Part 1: Equilibrium

1 The properties of gases

Solutions to exercises

Discussion questions

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

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

E1.3(b) The van der Waals equation is a cubic equation in the volume, V. Any cubic equation has certain properties, one of which is that there are some values of the coefficients of the variable where the number of real roots passes from three to one. In fact, any equation of state of odd degree higher than 1 can in principle account for critical behavior because for equations of odd degree in V there are necessarily some values of temperature and pressure for which the number of real roots of V passes from n(odd) to 1. That is, the multiple values of V converge from n to 1 as $T \rightarrow T_c$. This mathematical result is consistent with passing from a two phase region (more than one volume for a given T and p) to a one phase region (only one V for a given T and p and this corresponds to the observed experimental result as the critical point is reached.

Numerical exercises

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

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

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

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

$$pV = nRT$$

implying that the pressure would be

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

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

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

so $p = \dfrac{(0.62\bar{6}\,\text{mol}) \times (8.31 \times 10^{-2}\,\text{L bar K}^{-1}\,\text{mol}^{-1}) \times (30 + 273\,\text{K})}{1.5\,\text{L}} = \boxed{10.\bar{5}\,\text{bar}}$
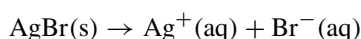
not 2.0 bar.

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

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

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

E2.36(b) The reaction is

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

$$\Delta_{\text{sol}} H^{\ominus} = \Delta_f H^{\ominus}(\text{Ag}^+) + \Delta_f H^{\ominus}(\text{Br}^-) - \Delta_f H^{\ominus}(\text{AgBr})$$

$$= [105.58 + (-121.55) - (-100.37)]\,\text{kJ mol}^{-1} = \boxed{+84.40\,\text{kJ mol}^{-1}}$$

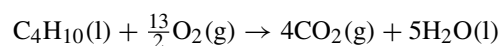**E2.37(b)** The difference of the equations is $C(\text{gr}) \rightarrow C(\text{d})$

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

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

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

(b) $\quad \Delta_c H^{\ominus} = \Delta_c U^{\ominus} + \Delta(pV) = \Delta_c U^{\ominus} + RT\Delta n_g \quad \text{so} \quad \Delta_c U^{\ominus} = \Delta_c H^{\ominus} - RT\Delta n_g$
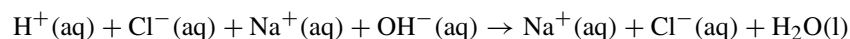
The reaction is

$$\text{C}_4\text{H}_{10}(\text{l}) + \tfrac{13}{2}\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{l})$$

so $\Delta n_g = -2.5$ and

$$\Delta_c U^{\ominus} = -2857\,\text{kJ mol}^{-1} - (8.3145 \times 10^{-3}\,\text{kJ K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K}) \times (-2.5)$$

$$= \boxed{-2851\,\text{kJ mol}^{-1}}$$

E2.39(b) **(a)** $\quad \Delta_r H^{\ominus} = \Delta_f H^{\ominus}(\text{propene, g}) - \Delta_f H^{\ominus}(\text{cyclopropane, g}) = [(20.42) - (53.30)]\,\text{kJ mol}^{-1}$

$$= \boxed{-32.88\,\text{kJ mol}^{-1}}$$

(b) The net ionic reaction is obtained from

$$\text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{H}_2\text{O(l)}$$

and is $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O(l)}$

$$\Delta_r H^{\ominus} = \Delta_f H^{\ominus}(\text{H}_2\text{O, l}) - \Delta_f H^{\ominus}(\text{H}^+, \text{aq}) - \Delta_f H^{\ominus}(\text{OH}^-, \text{aq})$$

$$= [(-285.83) - (0) - (-229.99)]\,\text{kJ mol}^{-1}$$

$$= \boxed{-55.84\,\text{kJ mol}^{-1}}$$

13 Atomic structure and atomic spectra

Solutions to exercises

Discussion questions

E13.1(b) (1) The principal quantum number, n, determines the energy of a hydrogenic atomic orbital through eqn 13.13.

