energy with gravitational potential energy of a 1000-kg mass. The efficiency is

$$\varepsilon = \frac{|w|}{|q_h|}\,[3.8] = \frac{|w|}{|\Delta H|} = \varepsilon_{\mathrm{rev}} = 1 - \frac{T_c}{T_h}\,[3.10] \quad \text{so} \quad |w| = |\Delta H|\left(1 - \frac{T_c}{T_h}\right)$$

$$|\Delta H| = 5512 \times 10^3\,\mathrm{J\,mol^{-1}} \times 1.00\,\mathrm{gal} \times \frac{3.00 \times 10^3\,\mathrm{g}}{1\,\mathrm{gal}} \times \frac{1\,\mathrm{mol}}{114.23\,\mathrm{g}} = 1.44\bar{8} \times 10^8\,\mathrm{J}$$

$$\text{so } |w| = 1.44\bar{8} \times 10^8\,\mathrm{J} \times \left(1 - \frac{1073\,\mathrm{K}}{2273\,\mathrm{K}}\right) = 7.64\bar{2} \times 10^7\,\mathrm{J}$$

If this work is converted completely to potential energy, it could lift a 1000-kg object to a height h given by $|w| = mgh$, so

$$h = \frac{|w|}{mg} = \frac{7.64\bar{2} \times 10^7\,\mathrm{J}}{(1000\,\mathrm{kg})(9.81\,\mathrm{m\,s^{-2}})} = 7.79 \times 10^3\,\mathrm{m} = \boxed{7.79\,\mathrm{km}}$$

P3.44 **(a)** As suggested, relate the work to the temperature-dependent coefficient of performance [*Impact* I3.1]:

$$|\mathrm{d}w| = \frac{|\mathrm{d}q_c|}{c} = \frac{|C_p\mathrm{d}T|}{\left(\dfrac{T}{T_h - T}\right)} = C_p\left|\frac{T_h\mathrm{d}T}{T} - \mathrm{d}T\right|$$

Integrating yields

$$|w| = C_p\left|T_h\int_{T_i}^{T_f}\frac{\mathrm{d}T}{T} + \int_{T_i}^{T_f}\mathrm{d}T\right| = C_p\left|T_h \ln\frac{T_f}{T_i} - (T_f - T_i)\right| = C_p\left(T_h \ln\frac{T_i}{T_f} - T_i + T_f\right)$$

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

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

The refrigerator must also remove the heat of fusion at the freezing temperature. For this isothermal process, the coefficient of performance does not change, so

$$|w|_{\mathrm{freeze}} = \frac{|q_c|}{c} = \frac{\Delta_{\mathrm{fus}}H}{\left(\dfrac{T_c}{T_h - T_c}\right)} = \Delta_{\mathrm{fus}}H\left(\frac{T_h - T_c}{T_c}\right)$$

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

The total work is

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

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 initials 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 $\Delta_{\mathrm{vap}}H$ is independent of temperature

$$\ln\frac{p^*}{p} = +\frac{\Delta_{\mathrm{vap}}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

$$\frac{1}{T} = \frac{1}{T^*} + \frac{R}{\Delta_{\rm vap}H}\ln\frac{p^*}{p}$$

$$= \frac{1}{293.2\,{\rm K}} + \frac{8.314\,{\rm J\,K^{-1}\,mol^{-1}}}{32.7\times 10^3\,{\rm J\,mol^{-1}}} \times \ln\left(\frac{58.0}{66.0}\right)$$

$$= 3.378\times 10^{-3}\,{\rm K^{-1}}$$

$$T = \frac{1}{3.37\overline{8}\times 10^{-3}\,{\rm K^{-1}}} = 296\,{\rm K} = \boxed{23\,°{\rm C}}$$

E4.2(b)

$$\frac{{\rm d}p}{{\rm d}T} = \frac{\Delta_{\rm fus}S}{\Delta_{\rm fus}V}$$

$$\Delta_{\rm fus}S = \Delta_{\rm fus}V\left(\frac{{\rm d}p}{{\rm d}T}\right) \approx \Delta_{\rm fus}V\frac{\Delta p}{\Delta T}$$

assuming $\Delta_{\rm fus}S$ and $\Delta_{\rm fus}V$ independent of temperature.

$$\Delta_{\rm fus}S = (152.6\,{\rm cm^3\,mol^{-1}} - 142.0\,{\rm cm^3\,mol^{-1}}) \times \frac{(1.2\times 10^6\,{\rm Pa}) - (1.01\times 10^5\,{\rm Pa})}{429.26\,{\rm K} - 427.15\,{\rm K}}$$

$$= (10.6\,{\rm cm^3\,mol^{-1}}) \times \left(\frac{1\,{\rm m^3}}{10^6\,{\rm cm^3}}\right) \times (5.21\times 10^5\,{\rm Pa\,K^{-1}})$$

$$= 5.52\,{\rm Pa\,m^3\,K^{-1}\,mol^{-1}} = \boxed{5.5\,{\rm J\,K^{-1}mol^{-1}}}$$

$$\Delta_{\rm fus}H = T_{\rm f}\Delta S = (427.15\,{\rm K}) \times (5.5\overline{2}\,{\rm J\,K^{-1}\,mol^{-1}})$$

$$= \boxed{2.4\,{\rm kJ\,mol^{-1}}}$$

E4.3(b) Use $\int {\rm d}\ln p = \int \frac{\Delta_{\rm vap}H}{RT^2}\,{\rm d}T$

$$\ln p = {\rm constant} - \frac{\Delta_{\rm vap}H}{RT}$$

Terms with $1/T$ dependence must be equal, so

$$-\frac{3036.8\,{\rm K}}{T/K} = -\frac{\Delta_{\rm vap}H}{RT}$$

$$\Delta_{\rm vap}H = (3036.8\,{\rm K})R = (8.314\,{\rm J\,K^{-1}\,mol^{-1}}) \times (3036.8\,{\rm K})$$

$$= \boxed{25.25\,{\rm kJ\,mol^{-1}}}$$

E4.4(b) **(a)** $\log p = {\rm constant} - \Delta_{\rm vap}H/(RT(2.303))$

Thus

$$\Delta_{\rm vap}H = (1625\,{\rm K}) \times (8.314\,{\rm J\,K^{-1}\,mol^{-1}}) \times (2.303)$$

$$= \boxed{31.11\,{\rm kJ\,mol^{-1}}}$$

(b) Normal boiling point corresponds to $p = 1.000\,\text{atm} = 760\,\text{Torr}$

$$\log(760) = 8.750 - \frac{1625}{T/\text{K}}$$

$$\frac{1625}{T/\text{K}} = 8.750 - \log(760)$$

$$T/\text{K} = \frac{1625}{8.750 - \log(760)} = 276.8\bar{7}$$

$$T_b = \boxed{276.9\,\text{K}}$$

E4.5(b)

$$\Delta T = \frac{\Delta_{\text{fus}}V}{\Delta_{\text{fus}}S} \times \Delta p = \frac{T_f \Delta_{\text{fus}}V}{\Delta_{\text{fus}}H} \times \Delta p = \frac{T_f \Delta p M}{\Delta_{\text{fus}}H} \times \Delta\left(\frac{1}{\rho}\right)$$

$[T_f = -3.65 + 273.15 = 269.50\,\text{K}]$

$$\Delta T = \frac{(269.50\,\text{K}) \times (99.9\,\text{MPa})M}{8.68\,\text{kJ mol}^{-1}} \times \left(\frac{1}{0.789\,\text{g cm}^{-3}} - \frac{1}{0.801\,\text{g cm}^{-3}}\right)$$

$$= (3.10\overline{17} \times 10^6\,\text{K Pa J}^{-1}\,\text{mol}) \times (M) \times (+0.01\overline{899}\,\text{cm}^3/\text{g}) \times \left(\frac{\text{m}^3}{10^6\,\text{cm}^3}\right)$$

$$= (+5.\overline{889} \times 10^{-2}\,\text{K Pa m}^3\,\text{J}^{-1}\,\text{g}^{-1}\,\text{mol})M = (+5.\overline{889} \times 10^{-2}\,\text{K g}^{-1}\,\text{mol})M$$

$$\Delta T = (46.07\,\text{g mol}^{-1}) \times (+5.\overline{889} \times 10^{-2}\,\text{K g}^{-1}\,\text{mol})$$

$$= +2.\overline{71}\,\text{K}$$

$$T_f = 269.50\,\text{K} + 2.\overline{71}\,\text{K} = \boxed{272\,\text{K}}$$

E4.6(b)

$$\frac{\text{d}m}{\text{d}t} = \frac{\text{d}n}{\text{d}t} \times M_{\text{H}_2\text{O}} \quad \text{where } n = \frac{q}{\Delta_{\text{vap}}H}$$

$$\frac{\text{d}n}{\text{d}t} = \frac{dq/\text{d}t}{\Delta_{\text{vap}}H} = \frac{(0.87 \times 10^3\,\text{W m}^{-2}) \times (10^4\,\text{m}^2)}{44.0 \times 10^3\,\text{J mol}^{-1}}$$

$$= 19\overline{7.7}\,\text{J s}^{-1}\,\text{J}^{-1}\,\text{mol}$$

$$= 20\bar{0}\,\text{mol s}^{-1}$$

$$\frac{\text{d}m}{\text{d}t} = (19\overline{7.7}\,\text{mol s}^{-1}) \times (18.02\,\text{g mol}^{-1})$$

$$= \boxed{3.6\,\text{kg s}^{-1}}$$

E4.7(b) The vapor pressure of ice at $-5\,°\text{C}$ 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)

$$\Delta_{\text{vap}}H = (85\,\text{J K}^{-1}\,\text{mol}^{-1}) \times T_b = (85\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (342.2\,\text{K}) = \boxed{29.\bar{1}\,\text{kJ mol}^{-1}}$$

(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 $T_2 = 342.2\,\mathrm{K}$, $p_2 = 1.000\,\mathrm{atm}$; thus at 25 °C

$$\ln p_1 = -\left(\frac{29.\bar{1} \times 10^3\,\mathrm{J\,mol^{-1}}}{8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}}\right) \times \left(\frac{1}{298.2\,\mathrm{K}} - \frac{1}{342.2\,\mathrm{K}}\right) = -1.50\bar{9}$$

$$p_1 = \boxed{0.22\,\mathrm{atm}} = 16\bar{8}\,\mathrm{Torr}$$

At 60 °C,

$$\ln p_1 = -\left(\frac{29.\bar{1} \times 10^3\,\mathrm{J\,mol^{-1}}}{8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}}\right) \times \left(\frac{1}{333.2\,\mathrm{K}} - \frac{1}{342.2\,\mathrm{K}}\right) = -0.27\bar{6}$$

$$p_1 = \boxed{0.76\,\mathrm{atm}} = 57\bar{6}\,\mathrm{Torr}$$

E4.9(b) $\Delta T = T_{\mathrm{fus}}(10\,\mathrm{MPa}) - T_{\mathrm{fus}}(0.1\,\mathrm{MPa}) = \dfrac{T_{\mathrm{fus}}\Delta p M}{\Delta_{\mathrm{fus}}H}\Delta\left(\dfrac{1}{\rho}\right)$ [See Exercise 4.5(b)]

$\Delta_{\mathrm{fus}}H = 6.01\,\mathrm{kJ\,mol^{-1}}$

$$\Delta T = \left\{\frac{(273.15\,\mathrm{K}) \times (9.9 \times 10^6\,\mathrm{Pa}) \times (18 \times 10^{-3}\,\mathrm{kg\,mol^{-1}})}{6.01 \times 10^3\,\mathrm{J\,mol^{-1}}}\right\}$$
$$\times \left\{\frac{1}{9.98 \times 10^2\,\mathrm{kg\,m^{-3}}} - \frac{1}{9.15 \times 10^2\,\mathrm{kg\,m^{-3}}}\right\}$$
$$= -0.74\,\mathrm{K}$$

$T_{\mathrm{fus}}(10\,\mathrm{MPa}) = 273.15\,\mathrm{K} - 0.74\,\mathrm{K} = \boxed{272.41\,\mathrm{K}}$

E4.10(b) $\Delta_{\mathrm{vap}}H = \Delta_{\mathrm{vap}}U + \Delta_{\mathrm{vap}}(pV)$

$\Delta_{\mathrm{vap}}H = 43.5\,\mathrm{kJ\,mol^{-1}}$

$\Delta_{\mathrm{vap}}(pV) = p\Delta_{\mathrm{vap}}V = p(V_{\mathrm{gas}} - V_{\mathrm{liq}}) = pV_{\mathrm{gas}} = RT$ [per mole, perfect gas]

$\Delta_{\mathrm{vap}}(pV) = (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (352\,\mathrm{K}) = 292\bar{7}\,\mathrm{J\,mol^{-1}}$

$$\text{Fraction} = \frac{\Delta_{\mathrm{vap}}(pV)}{\Delta_{\mathrm{vap}}H} = \frac{2.92\bar{7}\,\mathrm{kJ\,mol^{-1}}}{43.5\,\mathrm{kJ\,mol^{-1}}}$$
$$= \boxed{6.73 \times 10^{-2}} = 6.73\text{ percent}$$

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)].

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{\Delta_{\mathrm{vap}}H}{R} \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right); \quad T_1 = \text{normal boiling point}; \quad p_1 = 1.000\,\mathrm{atm}$$

$$\ln(p_2/\mathrm{atm}) = \left(\frac{20.25 \times 10^3\,\mathrm{J\,mol^{-1}}}{8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}}\right) \times \left(\frac{1}{244.0\,\mathrm{K}} - \frac{1}{313.2\,\mathrm{K}}\right) = 2.206$$

$p_2 = \boxed{9.07\,\mathrm{atm}} \approx 9\,\mathrm{atm}$

COMMENT. Three significant figures are not really warranted in this answer because of the approximations employed.

P4.4 (a)
$$\left(\frac{\partial\mu(\mathrm{l})}{\partial T}\right)_p - \left(\frac{\partial\mu(\mathrm{s})}{\partial T}\right)_p = -S_{\mathrm{m}}(\mathrm{l}) + S_{\mathrm{m}}(\mathrm{s}) \text{ [Section 4.7, eqn 13]}$$
$$= -\Delta_{\mathrm{fus}}S = \frac{-\Delta_{\mathrm{fus}}H}{T_{\mathrm{f}}}; \quad \Delta_{\mathrm{fus}}H = 6.01\,\mathrm{kJ\,mol^{-1}} \text{ [Table 2.3]}$$
$$= \frac{-6.01\,\mathrm{kJ\,mol^{-1}}}{273.15\,\mathrm{K}} = \boxed{-22.0\,\mathrm{J\,K^{-1}mol^{-1}}}$$

(b)
$$\left(\frac{\partial\mu(\mathrm{g})}{\partial T}\right)_p - \left(\frac{\partial\mu(\mathrm{l})}{\partial T}\right)_p = -S_{\mathrm{m}}(\mathrm{g}) + S_{\mathrm{m}}(\mathrm{l}) = -\Delta_{\mathrm{vap}}S$$
$$= \frac{-\Delta_{\mathrm{vap}}H}{T_{\mathrm{b}}} = \frac{-40.6\,\mathrm{kJ\,mol^{-1}}}{373.15\,\mathrm{K}} = \boxed{-109.0\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

(c)
$$\Delta\mu \approx \left(\frac{\partial\mu}{\partial T}\right)_p \Delta T = -S_{\mathrm{m}}\Delta T \text{ [4.1]}$$
$$\Delta\mu(\mathrm{l}) - \Delta\mu(\mathrm{s}) = \mu(\mathrm{l}, -5\,^{\circ}\mathrm{C}) - \mu(\mathrm{l}, 0\,^{\circ}\mathrm{C}) - \mu(\mathrm{s}, -5\,^{\circ}\mathrm{C}) + \mu(\mathrm{s}, 0\,^{\circ}\mathrm{C})$$
$$= \mu(\mathrm{l}, -5\,^{\circ}\mathrm{C}) - \mu(\mathrm{s}, -5\,^{\circ}\mathrm{C}) \; [\mu(\mathrm{l}, 0\,^{\circ}\mathrm{C}) = \mu(\mathrm{s}, 0\,^{\circ}\mathrm{C})]$$
$$\approx -\{S_{\mathrm{m}}(\mathrm{l}) - S_{\mathrm{m}}(\mathrm{s})\}\Delta T \approx -\Delta_{\mathrm{fus}}S\Delta T$$
$$= -(5\,\mathrm{K}) \times (-22.0\,\mathrm{J\,K^{-1}\,mol^{-1}}) = \boxed{+11\bar{0}\,\mathrm{J\,mol^{-1}}}$$

Since, $\mu(\mathrm{l}, -5\,^{\circ}\mathrm{C}) > \mu(\mathrm{s}, -5\,^{\circ}\mathrm{C})$, there is a thermodynamic tendency to freeze.

P4.6
$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{fus}}S}{\Delta_{\mathrm{fus}}V} \text{ [4.6]} = \frac{\Delta_{\mathrm{fus}}H}{T\Delta_{\mathrm{fus}}V}$$
$$\Delta T = \int_{T_{\mathrm{m,1}}}^{T_{\mathrm{m,2}}} \mathrm{d}T = \int_{p_{\mathrm{top}}}^{p_{\mathrm{bot}}} \frac{T_{\mathrm{m}}\Delta_{\mathrm{fus}}V}{\Delta_{\mathrm{fus}}H}\,\mathrm{d}p$$
$$\Delta T \approx \frac{T_{\mathrm{m}}\Delta_{\mathrm{fus}}V}{\Delta_{\mathrm{fus}}H} \times \Delta p \quad [T_{\mathrm{m}}, \Delta_{\mathrm{fus}}H, \text{ and } \Delta_{\mathrm{fus}}V \text{ assumed constant}]$$
$$\Delta p = p_{\mathrm{bot}} - p_{\mathrm{top}} = \rho g h$$

Therefore
$$\Delta T = \frac{T_{\mathrm{m}}\rho g h \Delta_{\mathrm{fus}}V}{\Delta_{\mathrm{fus}}H}$$
$$= \frac{(234.3\,\mathrm{K}) \times (13.6 \times 10^3\,\mathrm{kg\,m^{-3}}) \times (9.81\,\mathrm{m\,s^{-2}}) \times (10\,\mathrm{m}) \times (0.517 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}})}{2.292 \times 10^3\,\mathrm{J\,mol^{-1}}}$$
$$= 0.070\,\mathrm{K}$$

Therefore, the freezing point changes to $\boxed{234.4\,\mathrm{K}}$

P4.8
$$\frac{\mathrm{d}\ln p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}}H}{RT^2} \text{ [4.11], yields upon indefinite integration}$$
$$\ln p = \text{constant} - \frac{\Delta_{\mathrm{vap}}H}{RT}$$

Therefore, plot $\ln p$ against $1/T$ and identify $-\Delta_{vap}H/R$ as its slope. Construct the following table

$\theta/°C$	0	20	40	50	70	80	90	100
T/K	273	293	313	323	343	353	363	373
1000 K/T	3.66	3.41	3.19	3.10	2.92	2.83	2.75	2.68
ln (p/kPa)	0.652	1.85	2.87	3.32	4.13	4.49	4.83	5.14

The points are plotted in Figure 4.1. The slope is −4569 K, so

$$\frac{-\Delta_{vap}H}{R} = -4569\,\mathrm{K}, \quad \text{or} \quad \Delta_{vap}H = \boxed{+38.0\ \mathrm{kJ\,mol^{-1}}}$$

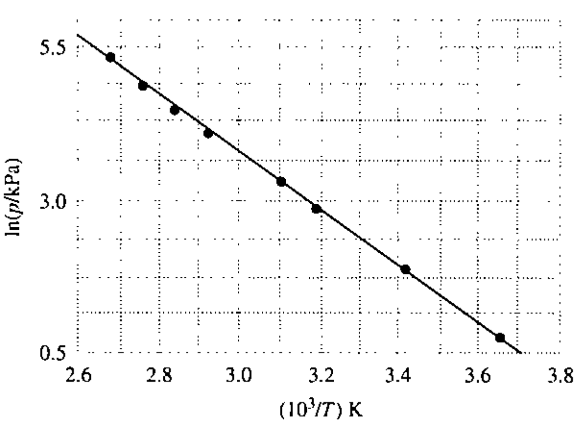


Figure 4.1

The normal boiling point occurs at p = 760 Torr, or at ln(p/Torr) = 6.633, which from the figure corresponds to 1000 K/$T \approx 2.80$. Therefore, $T_b = \boxed{357\ \mathrm{K}\ (84\,°\mathrm{C})}$ The accepted value is 83 °C.

P4.10 The equations describing the coexistence curves for the three states are

(a) Solid–liquid boundary

$$p = p^* + \frac{\Delta_{fus}H}{\Delta_{fus}V}\ln\frac{T}{T^*} \quad [4.8]$$

(b) Liquid–vapor boundary

$$p = p^*e^{-\chi}, \quad \chi = \frac{\Delta_{vap}H}{R}\times\left(\frac{1}{T}-\frac{1}{T^*}\right) \quad [4.12]$$

(c) Solid–vapor boundary

$$p = p^*e^{-\chi}, \quad \chi = \frac{\Delta_{sub}H}{R}\times\left(\frac{1}{T}-\frac{1}{T^*}\right) \quad \text{[similar to 4.12]}$$

We need $\Delta_{\text{sub}}H = \Delta_{\text{fus}}H + \Delta_{\text{vap}}H = 41.4\,\text{kJ mol}^{-1}$

$$\Delta_{\text{fus}}V = M \times \left(\frac{1}{\rho(\text{l})} - \frac{1}{\rho(\text{s})}\right) = \left(\frac{78.11\,\text{g mol}^{-1}}{\text{g cm}^{-3}}\right) \times \left(\frac{1}{0.879} - \frac{1}{0.891}\right) = +1.19\overline{7}\,\text{cm}^3\,\text{mol}^{-1}$$

After insertion of these numerical values into the above equations, we obtain

(a) $$p = p^* + \left(\frac{10.6 \times 10^3\,\text{J mol}^{-1}}{1.197 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1}}\right) \ln\frac{T}{T^*}$$

$$= p^* + 8.85\overline{5} \times 10^9\,\text{Pa} \times \ln\frac{T}{T^*} = p^* + (6.64 \times 10^7\,\text{Torr}) \ln\frac{T}{T^*} \quad (1\,\text{Torr} = 133.322\,\text{Pa})$$

This line is plotted as a in Figure 4.2, starting at $(p^*, T^*) = (36\,\text{Torr}, 5.50\,°\text{C}\,(278.65\,\text{K}))$.

(b) $$\chi = \left(\frac{30.8 \times 10^3\,\text{J mol}^{-1}}{8.314\,\text{J K}^{-1}\,\text{mol}^{-1}}\right) \times \left(\frac{1}{T} - \frac{1}{T^*}\right) = (370\overline{5}\,\text{K}) \times \left(\frac{1}{T} - \frac{1}{T^*}\right)$$

$$p = p^* \text{e}^{-370\overline{5}\,\text{K} \times (1/T - 1/T^*)}$$

This equation is plotted as line b in Figure 4.2, starting from $(p^*, T^*) = (36\,\text{Torr}, 5.50\,°\text{C}\,(278.65\,\text{K}))$.

(c) $$\chi = \left(\frac{41.4 \times 10^3\,\text{J mol}^{-1}}{8.314\,\text{J K}^{-1}\,\text{mol}^{-1}}\right) \times \left(\frac{1}{T} - \frac{1}{T^*}\right) = (4\overline{980}\,\text{K}) \times \left(\frac{1}{T} - \frac{1}{T^*}\right)$$

$$p = p^* \text{e}^{-498\overline{0}\,\text{K} \times (1/T - 1/T^*)}$$

These points are plotted as line c in Figure 4.2, starting at (36 Torr, 5.50 °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.

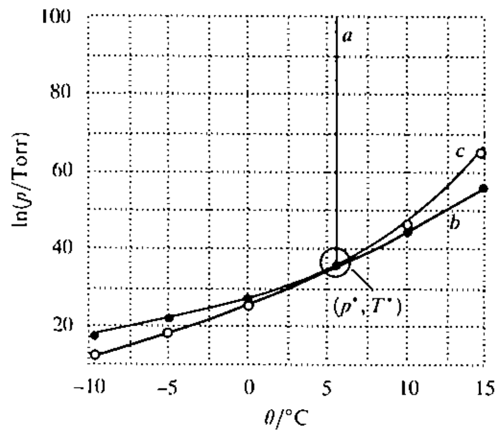


Figure 4.2

P4.12 The slope of the solid–vapor coexistence curve is given by

$$\frac{\text{d}p}{\text{d}T} = \frac{\Delta_{\text{sub}}H^\ominus}{T\Delta_{\text{sub}}V^\ominus} \quad \text{so} \quad \Delta_{\text{sub}}H^\ominus = T\Delta_{\text{sub}}V^\ominus \frac{\text{d}p}{\text{d}T}$$

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

$$\Delta_{\text{sub}}H^{\ominus} = (150 \text{ K}) \times (47.8 \text{ m}^3) \times (4.41 \text{ Pa K}^{-1}) = 3.16 \times 10^4 \text{ J mol}^{-1} = \boxed{31.6 \text{ kJ mol}^{-1}}$$

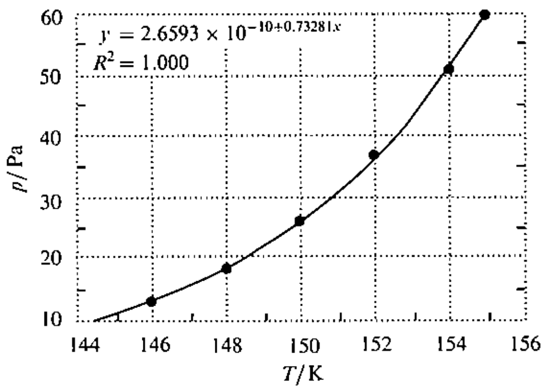


Figure 4.3

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

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} \text{ [Clapeyron equation, e.g. 4.6, 4.7, or 4.10]}$$

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 $p = p_0 e^{-Mgh/RT}$ [*Impact* I1.1]

$$p = p^* e^{-\chi} \quad \chi = \frac{\Delta_{\mathrm{vap}}H}{R} \times \left(\frac{1}{T} - \frac{1}{T^*}\right) \text{ [4.12]}$$

Let $T^* = T_{\mathrm{b}}$ the normal boiling point; then $p^* = 1$ atm. Let $T = T_{\mathrm{h}}$, 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, $T = T_{\mathrm{h}}$. Therefore, since $p_0 = p^*$, $p(T) = p(h)$ implies that

$$e^{-Mgh/RT} = \exp\left\{-\frac{\Delta_{\mathrm{vap}}H}{R} \times \left(\frac{1}{T_{\mathrm{h}}} - \frac{1}{T_{\mathrm{b}}}\right)\right\}$$

It follows that

$$\frac{1}{T_{\mathrm{h}}} = \frac{1}{T_{\mathrm{b}}} + \frac{Mgh}{T\Delta_{\mathrm{vap}}H}$$

where T is the ambient temperature and M the molar mass of the air. For water at 3000 m, using $M = 29\,\mathrm{g\,mol^{-1}}$

$$\frac{1}{T_{\mathrm{h}}} = \frac{1}{373\mathrm{K}} + \frac{(29 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}) \times (9.81\,\mathrm{m\,s^{-2}}) \times (3.000 \times 10^3\,\mathrm{m})}{(293\,\mathrm{K}) \times (40.7 \times 10^3\,\mathrm{J\,mol^{-1}})}$$

$$= \frac{1}{373\,\mathrm{K}} + \frac{1}{1.397 \times 10^4\,\mathrm{K}}$$

Hence, $T_{\mathrm{h}} = \boxed{363\,\mathrm{K}}$ (90 °C).

