5

Simple mixtures

This chapter begins by developing the concept of chemical potential to show that it is a particular case of a class of properties called partial molar quantities. Then it explores how to use the chemical potential of a substance to describe the physical properties of mixtures. The underlying principle to keep in mind is that at equilibrium the chemical potential of a species is the same in every phase. We see, by making use of the experimental observations known as Raoult's and Henry's laws, how to express the chemical potential of a substance in terms of its mole fraction in a mixture. With this result established, we can calculate the effect of a solute on certain thermodynamic properties of a solution. These properties include the lowering of vapour pressure of the solvent, the elevation of its boiling point, the depression of its freezing point, and the origin of osmotic pressure. Finally, we see how to express the chemical potential of a substance in a real mixture in terms of a property known as the activity. We see how the activity may be measured, and conclude with a discussion of how the standard states of solutes and solvents are defined and how ion–ion interactions are taken into account in electrolyte solutions.

Chemistry deals with mixtures, including mixtures of substances that can react together. Therefore, we need to generalize the concepts introduced so far to deal with substances that are mingled together. As a first step towards dealing with chemical reactions (which are treated in Chapter 7), here we consider mixtures of substances that do not react together. At this stage we deal mainly with *binary mixtures*, which are mixtures of two components, A and B. We shall therefore often be able to simplify equations by making use of the relation $x_A + x_B = 1$.

The thermodynamic description of mixtures

We have already seen that the partial pressure, which is the contribution of one component to the total pressure, is used to discuss the properties of mixtures of gases. For a more general description of the thermodynamics of mixtures we need to introduce other analogous 'partial' properties.

5.1 Partial molar quantities

The easiest partial molar property to visualize is the 'partial molar volume', the contribution that a component of a mixture makes to the total volume of a sample.

(a) Partial molar volume

Imagine a huge volume of pure water at 25°C. When a further 1 mol H_2O is added, the volume increases by 18 cm³ and we can report that 18 cm³ mol⁻¹ is the molar volume

of pure water. However, when we add 1 mol H_2O to a huge volume of pure ethanol, the volume increases by only 14 cm³. The reason for the different increase in volume is that the volume occupied by a given number of water molecules depends on the identity of the molecules that surround them. In the latter case there is so much ethanol present that each H_2O molecule is surrounded by ethanol molecules, and the packing of the molecules results in the H_2O molecules increasing the volume by only 14 cm³. The quantity 14 cm³ mol⁻¹ is the partial molar volume of water in pure ethanol. In general, the **partial molar volume** of a substance A in a mixture is the change in volume per mole of A added to a large volume of the mixture.

The partial molar volumes of the components of a mixture vary with composition because the environment of each type of molecule changes as the composition changes from pure A to pure B. It is this changing molecular environment, and the consequential modification of the forces acting between molecules, that results in the variation of the thermodynamic properties of a mixture as its composition is changed. The partial molar volumes of water and ethanol across the full composition range at 25°C are shown in Fig. 5.1.

The partial molar volume, V_J, of a substance J at some general composition is defined formally as follows:

$$V_J = \left(\frac{\partial V}{\partial n_J} \right)_{p,T,n'} \qquad [5.1]$$

where the subscript n' signifies that the amounts of all other substances present are constant.[1] The partial molar volume is the slope of the plot of the total volume as the amount of J is changed, the pressure, temperature, and amount of the other components being constant (Fig. 5.2). Its value depends on the composition, as we saw for water and ethanol. The definition in eqn 5.1 implies that, when the composition of the mixture is changed by the addition of dn_A of A and dn_B of B, then the total volume of the mixture changes by

$$dV = \left(\frac{\partial V}{\partial n_A} \right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B} \right)_{p,T,n_A} dn_B = V_A dn_A + V_B dn_B \qquad (5.2)$$

Provided the composition is held constant as the amounts of A and B are increased, the final volume of a mixture can be calculated by integration. Because the partial molar volumes are constant (provided the composition is held constant throughout the integration) we can write

$$V = \int_0^{n_A} V_A dn_A + \int_0^{n_B} V_B dn_B = V_A \int_0^{n_A} dn_A + V_B \int_0^{n_B} dn_B$$

$$= V_A n_A + V_B n_B \qquad (5.3)$$

Although we have envisaged the two integrations as being linked (in order to preserve constant composition), because V is a state function the final result in eqn 5.3 is valid however the solution is in fact prepared.