(2) The azimuthal quantum number, l, determines the magnitude of the angular momentum of a hydrogenic atomic orbital through the relation $\{l(l+1)\}^{1/2}\hbar$.

(3) The magnetic quantum number, m_l, determines the z-component of the angular momentum of a hydrogenic orbital through the relation $m_l\hbar$.

(4) The spin quantum number, s, determines the magnitude of the spin angular momentum through the relation $\{s(s+1)\}^{1/2}\hbar$. For a hydrogenic atomic orbitals, s can only be $1/2$.

(5) The spin quantum number, m_s, determines the z-component of the spin angular momentum through the relation $m_s\hbar$. For hydrogenic atomic orbitals, m_s can only be $\pm 1/2$.

E13.2(b) (a) A boundary surface for a hydrogenic orbital is drawn so as to contain most (say 90%) of the probability density of an electron in that orbital. Its shape varies from orbital to orbital because the electron density distribution is different for different orbitals.

(b) The radial distribution function gives the probability that the electron will be found anywhere within a shell of radius r around the nucleus. It gives a better picture of where the electron is likely to be found with respect to the nucleus than the probability density which is the square of the wavefunction.

E13.3(b) The first ionization energies increase markedly from Li to Be, decrease slightly from Be to B, again increase markedly from B to N, again decrease slightly from N to O, and finally increase markedly from N to Ne. The general trend is an overall increase of I_1 with atomic number across the period. That is to be expected since the principal quantum number (electron shell) of the outer electron remains the same, while its attraction to the nucleus increases. The slight decrease from Be to B is a reflection of the outer electron being in a higher energy subshell (larger l value) in B than in Be. The slight decrease from N to O is due to the half-filled subshell effect; half-filled sub-shells have increased stability. O has one electron outside of the half-filled p subshell and that electron must pair with another resulting in strong electron–electron repulsions between them.

E13.4(b) An electron has a magnetic moment and magnetic field due to its orbital angular momentum. It also has a magnetic moment and magnetic field due to its spin angular momentum. There is an interaction energy between magnetic moments and magnetic fields. That between the spin magnetic moment and the magnetic field generated by the orbital motion is called spin–orbit coupling. The energy of interaction is proportional to the scalar product of the two vectors representing the spin and orbital angular momenta and hence depends upon the orientation of the two vectors. See Fig. 13.29. The total angular momentum of an electron in an atom is the vector sum of the orbital and spin angular momenta as illustrated in Fig. 13.30 and expressed in eqn 13.46. The spin–orbit coupling results in a splitting of the energy levels associated with atomic terms as shown in Figs 13.31 and 13.32. This splitting shows up in atomic spectra as a fine structure as illustrated in Fig. 13.32.

19 Statistical thermodynamics: the concepts

Solutions to exercises

Discussion questions

E19.1(b) Consider the value of the partition function at the extremes of temperature. The limit of q as T approaches zero, is simply g_0, the degeneracy of the ground state. As T approaches infinity, each term in the sum is simply the degeneracy of the energy level. If the number of levels is infinite, the partition function is infinite as well. In some special cases where we can effectively limit the number of states, the upper limit of the partition function is just the number of states. In general, we see that the molecular partition function gives an indication of the average number of states thermally accessible to a molecule at the temperature of the system.

E19.2(b) The statistical entropy may be defined in terms of the Boltzmann formula, $S = k \ln W$, where W is the statistical weight of the most probable configuration of the system. The relation between the entropy and the partition function is developed in two stages. In the first stage, we justify Boltzmann's formula, in the second, we express W in terms of the partition function. The justification for Boltzmann's formula is presented in *Justification* 19.6. Without repeating the details of this justification, we can see that the entropy defined through the formula has the properties we expect of the entropy. W can be thought of as a measure of disorder, hence the greater W, the greater the entropy; and the logarithmic form is consistent with the additive properties of the entropy. We expect the total disorder of a combined system to be the product of the individual disorders and $S = k \ln W = k \ln W_1 W_2 = k \ln W_1 + k \ln W_2 = S_1 + S_2$.