P4.18 (1) $V = V(T,p)$

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

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

hence, $\mathrm{d}V = \alpha V\,\mathrm{d}T - \kappa_T V\,\mathrm{d}p$

This equation applies to both phases 1 and 2, and since V is continuous through a second-order transition

$$\alpha_1\,\mathrm{d}T - \kappa_{T,1}\,\mathrm{d}p = \alpha_2\,\mathrm{d}T - \kappa_{T,2}\,\mathrm{d}p$$

Solving for $\frac{\mathrm{d}p}{\mathrm{d}T}$ yields $\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\alpha_2 - \alpha_1}{\kappa_{T,2} - \kappa_{T,1}}$

(2) $S_{\mathrm{m}} = S_{\mathrm{m}}(T,p)$

$$\mathrm{d}S_{\mathrm{m}} = \left(\frac{\partial S_{\mathrm{m}}}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial S_{\mathrm{m}}}{\partial p}\right)_T \mathrm{d}p.$$

$$\left(\frac{\partial S_{\mathrm{m}}}{\partial T}\right)_p = \frac{C_{p,\mathrm{m}}}{T} \text{ [Problem 3.26]} \quad \left(\frac{\partial S_{\mathrm{m}}}{\partial p}\right)_T = -\left(\frac{\partial V_{\mathrm{m}}}{\partial T}\right)_p \text{ [Maxwell relation]}$$

$$= -\alpha V_{\mathrm{m}}$$

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

$$\frac{C_{p,m,1}}{T}\,dT - \alpha_1 V_m\,dp = \frac{C_{p,m,2}}{T}\,dT - \alpha_2 V_m\,dp$$

Solving for $\frac{dp}{dT}$ 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)** $$\Delta G_m = (n-4)\Delta_{hb}H_m - (n-2)T_m\Delta_{hb}S_m \quad (1)$$

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

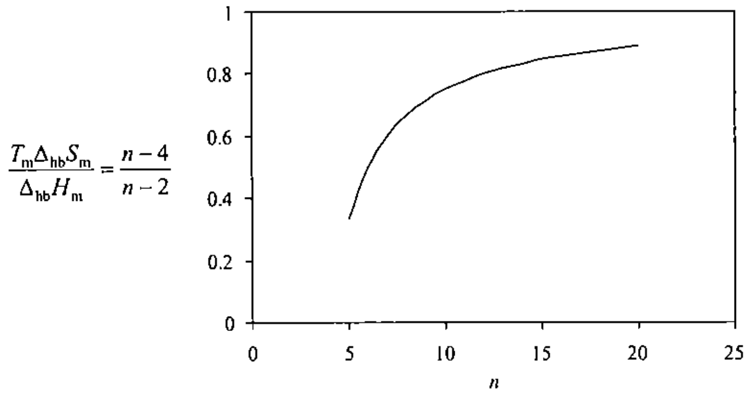


Figure 4.4

Consider $$\frac{1}{T_m}\frac{dT_m}{dn} = \frac{\Delta_{hb}H_m}{T_m\Delta_{hb}S_m}\frac{d(T_m\Delta_{hb}S_m/\Delta_{hb}H_m)}{dn} = \left(\frac{n-2}{n-4}\right)\frac{d}{dn}\left(\frac{n-4}{n-2}\right)$$
$$= \left(\frac{n-2}{n-4}\right)\left(\frac{2}{(n-2)^2}\right) = \frac{2}{(n-4)(n-2)}$$

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 $n \cong \boxed{17}$. 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.

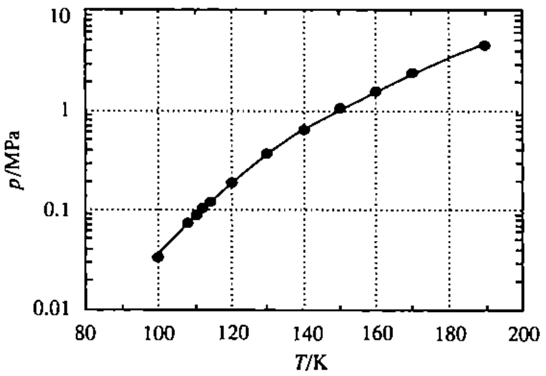


Figure 4.5

(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 $T_b = \boxed{112\ \text{K}}$

(c) The slope of the liquid–vapor coexistence curve is given by

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\Delta_{vap}V} \quad \text{so} \quad \Delta_{vap}H = (T\Delta_{vap}V)\frac{dp}{dT}$$

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

$$\Delta_{vap}H = (112\ \text{K}) \times \left(\frac{(8.89 - 0.0380)\ \text{dm}^3\ \text{mol}^{-1}}{1000\ \text{dm}^3\ \text{m}^3}\right) \times (8.14\ \text{k Pa K}^{-1}) = \boxed{8.07\ \text{kJ mol}^{-1}}$$

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 $\gamma_\pm$ will have a value different from unity which is its ideal value. The role of the solvent is more indirect. The solvent determines the dielectric constant, ε, of the solution. Looking at the details of the theory as outlined in *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 $(0.20) \times (96.87\ \text{g}) = 19.\overline{374}$ g is ethanol and $(0.80) \times (96.87\ \text{g}) = 77.\overline{496}$ g is water.

$$n_A = \frac{77.\overline{496}\ \text{g}}{18.02\ \text{g mol}^{-1}} = 4.3\bar{0}\ \text{mol}\ H_2O$$

$$n_B = \frac{19.374\ \text{g}}{46.07\ \text{g mol}^{-1}} = 0.42\overline{05}\ \text{mol ethanol}$$

$$\begin{aligned} \frac{V - n_B V_B}{n_A} = V_A &= \frac{100\ \text{cm}^3 - (0.42\overline{05}\ \text{mol}) \times (52.2\ \text{cm}^3\ \text{mol}^{-1})}{4.3\bar{0}\ \text{mol}} \\ &= 18.\overline{15}\ \text{cm}^3 \\ &= \boxed{18\ \text{cm}^3} \end{aligned}$$

E5.3(b) Check that p_B/x_B = a constant (K_B)

x_B	0.010	0.015	0.020
(p_B/x_B)/kPa	8.2×10^3	8.1×10^3	8.3×10^3

$K_B = p/x$, 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.

$$m(\text{A}) = 1000\,\text{g}, \quad \text{corresponding to } n(\text{A}) = \frac{1000\ \text{g}}{74.1\ \text{g mol}^{-1}} = 13.5\bar{0}\ \text{mol} \quad n(\text{B}) = 0.25\ \text{mol}$$

Therefore,

$$x_B = \frac{0.25\ \text{mol}}{0.25\ \text{mol} + 13.5\bar{0}\ \text{mol}} = 0.018\bar{2}$$

using $K_B = 8.2 \times 10^3$ kPa [Exercise 5.3(b)]

$$p = 0.018\bar{2} \times 8.2 \times 10^3\ \text{kPa} = \boxed{1.5 \times 10^2\ \text{kPa}}$$

E5.5(b) We assume that the solvent, 2-propanol, is ideal and obeys Raoult's law.

$$x_A(\text{solvent}) = p/p^* = \frac{49.62}{50.00} = 0.9924$$

$$M_A(C_3H_8O) = 60.096\ \text{g mol}^{-1}$$

$$n_A = \frac{250\ \text{g}}{60.096\ \text{g mol}^{-1}} = 4.16\overline{00}\ \text{mol}$$

$$x_A = \frac{n_A}{n_A + n_B} \quad n_A + n_B = \frac{n_A}{x_A}$$

$$n_B = n_A\left(\frac{1}{x_A} - 1\right)$$

$$= 4.16\overline{00}\ \text{mol}\left(\frac{1}{0.9924} - 1\right) = 3.1\overline{86} \times 10^{-2}\ \text{mol}$$

$$M_B = \frac{8.69\ \text{g}}{3.186 \times 10^{-2}\ \text{mol}} = 27\overline{3}\ \text{g mol}^{-1} = \boxed{270\ \text{g mol}^{-1}}$$

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) $\Delta T = K_f b_B$ and $b_B = \dfrac{n_B}{\text{mass of water}} = \dfrac{n_B}{V\rho}$

$\rho = 10^3\ \text{kg m}^{-3}$ (density of solution $\approx$ density of water)

$$n_B = \frac{\Pi V}{RT} \quad \Delta T = K_f\frac{\Pi}{RT\rho} \quad K_f = 1.86\ \text{K mol}^{-1}\ \text{kg}$$

$$\Delta T = \frac{(1.86\ \text{K kg mol}^{-1}) \times (99 \times 10^3\ \text{Pa})}{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (288\ \text{K}) \times (10^3\ \text{kg m}^{-3})} = 7.7 \times 10^{-2}\ \text{K}$$

$$T_f = \boxed{-0.077\ °\text{C}}$$

E5.8(b) $\Delta_{\text{mix}}G = nRT(x_A \ln x_A + x_B \ln x_B)$

$$n_{Ar} = n_{Ne}, \quad x_{Ar} = x_{Ne} = 0.5, \quad n = n_{Ar} + n_{Ne} = \frac{pV}{RT}$$

$$\Delta_{\text{mix}}G = pV(\tfrac{1}{2}\ln\tfrac{1}{2} + \tfrac{1}{2}\ln\tfrac{1}{2}) = -pV\ln 2$$

$$= -(100 \times 10^3\ \text{Pa}) \times (250\ \text{cm}^3)\left(\frac{1\ \text{m}^3}{10^6\ \text{cm}^3}\right)\ln 2$$

$$= -17.3\ \text{Pa m}^3 = -17.3\ \text{J}$$

$$\Delta_{\text{mix}}S = \frac{-\Delta_{\text{mix}}G}{T} = \frac{17.3\ \text{J}}{273\ \text{K}} = \boxed{6.34 \times 10^{-2}\ \text{J K}^{-1}}$$

E5.9(b) $$\Delta_{\text{mix}}G = nRT\sum_{\text{J}} x_{\text{J}} \ln x_{\text{J}} \; [5.18]$$

$$\Delta_{\text{mix}}S = -nR\sum_{\text{J}} x_{\text{J}} \ln x_{\text{J}} \; [5.19] = \frac{-\Delta_{\text{mix}}G}{T}$$

$$n = 1.00\,\text{mol} + 1.00\,\text{mol} = 2.00\,\text{mol}$$

$$x(\text{Hex}) = x(\text{Hep}) = 0.500$$

Therefore,

$$\Delta_{\text{mix}}G = (2.00\text{ mol}) \times (8.314\text{ J K}^{-1}\text{ mol}^{-1}) \times (298\text{ K}) \times (0.500\ln 0.500 + 0.500\ln 0.500)$$
$$= \boxed{-3.43\text{ kJ}}$$

$$\Delta_{\text{mix}}S = \frac{+3.43\text{ kJ}}{298\text{ K}} = \boxed{+11.5\text{ J K}^{-1}}$$

$\Delta_{\text{mix}}H$ 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

$$\Delta_{\text{mix}}S = -nR(x_{\text{A}}\ln x_{\text{A}} + x_{\text{B}}\ln x_{\text{B}})$$

To find maximum $\Delta_{\text{mix}}S$, differentiate with respect to x_{A} and find value of x_{A} at which the derivative is zero.

Note that $x_{\text{B}} = 1 - x_{\text{A}}$ so

$$\Delta_{\text{mix}}S = -nR(x_{\text{A}}\ln x_{\text{A}} + (1 - x_{\text{A}})\ln(1 - x_{\text{A}}))$$

use $\dfrac{\text{d}\ln x}{\text{d}x} = \dfrac{1}{x}$:

$$\frac{\text{d}}{\text{d}x}(\Delta_{\text{mix}}S) = -nR(\ln x_{\text{A}} + 1 - \ln(1 - x_{\text{A}}) - 1) = -nR\ln\frac{x_{\text{A}}}{1 - x_{\text{A}}}$$
$$= 0 \quad \text{when } x_{\text{A}} = \frac{1}{2}$$

Thus the maximum entropy of mixing is attained by mixing equal molar amounts of two components.

$$\frac{n_{\text{B}}}{n_{\text{E}}} = 1 = \frac{m_{\text{B}}/M_{\text{B}}}{m_{\text{E}}/M_{\text{E}}} \times \frac{m_{\text{E}}}{m_{\text{B}}} = \frac{M_{\text{E}}}{M_{\text{B}}} = \frac{106.169}{78.115} = 1.3591$$

$$\frac{m_{\text{B}}}{m_{\text{E}}} = \boxed{0.7358}$$

E5.11(b) With concentrations expressed in molalities, Henry's law [5.26] becomes $p_{\text{B}} = b_{\text{B}}K$.

Solving for b, the molality, we have $b_{\text{B}} = p_{\text{B}}/K = xp_{\text{total}}/\text{K}$ and $p_{\text{total}} = p_{\text{atm}}$

For N_2, $K = 1.56 \times 10^5$ 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, $K = 7.92 \times 10^4$ 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) $$b_B = \frac{p_B}{K} = \frac{2.0 \times 101.3\text{ kPa}}{3.01 \times 10^3\text{ kPa kg mol}^{-1}} = 0.067\text{ mol kg}^{-1}$$

The molality will be about 0.067 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).

$$\ln x_B = \frac{\Delta_{\text{fus}}H}{R} \times \left(\frac{1}{T^*} - \frac{1}{T}\right) \quad [5.39;\text{ B, the solute, is lead}]$$

$$= \left(\frac{5.2 \times 10^3\text{ J mol}^{-1}}{8.314\text{ J K}^{-1}\text{ mol}^{-1}}\right) \times \left(\frac{1}{600\text{ K}} - \frac{1}{553\text{ K}}\right)$$

$$= -0.088\bar{6},\ \text{implying that } x_B = 0.92$$

$$x_B = \frac{n(\text{Pb})}{n(\text{Pb}) + n(\text{Bi})},\ \text{implying that } n(\text{Pb}) = \frac{x_B n(\text{Bi})}{1 - x_B}$$

For 1 kg of bismuth, $n(\text{Bi}) = \dfrac{1000\text{ g}}{208.98\text{ g mol}^{-1}} = 4.785\text{ mol}$

Hence, the amount of lead that dissolves in 1 kg of bismuth is

$$n(\text{Pb}) = \frac{(0.92) \times (4.785\text{ mol})}{1 - 0.92} = 55\text{ mol}, \quad \text{or} \quad \boxed{11\text{ kg}}$$

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 $1.78\text{ cm}/(\text{mg cm}^{-3}) = 1.78\text{ cm}/(\text{g dm}^{-3}) = 1.78 \times 10^{-2}\text{ m}^4\text{ kg}^{-1}$.

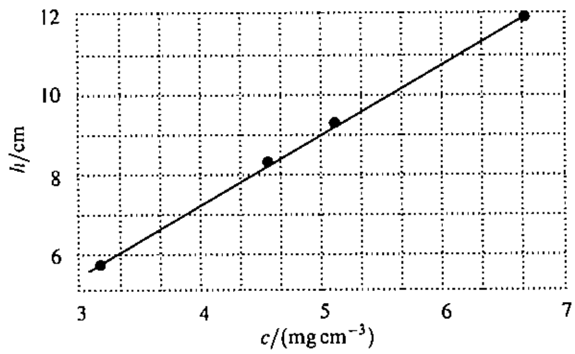


Figure 5.1

Therefore,

$$M = \frac{(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (293.15\ \mathrm{K})}{(1.000 \times 10^{3}\ \mathrm{kg\ m^{-3}}) \times (9.81\ \mathrm{m\ s^{-2}}) \times (1.78 \times 10^{-2}\ \mathrm{m^{4}\ kg^{-1}})} = \boxed{14.0\ \mathrm{kg\ mol^{-1}}}$$

E5.15(b) Let A = water and B = solute.

$$a_{\mathrm{A}} = \frac{p_{\mathrm{A}}}{p_{\mathrm{A}}^{*}}\ [5.43] = \frac{0.02239\ \mathrm{atm}}{0.02308\ \mathrm{atm}} = \boxed{0.9701}$$

$$\gamma_{\mathrm{A}} = \frac{a_{\mathrm{A}}}{x_{\mathrm{A}}} \quad \text{and} \quad x_{\mathrm{A}} = \frac{n_{\mathrm{A}}}{n_{\mathrm{A}} + n_{\mathrm{B}}}$$

$$n_{\mathrm{A}} = \frac{0.920\ \mathrm{kg}}{0.01802\ \mathrm{kg\ mol^{-1}}} = 51.0\bar{5}\ \mathrm{mol} \quad \text{and} \quad n_{\mathrm{B}} = \frac{0.122\ \mathrm{kg}}{0.241\ \mathrm{kg\ mol^{-1}}} = 0.506\ \mathrm{mol}$$

$$x_{\mathrm{A}} = \frac{51.0\bar{5}}{51.05 + 0.506} = 0.990 \quad \text{and} \quad \gamma_{\mathrm{A}} = \frac{0.9701}{0.990} = \boxed{0.980}$$

E5.16(b) B = Benzene $\mu_{\mathrm{B}}(\mathrm{l}) = \mu_{\mathrm{B}}^{*}(\mathrm{l}) + RT \ln x_{\mathrm{B}}$ [5.25, ideal solution]

$$RT \ln x_{\mathrm{B}} = (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (353.3\ \mathrm{K}) \times (\ln 0.30) = \boxed{-353\bar{6}\ \mathrm{J\ mol^{-1}}}$$

Thus, its chemical potential is lowered by this amount.

$$p_{\mathrm{B}} = a_{\mathrm{B}} p_{\mathrm{B}}^{*}\ [5.43] = \gamma_{\mathrm{B}} x_{\mathrm{B}} p_{\mathrm{B}}^{*} = (0.93) \times (0.30) \times (760\ \mathrm{Torr}) = \boxed{212\ \mathrm{Torr}}$$

Question. What is the lowering of the chemical potential in the nonideal solution with $\gamma = 0.93$?

E5.17(b)

$$y_{\mathrm{A}} = \frac{p_{\mathrm{A}}}{p_{\mathrm{A}} + p_{\mathrm{B}}} = \frac{p_{\mathrm{A}}}{101.3\ \mathrm{kPa}} = 0.314$$

$$p_{\mathrm{A}} = (101.3\ \mathrm{kPa}) \times (0.314) = 31.8\ \mathrm{kPa}$$

$$p_{\mathrm{B}} = 101.3\ \mathrm{kPa} - 31.8\ \mathrm{kPa} = 69.5\ \mathrm{kPa}$$

$$a_A = \frac{p_A}{p_A^*} = \frac{31.8\ \text{kPa}}{73.0\ \text{kPa}} = \boxed{0.436}$$

$$a_B = \frac{p_B}{p_B^*} = \frac{69.5\ \text{kPa}}{92.1\ \text{kPa}} = \boxed{0.755}$$

$$\gamma_A = \frac{a_A}{x_A} = \frac{0.436}{0.220} = \boxed{1.98}$$

$$\gamma_B = \frac{a_B}{x_B} = \frac{0.755}{0.780} = \boxed{0.968}$$

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

$$I = \tfrac{1}{2}(pz_+^2 + qz_-^2)b/b^\ominus$$

$$I = I(K_3[Fe(CN)_6]) + I(KCl) + I(NaBr) = \frac{1}{2}(3+3^2)\frac{b(K_3[Fe(CN)_6])}{b^\ominus} + \frac{b(KCl)}{b^\ominus} + \frac{b(NaBr)}{b^\ominus}$$

$$= (6)\times(0.040) + (0.030) + (0.050) = \boxed{0.320}$$

Question. Can you establish that the statement in the comment following the solution to Exercise 5.18(a) holds for the solution of this exercise?

E5.19(b) $I = I(KNO_3) = \dfrac{b}{b^\ominus}(KNO_3) = 0.110$

Therefore, the ionic strengths of the added salts must be 0.890.

(a) $I(KNO_3) = \dfrac{b}{b^\ominus}$, so $b(KNO_3) = 0.890\ \text{mol kg}^{-1}$

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) $I(Ba(NO_3)_2) = \dfrac{1}{2}(2^2 + 2\times 1^2)\dfrac{b}{b^\ominus} = 3\dfrac{b}{b^\ominus} = 0.890$

$$b = \frac{0.890}{3}b^\ominus = 0.296\bar{7}\ \text{mol kg}^{-1}$$

and $(0.296\bar{7}\ \text{mol kg}^{-1}) \times (0.500\ \text{kg}) = 0.148\bar{4}\ \text{mol}\ Ba(NO_3)_2$

So $(0.148\bar{4}\ \text{mol}) \times (261.32\ \text{g mol}^{-1}) = \boxed{38.8\ \text{g}\ Ba(NO_3)_2}$

E5.20(b) Since the solutions are dilute, use the Debye–Hückel limiting law

$$\log\gamma_\pm = -|z_+z_-|AI^{1/2}$$

$$I = \frac{1}{2}\sum_i z_i^2(b_i/b^\ominus) = \frac{1}{2}\{1\times(0.020) + 1\times(0.020) + 4\times(0.035) + 2\times(0.035)\}$$

$$= 0.125$$

$$\log\gamma_\pm = -1\times 1\times 0.509\times(0.125)^{1/2} = -0.1799\bar{6}$$

$$(\text{For NaCl})\ \gamma_\pm = 10^{-0.1799\bar{6}} = \boxed{0.661}$$

E5.21(b) The extended Debye–Hückel law is $\log \gamma_{\pm} = -\dfrac{A|z_+z_-|I^{1/2}}{1+BI^{1/2}}$

Solving for B

$$B = -\left(\frac{1}{I^{1/2}} + \frac{A|z_+z_-|}{\log \gamma_{\pm}}\right) = -\left(\frac{1}{(b/b^{\ominus})^{1/2}} + \frac{0.509}{\log \gamma_{\pm}}\right)$$

Draw up the following table

$b/(\text{mol kg}^{-1})$	5.0×10^{-3}	10.0×10^{-3}	50.0×10^{-3}
$\gamma_{\pm}$	0.927	0.902	0.816
B	$1.3\bar{2}$	$1.3\bar{6}$	$1.2\bar{9}$

$$B = \boxed{1.3}$$

Solutions to problems

Solutions to numerical problems

P5.2

$$V_A = \left(\frac{\partial V}{\partial n_A}\right)_{n_B} [5.1, \text{A} = \text{NaCl(aq)}, \text{B} = \text{water}] = \left(\frac{\partial V}{\partial b}\right)_{n(\text{H}_2\text{O})} \text{mol}^{-1} \ [\text{with } b \equiv b/(\text{mol kg}^{-1})]$$

$$= \left((16.62) + \tfrac{3}{2} \times (1.77) \times (b)^{1/2} + (2) \times (0.12b)\right) \text{cm}^3\,\text{mol}^{-1}$$

$$= 17.5\,\text{cm}^3\,\text{mol}^{-1} \text{ when } b = 0.100$$

For a solution consisting of 0.100 mol NaCl and 1.000 kg of water, corresponding to 55.49 mol H_2O, the total volume is given both by

$$V = [(1003) + (16.62) + (0.100) \times (1.77) \times (0.100)^{3/2} + (0.12) \times (0.100)^2]\,\text{cm}^3$$

$$= 1004.7\,\text{cm}^3$$

and by

$$V = n(\text{NaCl})V_{\text{NaCl}} + n(\text{H}_2\text{O})V_{\text{H}_2\text{O}} \ [5.3] = (0.100\,\text{mol}) \times (17.5\,\text{cm}^3\,\text{mol}^{-1}) + (55.49\,\text{mol}) \times V_{\text{H}_2\text{O}}$$

Therefore, $V_{\text{H}_2\text{O}} = \dfrac{1004.7\,\text{cm}^3 - 1.75\,\text{cm}^3}{55.49\,\text{mol}} = \boxed{18.07\,\text{cm}^3\,\text{mol}^{-1}}$

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 $CuSO_4$ 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

$$\rho = \frac{m_A + m_B}{V} \qquad n_A = \frac{m_A}{M_A}$$

the procedure runs as follows

$$\begin{aligned} V_A &= \left(\frac{\partial V}{\partial n_A}\right)_{n_B} = \left(\frac{\partial V}{\partial m_A}\right)_B M_A \\ &= \frac{\partial}{\partial m_A}\left(\frac{m_A + m_B}{\rho}\right) \times M_A \\ &= \frac{M_A}{\rho} + (m_A + m_B) M_A \frac{\partial}{\partial m_A}\frac{1}{\rho} \end{aligned}$$

$$\frac{\partial}{\partial m_A}\frac{1}{\rho} = \left(\frac{\partial w}{\partial m_A}\right)\frac{\partial}{\partial w}\frac{1}{\rho} = \frac{-w}{m_A + m_B}\frac{\partial}{\partial w}\frac{1}{\rho}$$

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
$\rho/(\mathrm{g\,cm^{-3}})$	1.051	1.107	1.167	1.230
$1/(\rho/\mathrm{g\,cm^{-3}})$	0.951	0.903	0.857	0.813

The values of $1/\rho$ are plotted against w in Figure 5.2.