Partial molar volumes can be measured in several ways. One method is to measure the dependence of the volume on the composition and to fit the observed volume to a function of the amount of the substance. Once the function has been found, its slope can be determined at any composition of interest by differentiation.
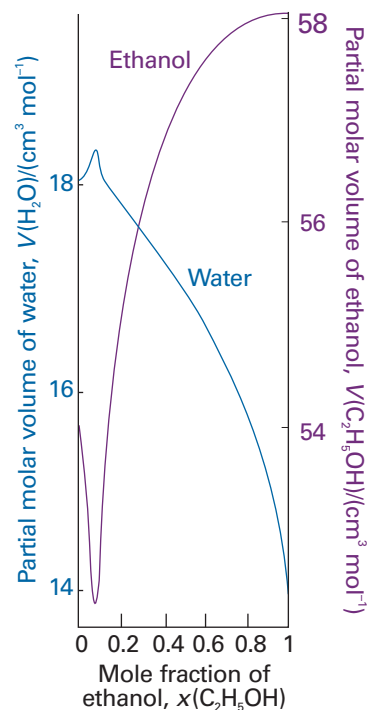

Fig. 5.1 The partial molar volumes of water and ethanol at 25°C. Note the different scales (water on the left, ethanol on the right).
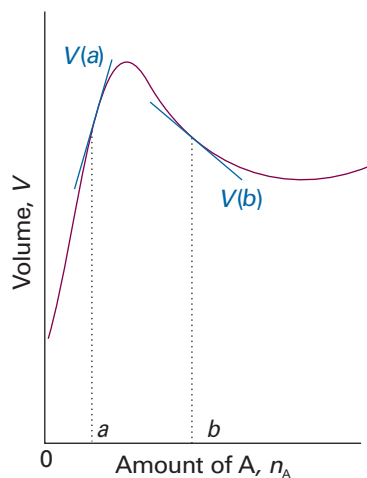
Fig. 5.2 The partial molar volume of a substance is the slope of the variation of the total volume of the sample plotted against the composition. In general, partial molar quantities vary with the composition, as shown by the different slopes at the compositions a and b. Note that the partial molar volume at b is negative: the overall volume of the sample decreases as A is added.

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[1] The IUPAC recommendation is to denote a partial molar quantity by $\bar{X}$, but only when there is the possibility of confusion with the quantity X. For instance, the partial molar volume of NaCl in water could be written $\bar{V}(NaCl, aq)$ to distinguish it from the volume of the solution, $V(NaCl, aq)$.

Fig. 5.3 The partial molar volume of ethanol as expressed by the polynomial in *Illustration 5.1*.

Exploration Using the data from *Illustration 5.1*, determine the value of b at which V_E has a minimum value.
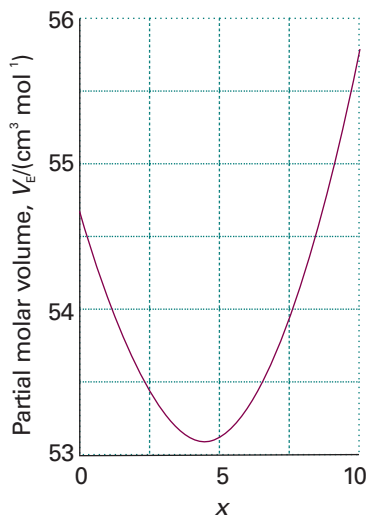
Illustration 5.1 *The determination of partial molar volume*