In the second stage the formula relating entropy and the partition function is derived. This derivation is presented in *Justification* 19.7. The expression for W, eqn 19.1, is recast in terms of probabilities, which in turn are expressed in terms of the partition function through eqn 10. The final expression which is eqn 19.34 then follows immediately.

E19.3(b) Since β and temperature are inversely related, strictly speaking one can never replace the other. The concept of temperature is useful in indicating the direction of the spontaneous transfer of energy in the form of heat. It seems natural to us to think of the spontaneous direction for this transfer to be from a body at high T to one at low T. In terms of β, the spontaneous direction would be from low to high and this has an unnatural feel.

On the other hand, β has a direct connection to the energy level pattern of systems of atoms and molecules. It arises in a natural, purely mathematical, manner from our knowledge of how energy is distributed amongst the particles of our atomic/molecular system. We would not have to invoke the abstract laws of thermodynamics, namely the zeroth and second laws in order to define our concept of temperature if we used β as the property to indicate the natural direction of heat flow. We can easily demonstrate that β is directly related to the statistical weight W through the relation $\beta = (\partial \ln W / \partial U)_N$. W, U, and N are all concrete properties of an atomic/molecular system.

E19.4(b) Identical particles can be regarded as distinguishable when they are localized as in a crystal lattice where we can assign a set of coordinates to each particle. Strictly speaking it is the lattice site that carries the set of coordinates, but as long as the particle is fixed to the site, it too can be considered distinguishable.
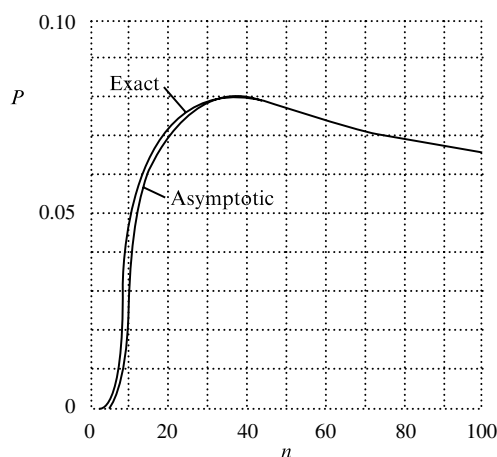
Figure 24.1

Solutions to applications

P24.33 The work required for a mass, m, to go from a distance r from the centre of a planet of mass m' to infinity is

$$w = \int_r^\infty F \, \mathrm{d}r$$

where F is the force of gravity and is given by Newton's law of universal gravitation, which is

$$F = \frac{Gmm'}{r^2}$$

G is the gravitational constant (not to be confused with g). Then

$$w' = \int_r^\infty \frac{Gmm'}{r^2} \, \mathrm{d}r = \frac{Gmm'}{r}$$

Since according to Newton's second law of motion, $F = mg$, we may make the identification

$$g = \frac{Gm'}{r^2}$$

Thus, $w = grm$. This is the kinetic energy that the particle must have in order to escape the planet's gravitational attraction at a distance r from the planet's centre; hence $w = \frac{1}{2}mv^2 = mgr$

$$v_e = (2g\,R_p)^{1/2} \quad [R_p = \text{radius of planet}]$$

which is the escape velocity.

(a) $v_e = [(2) \times (9.81 \, \mathrm{m \, s^{-2}}) \times (6.37 \times 10^6 \, \mathrm{m})]^{1/2} = \boxed{11.2 \, \mathrm{km \, s^{-1}}}$

(b) $g(\text{Mars}) = \dfrac{m(\text{Mars})}{m(\text{Earth})} \times \dfrac{R(\text{Earth})^2}{R(\text{Mars})^2} \times g(\text{Earth}) = (0.108) \times \left(\dfrac{6.37}{3.38}\right)^2 \times (9.81 \, \mathrm{m \, s^{-2}})$

$$= 3.76 \, \mathrm{m \, s^{-2}}$$

Hence, $v_e = [(2) \times (3.76 \, \mathrm{m \, s^{-2}}) \times (3.38 \times 10^6 \, \mathrm{m})]^{1/2} = \boxed{5.0 \, \mathrm{km \, s^{-1}}}$