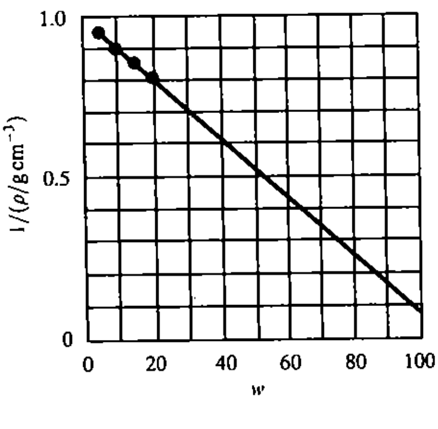


Figure 5.2

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 $0.075\,\mathrm{g^{-1}\,cm^3}$. Thus

$$V(\mathrm{CuSO_4}) = 0.075\,\mathrm{g^{-1}\,cm^3} \times 159.6\,\mathrm{g\,mol^{-1}} = \boxed{12.0\,\mathrm{cm^3\,mol^{-1}}}$$

P5.6

$$\Delta T = \frac{RT_f^{*2}x_B}{\Delta_{\mathrm{fus}}H}\ [5.36], \quad x_B \approx \frac{n_B}{n(\mathrm{CH_3COOH})} = \frac{n_B M(\mathrm{CH_3COOH})}{1000\,\mathrm{g}}$$

Hence, $\Delta T = \dfrac{n_B MRT_f^{*2}}{\Delta_{\mathrm{fus}}H \times 1000\,\mathrm{g}} = \dfrac{b_B MRT_f^{*2}}{\Delta_{\mathrm{fus}}H}$ [b_B: molality of solution]

$$= b_B \times \left(\frac{(0.06005\,\mathrm{kg\,mol^{-1}}) \times (8.314\,\mathrm{J\,K^{-1}mol^{-1}}) \times (290\,\mathrm{K})^2}{11.4 \times 10^3\,\mathrm{J\,mol^{-1}}}\right)$$

$$= 3.68\,\mathrm{K} \times b_B/(\mathrm{mol\,kg^{-1}})$$

Giving for b_B, the apparent molality,

$$b_B = \nu b_B^0 = \frac{\Delta T}{3.68\,\mathrm{K}}\mathrm{mol\,kg^{-1}}$$

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

$$M_B(\text{apparent}) = \frac{b_B^0}{b_B} \times M_B^0 = \frac{1}{\nu} \times M_B^0 = \frac{1}{\nu} \times (74.56\,\mathrm{g\,mol^{-1}})$$

where M_B^0 is the actual molar mass of KCl.

We can draw up the following table from the data.

$b_B^0/(\mathrm{mol\,kg^{-1}})$	0.015	0.037	0.077	0.295	0.602
$\Delta T/K$	0.115	0.295	0.470	1.381	2.67
$b_B/(\mathrm{mol\,kg^{-1}})$	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
$M_B(\mathrm{app})/(\mathrm{g\,mol^{-1}})$	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: $p_I^* = 47.12\,\mathrm{kPa}$, $p_A^* = 37.38\,\mathrm{kPa}$.

(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: $K_A = \boxed{60.0\text{ kPa}}$ and $K_I = \boxed{62.0\text{ kPa}}$

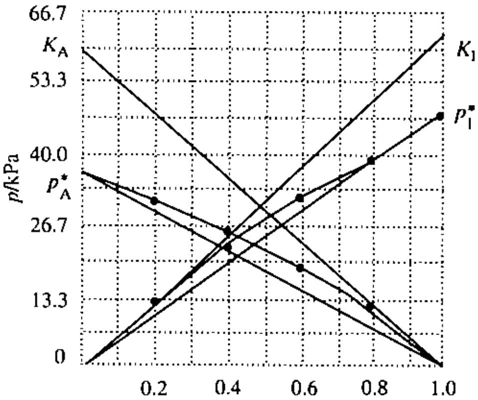


Figure 5.3

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‡
p_A/kPa	37.38†	30.7	24.7	18.0	10.7	0
$\gamma_I(\mathbf{R})$	—	1.30	1.17	1.09	1.03	$1.000[p_I/x_I p_I^*]$
$\gamma_A(\mathbf{R})$	1.000	1.03	1.10	1.20	1.43	$—[p_A/x_A p_A^*]$
$\gamma_I(\mathbf{H})$	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 $\gamma_A(\mathrm{H})$.

P5.10 The partial molar volume of cyclohexane is

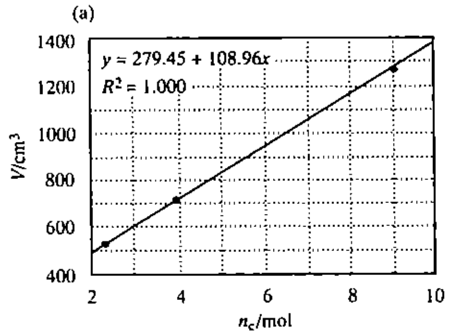
$$V_c = \left(\frac{\partial V}{\partial n_c}\right)_{p,T,n_2}$$

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

$$V = \frac{m}{\rho} = \frac{n_c M_c + n_p M_p}{\rho}$$



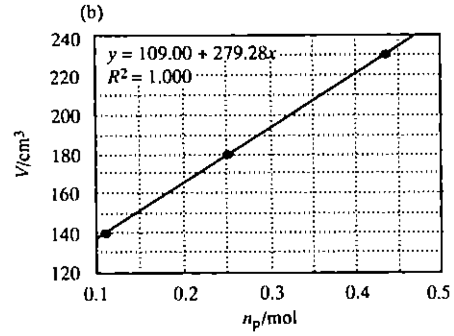


Figure 5.4

The following table is drawn up

n_c/mol($n_p = 1$)	V/cm^3	x_c	ρ/g cm^{-3}	n_p/mol($n_c = 1$)	V/cm^3
2.295	529.4	0.6965	0.7661	0.4358	230.7
3.970	712.2	0.7988	0.7674	0.2519	179.4
9.040	1264	0.9004	0.7697	0.1106	139.9

These values are plotted in Figures 5.4(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

$$V_c = \boxed{109.0\ \text{cm}^3\ \text{mol}^{-1}} \quad \text{and} \quad V_p = \boxed{279.3\ \text{cm}^3\ \text{mol}^{-1}}$$

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 $\boxed{\tau = 165\text{ K}}$, standard deviation = 2 K

$$\ln(S_0/\text{mol dm}^{-3}) = 2.990,\ \text{standard deviation} = 0.007;\ S_0 = e^{2.990}\text{mol dm}^{-3} = \boxed{19.89\text{ mol dm}^{-3}}$$

$$R = \boxed{0.99978}$$

The linear regression explains 99.98 percent of the variation.

Equation 5.39 is

$$x_B = e^{-\left(\frac{\Delta_{fus}H}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)\right)} = e^{-\Delta_{fus}H/RT}e^{\Delta_{fus}H/RT^*}$$

Comparing to $S = S_0 e^{\tau/T}$, we see that

$$\boxed{S_0 = e^{-\Delta_{fus}H/RT^*}}$$

where T^* is the normal melting point of the solute and $\Delta_{fus}H$ is its heat of fusion $\boxed{\tau = \Delta_{fus}H/R}$

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 mmol kg^{-1} we may solve for B.

$$B = -\frac{A}{\log \gamma_\pm} - \frac{1}{I^{1/2}} = -\frac{0.509}{(-0.0599)} - \frac{1}{0.141} = 1.40\bar{5}$$

Thus,

$$\log \gamma_\pm = -\frac{0.509 I^{1/2}}{1 + 1.40\bar{5} I^{1/2}}$$

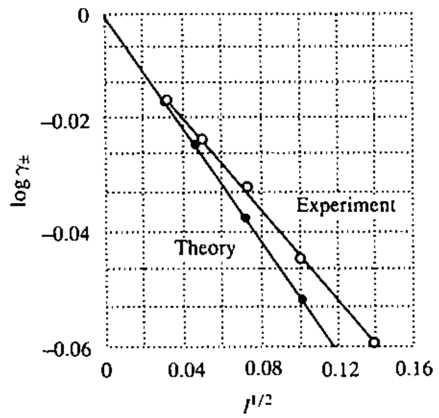


Figure 5.5

In order to determine whether or not the fit is improved, we use the data at 10.0 mmol kg^{-1}

$$\log \gamma_{\pm} = \frac{-(0.509) \times (0.100)}{(1) + (1.405) \times (0.100)} = -0.0446$$

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 $x_A + x_B = 1$

$$x_A\left(\frac{\partial \mu_A}{\partial x_A}\right)_{p,T} - x_B\left(\frac{\partial \mu_B}{\partial x_B}\right)_{p,T} = 0$$

or, $\left(\frac{\partial \mu_A}{\partial \ln x_A}\right)_{p,T} = \left(\frac{\partial \mu_B}{\partial \ln x_B}\right)_{p,T}$ $\left[d\ln x = \frac{dx}{x}\right]$

Then, since $\mu = \mu^{\ominus} + RT\ln\frac{f}{p^{\ominus}}$, $\left(\frac{\partial \ln f_A}{\partial \ln x_A}\right)_{p,T} = \left(\frac{\partial \ln f_B}{\partial \ln x_B}\right)_{p,T}$

On replacing f 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 $\ln x_A = -\Delta_{fus}G/RT$ (Section 5.5 analogous to equation for $\ln x_B$ used in derivation of eqn 5.39)

$$\frac{d\ln x_A}{dT} = -\frac{1}{R} \times \frac{d}{T}\left(\frac{\Delta_{fus}G}{T}\right) \quad \text{[Gibbs–Helmholtz equation]}$$

$$\int_1^{x_A} d\ln x_A = \int_{T^*}^{T} \frac{\Delta_{fus}H}{RT^2} dT \approx \frac{\Delta_{fus}H}{R} \int_{T^*}^{T} \frac{dT}{T^2}$$

$$\boxed{\ln x_A = \frac{-\Delta_{fus}H}{R} \times \left(\frac{1}{T} - \frac{1}{T^*}\right)}$$

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 cm^3 of blood in the lung containing 15 g of Hb at 97% saturated with O_2 binds

$$1.34\ \text{cm}^3\ \text{g}^{-1} \times 15\ \text{g} = 20\ \text{cm}^3\ O_2$$

The same 100 cm^3 of blood in the arteries would contain

$$20\ \text{cm}^3\ O_2 \times \frac{75\%}{97\%} = 15.5\ \text{cm}^3$$

Therefore, about $(20 - 15.5)\ \text{cm}^3$ or $\boxed{4.5\ \text{cm}^3}$ 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
$\dfrac{\nu/[\text{EB}]_{\text{out}}}{2\ \mu\text{mol}^{-1}}$	5.95	5.41	4.90	3.81	2.61

A plot of $\nu/[\text{EB}]_{\text{out}}$ is shown in Figure 5.6.

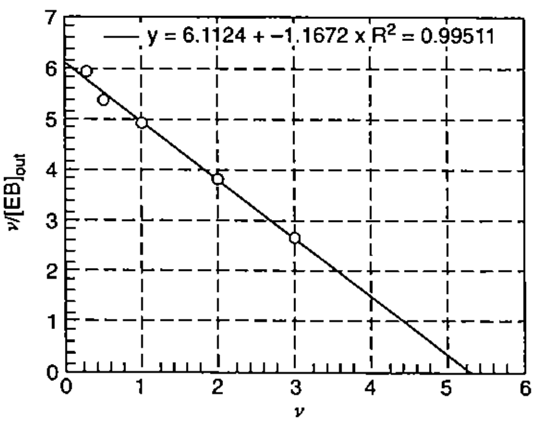


Figure 5.6

The slope is $-1.167\ \text{dm}^3\ \mu\text{mol}^{-1}$, hence $K = \boxed{1.167\ \text{dm}^3\ \mu\text{mol}^{-1}}$. The intercept at $\nu = 0$ is $\boxed{N = 5.24}$ 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 $\boxed{\text{is applicable}}$.

P5.28 $PX_\nu(s) \rightleftharpoons P^{\nu} + (aq) + \nu X^-(aq)$

This process is a solubility equilibrium described by a solubility constant K_s

$$K_s = a_{P^{\nu}} + a^{\nu}_{X^-}$$

Introducing activity coefficients and concentrations, b, we obtain

$$K_s = b_{P^{\nu}} + b^{\nu}_{X^-}\gamma_{\pm}^{\nu+1}$$

At low to moderate ionic strengths we can use the Debye–Hückel limiting law as a good approximation for $\gamma_\pm$

$$\log \gamma_\pm = -|z_+z_-|AI^{1/2}$$

Addition of a salt, such as $(NH_4)_2SO_4$ causes I to increase and log $\gamma_\pm$ to become more negative and $\gamma_\pm$ will decrease. However, K_s is a true equilibrium constant and remains unchanged. Therefore, the concentration of $P^{\nu+}$ 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 $(NH_4)_2SO_4$, the ions of the protein that are in solution attract one another less strongly, so that the equilibrium is shifted in the direction of increased solubility.

The explanation of the salting out effect is somewhat more complicated and can be related to the failure of the Debye-Hückel limiting law at higher ionic strengths. At high ionic strengths we may write

$$\log \gamma_\pm = -|z_+|AI^{1/2} + KI$$

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 $\Pi = \rho gh$, 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
$(\Pi/c)/(\text{N m}^{-2}\text{ mg}^{-1}\text{ cm}^3)$	$22.5\bar{6}$	$24.2\bar{9}$	$29.2\bar{0}$	$34.2\bar{6}$	$39.5\bar{1}$

The plot is shown in Figure 5.7. The intercept is $29.0\bar{9}\text{ N m}^{-2}/(\text{mg cm}^{-3})$. The slope is $1.974\text{ N m}^{-2}/(\text{mg cm}^{-3})^2$. Therefore

$$\begin{aligned} M &= \frac{RT}{29.0\bar{9}\text{ N m}^{-2}/(\text{mg cm}^{-3})} \\ &= \frac{8.3145\text{ J K}^{-1}\text{ mol}^{-1} \times 303.15\text{ K}}{20.09\text{ N m}^{-2}/(\text{mg cm}^{-3})} \times \left(\frac{1\text{g}}{10^3\text{ mg}}\right) \times \left(\frac{10^6\text{ cm}^3}{1\text{ m}^3}\right) \\ &= 1.25\bar{5} \times 10^5\text{ g mol}^{-1} = \boxed{1.26 \times 10^5\text{g mol}^{-1}} \end{aligned}$$

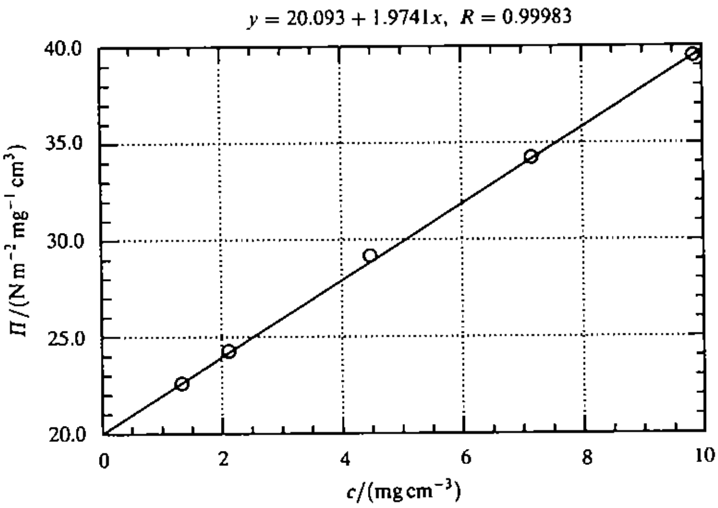


Figure 5.7

$$\begin{aligned}
B &= \frac{M}{RT} \times 1.974\,\mathrm{N\,m^{-2}/(mg\,cm^{-3})^2} \\
&= \frac{M}{\left(\dfrac{RT}{M}\right)} \times 1.974\,\mathrm{N\,m^{-2}/(mg\,cm^{-3})^2} \\
&= \frac{1.25\bar{5} \times 10^5\,\mathrm{g\,mol^{-1}} \times 1.974\,\mathrm{N\,m^{-2}/(mg\,cm^{-3})^2}}{20.09\,\mathrm{N\,m^{-2}/(mg\,cm^{-3})}} \\
&= 1.23 \times 10^4\,\mathrm{g\,mol^{-1}/(mg\,cm^{-3})} \\
&= 1.23 \times 10^7\,\mathrm{g\,mol^{-1}/(g\,cm^{-3})} \\
&= \boxed{1.23 \times 10^4\,\mathrm{dm^3\,mol^{-1}}}
\end{aligned}$$

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).

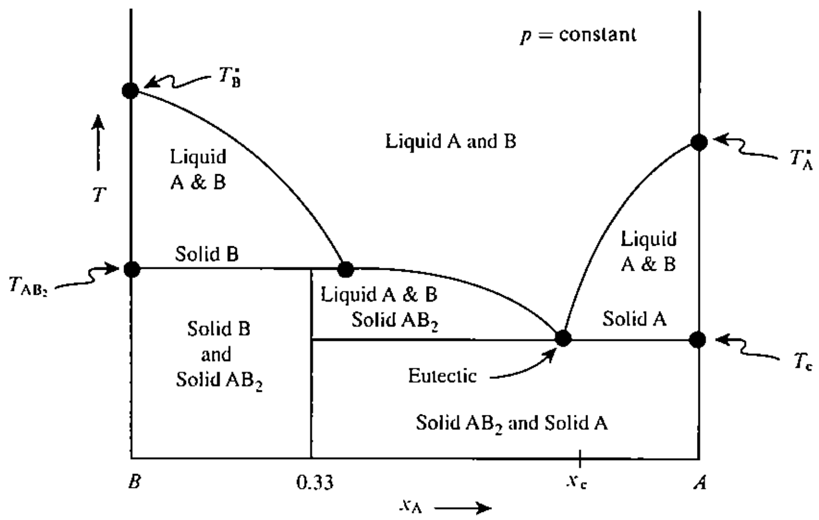


Figure 6.1(a)

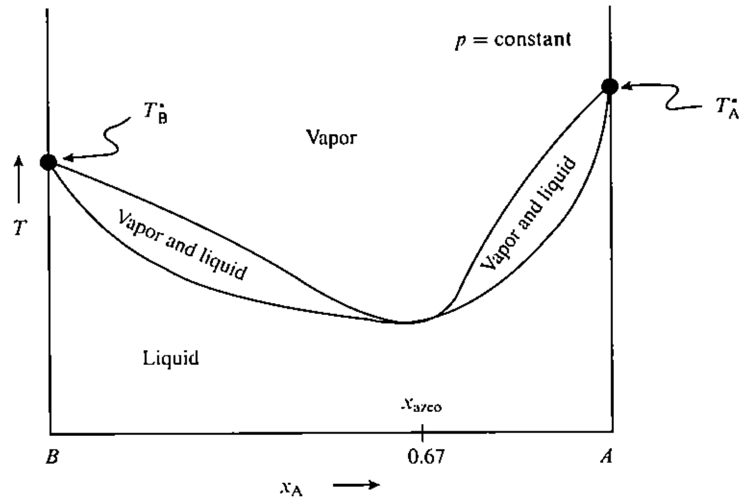


Figure 6.1(b)

D6.6 See Figure 6.2.

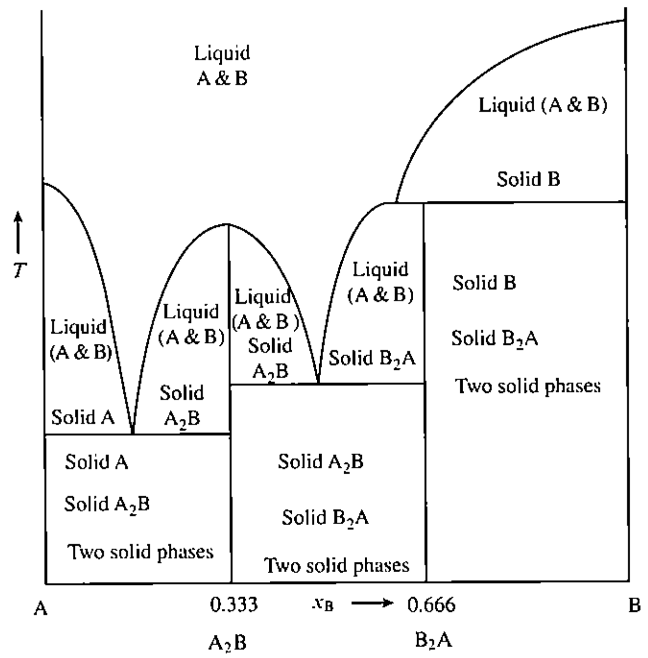


Figure 6.2

Solutions to exercises

E6.1(b) $p = p_A + p_B = x_A p_A^* + (1 - x_A) p_B^*$

$$x_A = \frac{p - p_B^*}{p_A^* - p_B^*}$$

$$x_A = \frac{19\,\text{kPa} - 18\,\text{kPa}}{20\,\text{kPa} - 18\,\text{kPa}} = \boxed{(0.5)} \text{ A is 1,2-dimethylbenzene}$$

$$y_A = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*)x_A} = \frac{(0.5)\times(20\,\text{kPa})}{18\,\text{kPa} + (20\,\text{kPa} - 18\,\text{kPa})0.5} = 0.5\overline{26} \approx \boxed{0.5}$$

$$y_B = 1 - 0.5\overline{26} = 0.4\overline{74} \approx 0.5$$

E6.2(b)

$$p_A = y_A p = 0.612p = x_A p_A^* = x_A(68.8\,\text{kPa})$$

$$p_B = y_B p = (1 - y_A)p = 0.388p = x_B p_B^* = (1 - x_A)\times 82.1\,\text{kPa}$$

$$\frac{y_A p}{y_B p} = \frac{x_A p_A^*}{x_B p_B^*} \text{ and } \frac{0.612}{0.388} = \frac{68.8 x_A}{82.1(1 - x_A)}$$

$$(0.388)\times(68.8)x_A = (0.612)\times(82.1) - (0.612)(82.1)x_A$$

$$26.6\overline{94}x_A = 50.2\overline{45} - 50.2\overline{45}x_A$$

$$x_A = \frac{50.2\overline{45}}{26.6\overline{94} + 50.2\overline{45}} = \boxed{0.653} \; x_B = 1 - 0.653 = \boxed{0.347}$$

$$p = x_A p_A^* + x_B p_B^* = (0.653)\times(68.8\,\text{kPa}) + (0.347)\times(82.1\,\text{kPa}) = \boxed{73.4\,\text{kPa}}$$

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 $\boxed{\text{the solution is ideal}}$.

(b)

$$y_A = \frac{p_A}{p} = \frac{46.43\,\text{kPa}}{101.33\,\text{kPa}} = \boxed{0.4582}$$

$$y_B = 1 - y_A = 1.000 - 0.4582 = \boxed{0.5418}$$

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

$$p = x_B p_B^* + x_T p_T^* \; [6.3] = (0.500)\times(9.9\,\text{kPa}) + (0.500)\times(2.9\,\text{kPa})$$

$$= 4.9\overline{5}\,\text{kPa} + 1.4\overline{5}\,\text{kPa} = \boxed{6.4\ \text{kPa}}$$

(b)

$$y_B = \frac{p_B}{p} \; [6.4] = \frac{4.9\overline{5}\,\text{kPa}}{6.4\,\text{kPa}} = \boxed{0.77} \; y_T = 1 - 0.77 = \boxed{0.23}$$

(c) Near the end of the distillation

$$y_B = z_B = 0.500 \text{ and } y_T = z_T = 0.500$$

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) $x_A = \boxed{0.67}$ $y_A = \boxed{0.925}$

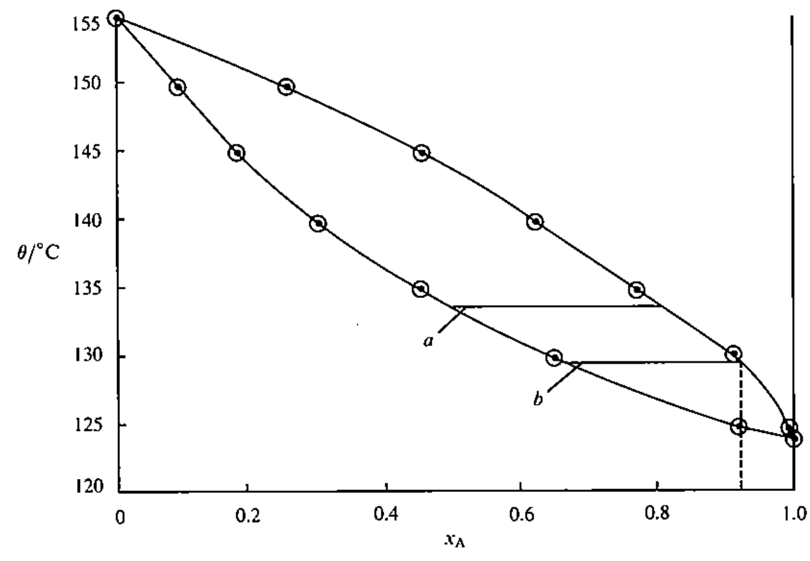


Figure 6.3

E6.6(b) Al^{3+}, H^+, $AlCl_3$, $Al(OH)_3$, OH^-, Cl^-, H_2O giving seven species. There are also three equilibria

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl$$

$$AlCl_3 \rightleftharpoons Al^{3+} + 3Cl^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

and one condition of electrical neutrality

$$[H^+] + 3[Al^{3+}] = [OH^-] + [Cl^-]$$

Hence, the number of independent components is

$$C = 7 - (3 + 1) = \boxed{3}$$

E6.7(b) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

(a) For this system $\boxed{C = 1}$ [Example 6.1] and $\boxed{P = 2}$ (s and g).

(b) If ammonia is added before heating, $\boxed{C = 2}$ (because NH_4Cl, NH_3 are now independent) and $\boxed{P = 2}$ (s and g).

E6.8(b) (a) Still $\boxed{C = 2}$ (Na_2SO_4, H_2O), but now there is no solid phase present, so $\boxed{P = 2}$ (liquid solution, vapor).