A polynomial fit to measurements of the total volume of a water/ethanol mixture at 25°C that contains 1.000 kg of water is

$$v = 1002.93 + 54.6664x - 0.363\,94x^2 + 0.028\,256x^3$$

where $v = V/cm^3$, $x = n_E/mol$, and n_E is the amount of CH_3CH_2OH present. The partial molar volume of ethanol, V_E, is therefore

$$V_E = \left(\frac{\partial V}{\partial n_E}\right)_{p,T,n_W} = \left(\frac{\partial(V/cm^3)}{\partial(n_E/mol)}\right)_{p,T,n_W} cm^3\,mol^{-1} = \left(\frac{\partial v}{\partial x}\right)_{p,T,n_W} cm^3\,mol^{-1}$$

Then, because

$$\frac{dv}{dx} = 54.6664 - 2(0.36394)x + 3(0.028256)x^2$$

we can conclude that

$$V_E/(cm^3\,mol^{-1}) = 54.6664 - 0.72788x + 0.084768x^2$$

Figure 5.3 is a graph of this function.

Self-test 5.1 At 25°C, the density of a 50 per cent by mass ethanol/water solution is 0.914 g cm^{-3}. Given that the partial molar volume of water in the solution is 17.4 cm^3 mol^{-1}, what is the partial molar volume of the ethanol?

[56.4 cm^3 mol^{-1}]

Molar volumes are always positive, but partial molar quantities need not be. For example, the limiting partial molar volume of $MgSO_4$ in water (its partial molar volume in the limit of zero concentration) is -1.4 cm^3 mol^{-1}, which means that the addition of 1 mol $MgSO_4$ to a large volume of water results in a decrease in volume of 1.4 cm^3. The mixture contracts because the salt breaks up the open structure of water as the ions become hydrated, and it collapses slightly.

(b) Partial molar Gibbs energies

The concept of a partial molar quantity can be extended to any extensive state function. For a substance in a mixture, the chemical potential is *defined* as the partial molar Gibbs energy:

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'} \tag{5.4}$$

That is, the chemical potential is the slope of a plot of Gibbs energy against the amount of the component J, with the pressure and temperature (and the amounts of the other substances) held constant (Fig. 5.4). For a pure substance we can write $G = n_J G_{J,m}$, and from eqn 5.4 obtain $\mu_J = G_{J,m}$: in this case, the chemical potential is simply the molar Gibbs energy of the substance, as we used in Chapter 4.

By the same argument that led to eqn 5.3, it follows that the total Gibbs energy of a binary mixture is

$$G = n_A\mu_A + n_B\mu_B \tag{5.5}$$

where μ_A and μ_B are the chemical potentials at the composition of the mixture. That is, the chemical potential of a substance in a mixture is the contribution of that
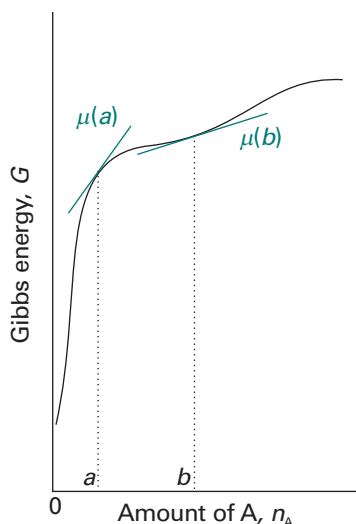

Fig. 5.4 The chemical potential of a substance is the slope of the total Gibbs energy of a mixture with respect to the amount of substance of interest. In general, the chemical potential varies with composition, as shown for the two values at a and b. In this case, both chemical potentials are positive.

substance to the total Gibbs energy of the mixture. Because the chemical potentials depend on composition (and the pressure and temperature), the Gibbs energy of a mixture may change when these variables change, and for a system of components A, B, etc., the equation $dG = Vdp - SdT$ becomes

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \cdots \tag{5.6}$$

This expression is the **fundamental equation of chemical thermodynamics**. Its implications and consequences are explored and developed in this and the next two chapters.