(b) The variance is $F = 2 - 2 + 2 = \boxed{2}$. We are free to change any two of the three variables, amount of dissolved salt, pressure, or temperature, but not the third. If we change the amount of dissolved salt and the pressure, the temperature is fixed by the equilibrium condition between the two phases.

E6.9(b) See Figure 6.4.

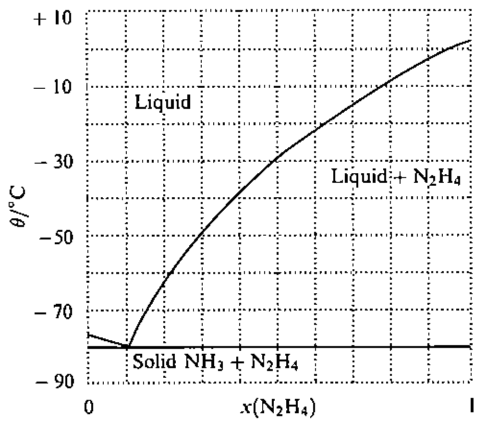


Figure 6.4

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

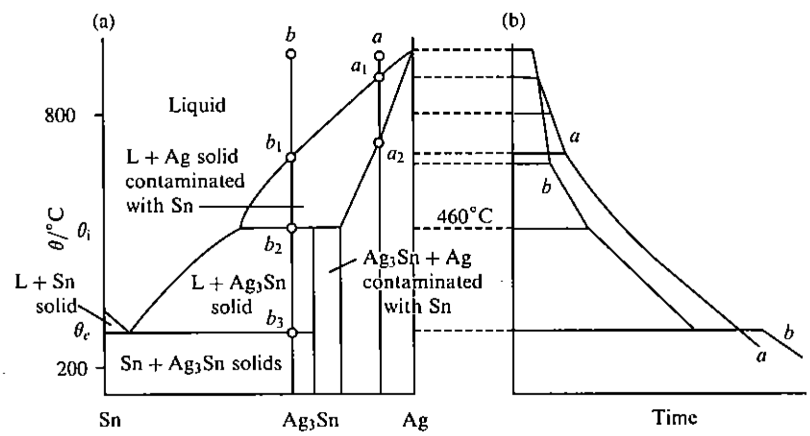


Figure 6.5

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 $x_B = \boxed{0.53}$, $T = \boxed{T_2}$; another at $x_B = \boxed{0.82}$, $T = \boxed{T_3}$.

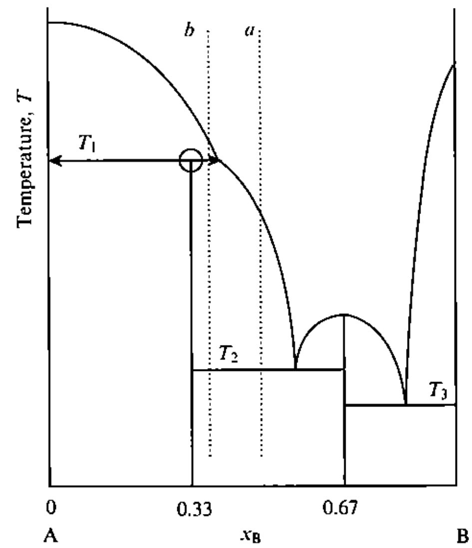


Figure 6.6

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.

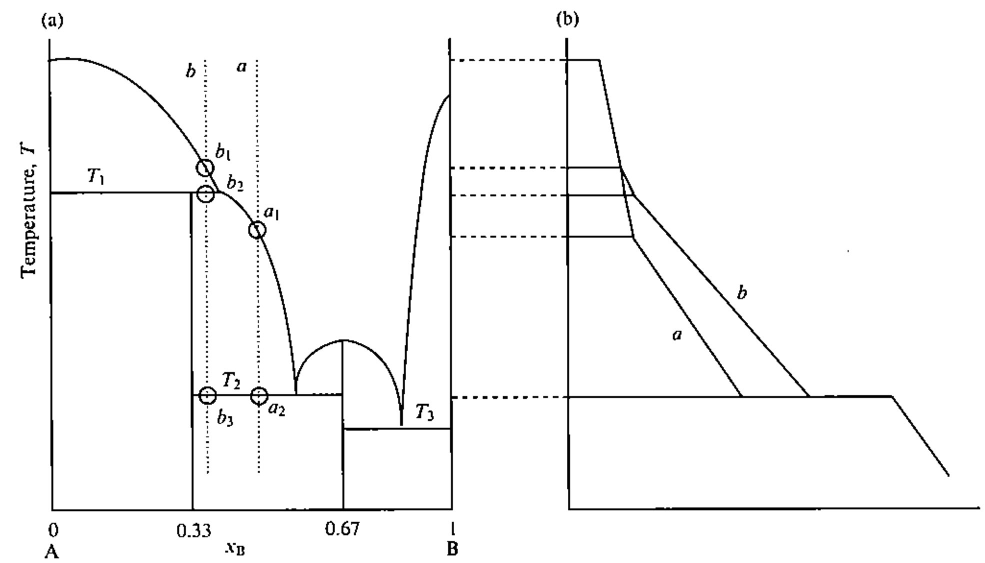


Figure 6.7

E6.13(b) Rough estimates based on Figure 6.37 of the text are

(a) $x_B \approx \boxed{0.75}$ (b) $x_{AB_2} \approx \boxed{0.8}$ (c) $x_{AB_2} \approx \boxed{0.6}$

E6.14(b) The phase diagram is shown in Figure 6.8. The given data points are circled. The lines are schematic at best.

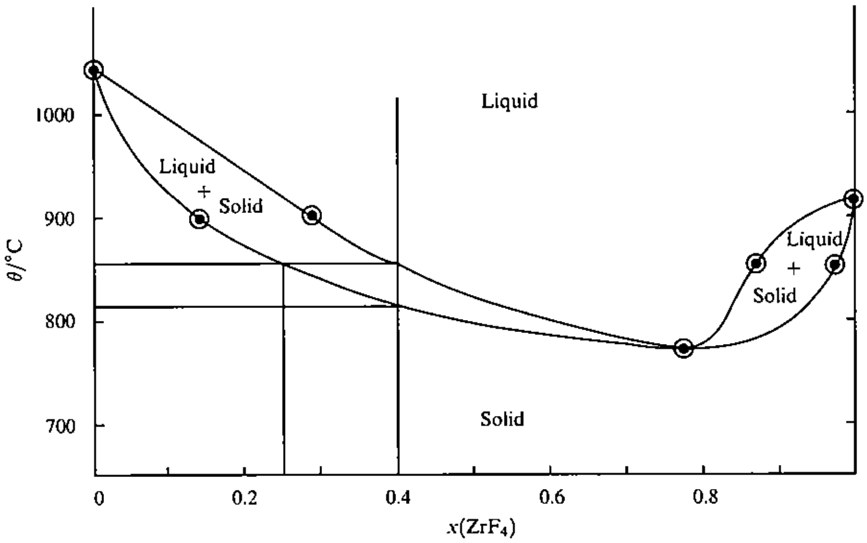


Figure 6.8

A solid solution with $x(ZrF_4) = 0.24$ appears at 855 °C. The solid solution continues to form, and its ZrF_4 content increases until it reaches $x(ZrF_4) = 0.40$ 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.

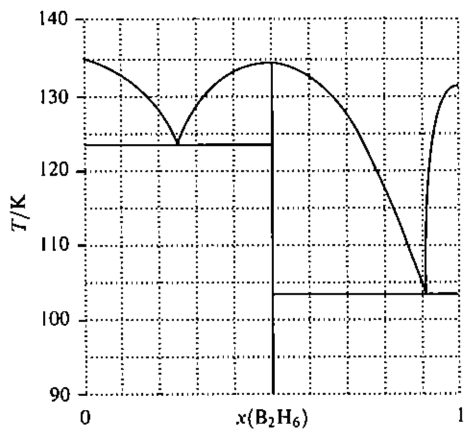


Figure 6.9

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.

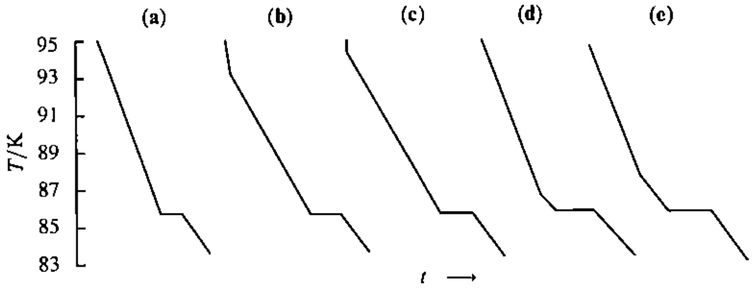


Figure 6.10

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.

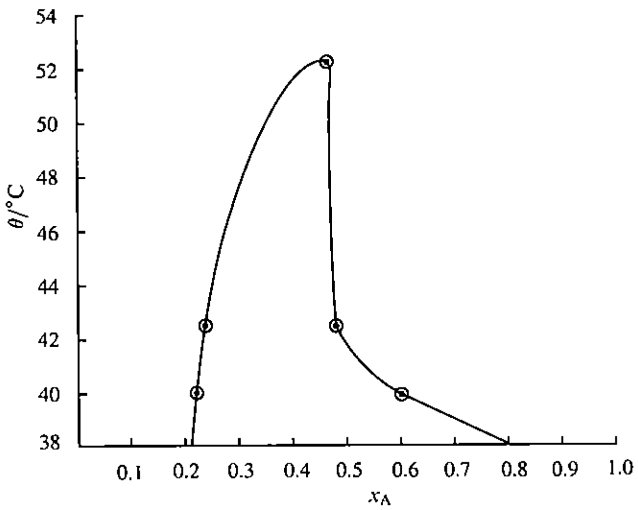


Figure 6.11

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

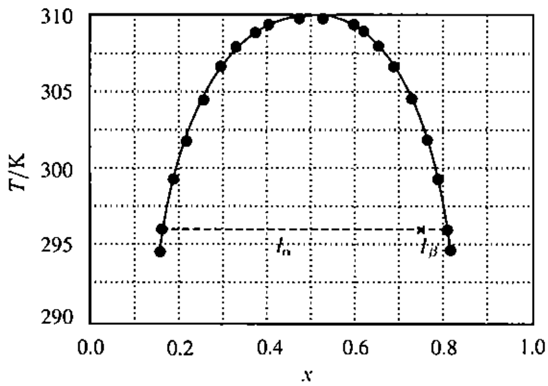


Figure 6.12

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.

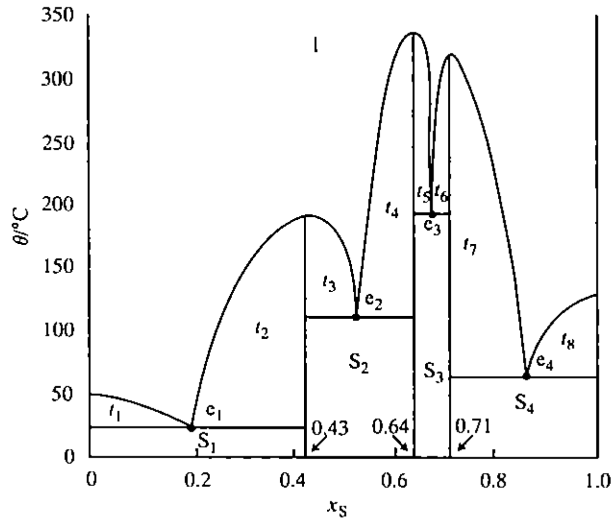


Figure 6.13(a)

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 $b_1 \approx 125\,°C$ as a result of solid P_4S_3 forming; a eutectic halt occurs at point $e_1 \approx 20\,°C$.

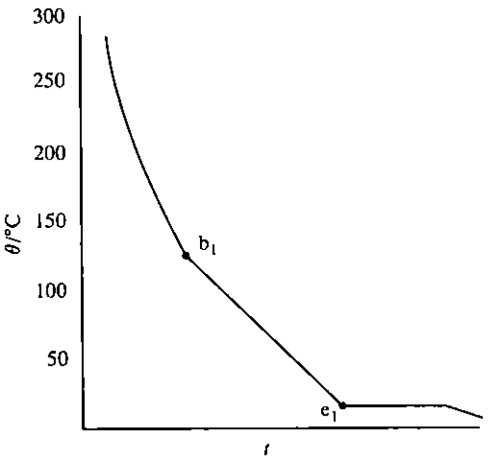


Figure 6.13(b)

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

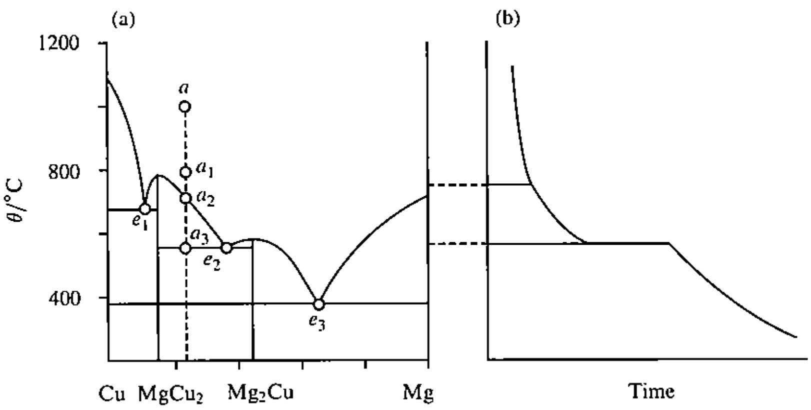


Figure 6.14(a)

$b(3,2)$, $d(2,2)$, $e(4,3)$, $f(4,3)$, $g(4,3)$, $k(2,2)$

[Liquid A and solid A are here considered distinct species.]

The cooling curves are shown in Figure 6.14(b).

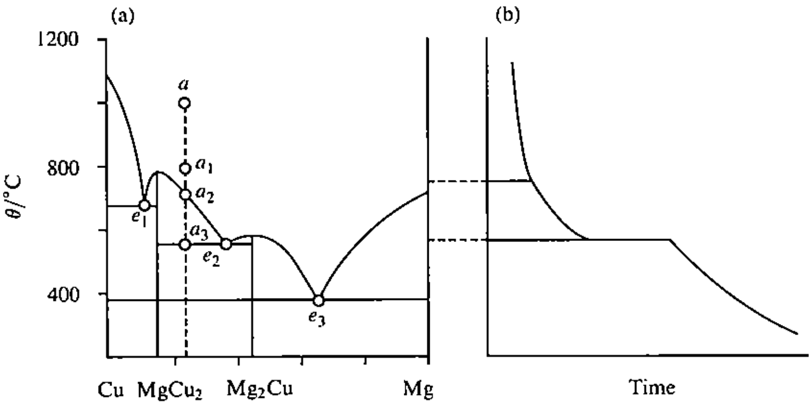


Figure 6.14(b)

P6.8 **(a)** The $\Delta_{mix}G(x_{Pb})$ 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 $x_{Pb} = 0.1$ is cooled from 1500 K to 1100 K, no phase separation occurs. The solution composition does not change.

If an $x_{Pb} = 0.7$ 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 $\Delta_{mix}G$ 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 $\Delta_{mix}G$ curve, we conclude that the straight line that is tangent to $\Delta_{mix}G(x)$ 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 $\boxed{x_{Pb}(\alpha) = 0.19}$ and $\boxed{x_{Pb}(\beta) = 0.86}$. 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 $\Delta_{mix}G$ curve. The maximum amount of lead that can be dissolved in copper yields a mixture that has $x_{Pb} = 0.17$, any more lead produces a second phase.

$$\text{solubility of Pb in Cu} = \left(\frac{0.17\,\cancel{\text{mol Pb}}}{0.83\,\cancel{\text{mol Cu}}}\right) \times \left(\frac{207.19\,\text{g Pb}}{1\,\cancel{\text{mol Pb}}}\right) \times \left(\frac{1\,\cancel{\text{mol Cu}}}{63.54\,\text{g Cu}}\right) = \boxed{0.67\text{g Pb/g Cu}}$$

The second minumum in the $\Delta_{\text{mix}}G$ curve at 1100 K is at $x_{\text{Pb}} = 0.86$.

$$\text{solubility of Cu in Pb} = \left(\frac{0.14\,\cancel{\text{mol Cu}}}{0.86\,\text{mol Pb}}\right) \times \left(\frac{63.54\,\text{g Cu}}{1\,\cancel{\text{mol Cu}}}\right) \times \left(\frac{1\,\text{mol Pb}}{207.19\,\text{g Pb}}\right)$$

$$= \boxed{0.050\text{ g Cu/g Pb}}$$

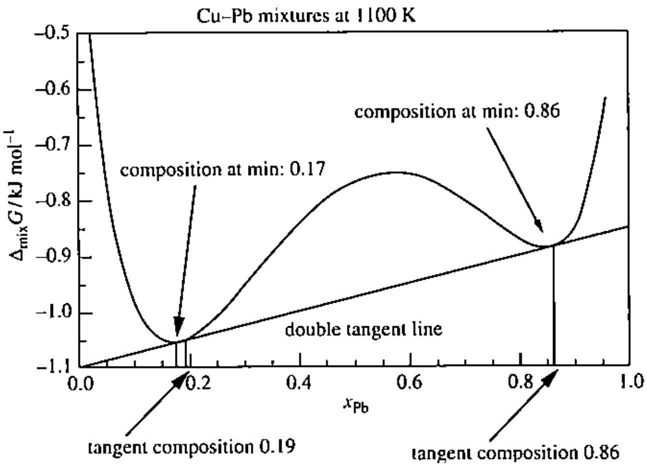


Figure 6.15

P6.10 The data are plotted in Figure 6.16. At 360 °C, K_2FeCl_4(s) appears. The solution becomes richer in $FeCl_2$ until the temperature reaches 351 °C, at which point $KFeCl_3$(s) also appears. Below 351 °C the system is a mixture of K_2FeCl_4(s) and $KFeCl_3$(s).

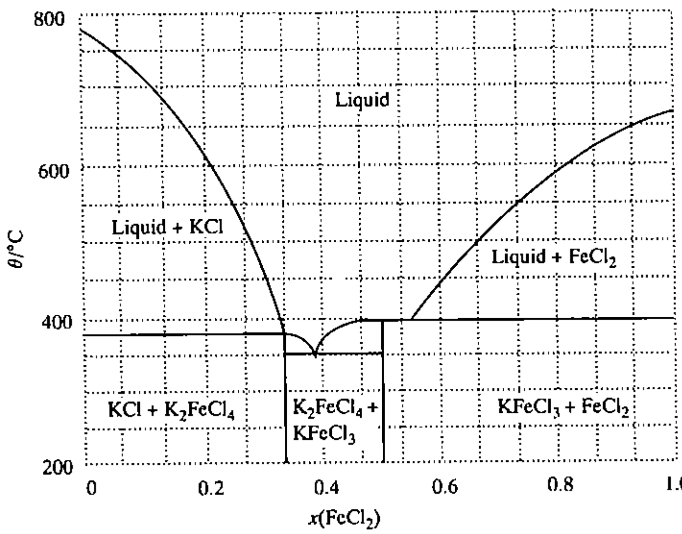


Figure 6.16

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, $U_\alpha + U_\beta$ = constant and $V_\alpha + V_\beta$ = constant. Hence,

$$\mathrm{d}U_\beta = -\mathrm{d}U_\alpha \text{ (b)} \quad \text{and} \quad \mathrm{d}V_\beta = -\mathrm{d}V_\alpha \text{ (c)}$$

The general condition of equilibrium in an isolated system is $\mathrm{d}S = 0$; hence

$$\mathrm{d}S = \mathrm{d}S_\alpha + \mathrm{d}S_\beta = 0 \text{ (a)}$$

$$S = S(U, V)$$

$$\mathrm{d}S = \left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)_{V_\alpha} \mathrm{d}U_\alpha + \left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)_{U_\alpha} \mathrm{d}V_\alpha + \left(\frac{\partial S_\beta}{\partial U_\beta}\right)_{V_\beta} \mathrm{d}U_\beta + \left(\frac{\partial S_\beta}{\partial V_\beta}\right)_{U_\beta} \mathrm{d}V_\beta$$

Using conditions (b) and (c), and eqn 3.45

$$\mathrm{d}S = \left(\frac{1}{T_\alpha} - \frac{1}{T_\beta}\right)\mathrm{d}U_\alpha + \left(\frac{p_\alpha}{T_\alpha} - \frac{p_\beta}{T_\beta}\right)\mathrm{d}V_\alpha = 0$$

The only way in which this expression may, in general, equal zero is for

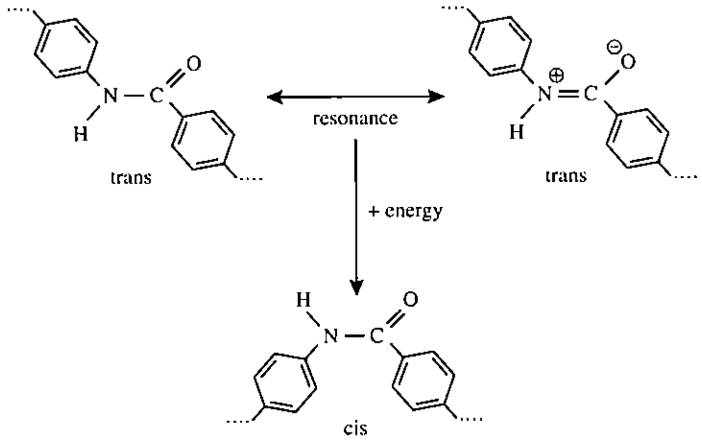
$$\frac{1}{T_\alpha} - \frac{1}{T_\beta} = 0 \quad \text{and} \quad \frac{p_\alpha}{T_\alpha} - \frac{p_\beta}{T_\beta} = 0$$

Therefore, $\boxed{T_\alpha = T_\beta \text{ and } p_\alpha = p_\beta}$

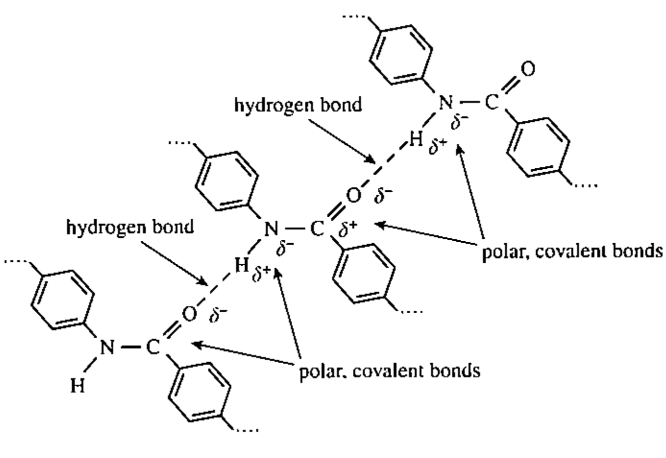
Solutions to applications

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 hinderance 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

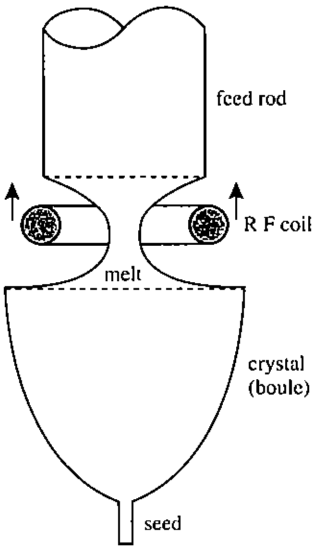


Figure 6.17

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].

$$\Delta T \approx \frac{RT^{*2}x_B}{\Delta_{fus}H}$$

For bismuth

$$\frac{RT^{*2}}{\Delta_{fus}H} = \frac{(8.314\,J\,K^{-1}\,mol^{-1}) \times (544.5\,K)^2}{10.88 \times 10^3\,J\,mol^{-1}} = 227\,K$$

For cadmium

$$\frac{RT^{*2}}{\Delta_{fus}H} = \frac{(8.314\,J\,K^{-1}\,mol^{-1}) \times (594.5\,K)^2}{6.07 \times 10^3\,J\,mol^{-1}} = 483\,K$$

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	45.4	$(T_f = T_f^* - \Delta T)$

$x(\text{Bi})$	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).

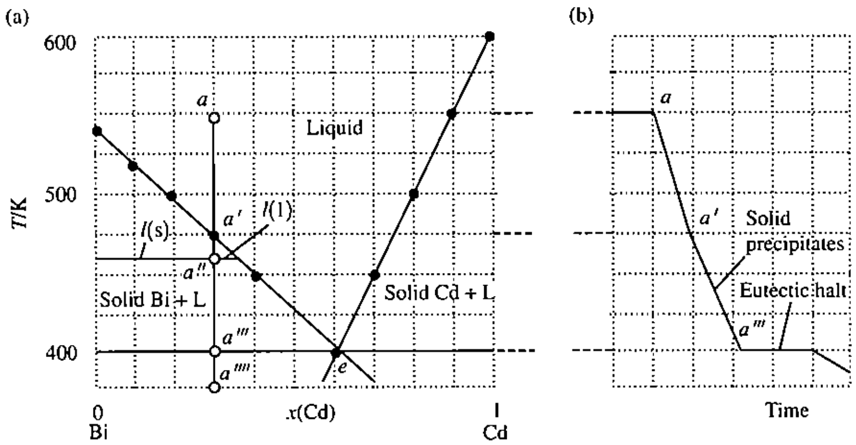


Figure 6.18

The eutectic temperature and concentration are located by extrapolation of the plotted freezing point lines until they intersect at e, which corresponds to $T_E \approx 400$ K and $x_E(\text{Cd}) \approx 0.6\bar{0}$

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 solidfies to solid Bi + solid Cd.

(a) At 460 K (point a'), $\dfrac{n(l)}{n(\text{s})} = \dfrac{l(\text{s})}{l(\text{l})} \approx 5$ by the lever rule.