At constant pressure and temperature, eqn 5.6 simplifies to

$$dG = \mu_A dn_A + \mu_B dn_B + \cdots \tag{5.7}$$

We saw in Section 3.5e that under the same conditions $dG = dw_{add,max}$. Therefore, at constant temperature and pressure,

$$dw_{add,max} = \mu_A dn_A + \mu_B dn_B + \cdots \tag{5.8}$$

That is, additional (non-expansion) work can arise from the changing composition of a system. For instance, in an electrochemical cell, the chemical reaction is arranged to take place in two distinct sites (at the two electrodes). The electrical work the cell performs can be traced to its changing composition as products are formed from reactants.

(c) The wider significance of the chemical potential

The chemical potential does more than show how G varies with composition. Because $G = U + pV - TS$, and therefore $U = -pV + TS + G$, we can write a general infinitesimal change in U for a system of variable composition as

$$dU = -pdV - Vdp + SdT + TdS + dG$$
$$= -pdV - Vdp + SdT + TdS + (Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \cdots)$$
$$= -pdV + TdS + \mu_A dn_A + \mu_B dn_B + \cdots$$

This expression is the generalization of eqn 3.43 (that $dU = TdS - pdV$) to systems in which the composition may change. It follows that at constant volume and entropy,

$$dU = \mu_A dn_A + \mu_B dn_B + \cdots \tag{5.9}$$

and hence that

$$\mu_J = \left(\frac{\partial U}{\partial n_J}\right)_{S,V,n'} \tag{5.10}$$

Therefore, not only does the chemical potential show how G changes when the composition changes, it also shows how the internal energy changes too (but under a different set of conditions). In the same way it is easy to deduce that

$$\text{(a)}\ \ \mu_J = \left(\frac{\partial H}{\partial n_J}\right)_{S,p,n'} \qquad \text{(b)}\ \ \mu_J = \left(\frac{\partial A}{\partial n_J}\right)_{V,T,n'} \tag{5.11}$$

Thus we see that the μ_J shows how all the extensive thermodynamic properties U, H, A, and G depend on the composition. This is why the chemical potential is so central to chemistry.

(d) The Gibbs–Duhem equation

Because the total Gibbs energy of a binary mixture is given by eqn 5.5 and the chemical potentials depend on the composition, when the compositions are changed infinitesimally we might expect G of a binary system to change by

$$dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B$$

However, we have seen that at constant pressure and temperature a change in Gibbs energy is given by eqn 5.7. Because G is a state function, these two equations must be equal, which implies that at constant temperature and pressure

$$n_A d\mu_A + n_B d\mu_B = 0 \tag{5.12a}$$

This equation is a special case of the **Gibbs–Duhem equation**:

$$\sum_J n_J d\mu_J = 0 \tag{5.12b}$$

The significance of the Gibbs–Duhem equation is that the chemical potential of one component of a mixture cannot change independently of the chemical potentials of the other components. In a binary mixture, if one partial molar quantity increases, then the other must decrease, with the two changes related by

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A \tag{5.13}$$

The same line of reasoning applies to all partial molar quantities. We can see in Fig. 5.1, for example, that, where the partial molar volume of water increases, that of ethanol decreases. Moreover, as eqn 5.13 shows, and as we can see from Fig. 5.1, a small change in the partial molar volume of A corresponds to a large change in the partial molar volume of B if n_A/n_B is large, but the opposite is true when this ratio is small. In practice, the Gibbs–Duhem equation is used to determine the partial molar volume of one component of a binary mixture from measurements of the partial molar volume of the second component.

Comment 5.1

The *molar concentration* (colloquially, the 'molarity', [J] or c_J) is the amount of solute divided by the volume of the solution and is usually expressed in moles per cubic decimetre (mol dm^{-3}). We write $c^\ominus = 1$ mol dm^{-3}. The term *molality*, b, is the amount of solute divided by the mass of solvent and is usually expressed in moles per kilogram of solvent (mol kg^{-1}). We write $b^\ominus = 1$ mol kg^{-1}.

Example 5.1 *Using the Gibbs–Duhem equation*

The experimental values of the partial molar volume of K_2SO_4(aq) at 298 K are found to fit the expression

$$v_B = 32.280 + 18.216x^{1/2}$$

where $v_B = V_{K_2SO_4}/(\text{cm}^3 \text{ mol}^{-1})$ and x is the numerical value of the molality of K_2SO_4 ($x = b/b^\ominus$; see *Comment 5.1*). Use the Gibbs–Duhem equation to derive an equation for the molar volume of water in the solution. The molar volume of pure water at 298 K is 18.079 cm^3 mol^{-1}.

Method Let A denote H_2O, the solvent, and B denote K_2SO_4, the solute. The Gibbs–Duhem equation for the partial molar volumes of two components is $n_A dV_A + n_B dV_B = 0$. This relation implies that $dv_A = -(n_B/n_A)dv_B$, and therefore that v_A can be found by integration:

$$v_A = v_A^\star - \int \frac{n_B}{n_A} dv_B$$

where $v_A^\star = V_A/(\text{cm}^3 \text{ mol}^{-1})$ is the numerical value of the molar volume of pure A. The first step is to change the variable v_B to $x = b/b^\ominus$ and then to integrate the right-hand side between $x = 0$ (pure B) and the molality of interest.

Answer It follows from the information in the question that, with B = K_2SO_4, $dv_B/dx = 9.108x^{-1/2}$. Therefore, the integration required is

$$v_B = v_B^\star - 9.108 \int_0^{b/b^\ominus} \frac{n_B}{n_A} x^{-1/2} dx$$

However, the ratio of amounts of A (H_2O) and B (K_2SO_4) is related to the molality of B, $b = n_B/(1 \text{ kg water})$ and $n_A = (1 \text{ kg water})/M_A$ where M_A is the molar mass of water, by

$$\frac{n_B}{n_A} = \frac{n_B}{(1 \text{ kg})/M_A} = \frac{n_B M_A}{1 \text{ kg}} = bM_A = xb^{\ominus}M_A$$

and hence

$$v_A = v_A^\star - 9.108 M_A b^{\ominus} \int_0^{b/b^{\ominus}} x^{1/2}dx = v_A^\star - \tfrac{2}{3}\{9.108 M_A b^{\ominus}(b/b^{\ominus})^{3/2}\}$$

It then follows, by substituting the data (including $M_A = 1.802 \times 10^{-2}$ kg mol^{-1}, the molar mass of water), that

$$V_A/(\text{cm}^3 \text{ mol}^{-1}) = 18.079 - 0.1094(b/b^{\ominus})^{3/2}$$

The partial molar volumes are plotted in Fig. 5.5.

Self-test 5.2 Repeat the calculation for a salt B for which $V_B/(\text{cm}^3 \text{ mol}^{-1}) = 6.218 + 5.146b - 7.147b^2$. $[V_A/(\text{cm}^3 \text{ mol}^{-1}) = 18.079 - 0.0464b^2 + 0.0859b^3]$
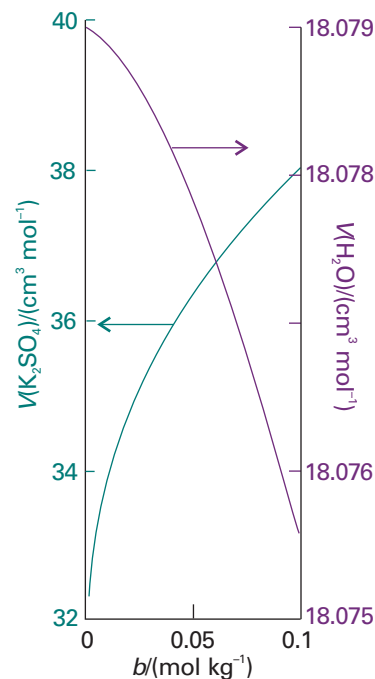

Fig. 5.5 The partial molar volumes of the components of an aqueous solution of potassium sulfate.