(b) At 375 K (point a'''') there is $\boxed{\text{no liquid}}$. 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

E7.1(b) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Amount at equilibrium	$(1-\alpha)n$	$2\alpha n$
Mole fraction	$\dfrac{1-\alpha}{1+\alpha}$	$\dfrac{2\alpha}{1+\alpha}$
Partial pressure	$\dfrac{(1-\alpha)P}{1+\alpha}$	$\dfrac{2\alpha P}{1+\alpha}$

Assuming that the gases are perfect, $a_J = \dfrac{p_J}{p^{\ominus}}$

$$K = \frac{(p_{NO_2}/p^{\ominus})^2}{(p_{N_2O_4}/p^{\ominus})} = \frac{4\alpha^2 p}{(1-\alpha^2)p^{\ominus}}$$

For $p = p^{\ominus}$, $K = \dfrac{4\alpha^2}{1-\alpha^2}$

(a) $\boxed{\Delta_r G = 0}$ at equilibrium

(b) $\alpha = 0.201 \qquad K = \dfrac{4(0.201)^2}{1-0.201^2} = \boxed{0.168\overline{41}}$

(c) $\Delta_r G^{\ominus} = -RT\ln K = -(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K}) \times \ln(0.168\overline{41})$

$$= \boxed{4.41\,\mathrm{kJ\,mol^{-1}}}$$

E7.2(b) (a) $Br_2(g) \rightleftharpoons 2Br(g) \quad \alpha = 0.24$

Amount at equilibrium	$(1-\alpha)n$	$2\alpha n$
Mole fraction	$\dfrac{1-\alpha}{1+\alpha}$	$\dfrac{2\alpha}{1+\alpha}$
Partial pressure	$\dfrac{(1-\alpha)P}{1+\alpha}$	$\dfrac{2\alpha P}{1+\alpha}$

Assuming both gases are perfect $a_J = \dfrac{p_J}{p^{\ominus}}$

$$K = \frac{(p_{Br}/p^{\ominus})^2}{p_{Br_2}/p^{\ominus}} = \frac{4\alpha^2 p}{(1-\alpha^2)p^{\ominus}} = \frac{4\alpha}{1-\alpha} \quad [p = p^{\ominus}]$$

$$= \frac{4(0.24)^2}{1-(0.24)^2} = 0.24\overline{45} = \boxed{0.24}$$

(b) $$\Delta_r G^{\ominus} = -RT\ln K = -(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (1600\,\mathrm{K}) \times \ln(0.24\overline{45})$$

$$\boxed{= 19\,\mathrm{kJ\,mol^{-1}}}$$

(c) $$\ln K(2273\,\mathrm{K}) = \ln K(1600\,\mathrm{K}) - \frac{\Delta_r H^{\ominus}}{R}\left(\frac{1}{2273\,\mathrm{K}} - \frac{1}{1600\,\mathrm{K}}\right)$$

$$= \ln(0.24\overline{45}) - \left(\frac{112 \times 10^3\,\mathrm{mol^{-1}}}{8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}}\right) \times (-1.851 \times 10^{-4})$$

$$= 1.08\overline{4}$$

$$K(2273\,\mathrm{K}) = \mathrm{e}^{1.08\overline{4}} = \boxed{2.96}$$

E7.3(b) $\nu(CHCl_3) = 1, \quad \nu(HCl) = 3, \quad \nu(CH_4) = -1, \quad \nu(Cl_2) = -3$

(a) $$\Delta_r G^{\ominus} = \Delta_f G^{\ominus}(CHCl_3, l) + 3\Delta_f G^{\ominus}(HCl, g) - \Delta_f G^{\ominus}(CH_4, g)$$

$$= (-73.66\,\mathrm{kJ\,mol^{-1}}) + (3) \times (-95.30\,\mathrm{kJ\,mol^{-1}}) - (-50.72\,\mathrm{kJ\,mol^{-1}})$$

$$= \boxed{-308.84\,\mathrm{kJ\,mol^{-1}}}$$

$$\ln K = -\frac{\Delta_r G^{\ominus}}{RT}[7.8] = \frac{-(-308.84 \times 10^3\,\mathrm{J\,mol^{-1}})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298.15\,\mathrm{K})} = 124.58\overline{4}$$

$$K = \boxed{1.3 \times 10^{54}}$$

(b) $$\Delta_r H^{\ominus} = \Delta_f H^{\ominus}(CHCl_3, l) + 3\Delta_f H^{\ominus}(HCl,\ g) - \Delta_f H^{\ominus}(CH_4, g)$$

$$= (-134.47\,\mathrm{kJ\,mol^{-1}}) + (3) \times (-92.31\,\mathrm{kJ\,mol^{-1}}) - (-74.81\,\mathrm{kJ\,mol^{-1}})$$

$$= -336.59\,\mathrm{kJ\,mol^{-1}}$$

$$\ln K(50\,°\mathrm{C}) = \ln K(25\,°\mathrm{C}) - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{323.2\,\mathrm{K}} - \frac{1}{298.2\,\mathrm{K}}\right) [7.25]$$

$$= 124.58\bar{4} - \left(\frac{-336.59 \times 10^3\,\mathrm{J\,mol^{-1}}}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\right) \times (-2.594 \times 10^{-4}\,\mathrm{K^{-1}}) = 114.08\bar{3}$$

$$K(50\,°\mathrm{C}) = \boxed{3.5 \times 10^{49}}$$

$$\Delta_r G^\ominus(50\,°\mathrm{C}) = -RT\ln K(50\,°\mathrm{C})\ [7.17] = -(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (323.15\,\mathrm{K}) \times (114.08\bar{3})$$

$$= \boxed{306.52\,\mathrm{kJ\,mol^{-1}}}$$

E7.4(b) Draw up the following table.

	A	+	B	⇌	C	+	2D	Total
Initial amounts/mol	2.00		1.00		0		3.00	6.00
Stated change/mol					+0.79			
Implied change/mol	−7.09		−7.09		+7.09		+1.58	
Equilibrium amounts/mol	1.21		0.21		0.79		4.58	6.79
Mole fractions	$0.178\bar{2}$		$0.030\bar{2}$		$0.116\bar{2}$		$0.674\bar{2}$	$0.999\bar{9}$

(a) Mole fractions are given in the table.

(b) $K_x = \prod_J x_J^{\nu_J}$,

$$K_x = \frac{(0.116\bar{3}) \times (0.674\bar{5})^2}{(0.178\bar{2}) \times (0.030\bar{9})} = \boxed{9.6}$$

(c) $p_J = x_J p$. Assuming the gases are perfect, $a_J = p_J/p^\ominus$, so

$$K = \frac{(p_C/p^\ominus) \times (p_D/p^\ominus)^2}{(p_A/p^\ominus) \times (p_B/p^\ominus)} = K_x\left(\frac{p}{p^\ominus}\right) = K_x \quad \text{when } p = 1.00\,\mathrm{bar}$$

$$K = K_x = \boxed{9.6}$$

(d) $\Delta_r G^\ominus = -RT\ln K = -(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K}) \times \ln(9.60\bar{9})$

$$= \boxed{-5.6\,\mathrm{kJ\,mol^{-1}}}$$

E7.5(b) At 1120 K, $\Delta_r G^\ominus = +22 \times 10^3\,\mathrm{J\,mol^{-1}}$

$$\ln K(1120\,\mathrm{K}) = \frac{\Delta_r G^\ominus}{RT} = -\frac{(22 \times 10^3\,\mathrm{J\,mol^{-1}})}{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (1120\,\mathrm{K})} = -2.3\overline{63}$$

$$K = \mathrm{e}^{-2.3\overline{63}} = 9.\overline{41} \times 10^{-2}$$

$$\ln K_2 = \ln K_1 - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Solve for T_2 at $\ln K_2 = 0\,(K_2 = 1)$

$$\frac{1}{T_2} = \frac{R\ln K_1}{\Delta_r H^\ominus} + \frac{1}{T_1} = \frac{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (-2.3\overline{63})}{(125 \times 10^3\,\mathrm{J\,mol^{-1}})} + \frac{1}{1120\,\mathrm{K}} = 7.3\overline{6} \times 10^{-4}$$

$$T_2 = \boxed{1.4 \times 10^3\,\mathrm{K}}$$

E7.6(b) Use $\dfrac{\mathrm{d}(\ln K)}{\mathrm{d}(1/T)} = \dfrac{-\Delta_r H^\ominus}{R}$

We have $\ln K = -2.04 - 1176\,\mathrm{K}\left(\dfrac{1}{T}\right) + 2.1 \times 10^7\,\mathrm{K}^3\left(\dfrac{1}{T}\right)^3$

$$-\frac{\Delta_r H^\ominus}{R} = -1176\,\mathrm{K} + (2.1 \times 10^7\,\mathrm{K}^3) \times 3\left(\frac{1}{T}\right)^2$$

$T = 450\,\mathrm{K}$ so

$$-\frac{\Delta_r H^\ominus}{R} = -1176\,\mathrm{K} + (2.1 \times 10^7\,\mathrm{K}^3) \times 3\left(\frac{1}{450\,\mathrm{K}}\right)^2 = -86\overline{5}\,\mathrm{K}$$

$$\Delta_r H^\ominus = +(86\overline{5}\,\mathrm{K}) \times (8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}) = \boxed{7.1\overline{91}\,\mathrm{kJ\,mol^{-1}}}$$

Find $\Delta_r S^\ominus$ from $\Delta_r G^\ominus$

$$\begin{aligned}\Delta_r G^\ominus &= -RT\ln K \\ &= -(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (450\,\mathrm{K}) \times \left\{-2.04 - \frac{1176\,\mathrm{K}}{450\,\mathrm{K}} + \frac{2.1 \times 10^7\,\mathrm{K}^3}{(450\,\mathrm{K})^3}\right\} \\ &= 16.\overline{55}\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta_r G^\ominus &= \Delta_r H^\ominus - T\Delta_r S^\ominus \\ \Delta_r S^\ominus &= \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T} = \frac{7.1\overline{91}\,\mathrm{kJ\,mol^{-1}} - 16.5\overline{5}\,\mathrm{kJ\,mol^{-1}}}{450\,\mathrm{K}} = -20.\overline{79}\,\mathrm{J\,K^{-1}\,mol^{-1}} \\ &= \boxed{-21\,\mathrm{J\,K^{-1}\,mol^{-1}}}\end{aligned}$$

E7.7(b) $U(s) + \frac{3}{2}H_2(g) \rightleftharpoons UH_3(s), \quad \Delta_f G^\ominus = -RT\ln K$

At this low pressure, hydrogen is nearly a perfect gas, $a(H_2) = (p/p^\ominus)$. The activities of the solids are 1.

Hence, $\ln K = \ln\left(\dfrac{p}{p^\ominus}\right)^{-3/2} = -\dfrac{3}{2}\ln\dfrac{p}{p^\ominus}$

$$\begin{aligned}\Delta_f G^\ominus &= \frac{3}{2}RT\ln\frac{p}{p^\ominus} \\ &= \left(\frac{3}{2}\right) \times (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (500\,\mathrm{K}) \times \ln\left(\frac{139\,\mathrm{Pa}}{1.00 \times 10^5\,\mathrm{Pa}}\right) \\ &= \boxed{-41.0\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

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

$$K_x = \prod_J \left(\frac{p_J}{p^\ominus}\right)^{\nu_J} \left[7.16 \text{ with } a_J = \frac{p_J}{p^\ominus}\right]$$

$$= \prod_J x_J^{\nu_J} \left(\frac{p_J}{p^\ominus}\right)^{\sum_J \nu_J} [p_J = x_J p] = K_x \times \left(\frac{p}{p^\ominus}\right)^{\nu} \left[\nu \equiv \sum_J \nu_J\right]$$

Therefore, $K_x = K\left(p/p^\ominus\right)^{-\nu}$, $K_x \propto p^{-\nu}$ [K and $p^\ominus$ are constants]

$\nu = 1 + 1 - 1 - 1 = 0$, thus $\boxed{K_x(2\text{ bar}) = K_x(1\text{ bar})}$

E7.9(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \quad K = 1.69 \times 10^{-3}$ at 2300 K

$$\text{Initial moles } N_2 = \frac{5.0\text{ g}}{28.01\text{ g mol}^{-1}} = 0.23\overline{80}\text{ mol } N_2$$

$$\text{Initial moles } O_2 = \frac{2.0\text{ g}}{32.00\text{ g mol}^{-1}} = 6.2\overline{50} \times 10^{-2}\text{ mol } O_2$$

	N_2	O_2	NO	Total
Initial amount/mol	$0.23\overline{80}$	$0.062\overline{5}$	0	0.300
Change/mol	$-z$	$-z$	$+2z$	0
Equilibrium amount/mol	$0.23\overline{80} - z$	$0.062\overline{5} - z$	$2z$	0.300
Mole fractions	$\frac{0.23\overline{80} - z}{0.300}$	$\frac{0.062\overline{5} - z}{0.300}$	$\frac{2z}{0.300}$	(1)

$$K = K_x \left(\frac{p}{p^\ominus}\right)^{\nu} \left[\nu = \sum_J \nu_J = 0\right], \text{ then}$$

$$K = K_x = \frac{(2z/0.300)^2}{\left(\frac{0.2380 - z}{0.300}\right) \times \left(\frac{0.0625 - z}{0.300}\right)}$$

$$= \frac{4z^2}{(0.2380 - z)(0.0625 - z)} = 1.69 \times 10^{-3}$$

$$4z^2 = 1.69 \times 10^{-3}\{0.014\overline{88} - 0.30\overline{05}z + z^2\}$$

$$= 2.5\overline{14} \times 10^{-5} - (5.0\overline{78} \times 10^{-4})z + (1.69 \times 10^{-3})z^2$$

$4.00 - 1.69 \times 10^{-3} = 4.00$ so

$$4z^2 + (5.0\overline{78} \times 10^{-4})z - 2.5\overline{14} \times 10^{-5} = 0$$

$$z = \frac{-5.0\overline{78} \times 10^{-4} \pm \{(5.078 \times 10^{-4})^2 - 4 \times (4) \times (-2.514 \times 10^{-5})\}^{1/2}}{8}$$

$$= \frac{1}{8}(-5.078 \times 10^{-4} \pm 2.0\overline{06} \times 10^{-2})$$

$z > 0$ [$z < 0$ is physically impossible] so

$z = 2.4\overline{44} \times 10^{-3}$

$$x_{NO} = \frac{2z}{0.300} = \frac{2(2.4\overline{44} \times 10^{-3})}{0.300} = \boxed{1.6 \times 10^{-2}}$$

E7.10(b) $$\ln\frac{K'}{K} = \frac{\Delta_f H^\ominus}{R}\left(\frac{1}{T} - \frac{1}{T'}\right) \quad \text{so} \quad \Delta_f H^\ominus = \frac{R\ln\left(\frac{K'}{K}\right)}{\left(\frac{1}{T} - \frac{1}{T'}\right)}$$

$T = 310\,K$, $T' = 325\,K$; let $\frac{K'}{K} = \kappa$

Now $$\Delta_f H^\ominus = \frac{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}})}{((1/310\,\mathrm{K}) - (1/325\,\mathrm{K}))} \times \ln\kappa = 55.\overline{84}\,\mathrm{kJ\,mol^{-1}}\ln\kappa$$

(a) $\kappa = 2$ $\quad \Delta_f H^\ominus = (55.\overline{84}\,\mathrm{kJ\,mol^{-1}}) \times (\ln 2) = \boxed{39\,\mathrm{kJ\,mol^{-1}}}$

(b) $\kappa = \frac{1}{2}$ $\quad \Delta_r H^\ominus = (55.\overline{84}\,\mathrm{kJ\,mol^{-1}}) \times (\ln\frac{1}{2}) = \boxed{-39\,\mathrm{kJ\,mol^{-1}}}$

E7.11(b) $NH_4Cl(s) \rightleftharpoons NH_2(g) + HCl(g)$

$p = p(NH_3) + p(HCl) = 2p(NH_3)$ $\quad [p(NH_3) = p(HCl)]$

(a) $K = \prod_J a_J^{\nu_J}$ [7.16]; $\quad a(\text{gases}) = \frac{p_J}{p^\ominus}$; $\quad a(NH_4Cl,\ s) = 1$

$$K = \left(\frac{p(NH_3)}{p^\ominus}\right) \times \left(\frac{p(HCl)}{p^\ominus}\right) = \frac{p(NH_3)^2}{p^{\ominus 2}} = \frac{1}{4} \times \left(\frac{p}{p^\ominus}\right)^2$$

At 427 °C (700 K), $K = \frac{1}{4} \times \left(\frac{608\,\mathrm{kPa}}{100\,\mathrm{kPa}}\right)^2 = \boxed{9.24}$

At 459 °C (732 K), $K = \frac{1}{4} \times \left(\frac{1115\,\mathrm{kPa}}{100\,\mathrm{kPa}}\right)^2 = \boxed{31.08}$

(b) $\Delta_r G^\ominus = -RT\ln K$ [7.8] $= (-8.314\,\mathrm{J\,K^{-1}mol^{-1}}) \times (700\,\mathrm{K}) \times (\ln 9.24)$

$= \boxed{-12.9\,\mathrm{kJ\,mol^{-1}}}$ (at 427° C)

(c) $$\Delta_r H^\ominus \approx \frac{R\ln(K'/K)}{(1/T - 1/T')}\ [7.25]$$

$$\approx \frac{(8.314\,\mathrm{J\,K^{-1}mol^{-1}}) \times \ln(31.08/9.24)}{(1/700\,\mathrm{K}) - (1/732\,\mathrm{K})} = \boxed{+161\,\mathrm{kJ\,mol^{-1}}}$$

(d) $$\Delta_r S^\ominus = \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T} = \frac{(161\,\mathrm{kJ\,mol^{-1}}) - (-12.9\,\mathrm{kJ\,mol^{-1}})}{700\,\mathrm{K}} = \boxed{+248\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

E7.12(b) The reaction is

$$CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(g)$$

For the purposes of this exercise we may assume that the required temperature is that temperature at which K=1, which corresponds to a pressure of 1 bar for the gaseous products. For $K = 1, \ln K = 0$, and $\Delta_r G^\ominus = 0$.

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus = 0 \quad \text{when } \Delta_r H^\ominus = T\Delta_r S^\ominus$$

Therefore, the decomposition temperature (when $K = 1$) is

$$T = \frac{\Delta_r H^\ominus}{\Delta_r S^\ominus}$$

$$CuSO_4 \cdot 5H_2O\,(s) \rightleftharpoons CuSO_4\,(s) + 5H_2O\,(g)$$

$$\Delta_r H^\ominus = [(-771.36) + (5) \times (-241.82) - (-2279.7)]\ \text{kJ mol}^{-1} = +299.2\ \text{kJ mol}^{-1}$$

$$\Delta_r S^\ominus = [(109) + (5) \times (188.83) - (300.4)]\ \text{J K}^{-1}\,\text{mol}^{-1} = 752.\bar{8}\ \text{J K}^{-1}\,\text{mol}^{-1}$$

Therefore, $T = \dfrac{299.2 \times 10^3\ \text{J mol}^{-1}}{752.8\ \text{J K}^{-1}\,\text{mol}^{-1}} = \boxed{397\ \text{K}}$

Question. What would the decomposition temperature be for decomposition defined as the state at which $K = 1/2$?

E7.13(b) $PbI_2(s) \rightleftharpoons PbI_2(aq) \qquad K_S = 1.4 \times 10^{-8}$

$$\Delta_r G^\ominus = -RT \ln K_S = -(8.314\ \text{J K}^{-1}\,\text{mol}^{-1}) \times (298.15\ \text{K}) \times \ln\left(1.4 \times 10^{-8}\right)$$

$$= 44.83\ \text{kJ mol}^{-1}$$

$$\Delta_r G^\ominus = \Delta_f G^\ominus\,(PbI_2, aq) - \Delta_f G^\ominus\,(PbI_2, s)$$

$$\Delta_f G^\ominus\,(PbI_2, aq) = \Delta_r G^\ominus \Delta + \Delta_f G^\ominus\,(PbI_2, s)$$

$$= 44.8\bar{3}\ \text{kJ mol}^{-1} - 173.64\ \text{kJ mol}^{-1}$$

$$= \boxed{-128.8\ \text{kJ mol}^{-1}}$$

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.

(a) R: $Ag_2CrO_4(s) + 2e^- \rightarrow 2Ag(s) + CrO_4^{2-}(aq)$ $\quad +0.45$ V

L: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $\quad +1.36$ V

Overall (R − L): $Ag_2CrO_4(s) + 2Cl^-(aq) \rightarrow 2Ag(s) + CrO_4^{2-}(aq) + (Cl_2g)$ $\quad -0.91$ V

(b) R: $Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$ $\quad +0.15\,V$

L: $2Fe^{3+}(aq) + 2e^- \rightarrow 2Fe^{2+}(aq)$ $\quad +0.77\,V$

Overall (R − L): $Sn^{4+}(aq) + 2Fe^{2+}(aq) \rightarrow Sn^{2+}(aq) + 2Fe^{3+}(aq)$ $\quad -0.62\,V$

(c) R: $MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2Fe^{3+}(aq)$ $\quad +1.23\,V$

L: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $\quad +0.34\,V$

Overall (R − L): $Cu(s) + MnO_2(s) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + Mn^{2+}(aq) + 2H_2O(l)$ $\quad +0.89\,V$

COMMENT. Those cells for which $E^\ominus > 0$ may operate as spontaneous galvanic cells under standard conditions. Those for which $E^\ominus < 0$ may operate as nonspontaneous electrolytic cells. Recall that $E^\ominus$ informs us of the spontaneity of a cell under standard conditions only. For other conditions we require E.

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.

(a) R: $2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$ $\quad -0.83\,V$

L: $2Na^+(aq) + 2e^- \rightarrow 2Na(s)$ $\quad -2.71\,V$

and the cell is

$Na(s)|Na^+(aq)|, OH^-(aq)\,|H_2(g)\,Pt$ $\quad \boxed{+1.88\,V}$

or more simply

$\boxed{Na(s)|NaOH(aq)|H_2(g)|Pt}$

(b) R: $I_2(s) + 2e^- \rightarrow 2I^-(aq)$ $\quad +0.54\,V$

L: $2H^+(aq) + 2e^- \rightarrow H_2(g)$ $\quad 0$

and the cell is

$Pt\,|H_2(g)|\,H^+(aq), I^-(aq)\,|I_2(s)|\,Pt$ $\quad \boxed{+0.54\,V}$

or more simply

$\boxed{Pt|H_2(g)|H^+(aq)|\,I_2(s)|\,Pt}$

(c) R: $2H^+(aq) + 2e^- \rightarrow H_2(g)$ $\quad 0.00\,V$

L: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $\quad 0.083\,V$

and the cell is

$Pt\,|H_2(g)|\,H^+(aq), OH^-(aq)|H_2\,(g)|Pt$ $\quad \boxed{0.083\,V}$

or more simply

$$\boxed{\mathrm{Pt|H_2(g)|H_2O(l)|H_2(g)|Pt}}$$

COMMENT. All of these cells have $E^\ominus > 0$, corresponding to a spontaneous cell reaction under standard conditions. If $E^\ominus$ had turned out to be negative, the spontaneous reaction would have been the reverse of the one given, with the right and left electrodes of the cell also reversed.

E7.16(b) (a) $$E = E^\ominus - \frac{RT}{\nu F}\ln Q \quad \nu = 2$$

$$Q = \prod_J a_J^{\nu_J} = a_{H^+}^2 a_{Cl^-}^2 \quad \text{[all other activities} = 1]$$

$$= a_+^2 a_-^2 = (\gamma_+ b_+)^2 \times (\gamma_- b_-)^2 \quad \left[b \equiv \frac{b}{b^\ominus}\text{here and below}\right]$$

$$= (\gamma_+\gamma_-)^2 \times (b_+ b_-)^2 = \gamma_\pm^4 b^4 \quad [5.66,\ b_+ = b,\ b_- = b]$$

Hence, $E = E^\ominus - \dfrac{RT}{2F}\ln\left(\gamma_\pm^4 b^4\right) = \boxed{E^\ominus - \dfrac{2RT}{F}\ln\left(\gamma_\pm b\right)}$

(b) $$\Delta_r G = -\nu FE\ [7.27] = -(2) \times \left(9.6485 \times 10^4\ \mathrm{C\,mol^{-1}}\right) \times (0.4658\ \mathrm{V}) = \boxed{-89.89\ \mathrm{kJ\,mol^{-1}}}$$

(c) $$\log \gamma_\pm = -|z_+z_-|AI^{1/2}[5.69] = -(0.509) \times (0.010)^{1/2}\left[I = b \text{ for HCl(aq)}\right] = -0.0509$$

$$\gamma_\pm = 0.889$$

$$E^\ominus = E + \frac{2RT}{F}\ln\left(\gamma_\pm b\right) = (0.4658\ \mathrm{V}) + (2) \times \left(25.693 \times 10^{-3}\ \mathrm{V}\right) \times \ln(0.889 \times 0.010)$$

$$= \boxed{+0.223\ \mathrm{V}}$$

The value compares favorably to that given in Table 7.2.

E7.17(b) In each case $\ln K = \dfrac{\nu FE^\ominus}{RT}$ [7.30]

(a) $\mathrm{Sn(s) + CuSO_4(aq) \rightleftharpoons Cu(s) + SnSO_4(aq)}$

$$\left.\begin{array}{lll} \mathrm{R:} & \mathrm{Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)} & +0.34\ \mathrm{V} \\ \mathrm{L:} & \mathrm{Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)} & -0.14\ \mathrm{V} \end{array}\right\} +0.48\ \mathrm{V}$$

$$\ln K = \frac{(2) \times (0.48\ \mathrm{V})}{25.693\ \mathrm{mV}} = +37.\bar{4}, \qquad K = \boxed{1.7 \times 10^{16}}$$

(b) $\mathrm{Cu^{2+}(aq) + Cu(s) \rightleftharpoons 2Cu^+(aq)}$

$$\left.\begin{array}{lll} \mathrm{R:} & \mathrm{Cu^{2+}(aq) + e^- \rightarrow Cu(aq)} & +0.16\ \mathrm{V} \\ \mathrm{L:} & \mathrm{Cu^{+}(aq) + e^- \rightarrow Cu(s)} & +0.52\ \mathrm{V} \end{array}\right\} -0.36\ \mathrm{V}$$

$$\ln K = \frac{-0.36\ \mathrm{V}}{25.693\ \mathrm{mV}} = -14.\bar{0}, \qquad K = \boxed{8.2 \times 10^{-7}}$$

E7.18(b) R: $2Bi^{3+}(aq) + 6e^- \rightarrow 2Bi(s)$

L: $Bi_2S_3(s) + 6e^- \rightarrow 2Bi(s) + 3S^{2-}(aq)$

Overall (R − L): $2Bi^{3+}(aq) + 3S^{2-}(aq) \rightarrow Bi_2S_3(s) \quad \nu = 6$

$$\ln K = \frac{\nu FE^{\ominus}}{RT} = \frac{6(0.96\,\mathrm{V})}{(25.693 \times 10^{-3}\,\mathrm{V})} = 22\bar{4}$$

$$K = e^{22\bar{4}}$$

(a) $$K = \frac{a_{Bi_2S_3(s)}}{a^2_{Bi^{3+}(aq)}a^3_{S^{2-}(aq)}} = \frac{M^5}{[Bi^{3+}]^2[S^{2-}]^3} = e^{22\bar{4}}$$

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 $[S^{2-}] = 1.5[Bi^{3+}]$ and solving for $[Bi^{3+}]$ gives $[Bi^{3+}] = 2.7 \times 10^{-20}$ M. Bi_2S_3 has a solubility equal $\boxed{\text{to } 1.4 \times 10^{-20}\text{ M.}}$

(b) The solubility equilibrium is written as the reverse of the cell reaction. Therefore,

$$K_S = K^{-1} = 1/e^{22\bar{4}} = \boxed{5.2 \times 10^{-98}}.$$

Solutions to problems

Solutions to numerical problems

P7.2 $CH_4(g) \rightleftharpoons C(s) + 2H_2(g)$

This reaction is the reverse of the formation reaction.

(a) $$\Delta_r G^{\ominus} = -\Delta_f G^{\ominus}$$

$$\Delta_f G^{\ominus} = \Delta_f H^{\ominus} - T\Delta_f S^{\ominus}$$

$$= -74850\,\mathrm{J\,mol^{-1}} - 298\,\mathrm{K} \times (-80.67\,\mathrm{J\,K^{-1}\,mol^{-1}})$$

$$= -5.08 \times 10^4\,\mathrm{J\,mol^{-1}}$$

$$\ln K = \frac{\Delta_r G^{\ominus}}{-RT}[7.8] = \frac{5.08 \times 10^4\,\mathrm{J\,mol^{-1}}}{-8.314\,\mathrm{J\,K^{-1}\,mol^{-1}} \times 298\,\mathrm{K}} = -20.508$$

$$K = \boxed{1.24 \times 10^{-9}}$$

(b) $$\Delta_r H^{\ominus} = -\Delta_f H^{\ominus} = 74.85\,\mathrm{kJmol^{-1}}$$

$$\ln K(50\,^{\circ}\mathrm{C}) = \ln K(298\,\mathrm{K}) - \frac{\Delta_r H^{\ominus}}{R}\left(\frac{1}{323\,\mathrm{K}} - \frac{1}{298\,\mathrm{K}}\right)[7.25]$$

$$= -20.508 - \left(\frac{7.4850 \times 10^4\,\mathrm{J\,mol^{-1}}}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\right) \times \left(-2.59\bar{7} \times 10^{-4}\right) = -18.17\bar{0}$$

$$K(50\,^{\circ}\mathrm{C}) = \boxed{1.29 \times 10^{-8}}$$

(c) Draw up the equilibrium table

	$CH_4(g)$	$H_2(g)$
Amounts	$(1-\alpha)n$	$2\alpha n$
Mole fractions	$\dfrac{1-\alpha}{1+\alpha}$	$\dfrac{2\alpha}{1+\alpha}$
Partial pressures	$\left(\dfrac{1-\alpha}{1+\alpha}\right)p$	$\dfrac{2\alpha}{1+\alpha}$

$$K = \prod_J a_J^{\nu_J}\,[7.16] = \frac{(p_{H_2}/p^{\ominus})^2}{(p_{CH_4}/p^{\ominus})}$$

$$1.24 \times 10^{-9} = \frac{(2\alpha)^2}{1-\alpha^2}\left(\frac{p}{p^{\ominus}}\right) \approx 4\alpha^2 p \quad [\alpha \ll 1]$$

$$\alpha = \frac{1.24 \times 10^{-9}}{4 \times 0.010} = \boxed{1.8 \times 10^{-4}}$$

(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 $CO_2(g) \rightleftharpoons CO(g) + \frac{1}{2}O_2(g)$

Draw up the following equilibrium table

	CO_2	CO	O_2
Amounts	$(1-\alpha)n$	αn	$\frac{1}{2}\alpha n$
Mole fractions	$\dfrac{(1-\alpha)}{(1+(\alpha/2))}$	$\dfrac{\alpha}{(1+(\alpha/2))}$	$\dfrac{(1/2)\alpha}{(1+(\alpha/2))}$
Partial pressures	$\dfrac{(1-\alpha)p}{(1+(\alpha/2))}$	$\dfrac{\alpha p}{(1+(\alpha/2))}$	$\dfrac{\alpha p}{2(1+(\alpha/2))}$

$$K = \left(\prod_J a_J^{\nu_J}\right)_{\text{equilibrium}} [7.16] = \frac{(p_{CO}/p^{\ominus}) \times (p_{O_2}/p^{\ominus})^{1/2}}{(p_{CO_2}/p^{\ominus})}$$

$$= \frac{(\alpha)/((1+(\alpha/2)) \times ((\alpha/2))/(1+(\alpha/2))^{1/2} \times (p/p^{\ominus})^{1/2}}{(1-\alpha)/(1+(\alpha/2))}$$

$$K \approx \frac{\alpha^{3/2}}{\sqrt{2}} \quad [\alpha \ll 1 \text{ at all the specified temperatures}]$$

$$\Delta_r G^{\ominus} = -RT \ln K\,[7.8]$$

The calculated values of K and $\Delta_r G$ are given in the table below. From any two pairs of K and T, $\Delta_r H$ 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 $\Delta_r H^\ominus$

$$\Delta_r H^\ominus = \frac{R \ln\left(\frac{K_2}{K_1}\right)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \text{ [Exercise 7.10]} = \frac{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln\left(\frac{7.23 \times 10^{-6}}{1.22 \times 10^{-6}}\right)}{\left(\frac{1}{1395\,\mathrm{K}} - \frac{1}{1498\,\mathrm{K}}\right)}$$

$$= \boxed{3.00 \times 10^5\,\mathrm{J\,mol^{-1}}}$$

$$\Delta_r S^\ominus = \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T}$$

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
$\Delta_r G^\ominus/(\mathrm{kJ\,mol^{-1}})$	158	153	147
$\Delta_r S^\ominus/(\mathrm{J\,K^{-1}\,mol^{-1}})$	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 $\Delta_r G^\ominus(\mathrm{H_2CO, g}) = \Delta_r G^\ominus(\mathrm{H_2CO, l}) + \Delta_{vap} G^\ominus(\mathrm{H_2CO, l})$

For $\mathrm{H_2CO(l) \rightleftharpoons H_2CO(g)}$, $K(\mathrm{vap}) = \frac{p}{p^\ominus}$

$$\Delta_{vap} G^\ominus = -RT \ln K(\mathrm{vap}) = -RT \ln \frac{p}{p^\ominus} \quad p^\ominus = 750\,\mathrm{Torr}$$

$$= -(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K}) \times \ln\left(\frac{1500\,\mathrm{Torr}}{750\,\mathrm{Torr}}\right) = -1.72\,\mathrm{kJ\,mol^{-1}}$$

Therefore, for the reaction

$$\mathrm{CO(g) + H_2(g) \rightleftharpoons H_2CO(g)},$$

$$\Delta_r G^\ominus = (+28.95) + (-1.72)\,\mathrm{kJ\,mol^{-1}} = +27.23\,\mathrm{kJ\,mol^{-1}}$$

$$\text{Hence, } K = e^{(-27.23\times 10^3\,\mathrm{J\,mol^{-1}})/(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})} = e^{-10.99} = \boxed{1.69 \times 10^{-5}}$$

P7.8 Draw up the following table using $H_2(g) + I_2 \rightleftharpoons 2HI(g)$

	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

$$K = \frac{\left(\frac{p(\mathrm{HI})}{p^\ominus}\right)^2}{\left(\frac{p(\mathrm{H_2})}{p^\ominus}\right)\left(\frac{p(\mathrm{I_2})}{p^\ominus}\right)} = \frac{x(\mathrm{HI})^2}{x(\mathrm{H_2})x(\mathrm{I_2})}[p(\mathrm{J}) = x_\mathrm{J}p] = \frac{(0.200 + 2x)^2}{(0.300 - x)(0.400 - x)} = 870 \text{ [given]}$$

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 $\boxed{0.007 \text{ mol } \mathrm{H_2}}$, 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 $\Delta_f H^\ominus(\mathrm{HClO})$ from

$$\Delta_r H^\ominus = 2\Delta_f H^\ominus(\mathrm{HClO}) - \Delta_f H^\ominus(\mathrm{Cl_2O}) - \Delta_f H^\ominus(\mathrm{H_2O})$$

We can find $\Delta_r H^\ominus$ if we know $\Delta_r G^\ominus$ and $\Delta_r S^\ominus$, since

$$\Delta_r G^\ominus = \Delta_r H - T\Delta_r S$$

And we can find $\Delta_r G^\ominus$ from the equilibrium constant.

$$K = \exp(-\Delta_r G^\ominus/RT) \quad \text{so} \quad \Delta_r G^\ominus = -RT\ln K,$$

$$\Delta_r G^\ominus = -(8.3145 \times 10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K}) \ln 8.2 \times 10^{-2}$$

$$= 6.2\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta_r H^\ominus = \Delta_r G^\ominus + T\Delta_r S^\ominus$$

$$= 6.2\,\mathrm{kJ\,mol^{-1}} + (298\,\mathrm{K}) \times (16.38 \times 10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}}),$$

$$\Delta_r H^\ominus = 11.1\,\mathrm{kJ\,mol^{-1}}$$

Finally,

$$\Delta_f H^\ominus(\mathrm{HClO}) = \frac{1}{2}[\Delta_r H^\ominus + \Delta_f H^\ominus(\mathrm{Cl_2O}) + \Delta_f H^\ominus(\mathrm{H_2O})],$$

$$\Delta_f H^\ominus(\mathrm{HClO}) = \frac{1}{2}[11.1 + 77.2 + (-241.82)]\,\mathrm{kJ\,mol^{-1}}$$

$$= \boxed{76.8\,\mathrm{kJ\,mol^{-1}}}$$

P7.12 The equilibrium to be considered is (A = gas)

$$A(g, 1\text{ bar}) \rightleftharpoons A(\text{sol'n}) \quad K = \frac{(c/c^{\ominus})}{(p/p^{\ominus})} = \frac{s}{s^{\ominus}}$$

$$\Delta_r H^{\ominus} = -R \times \frac{d \ln K}{d\,(1/T)} \text{ [7.23]}$$

$$\ln K = \ln\left(\frac{s}{s^{\ominus}}\right) = 2.303 \log\left(\frac{s}{s^{\ominus}}\right)$$

$$\Delta_r H^{\ominus}(H_2) = -(2.303) \times (R) \times \frac{d}{d\,(1/T)}\left(-5.39 - \frac{768\text{ K}}{T}\right)$$

$$= 2.303R \times 768\text{ K} = \boxed{+14.7\text{ kJ mol}^{-1}}$$

$$\Delta_r H^{\ominus}(CO) = -(2.303) \times (R) \times \frac{d}{d\,(1/T)}\left(-5.98 - \frac{980\text{ K}}{T}\right)$$

$$= 2.303R \times 980\text{ K} = \boxed{+18.8\text{ kJ mol}^{-1}}$$

P7.14 **(a)** The cell reaction is

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l)$$

$$\Delta_r G^{\ominus} = \Delta_f G^{\ominus}(H_2O, l) = -237.13\text{ kJ mol}^{-1} \text{ [Table 2.7]}$$

$$E^{\ominus} = \frac{\Delta_r G^{\ominus}}{\nu F} \text{ [7.28]} = \frac{+237.13\text{ kJ mol}^{-1}}{(2) \times (96.485\text{ kC mol}^{-1})} = \boxed{+1.23\text{ V}}$$

(b)

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

$$\Delta_f G^{\ominus} = 4\Delta_f G^{\ominus}(CO_2, g) + 5\Delta_f G^{\ominus}(H_2O, l) - \Delta_f G^{\ominus}(C_4H_{10}, g)$$

$$= (4) \times (-394.36) + (5) \times (-237.13) - (-17.03)]\text{ kJ mol}^{-1} \text{ [Table 2.7]}$$

$$= -2746.06\text{ kJ mol}^{-1}$$

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

$$R: \quad \tfrac{13}{2}O_2(g) + 26e^- + 26H^+(aq) \rightarrow 13H_2O(l)$$

$$L: \quad 4CO_2(g) + 26e^- + 26H^+(aq) \rightarrow C_4H_{10}(g) + 8H_2O(l)$$

$$R - L: \quad C_4H_{10}(g) + \tfrac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 8H_2O(l)$$

Hence, $\nu = 26$.

Therefore, $E = \dfrac{-\Delta G^{\ominus}}{\nu F} = \dfrac{+2746.06\text{ kJ mol}^{-1}}{(26) \times (96.485\text{ kC mol}^{-1})} = \boxed{+1.09\text{ V}}$

P7.16 **(a)** $E = E^{\ominus} - \dfrac{25.693\,\text{mV}}{\nu}\ln Q$ [*Illustration* 7.10, 25 °C]

$Q = a(\text{Zn}^{2+})a^2(\text{Cl}^-)$

$= \gamma_+\left(\dfrac{b}{b^{\ominus}}\right)(\text{Zn}^{2+})\gamma_-^2\left(\dfrac{b}{b^{\ominus}}\right)^2(\text{Cl}^-);\ \ b(\text{Zn}^{2+}) = b;\ \ b(\text{Cl}^-) = 2b;\ \ \gamma_+\gamma_-^2 = \gamma_\pm^3$

Therefore, $Q = \gamma_\pm^3 \times 4b^3\ \left[b \equiv \dfrac{b}{b^{\ominus}} \text{ here and below}\right]$

and $E = E^{\ominus} - \dfrac{25.693\,\text{mV}}{2}\ln(4b^3\gamma_\pm^3) = E^{\ominus} - \left(\dfrac{3}{2}\right) \times (25.693\,\text{mV}) \times \ln(4^{1/3}b\gamma_\pm)$

$= \boxed{E^{\ominus} - (38.54\,\text{mV}) \times \ln(4^{1/3}b) - (38.54\,\text{mV})\ln(\gamma_\pm)}$

(b) $E^{\ominus}(\text{Cell}) = E_\text{R}^{\ominus} - E_\text{L}^{\ominus} = E^{\ominus}(\text{Hg}_2\text{Cl}_2,\text{Hg}) - E^{\ominus}(\text{Zn}^{2+},\text{Zn})$

$= (0.2676\,\text{V}) - (-0.7628\,\text{V}) = \boxed{+1.0304\,\text{V}}$

(c) $\Delta_\text{r}G = -\nu FE = -(2) \times (9.6485 \times 10^4\,\text{C mol}^{-1}) \times (1.2272\,\text{V}) = -236.81\,\text{kJ mol}^{-1}$

$\Delta_\text{r}G^{\ominus} = -\nu FE^{\ominus} = -(2) \times (9.6485 \times 10^4\,\text{C mol}^{-1}) \times (1.0304\,\text{V}) = \boxed{-198.84\,\text{kJ mol}^{-1}}$

$\ln K = -\dfrac{\Delta_\text{r}G^{\ominus}}{RT} = \dfrac{1.9884 \times 10^5\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298.15\,\text{K})} = 80.211 \quad K = \boxed{6.84 \times 10^{34}}$

(d) From part (a)

$1.2272\,\text{V} = 1.0304\,\text{V} - (38.54\,\text{mV}) \times \ln(4^{1/3} \times 0.0050) - (38.54\,\text{mV}) \times \ln\gamma_\pm$

$\ln\gamma_\pm = -\dfrac{(1.2272\,\text{V}) - (1.0304\,\text{V}) - (0.186\bar{4}\,\text{V})}{0.03854\,\text{V}} = -0.269\bar{8};\quad \gamma_\pm = \boxed{0.763}$

(e) $\log\gamma_\pm = -|z_-z_+|AI^{1/2}$ [5.69]

$I = \dfrac{1}{2}\sum_i z_i^2\left(\dfrac{b_i}{b^{\ominus}}\right)$ [5.70]

$b(\text{Zn}^{2+}) = b = 0.0050\,\text{mol kg}^{-1} \quad b(\text{Cl}^-) = 2b = 0.010\,\text{mol kg}^{-1}$

$I = \frac{1}{2}[(4) \times (0.0050) + (0.010)] = 0.015$

$\log\gamma_\pm = -(2) \times (0.509) \times (0.015)^{1/2} = -0.12\bar{5};\quad \gamma_\pm = \boxed{0.75}$

This compares remarkably well to the value obtained from experimental data in part (d).

(f) $\Delta_\text{r}S = -\left(\dfrac{\partial\Delta_\text{r}G}{\partial T}\right)_p$

$= \nu F\left(\dfrac{\partial E}{\partial T}\right)_p$ [7.39] $= (2) \times (9.6485 \times 10^4\,\text{C mol}^{-1}) \times (-4.52 \times 10^{-4}\,\text{V K}^{-1})$

$= \boxed{-87.2\,\text{J K}^{-1}\,\text{mol}^{-1}}$

$\Delta_\text{r}H = \Delta_\text{r}G + T\Delta_\text{r}S = (-236.81\,\text{kJ mol}^{-1}) + (298.15\,\text{K}) \times (-87.2\,\text{J K}^{-1}\,\text{mol}^{-1})$

$= \boxed{-262.4\,\text{kJ mol}^{-1}}$

P7.18 $Pt|H_2(g)|NaOH(aq), NaCl(aq)|AgCl(s)|Ag(s)$

$H_2(s) + 2AgCl(s) \rightarrow 2Ag(s) + 2Cl^-(aq) + 2H^+(aq) \quad \nu = 2$

$$E = E^\ominus - \frac{RT}{2F}\ln Q, \quad Q = a(H^+)^2 a(Cl^-)^2 \quad [f/p^\ominus = 1]$$

$$= E^\ominus - \frac{RT}{F}\ln a(H^+)a(Cl) = E^\ominus - \frac{RT}{F}\ln\frac{K_w a(Cl^-)}{a(OH^-)} = E^\ominus - \frac{RT}{F}\ln\frac{K_w\gamma_\pm b(Cl^-)}{\gamma_\pm b(OH^-)}$$

$$= E^\ominus - \frac{RT}{F}\ln\frac{K_w b(Cl^-)}{b(OH^-)} = E^\ominus - \frac{RT}{F}\ln K_w - \frac{RT}{F}\ln\frac{b(Cl^-)}{b(OH^-)}$$

$$= E^\ominus + (2.303)\frac{RT}{F}\times pK_w - \frac{RT}{F}\ln\frac{b(Cl^-)}{b(OH^-)} \quad \left(pK_w = -\log K_w = \frac{-\ln K_w}{2.303}\right)$$

$$\text{Hence, } pK_w = \frac{E - E^\ominus}{2.303RT/F} + \frac{\ln\left(\dfrac{b(Cl^-)}{b(OH^-)}\right)}{2.303} = \frac{E - E^\ominus}{2.303RT/F} + 0.05114$$

$$E^\ominus = E^\ominus_R - E^\ominus_L = E^\ominus(AgCl, Ag) - E^\ominus(H^+/H_2) = +0.22\text{ V} - 0 \quad [\text{Table 7.2}]$$

We then draw up the following table with the more precise value for $E^\ominus = +0.2223$ V [See the solution to Problem 10.8, 7th edition]

$\theta/°C$	20.0	25.0	30.0
E/V	1.04774	1.04864	1.04942
$\dfrac{(2.303RT/F)}{V}$	0.05819	0.05918	0.06018
pK_w	$\boxed{14.23}$	14.01	13.79

$$\frac{d\ln K_w}{dT} = \frac{\Delta_r H^\ominus}{RT^2} \quad [7.23]$$

Hence, $\Delta_r H^\ominus = -(2.303)RT^2\dfrac{d}{dT}(pK_w)$

then with $\dfrac{d\,pK_w}{dT} \approx \dfrac{\Delta pK_w}{\Delta T}$

$$\Delta_r H^\ominus \approx -(2.303)\times(8.314\text{ J K}^{-1}\text{ mol}^{-1})\times(298.15\text{ K})^2\times\frac{13.79 - 14.23}{10\text{ K}}$$

$$= \boxed{+74.9\text{ kJ mol}^{-1}}$$

$$\Delta_r G^\ominus = -RT\ln K_w = 2.303\,RT\times pK_w = \boxed{+80.0\text{ kJ mol}^{-1}}$$

$$\Delta_r S^\ominus = \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T} = \boxed{-17.1\text{ J K}^{-1}\text{ mol}^{-1}}$$

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

$$\tfrac{1}{2}H_2(g) + AgCl(s) \rightarrow Ag(s) + HCl(aq)$$

and then, from the values of these quantities and the known values of $\Delta_f G^\ominus$, $\Delta_f H^\ominus$, and $S^\ominus$, for all the species other than $Cl^-(aq)$, to calculate $\Delta_f G^\ominus$, $\Delta_f H^\ominus$, and $S^\ominus$ for $Cl^-(aq)$.

$$\Delta_r G^\ominus = -\nu F E^\ominus$$

At 298.15 K (25.00 °C)

$$E^\ominus/\mathrm{V} = (0.23659) - (4.8564 \times 10^{-4}) \times (25.00) - (3.4205 \times 10^{-6}) \times (25.00)^2$$
$$+ (5.869 \times 10^{-9}) \times (25.00)^3 = +0.22240\,\mathrm{V}$$

Therefore, $\Delta G^\ominus = -(96.485\,\mathrm{kC\,mol^{-1}}) \times (0.22240\,\mathrm{V}) = -21.46\,\mathrm{kJ\,mol^{-1}}$

$$\Delta_r S^\ominus = -\left(\frac{\partial \Delta_r G^\ominus}{\partial T}\right)_p = \left(\frac{\partial E^\ominus}{\partial T}\right)_p \times \nu F = \nu F \left(\frac{\partial E^\ominus}{\partial \theta}\right)_p \frac{^\circ\mathrm{C}}{\mathrm{K}} \quad [\mathrm{d}\theta/^\circ\mathrm{C} = \mathrm{d}T/K] \qquad \text{(a)}$$

$$\frac{(\partial E^\ominus/\partial\theta)_p}{\mathrm{V}} = (-4.8564 \times 10^{-4}/^\circ\mathrm{C}) - (2) \times (3.4205 \times 10^{-6}\theta/(^\circ\mathrm{C})^2)$$
$$+ (3) \times \left(5.869 \times 10^{-9}\theta^2/(^\circ\mathrm{C})^3\right)$$

$$\frac{(\partial E^\ominus/\partial\theta)_p}{\mathrm{V}/^\circ\mathrm{C}} = \left(-4.8564 \times 10^{-4}\right) - \left(6.8410 \times 10^{-6}\,(\theta/^\circ\mathrm{C})\right) + \left(1.7607 \times 10^{-8}\,(\theta/^\circ\mathrm{C})^2\right)$$

Therefore, at 25.00 °C,

$$\left(\frac{\partial E^\ominus}{\partial \theta}\right)_p = -6.4566 \times 10^{-4}\,\mathrm{V}/^\circ\mathrm{C}$$

and

$$\left(\frac{\partial E^\ominus}{\partial T}\right)_p = (-6.4566 \times 10^{-4}\,\mathrm{V}/^\circ\mathrm{C}) \times (^\circ\mathrm{C}/\mathrm{K}) = -6.4566 \times 10^{-4}\,\mathrm{V\,K^{-1}}$$

Hence, from equation (a)

$$\Delta_r S^\ominus = (-96.485\,\mathrm{kC\,mol^{-1}}) \times (6.4566 \times 10^{-4}\,\mathrm{V\,K^{-1}}) = -62.30\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

and $\Delta_r H^\ominus = \Delta_r G^\ominus + T\Delta_r S^\ominus$

$$= -(21.46\,\mathrm{kJ\,mol^{-1}}) + (298.15\,\mathrm{K}) \times (-62.30\,\mathrm{J\,K^{-1}mol^{-1}}) = -40.03\,\mathrm{kJ\,mol^{-1}}$$

For the cell reaction

$$\tfrac{1}{2}H_2(g) + AgCl(s) \rightarrow Ag(s) + HCl(aq)$$

$$\Delta_r G^\ominus = \Delta_f G^\ominus(H^+) + \Delta_f G^\ominus(Cl^-) - \Delta_f G^\ominus(AgCl)$$
$$= \Delta_f G^\ominus(Cl^-) - \Delta_f G^\ominus(AgCl) \quad \left[\Delta_f G^\ominus(H^+) = 0\right]$$

Hence, $\Delta_f G^{\ominus}(Cl^-) = \Delta_r G^{\ominus} + \Delta_f G^{\ominus}(AgCl) = [(-21.46) - (109.79)\,kJ\,mol^{-1}]$

$$= \boxed{-131.25\,kJ\,mol^{-1}}$$

Similarly, $\Delta_f H^{\ominus}(Cl^-) = \Delta_r H^{\ominus} + \Delta_f H^{\ominus}(AgCl) = (-40.03) - (127.07\,kJ\,mol^{-1})$

$$= \boxed{-167.10\,kJ\,mol^{-1}}$$

For the entropy of Cl^- in solution we use

$$\Delta_r S^{\ominus} = S^{\ominus}(Ag) + S^{\ominus}(H^+) + S^{\ominus}(Cl^-) - \tfrac{1}{2}S^{\ominus}(H_2) - S^{\ominus}(AgCl)$$

with $S^{\ominus}(H^+) = 0$. Then,

$$S^{\ominus}(Cl^-) = \Delta_r S^{\ominus} - S^{\ominus}(Ag) + \tfrac{1}{2}S^{\ominus}(H_2) + S^{\ominus}(AgCl)$$

$$= (-62.30) - (42.55) + \left(\tfrac{1}{2}\right) \times (130.68) + (96.2) = \boxed{+56.7\ J\,K^{-1}\,mol^{-1}}$$

P7.22 Electrochemical cell equation:

$$\tfrac{1}{2}H_2(g, 1\,bar) + AgCl(s) \rightleftharpoons H^+(aq) + Cl^-(aq) + Ag(s)$$

where $f(H_2) = 1\,bar = p^{\ominus} a_{Cl^-} = \gamma_{Cl^-} b$

Weak acid equilibrium:

$$BH^+ \rightleftharpoons B + H^+$$

where $b_{BH} = b_B = b$

and $K_a = a_B a_{H^+}/a_{BH} = \gamma_B\, b\, a_{H^+}/\gamma_{BH}\, b = \gamma_B\, a_{H^+}/\gamma_{BH}$

or $a_H = \gamma_{BH} K_a/\gamma_B$

Ionic strength (neglect b_{H^+} because $b_{H^+} \ll b$):

$$I = \frac{1}{2}\{z_{BH}^2 b_{BH} + z_{Cl^-}^2 b_{Cl^-}\} = b$$

according to the Nernst equation [7.29]

$$E = E^{\ominus} - \frac{RT}{F}\ln\left(\frac{a_H + a_{Cl^-}}{f(H_2/p^{\ominus}}\right) = E^{\ominus} - \frac{RT\ \ln(10)}{F}\log(a_H + a_{Cl^-})$$

$$\frac{F}{RT\ln(10)}(E - E^{\ominus}) = -\log(a_{H^+}\gamma_{Cl^-} b) = -\log\left(\frac{K_a \gamma_{BH}\gamma_{Cl^-} b}{\gamma_B}\right)$$

$$= pK_a - \log(b) - 2\log(\gamma_{\pm})$$

$$\frac{F}{RT\ln(10)}(E - E^{\ominus}) = pK_a - \log(b) + \frac{2A\sqrt{b}}{1 + B\sqrt{b}} - 2kb$$

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.

$$\boxed{\begin{array}{l} pK_a = 6.736, \quad B = 1.997\,\text{kg}^{0.5}\text{mol}^{-0.5} \\ k = -0.121\,\text{kg mol}^{-1} \end{array}}$$

$$\gamma_\pm = 10^{\left(\frac{-AI^{1/2}}{1+BI^{1/2}}+kb\right)}$$

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 Ka.

$$K_a = \frac{a_{H^+}a_{F-}}{a_{HF}}, \quad a_{F-} = \frac{K_a a_{HF}}{a_{H^+}} = \frac{3.5\times10^{-4}a_{HF}}{a_{H^+}}$$

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 $E - E_{ap}$

$[F^-]\backslash$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 pH $\leq$ 8 the emf responds linearly to log a_{F-}. At pH = 5 and below, the ratio

$$\frac{a_{HF}}{a_{F^-}} = \frac{a_{H^+}}{K_a} = \frac{a_{H^+}}{3.5\times10^{-4}} = \frac{10^{-5}}{3.5\times10^{-4}} = 0.029$$

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

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

$$\Delta_r H' = \Delta_r H + \int_T^{T'} \Delta_r C_p \mathrm{d}T \ [2.36]$$

$$\Delta_r S' = \Delta_r S + \int_T^{T'} \frac{\Delta_r C_p}{T} \mathrm{d}T \ [3.19, \text{with } \Delta_r S \text{ in place of } S]$$

$$\Delta_r G' = \Delta_r G + \int_T^{T'} \Delta_r C_p \, \mathrm{d}T + (T - T')\Delta_r S - T' \int_T^{T'} \frac{\Delta_r C_p}{T} \mathrm{d}T$$

$$= \Delta_r G + (T - T')\Delta_r S + \int_T^{T'} \left(1 - \frac{T'}{T}\right) \Delta_r C_p \, \mathrm{d}T$$

$$\Delta_r C_p = \Delta a + T\Delta b + \frac{\Delta c}{T^2}$$

$$\left(1 - \frac{T'}{T}\right) \Delta_r C_p = \Delta a + T\Delta b + \frac{\Delta c}{T^2} - \frac{T'\Delta a}{T} - T'\Delta b - \frac{T'\Delta c}{T^3}$$

$$= \Delta a - T'\Delta b + T\Delta b - \frac{T'\Delta a}{T} + \frac{\Delta c}{T^2} - \frac{T'\Delta c}{T^3}$$

$$\int_T^{T'} \left(1 - \frac{T'}{T}\right) \Delta_r C_p \, \mathrm{d}T = (\Delta a - T'\Delta b)(T' - T) + \frac{1}{2}(T'^2 - T^2)\Delta b - T'\Delta a \ln \frac{T'}{T}$$

$$+ \Delta c \left(\frac{1}{T} - \frac{1}{T'}\right) - \frac{1}{2}T'\Delta c \left(\frac{1}{T^2} - \frac{1}{T'^2}\right)$$

Therefore, $\boxed{\Delta_r G' = \Delta_r G + (T - T')\Delta_r S + \alpha\Delta a + \beta\Delta b + \gamma\Delta c}$

where $\alpha = T' - T - T' \ln \dfrac{T'}{T}$

$$\beta = \frac{1}{2}(T'^2 - T^2) - T'(T' - T)$$

$$\gamma = \frac{1}{T} - \frac{1}{T'} + \frac{1}{2}T'\left(\frac{1}{T'^2} - \frac{1}{T^2}\right)$$

For water,

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta_f G^\ominus(T) = -237.13 \text{ kJ mol}^{-1}$$

$$\Delta_r S^\ominus(T) = -163.34 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta a = a(\mathrm{H_2O}) - a(\mathrm{H_2}) - \frac{1}{2}a(\mathrm{O_2}) = (75.29 - 27.88 - 14.98)\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

$$= +33.03\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

$$\Delta b = [(0) - (3.26\times 10^{-3}) - (2.09\times 10^{-3})]\,\mathrm{J\,K^{-2}\,mol^{-1}} = -5.35\times 10^{-3}\,\mathrm{J\,K^{-2}\,mol^{-1}}$$

$$\Delta c = [(0) - (0.50\times 10^{5}) + (0.83\times 10^{5})]\,\mathrm{J\,K\,mol^{-1}} = +0.33\times 10^{5}\,\mathrm{J\,K\,mol^{-1}}$$

$$T = 298\,\mathrm{K}, \qquad T' = 372\,\mathrm{K},\ \text{so}$$

$$\alpha = -8.5\,\mathrm{K}, \qquad \beta = -2738\,\mathrm{K^2}, \qquad \gamma = -8.288\times 10^{-5}\,\mathrm{K^{-1}}$$

and so

$$\begin{aligned}\Delta_f G^{\ominus}(372\,\mathrm{K}) &= (-237.13\,\mathrm{kJ\,mol^{-1}}) + (-74\,\mathrm{K})\times(-163.34\,\mathrm{J\,K^{-1}\,mol^{-1}}) \\ &\quad + (-8.5\,\mathrm{K})\times(33.03\times 10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}}) \\ &\quad + (-2738\,\mathrm{K^2})\times(-5.35\times 10^{-6}\,\mathrm{kJ\,K^{-2}\,mol^{-1}}) \\ &\quad + (-8.288\times 10^{-5}\,\mathrm{K^{-1}})\times(0.33\times 10^{2}\,\mathrm{kJ\,K\,mol^{-1}}) \\ &= [(-237.13) + (12.09) - (0.28) + (0.015) - (0.003)]\,\mathrm{kJ\,mol^{-1}} \\ &= \boxed{-225.31\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

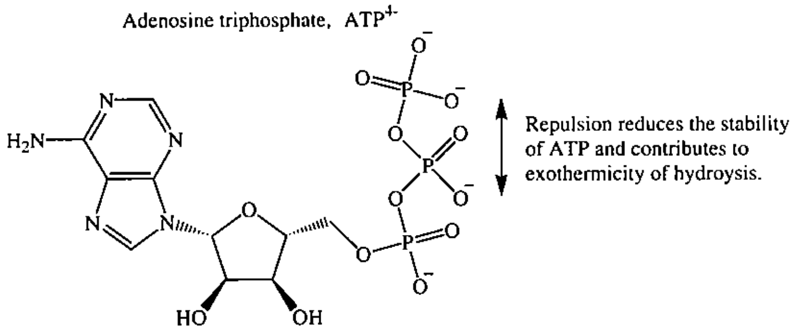
Note that the β and γ terms are not significant (for this reaction and temperature range).

Solutions to applications

P7.28 (a) ATP hydrolysis at physiological pH, $\mathrm{ATP(aq)+H_2O(l)} \rightarrow \mathrm{ADP(aq)+P_i^-(aq)+H_3O^+(aq)}$, 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 $\mathrm{ATP^{4-}}$. The electrostatic repulsions between the highly charged oxygen atoms of $\mathrm{ATP^{4-}}$ is expected to give it an exergonic hydrolysis free energy by making the hydrolysis enthalpy negative. Also, the deprotonated phosphate species, $\mathrm{P_i(aq)}$, produced in the hydrolysis ATP has more resonance structures than $\mathrm{ATP^{4-}}$. 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 $\mathrm{ATP^{4-}}$ is a hypothesis that is consistent with the observation that protonated ATP, $\mathrm{H_4ATP}$, has an exergonic hydrolysis free energy of smaller magnitude because the negative repulsions of oxygen atoms are not present. Likewise for $\mathrm{MgATP^{2-}}$ because the $\mathrm{Mg^{2+}}$ ion lies between negatively charged oxygen atoms, thereby, reducing repulsions and stabilizing the ATP molecule.



P7.30 Refer to *Impact* I7.2 for information necessary to the solution of this problem. The biological standard value of the Gibbs energy for ATP hydrolysis is $\approx -30\,\mathrm{kJ\,mol^{-1}}$. The standard Gibbs energy of combustion of glucose is $-2880\,\mathrm{kJ\,mol^{-1}}$.

(a) If we assume that each mole of ATP formed during the aerobic breakdown of glucose produces about $-30\,\mathrm{kJ\,mol^{-1}}$, then

$$\text{efficiency} = \frac{38 \times (-30\,\mathrm{kJ\,mol^{-1}})}{-2880\,\mathrm{kJ\,mol^{-1}}} \times 100\% \approx \boxed{40\%}$$

(b) For the oxidation of glucose under the biological conditions of
$p_{CO_2} = 5.3 \times 10^{-2}\,\mathrm{atm}$ $\quad p_{O_2} = 0.132\,\mathrm{atm}$, and $[\text{glucose}] = 5.6 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ we have

$$\Delta_r G' = \Delta_r G^{\ominus} + RT \ln Q$$

where $$Q = \frac{(p_{CO_2}/p^{\ominus})^6}{[\text{glucose}] \times (p_{O_2}/p^{\ominus})^9} = \frac{(5.3 \times 10^{-2})^6}{5.6 \times 10^{-2} \times (0.132)^9}$$

$$= 32.\bar{5}$$

Then

$$\Delta_r G' = -2880\,\mathrm{kJ\,mol^{-1}} + 8.314\,\mathrm{J\,K^{-1}\,mol^{-1}} \times 310\,\mathrm{K} \times \ln(32.\bar{5})$$

$$= \boxed{-2871\,\mathrm{kJ\,mol^{-1}}}$$

which is not much different from the standard value.

For the ATP $\rightarrow$ ADP conversion under the given conditions

$$\Delta_r G' = \Delta_r G^{\ominus} + RT \ln \frac{Q'}{Q^{\ominus}}$$

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 $14.8\,\text{kJ mol}^{-1}$.

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).

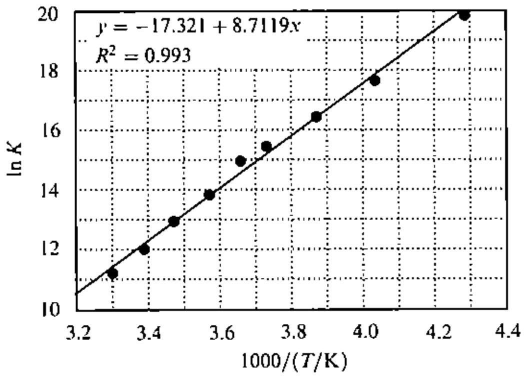


Figure 7.1

$$\text{So } \Delta_r H^\ominus = -R \times \text{slope} = -\left(8.3145 \times 10^{-3}\,\text{kJ mol}^{-1}\,\text{K}^{-1}\right) \times \left(8.71 \times 10^3\,\text{K}\right)$$

$$= \boxed{-72.4\,\text{kJ mol}^{-1}}$$

$$\text{and } \Delta_r S^\ominus = R \times \text{intercept} = \left(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}\right) \times (-17.3) = \boxed{-144\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

(b) $\Delta_r H^\ominus = \Delta_r H^\ominus\,((\text{ClO})_2) - 2\Delta_f H^\ominus\,(\text{ClO})$ so $\Delta_f H^\ominus\,((\text{ClO})_2) = \Delta_r H^\ominus + 2\Delta_f H^\ominus\,(\text{ClO})$,

$$\Delta_f H^\ominus\,((\text{ClO})_2) = [-72.4 + 2\,(101.8)]\,\text{kJ mol}^{-1} = \boxed{+131.2\,\text{kJ mol}^{-1}}$$

$$S^\ominus\,((\text{ClO})_2) = [-144 + 2\,(226.6)]\,\text{J K}^{-1}\,\text{mol}^{-1} = \boxed{+309.2\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

P7.36 $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$; $\Delta\nu = -1/2$

First, calculate the standard reaction thermodynamic functions with formation thermodynamic properties found in the appendix (Table 2.7).

$$\Delta_r H^\ominus(298) = -46.11\,\text{kJ} \qquad \text{and} \qquad \Delta_r S^\ominus(298) = -99.38\,\text{J K}^{-1}$$

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).

$$\Delta_r H^\ominus(T) = \Delta_r H^\ominus(298) + \int_{298.15\,\text{K}}^{T} \Delta_r C_p^\ominus(T)\text{d}T$$

$$\Delta_r S^\ominus(T) = \Delta_r S^\ominus(298) + \int_{298.15\,\text{K}}^{T} \frac{\Delta_r C_p^\ominus(T)}{T}\text{d}T$$

For a prefect 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:

$$\begin{aligned}
\Delta_r S(T_p) &= \Delta_r S^{\ominus}(T) + \sum_{\text{Products}-\text{Reactants}} \nu \int_{1\,\text{bar}}^{p} \left(\frac{\partial S_m}{\partial p}\right)_T \mathrm{d}P \\
&= \Delta_r S^{\ominus}(T) - \sum_{\text{Products}-\text{Reactants}} \nu \int_{1\,\text{bar}}^{p} \left(\frac{\partial V_m}{\partial T}\right)_p \mathrm{d}P \text{ [Table 3.5]} \\
&= \Delta_r S^{\ominus}(T) - \sum_{\text{Products}-\text{Reactants}} \nu \int_{1\,\text{bar}}^{p} \frac{R}{p} \mathrm{d}p \\
&= \Delta_r S^{\ominus}(T) - \left[\sum_{\text{Products}-\text{Reactants}} \nu\right] R \ln\left(\frac{p}{1\text{bar}}\right) \\
&= \Delta_r S^{\ominus}(T) - 1/2 R \ln\left(\frac{p}{1\text{bar}}\right)
\end{aligned}$$

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:

$$\text{For } T = (450 + 273.15)\,\text{K} = 723.15\,\text{K}, \text{root}(\Delta_r G(723.15\,\text{K}, p) + 500\,\text{J}) = \boxed{156.5\,\text{bar}}$$

$$\text{For } T = (400 + 273.15)\,\text{K} = 673.15\,\text{K}, \text{root}(\Delta_r G(673.15\,\text{K}, p) + 500\,\text{J}) = \boxed{81.8\,\text{bar}}$$

For a van der Waals gas mixture $\Delta_r H$ does depend upon pressure. The calculational equation is:

$$\begin{aligned}
\Delta_r H(T,P) &= \Delta_r H^{\ominus}(T) + \sum_{\text{Products}-\text{Reactants}} \nu \int_{1\,\text{bar}}^{p} \left(\frac{\partial H_m}{\partial p}\right)_T \mathrm{d}p \\
&= \Delta_r H^{\ominus}(T) + \sum_{\text{Products}-\text{Reactants}} \nu \int_{1\,\text{bar}}^{p} \left[V_m - T\left(\frac{\partial H_m}{\partial p}\right)_p\right] \mathrm{d}p
\end{aligned}$$

[Theoretical Problem 3.28]

where $(\partial V_m/\partial T)_p = R(V_m - b)^{-1}(RT(V_m - b)^{-2} - 2aV_m^{-3})^{-1}$

and $V_m(T,p) = \text{root}\left(P - \dfrac{RT}{V_m - b} + \dfrac{a}{V_m^2}\right)$

The functional equation for $\Delta_r S$ calculations is:

$$\Delta_r S(T,P) = \Delta_r S^{\ominus}(T) - \sum_{\text{Products}-\text{Reactants}} \nu \int_{1\,\text{bar}}^{p} \left(\frac{\partial V_m}{\partial T}\right)_p \mathrm{d}p$$

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:

$$\text{For } T = 723.15\,\text{K},\ \ \text{root}(\Delta_r G(723.15\,\text{K}, p) + 500\,\text{J}) = \boxed{132.5\,\text{bar}}$$

$$\text{For } T = 673.15\,\text{K},\ \ \text{root}(\Delta_r G(673.15\,\text{K}, p) + 500\,\text{J}) = \boxed{73.7\,\text{bar}}$$

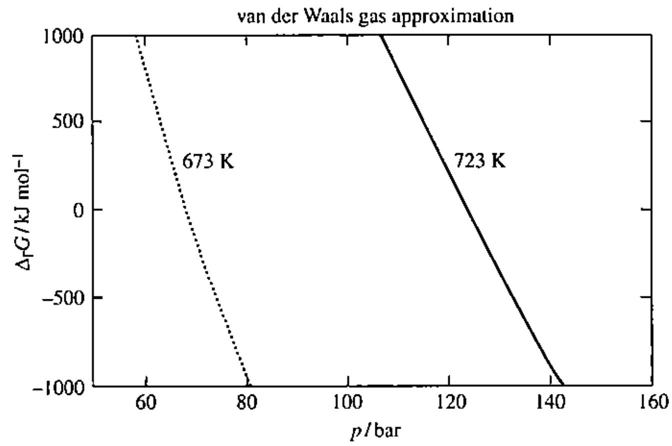


Figure 7.2

(c) $\Delta_r G(T, p)$ isotherms $\boxed{\text{confirm}}$ Le Chatelier's principle. Along an isotherm, $\Delta_r G$ decreases as pressure increases. This corresponds to a shift to the right in the reaction equation and reduces the stress by shifting to the side that has fewer total moles of gas. Additionally the reaction is exothermic, so Chatelier's principle predicts a shift to the left with an increase in temperature. The isotherms confirm this as an increase in $\Delta_r G$ as temperature is increased at constant pressure. 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 $\lambda \to 0$. Classical theory predicts the opposite. However, if we assume, as did Planck, that the energy of the oscillators that constitute electromagnetic radiation are quantized according to the relation $E = nh\nu = nhc/\lambda$, we see that at short wavelengths the energy of the oscillators is very large. This energy is too large for the walls to supply it, so the short-wavelength oscillators remain unexcited. The effect of quantization is to reduce the contribution to the total energy emitted by the black-body from the high-energy short-wavelength oscillators, for they cannot be sufficiently excited with the energy available.

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.

$$(\Omega) = \int \Psi^*\Omega\Psi \mathrm{d}\tau.$$

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

$$\Delta p \Delta x \geq \tfrac{1}{2}\hbar$$

so the minimum uncertainty in position is

$$\Delta x = \frac{\hbar}{2\Delta p} = \frac{\hbar}{2m\Delta v} = \frac{1.0546 \times 10^{-34}\,\text{J s}}{2(9.11 \times 10^{-31}\,\text{kg}) \times (0.000\,010) \times (995 \times 10^{3}\,\text{m s}^{-1})}$$

$$= \boxed{5.8 \times 10^{-6}\,\text{m}}$$

E8.4(b) $E = h\nu = \dfrac{hc}{\lambda}$; $E(\text{per mole}) = N_A E = \dfrac{N_A hc}{\lambda}$

$$hc = (6.626\,08 \times 10^{-34}\,\text{J s}) \times (2.997\,92 \times 10^{8}\,\text{m s}^{-1}) = 1.986 \times 10^{-25}\,\text{J m}$$

$$N_A hc = (6.022\,14 \times 10^{23}\,\text{mol}^{-1}) \times (1.986 \times 10^{-25}\,\text{J m}) = 0.1196\,\text{J m mol}^{-1}$$

Thus, $E = \dfrac{1.986 \times 10^{-25}\,\text{J m}}{\lambda}$; $E(\text{per mole}) = \dfrac{0.1196\,\text{J m mol}^{-1}}{\lambda}$

We can therefore draw up the following table

λ	E/J	$E/(\text{kJ mol}^{-1})$
(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 ^{4}He atom is free and stationary, if a photon is absorbed, the atom acquires its momentum p achieving a speed v such that $p = mv$.

$$v = \frac{p}{m} \quad m = 4.00 \times 1.6605 \times 10^{-27}\,\text{kg} = 6.64\bar{2} \times 10^{-27}\,\text{kg}$$

$$p = \frac{h}{\lambda}$$

(a) $$p = \frac{6.626 \times 10^{-34}\,\text{J s}}{200 \times 10^{-9}\,\text{m}} = 3.31\bar{3} \times 10^{-27}\,\text{kg m s}^{-1}$$

$$v = \frac{p}{m} = \frac{3.31\bar{3} \times 10^{-27}\,\text{kg m s}^{-1}}{6.642 \times 10^{-27}\,\text{kg}} = \boxed{0.499\,\text{m s}^{-1}}$$

(b) $$p = \frac{6.626 \times 10^{-34}\,\text{J s}}{150 \times 10^{-12}\,\text{m}} = 4.41\bar{7} \times 10^{-24}\,\text{kg m s}^{-1}$$

$$v = \frac{p}{m} = \frac{4.41\bar{7} \times 10^{-27}\,\text{kg m s}^{-1}}{6.642 \times 10^{-27}\,\text{kg}} = \boxed{665\ \text{m s}^{-1}}$$

(c) $$p = \frac{6.626 \times 10^{-34}\,\text{J s}}{1.00 \times 10^{-2}\,\text{m}} = 6.626 \times 10^{-32}\,\text{kg m s}^{-1}$$

$$v = \frac{p}{m} = \frac{6.626 \times 10^{-32}\,\text{kg m s}^{-1}}{6.642 \times 10^{-27}\,\text{kg}} = \boxed{9.98 \times 10^{-6}\,\text{m s}^{-1}}$$

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) $$\text{rate} = \frac{P\lambda}{hc} = \frac{(0.10\,\text{W}) \times (700 \times 10^{-9}\,\text{m})}{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^8\,\text{m s}^{-1})} = \boxed{3.52 \times 10^{17}\ \text{s}^{-1}}$$

(b) $$\text{rate} = \frac{(1.0\,\text{W}) \times (700 \times 10^{-9}\,\text{J s})}{(6.626 \times 10^{-34}\,\text{J s}) \times (2.998 \times 10^8\,\text{m s}^{-1})} = \boxed{3.52 \times 10^{18}\ \text{s}^{-1}}$$

E8.8(b) Conservation of energy requires

$$E_{\text{photon}} = \Phi + E_{\text{K}} = h\nu = hc/\lambda \quad \text{so} \quad E_{\text{K}} = hc/\lambda - \Phi$$

$$\text{and } E_{\text{K}} = \tfrac{1}{2}m_{\text{e}}v^2 \quad \text{so} \quad v = \left(\frac{2E_{\text{K}}}{m_{\text{e}}}\right)^{1/2}$$

(a) $E_K = \dfrac{(6.626 \times 10^{-34}\,\mathrm{J\,s}) \times (2.998 \times 10^{8}\,\mathrm{m\,s^{-1}})}{650 \times 10^{-9}\,\mathrm{m}} - (2.09\,\mathrm{eV}) \times (1.60 \times 10^{-19}\,\mathrm{J\,eV^{-1}})$

But this expression is negative, which is unphysical. There is no kinetic energy or velocity because the photon does not have enough energy to dislodge the electron.

(b) $E_K = \dfrac{(6.626 \times 10^{-34}\,\mathrm{J\,s}) \times (2.998 \times 10^{8}\,\mathrm{m\,s^{-1}})}{195 \times 10^{-9}\,\mathrm{m}} - (2.09\,\mathrm{eV}) \times (1.60 \times 10^{-19}\,\mathrm{J\,eV^{-1}})$

$$= \boxed{6.84 \times 10^{-19}\,\mathrm{J}}$$

and $v = \left(\dfrac{2(6.84 \times 10^{-19}\mathrm{J})}{9.11 \times 10^{-31}\,\mathrm{kg}}\right)^{1/2} = \boxed{1.23 \times 10^{6}\ \mathrm{m\ s^{-1}}}$

E8.9(b) $E = h\nu = h/\tau$, so

(a) $E = 6.626 \times 10^{-34}\,\mathrm{J\,s}/2.50 \times 10^{-15}\,\mathrm{s} = \boxed{2.65 \times 10^{-19}\ \mathrm{J} = 160\ \mathrm{kJ\ mol^{-1}}}$

(b) $E = 6.626 \times 10^{-34}\,\mathrm{J\,s}/2.21 \times 10^{-15}\,\mathrm{s} = \boxed{3.00 \times 10^{-19}\ \mathrm{J} = 181\ \mathrm{kJ\ mol^{-1}}}$

(c) $E = 6.626 \times 10^{-34}\mathrm{J\,s}/1.0 \times 10^{-3}\,\mathrm{s} = \boxed{6.62 \times 10^{-31}\ \mathrm{J} = 4.0 \times 10^{-10}\ \mathrm{kJ\ mol^{-1}}}$

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) $\lambda = \dfrac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{(2(9.11 \times 10^{-31}\,\mathrm{kg}) \times (100\,\mathrm{eV}) \times (1.60 \times 10^{-19}\,\mathrm{J\,eV^{-1}}))^{1/2}}$

$$= \boxed{1.23 \times 10^{-10}\,\mathrm{m}}$$

(b) $\lambda = \dfrac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{(2(9.11 \times 10^{-31}\,\mathrm{kg}) \times (1.0 \times 10^{3}\,\mathrm{eV}) \times (1.60 \times 10^{-19}\,\mathrm{J\,eV^{-1}}))^{1/2}}$

$$= \boxed{3.9 \times 10^{-11}\,\mathrm{m}}$$

(c) $\lambda = \dfrac{6.626 \times 10^{-34}\,\mathrm{J\,s}}{(2(9.11 \times 10^{-31}\,\mathrm{kg}) \times (100 \times 10^{3}\,\mathrm{eV}) \times (1.60 \times 10^{-19}\,\mathrm{J\,eV^{-1}}))^{1/2}}$

$$= \boxed{3.88 \times 10^{-12}\,\mathrm{m}}$$

E8.11(b) The upper sign in the following equations represents the math using the $\hat{A} + \mathrm{i}\hat{B}$ operator. The lower sign is for the $\hat{A} - \mathrm{i}\hat{B}$ operator. τ is a generalized coordinate.

$$\begin{aligned}
\int \psi_i^* |\hat{A} \pm \mathrm{i}\hat{B}|\psi_j \mathrm{d}\tau &= \int \psi_i^* |\hat{A}|\psi_j \mathrm{d}\tau \pm \mathrm{i} \int \psi_i^* |\hat{B}|\psi_j \mathrm{d}\tau \\
&= \left\{\int \psi_j^* |\hat{A}|\psi_i \mathrm{d}\tau\right\}^* \pm \mathrm{i} \left\{\int \psi_j^* |\hat{B}|\psi_i \mathrm{d}\tau\right\}^* \quad \hat{A} \text{ and } \hat{B} \text{ are hermitian [8.30]} \\
&= \left\{\int \psi_j^* |\hat{A}|\psi_i \mathrm{d}\tau \mp \mathrm{i} \int \psi_j^* |\hat{B}|\psi_i \mathrm{d}\tau\right\}^* \\
&= \left\{\int \psi_j^* |\hat{A} \mp \mathrm{i}\hat{B}|\psi_i \mathrm{d}\tau\right\}^*
\end{aligned}$$

This shows that the $\hat{A} \pm \mathrm{i}\hat{B}$ operators are not hermitian. If they were hermitian, the result would be $\left\{\int \psi_j^* |\hat{A} \pm \mathrm{i}\hat{B}|\psi_i \mathrm{d}\tau\right\}^*$.

E8.12(b) The minimum uncertainty in position is $\boxed{100 \text{ pm}}$. Therefore, since $\Delta x \Delta p \geq \frac{1}{2}\hbar$

$$\Delta p \geq \frac{\hbar}{2\Delta x} = \frac{1.0546 \times 10^{-34}\,\mathrm{J\,s}}{2(100 \times 10^{-12}\,\mathrm{m})} = 5.3 \times 10^{-25}\,\mathrm{kg\,m\,s^{-1}}$$

$$\Delta v = \frac{\Delta p}{m} = \frac{5.3 \times 10^{-25}\,\mathrm{kg\,m\,s^{-1}}}{9.11 \times 10^{-31}\,\mathrm{kg}} = \boxed{5.8 \times 10^5\ \mathrm{m\ s^{-1}}}$$

E8.13(b) Conservation of energy requires

$$E_{\text{photon}} = E_{\text{binding}} + \tfrac{1}{2}m_e v^2 = h\nu = hc/\lambda \quad \text{so} \quad E_{\text{binding}} = hc/\lambda - \tfrac{1}{2}m_e v^2$$

$$\begin{aligned}
\text{and } E_{\text{binding}} &= \frac{(6.626 \times 10^{-34}\,\mathrm{J\,s}) \times (2.998 \times 10^8\,\mathrm{m\,s^{-1}})}{121 \times 10^{-12}\,\mathrm{m}} \\
&\quad - \tfrac{1}{2}(9.11 \times 10^{-31}\,\mathrm{kg}) \times (5.69 \times 10^7\,\mathrm{m\,s^{-1}})^2 \\
&= \boxed{1.67 \times 10^{-16}\ \mathrm{J}}
\end{aligned}$$

COMMENT. This calculation uses the non-relativistic kinetic energy, which is only about 3 percent less than the accurate (relativistic) value of 1.52×10^{-15} J. In this exercise, however, E_{binding} is a small difference of two larger numbers, so a small error in the kinetic energy results in a larger error in E_{binding}: the accurate value is $E_{\text{binding}} = 1.26 \times 10^{-16}$ J.

E8.14(b) The quality $\hat{\Omega}_1\hat{\Omega}_2 - \hat{\Omega}_2\hat{\Omega}_1$ [*Illustration* 8.3] is referred to as the commutator of the operators $\hat{\Omega}_1$ and $\hat{\Omega}_2$. In obtaining the commutator it is necessary to realize that the operators operate on functions; thus, we form

$$\hat{\Omega}_1\hat{\Omega}_2 f(x) - \hat{\Omega}_2\hat{\Omega}_1 f(x)$$

$$p_x = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}$$

Therefore $a = \left(\hat{x} + \hbar\dfrac{\mathrm{d}}{\mathrm{d}x}\right)$ and $a^\dagger = \left(\hat{x} - \hbar\dfrac{\mathrm{d}}{\mathrm{d}x}\right)$

Then $aa^{\dagger}f(x) = \frac{1}{2}\left(\hat{x} + \hbar\frac{\mathrm{d}}{\mathrm{d}x}\right) \times \left(\hat{x} - \hbar\frac{\mathrm{d}}{\mathrm{d}x}\right)f(x)$

and $a^{\dagger}af(x) = \frac{1}{2}\left(\hat{x} - \hbar\frac{\mathrm{d}}{\mathrm{d}x}\right) \times \left(\hat{x} + \hbar\frac{\mathrm{d}}{\mathrm{d}x}\right)f(x)$

The terms in $\hat{x}^2$ and $(\mathrm{d}/\mathrm{d}x)^2$ obviously drop out when the difference is taken and are ignored in what follows; thus

$$aa^{\dagger}f(x) = \frac{1}{2}\left(-\hat{x}\hbar\frac{\mathrm{d}}{\mathrm{d}x} + \hbar\frac{\mathrm{d}}{\mathrm{d}x}x\right)f(x)$$

$$a^{\dagger}af(x) = \frac{1}{2}\left(x\hbar\frac{\mathrm{d}}{\mathrm{d}}x - \hbar\frac{\mathrm{d}}{\mathrm{d}x}x\right)f(x)$$

These expressions are the negative of each other, therefore

$$(aa^{\dagger} - a^{\dagger}a)f(x) = \hbar\frac{\mathrm{d}}{\mathrm{d}x}\hat{x}f(x) - \hbar\hat{x}\frac{\mathrm{d}}{\mathrm{d}x}f(x)$$

$$= \hbar\left(\frac{\mathrm{d}}{\mathrm{d}x}\hat{x} - \hat{x}\frac{\mathrm{d}}{\mathrm{d}x}\right)f(x) = \hbar f(x)$$

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.

$\theta/°\mathrm{C}$	1000	1500	2000	2500	3000	3500
T/K	1273	1773	2273	2773	3273	3773
$\lambda_{\max}/\mathrm{nm}$	2181	1600	1240	1035	878	763
$\lambda_{\max}T\,/\,(10^6\,\mathrm{nm\,K})$	2.776	2.837	2.819	2.870	2.874	2.879

The mean is 2.84×10^6 nm K with a standard deviation of 0.04×10^6 nm K

and $h = \dfrac{(5) \times (1.38066 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (2.84 \times 10^{-3}\,\mathrm{m\,K})}{2.99792 \times 10^{8}\,\mathrm{m\,s^{-1}}} = \boxed{6.54 \times 10^{-34}\,\mathrm{J\,s}}$

COMMENT. Planck's estimate of the constant h in his first paper of 1900 on black body radiation was 6.55×10^{-27} erg sec(1 erg $= 10^{-7}$ J) which is remarkably close to the current value of 6.626×10^{-34} 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

$$P(a,b) = \int_a^b \psi^2 \mathrm{d}x \text{ [Section 8.4]}$$

$$= \frac{2}{L}\int_a^b \sin^2\frac{\pi x}{L}\mathrm{d}x = \left(\frac{x}{L} - \frac{1}{2\pi}\sin\frac{2\pi x}{L}\right)\Bigg|_a^b$$

$$= \frac{b-a}{L} - \frac{1}{2\pi}\left(\sin\frac{2\pi b}{L} - \sin\frac{2\pi a}{L}\right)$$

$L = 10.0\,\mathrm{nm}$

(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) $$P(9.90, 10.0) = \frac{0.10}{10.0} - \frac{1}{2\pi}\left(\sin\frac{(2\pi)\times(10.0)}{10.0} - \sin\frac{(2\pi)\times(9.90)}{10.0}\right)$$

$$= 0.010 - 0.009993 = \boxed{7\times10^{-6}}$$

(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:

$$\langle\phi\rangle = \int \psi^*\phi\psi\,\mathrm{d}\tau = \int_0^{2\pi} \frac{\mathrm{e}^{im\phi}}{(2\pi)^{1/2}}\phi\frac{\mathrm{e}^{-im\phi}}{(2\pi)^{1/2}}\,\mathrm{d}\phi = \frac{1}{2\pi}\int_0^{2\pi}\phi\,\mathrm{d}\phi = \frac{1}{2\pi}\frac{\phi^2}{2}\Bigg|_0^{2\pi} = \boxed{\pi}.$$

Note: this result applies to all values of the quantum number m, for it drops out of the calculation.

P8.8 The expectation value of the commutator is:

$$\langle[\hat{x},\hat{p}]\rangle = \int \psi^*[\hat{x},\hat{p}]\psi\,\mathrm{d}\tau.$$

First evaluate the commutator acting on the wavefunction. The commutator of the position and momentum operators is defined as

$$[\hat{x},\hat{p}] = \hat{x}\hat{p} - \hat{p}\hat{x} = x\times\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x} - \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}x,$$

so the commutator acting on the wavefunction is

$$[\hat{x},\hat{p}]\psi = x \times \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\psi}{\mathrm{d}x} - \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}(x\psi),$$

where $\psi = (2a)^{1/2}\mathrm{e}^{-ax}$.

Evaluating this expression yields

$$[\hat{x},\hat{p}]\psi = \frac{x\hbar}{\mathrm{i}}(2a)^{1/2}a\,\mathrm{e}^{-ax} - \frac{\hbar}{\mathrm{i}}[(2a)^{1/2}\,\mathrm{e}^{-ax} + xa(2a)^{1/2}\,\mathrm{e}^{-ax}],$$

$$[\hat{x},\hat{p}]\psi = \frac{\hbar(2a)^{1/2}\mathrm{e}^{-ax}}{\mathrm{i}}(xa - 1 - xa) = \mathrm{i}\hbar(2a)^{1/2}\,\mathrm{e}^{-ax},$$

which is just $\mathrm{i}\hbar$ times the original wavefunction. Putting this result into the expectation value yields:

$$\langle[\hat{x},\hat{p}]\rangle = \int_0^\infty (2a)^{1/2}\mathrm{e}^{-ax}(\mathrm{i}\hbar)(2a)^{1/2}\,\mathrm{e}^{-ax}\,\mathrm{d}x = 2\mathrm{i}a\hbar\int_0^\infty \mathrm{e}^{-2ax}\mathrm{d}x$$

$$\langle[\hat{x},\hat{p}]\rangle = 2\mathrm{i}a\hbar \times \left.\frac{\mathrm{e}^{-2ax}}{-2a}\right|_0^\infty = \boxed{\mathrm{i}\hbar}.$$

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

$$\rho = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{\mathrm{e}^{hc/\lambda kT} - 1}\right) \text{[8.5]}$$

$$\frac{\mathrm{d}\rho}{\mathrm{d}\lambda} = -\frac{5}{\lambda}\rho + \frac{hc}{\lambda^2 kT}\left(\frac{\mathrm{e}^{hc/\lambda kT}}{\mathrm{e}^{hc/\lambda kT} - 1}\right)\rho = 0 \quad \text{at } \lambda = \lambda_{\max}$$

Then, $-5 + \dfrac{hc}{\lambda kT} \times \dfrac{\mathrm{e}^{hc/\lambda kT}}{\mathrm{e}^{hc/\lambda kT} - 1} = 0$

Hence, $5 - 5\mathrm{e}^{hc/\lambda kT} + \dfrac{hc}{\lambda kT}\mathrm{e}^{hc/\lambda kT} = 0$

If $hc/\lambda kT \gg 1$ [short wavelengths, high frequencies], this expression simplifies. We neglect the initial 5, cancel the two exponents, and obtain

$$hc = 5\lambda kT \quad \text{for } \lambda = \lambda_{\max} \text{ and } \frac{hc}{\lambda kT} \gg 1$$

or $\boxed{\lambda_{\max}T = \dfrac{hc}{5k} = \dfrac{c_2}{5}}$, 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,

$$\rho_{\text{Planck}} = \frac{8\pi hc}{\lambda^5(\mathrm{e}^{hc/\lambda kT} - 1)},$$

for small-wavelength behavior. The factor λ^{-5} gets large as λ itself gets small, but the other factor, namely $1/(\mathrm{e}^{hc/\lambda kT} - 1)$ gets small even faster. Focus on that factor, and try to express it in terms of a single decaying exponential (as in Wien's formula), at least in the small-λ limit. Multiplying it by one in the form of $\mathrm{e}^{-hc/\lambda kT}/\mathrm{e}^{-hc/\lambda kT}$, yields $\mathrm{e}^{-hc/\lambda kT}/1 - \mathrm{e}^{-hc/\lambda kT}$, where $\mathrm{e}^{-hc/\lambda kT}$ is small, so let us call it ε. The factor, then, becomes $\varepsilon/(1-\varepsilon)$, which can be expressed as a power series in ε as $\varepsilon(1+\varepsilon+\cdots)$. For sufficiently small wavelengths, then, the Planck distribution may be approximated as:

$$\rho_{\text{Planck}} \approx \frac{8\pi hc\varepsilon}{\lambda^5} = \frac{8\pi hc\mathrm{e}^{-hc/\lambda kT}}{\lambda^5}.$$

This has the same form as Wien's formula:

$$\rho_{\text{Wien}} = \frac{a}{\lambda^5}\,\mathrm{e}^{-b/\lambda kT}.$$

Comparing the two formulas gives the values of the Wien constants:

$$a = \boxed{8\pi hc} \quad \text{and} \quad b = \boxed{hc}.$$

(b) The wavelength at which the Wien distribution is a maximum is found by setting the derivative of the distribution function to zero:

$$\frac{\mathrm{d}\rho_{\text{Wein}}}{\mathrm{d}\lambda} = 0 = \frac{a}{\lambda^5}\mathrm{e}^{-b/\lambda kT}\left(\frac{b}{\lambda^2 kT}\right) - \frac{5a}{\lambda^6}\mathrm{e}^{-b/\lambda kT} = \frac{a}{\lambda^6}\mathrm{e}^{-b/\lambda kT}\left(\frac{b}{\lambda kT} - 5\right),$$

so $\dfrac{b}{\lambda kT} - 5 = 0$ and $\lambda_{\max} = \dfrac{b}{5kT} = \dfrac{hc}{5kT}$.

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:

$$\mathrm{d}E = \rho\,\mathrm{d}\lambda \quad \text{so} \quad E = \int_0^\infty \rho\,d\lambda.$$

The energy density implied by the Wien distribution is:

$$E = \int_0^\infty \frac{a}{\lambda^5}\,\mathrm{e}^{-b/\lambda kT}\mathrm{d}\lambda.$$

Integration by parts several times yields:

$$E = e^{-b/\lambda kT}\left(\left(\frac{b}{k\lambda}\right)^3 + 3\left(\frac{b}{k\lambda}\right)^2 T + \frac{6bT^2}{k\lambda} + 6T^3\right)\frac{aTk^4}{b^4}\Bigg|_0^\infty = \frac{6aT^4k^4}{b^4},$$

$$E = \frac{48\pi k^4 T^4}{h^3c^3},$$

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) $$\psi = N\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$$

$$\psi^2 = N^2\left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0}$$

$$\int \psi^2\, d\tau = N^2 \int_0^\infty \left(4r^2 - \frac{4r^3}{a_0} + \frac{r^4}{a_0^2}\right)e^{-r/a_0}\, dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi$$

$$= N^2\left(4 \times 2a_0^3 - 4 \times \frac{6a_0^4}{a_0} + \frac{24a_0^5}{a_0^2}\right) \times (2) \times (2\pi) = 32\pi a_0^3 N^2;$$

hence $\boxed{N = \left(\dfrac{1}{32\pi a_0^3}\right)^{1/2}}$

where we have used

$$\int_0^\infty x^n e^{-ax}\, dx = \frac{n!}{a^{n+1}}$$ [Problem 8.13 and inside front cover]

$$\psi = Nr\sin\theta\cos\phi\, e^{-r/(2a_0)}$$

$$\int \psi^2\, d\tau = N^2 \int_0^\infty r^4 e^{-r/a_0}\, dr \int_0^\pi \sin^2\theta \sin\theta\, d\theta \int_0^{2\pi} \cos^2\phi\, d\phi$$

$$= N^2 4! a_0^5 \int_{-1}^1 (1 - \cos^2\theta)\, d\cos\theta \times \pi$$

$$= N^2 4! a_0^5\left(2 - \frac{2}{3}\right)\pi = 32\pi a_0^5 N_0^2;$$ hence $\boxed{N = \left(\dfrac{1}{32\pi a_0^5}\right)^{1/2}}$

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.

$$\int \psi_1\psi_2 d\tau = \int \left\{\left(2 - \frac{r}{a_0}\right) e^{\frac{r}{2a_0}}\right\} \left\{r \sin\theta \, \cos\phi \, e^{\frac{r}{2a_0}}\right\} d\tau$$
$$= \int_0^{\infty} \left\{\left(2r - \frac{r^2}{a_0}\right) e^{\frac{r}{a_0}}\right\} dr \int_0^{\pi} \sin^2\theta \, d\theta \int_0^{2\pi} \cos\phi \, d\phi$$

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 $\hat{\imath}$; if the function is regenerated multiplied by a constant, it is an eigenfunction of $\hat{\imath}$ and the constant is the eigenvalue.

(a) $f = x^3 - kx$

$\hat{\imath}(x^3 - kx) = -x^3 + kx = -f$

Therefore, f is an eigenfunction with eigenvalue, $\boxed{-1}$

(b) $f = \cos kx$

$\hat{\imath} \cos kx = \cos(-kx) = \cos kx = f$

Therefore, f is an eigenfunction with eigenvalue, $\boxed{+1}$

(c) $f = x^2 + 3x - 1$

$\hat{\imath}(x^2 + 3x - 1) = x^2 - 3x - 1 \neq \text{constant} \times f$

Therefore, f is not an eigenfunction of $\hat{\imath}$.

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) $c_1^2 = 0.90 = \cos^2\chi$, so $\cos\chi = 0.95$

$c_2^2 = 0.10 = \sin^2\chi$, so $\sin\chi = \pm 0.32$; hence

$$\boxed{\psi = 0.95\mathrm{e}^{ikx} \pm 0.32\mathrm{e}^{-ikx}}$$

P8.20 $p_x = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}$ [8.26]

$$\langle p_x\rangle = N^2\int \psi^*\hat{p}_x\psi\,\mathrm{d}x;\quad N^2 = \frac{1}{\int\psi^*\psi\,\mathrm{d}\tau}$$

$$= \frac{\int\psi^*\hat{p}_x\psi\,\mathrm{d}x}{\int\psi^*\psi\,\mathrm{d}x} = \frac{\frac{\hbar}{i}\int\psi^*\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)\mathrm{d}x}{\int\psi^*\psi\,\mathrm{d}x}$$

(a) $\psi = \mathrm{e}^{\mathrm{i}kx}$, $\frac{\mathrm{d}\psi}{\mathrm{d}x} = \mathrm{i}k\psi$

Hence,

$$\langle p_x\rangle = \frac{\frac{\hbar}{\mathrm{i}}\times \mathrm{i}k\int\psi^*\psi\,\mathrm{d}x}{\int\psi^*\psi\,\mathrm{d}x} = \boxed{k\hbar}$$

(b) $\psi = \cos kx$, $\frac{d\psi}{dx} = -k\sin kx$

$$\int_{-\infty}^{\infty}\psi^*\frac{\mathrm{d}\psi}{\mathrm{d}x}\mathrm{d}x = -k\int_{-\infty}^{\infty}\cos kx\sin kx\,\mathrm{d}x = 0$$

Therefore, $\langle p_x\rangle = \boxed{0}$

(c) $\psi = \mathrm{e}^{-\alpha x^2}$, $\frac{\mathrm{d}\psi}{\mathrm{d}x} = -2\alpha x\mathrm{e}^{-\alpha x^2}$

$$\int_{-\infty}^{\infty}\psi^*\frac{\mathrm{d}\psi}{\mathrm{d}x}\mathrm{d}x = -2\alpha\int_{-\infty}^{\infty}x\mathrm{e}^{-2\alpha x^2}\mathrm{d}x = 0$$ [by symmetry, since x is an odd function]

Therefore, $\langle p_x\rangle = \boxed{0}$

P8.22 $\psi = \left(\frac{1}{\pi a_0^3}\right)^{1/2}\mathrm{e}^{-r/a_0}$ [Example 8.4]

(a) $\langle V\rangle = \int\psi^*\hat{V}\psi\,\mathrm{d}\tau\left[\hat{V} = -\frac{e^2}{4\pi\varepsilon_0 r}\text{, Section 10.1}\right]$

$$\langle V\rangle = \int\psi^*\left(\frac{-e^2}{4\pi\varepsilon_0}\cdot\frac{1}{r}\right)\psi\,\mathrm{d}\tau = \frac{1}{\pi a_0^3}\left(\frac{-e^2}{4\pi\varepsilon_0}\right)\int_0^{\infty}r\mathrm{e}^{-2r/a_0}\mathrm{d}r\times 4\pi$$

$$= \frac{1}{\pi a_0^3}\left(\frac{-e^2}{4\pi\varepsilon_0}\right)\times\left(\frac{a_0}{2}\right)^2\times 4\pi = \boxed{\frac{-e^2}{4\pi\varepsilon_0 a_0}}$$

(b) For three-dimensional systems such as the hydrogen atom the kinetic energy operator is

$$\hat{T} = -\frac{\hbar^2}{2m_e}\nabla^2 \text{ [Table 8.1, } m_e \approx \mu \text{ for the hydrogen atom]}$$

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2 = \left(\frac{1}{r}\right) \times \left(\frac{\partial^2}{\partial r^2}\right) r + \frac{1}{r^2}\Lambda^2$$

$$\Lambda^2\psi = 0 \quad [\psi \text{ has no angular coordinates}]$$

$$\nabla^2\psi = \left(\frac{1}{\pi a_0^3}\right)^{1/2} \times \left(\frac{1}{r}\right) \times \left(\frac{\mathrm{d}^2}{\mathrm{d}r^2}\right) r\,\mathrm{e}^{-r/a_0}$$

$$= \left(\frac{1}{\pi a_0^3}\right)^{1/2} \times \left[-\left(\frac{2}{a_0 r}\right) + \frac{1}{a_0^2}\right] \mathrm{e}^{-r/a_0}$$

$$\text{Then, } \langle T\rangle = -\left(\frac{\hbar^2}{2m_e}\right) \times \left(\frac{1}{\pi a_0^3}\right) \int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \sin\theta\,\mathrm{d}\theta \int_0^{\infty} \left[-\left(\frac{2}{a_0 r}\right) + \left(\frac{1}{a_0^2}\right)\right] \mathrm{e}^{-2r/a_0} r^2\,\mathrm{d}r$$

$$= -\left(\frac{2\hbar^2}{m_e a_0{}^3}\right) \int_0^{\infty} \left[-\left(\frac{2r}{a_0}\right) + \left(\frac{r^2}{a_0^2}\right)\right] \mathrm{e}^{-2r/a_0}\,\mathrm{d}r$$

$$= -\left(\frac{2\hbar^2}{m_e a_0{}^3}\right) \times \left(-\frac{a_0}{4}\right) \left[\int_0^{\infty} x^n \mathrm{e}^{-ax}\,\mathrm{d}x = \frac{n!}{a^{n+1}}\right] = \boxed{\frac{\hbar^2}{2m_e a_0^2}}$$

Inserting $a_0 = \dfrac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$ [Chapter 10]

$$\langle T\rangle = \frac{e^2}{8\pi\varepsilon_0 a_0} = -\frac{1}{2}\langle V\rangle$$

P8.24 $\left\langle \Omega^2 \right\rangle = \int \psi^* \hat{\Omega}^2 \psi\,\mathrm{d}\tau = \int \psi^* \hat{\Omega}\hat{\Omega}\psi\,\mathrm{d}\tau = \left\{\int \left(\hat{\Omega}\psi\right)^* \hat{\Omega}\psi\,\mathrm{d}\tau\right\}^*$ 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 $\lambda_{\max} = \dfrac{1.44\,\mathrm{cm\,K}}{5T}$ [See problems 8.2 and 8.10]

$$= \frac{1.44\,\mathrm{cm\,K}}{5(5800\,\mathrm{K})} = 5.0 \times 10^{-5}\,\mathrm{cm}\left(\frac{10^9\,\mathrm{nm}}{10^2\,\mathrm{cm}}\right)$$

$\lambda_{\max} = \boxed{500\,\text{nm, blue-green}}$ [see Figure 10.1 in the text]

P8.28 $I = aI + M = aI + \sigma T^4$ so $T = \left(\dfrac{I(1-a)}{\sigma}\right)^{1/4} = \left(\dfrac{(343\,\mathrm{W\,m^{-2}}) \times (1-0.30)}{5.67 \times 10^{-8}\,\mathrm{W\,m^{-2}\,K^{-4}}}\right)^{1/4}$

$$= \boxed{255\,\mathrm{K}}$$

where I is the incoming energy flux, a the albedo (fraction of incoming radiation absorbed), M the excitance 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

$$T\lambda_{\max} = c_2/5, \quad \text{so } \lambda_{\max} = \frac{c_2}{5T} = \frac{1.44\,\text{cm K}}{5(255\,\text{K})}$$

$$= 1.13 \times 10^{-3}\text{cm} = \boxed{11.3\,\mu\text{m}} \text{ in the infrared.}$$