5.2 The thermodynamics of mixing

The dependence of the Gibbs energy of a mixture on its composition is given by eqn 5.5, and we know that at constant temperature and pressure systems tend towards lower Gibbs energy. This is the link we need in order to apply thermodynamics to the discussion of spontaneous changes of composition, as in the mixing of two substances. One simple example of a spontaneous mixing process is that of two gases introduced into the same container. The mixing is spontaneous, so it must correspond to a decrease in G. We shall now see how to express this idea quantitatively.

(a) The Gibbs energy of mixing of perfect gases

Let the amounts of two perfect gases in the two containers be n_A and n_B; both are at a temperature T and a pressure p (Fig. 5.6). At this stage, the chemical potentials of the two gases have their 'pure' values, which are obtained by applying the definition $\mu = G_m$ to eqn 3.57:

$$\mu = \mu^{\ominus} + RT \ln \frac{p}{p^{\ominus}} \tag{5.14a}°$$

where $\mu^{\ominus}$ is the **standard chemical potential**, the chemical potential of the pure gas at 1 bar. It will be much simpler notationally if we agree to let p denote the pressure relative to $p^{\ominus}$; that is, to replace $p/p^{\ominus}$ by p, for then we can write

$$\mu = \mu^{\ominus} + RT \ln p \tag{5.14b}°$$

Equations for which this convention is used will be labelled {1}, {2}, . . . ; to use the equations, we have to remember to replace p by $p/p^{\ominus}$ again. In practice, that simply means using the numerical value of p in bars. The Gibbs energy of the total system is then given by eqn 5.5 as

$$G_i = n_A\mu_A + n_B\mu_B = n_A(\mu_A^{\ominus} + RT \ln p) + n_B(\mu_B^{\ominus} + RT \ln p) \tag{5.15}°$$
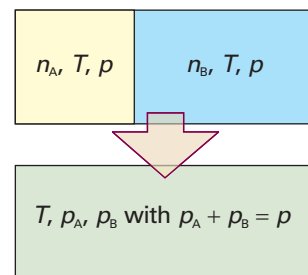

Fig. 5.6 The arrangement for calculating the thermodynamic functions of mixing of two perfect gases.
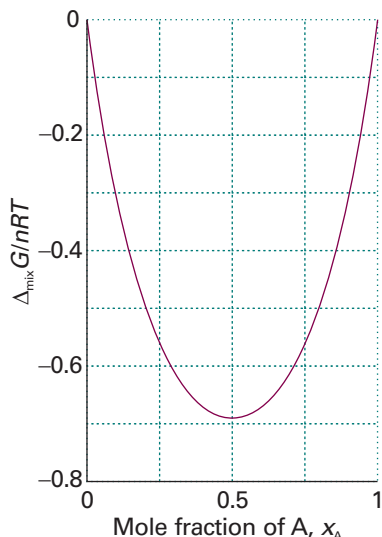
Fig. 5.7 The Gibbs energy of mixing of two perfect gases and (as discussed later) of two liquids that form an ideal solution. The Gibbs energy of mixing is negative for all compositions and temperatures, so perfect gases mix spontaneously in all proportions.

Exploration Draw graphs of $\Delta_{mix}G$ against x_A at different temperatures in the range 298 K to 500 K. For what value of x_A does $\Delta_{mix}G$ depend on temperature most strongly?
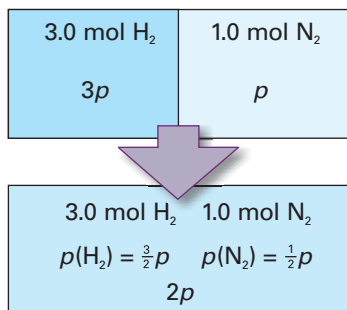

Fig. 5.8 The initial and final states considered in the calculation of the Gibbs energy of mixing of gases at different initial pressures.

After mixing, the partial pressures of the gases are p_A and p_B, with $p_A + p_B = p$. The total Gibbs energy changes to

$$G_f = n_A(\mu_A^{\ominus} + RT\ln p_A) + n_B(\mu_B^{\ominus} + RT\ln p_B) \qquad \{5.16\}°$$

The difference $G_f - G_i$, the **Gibbs energy of mixing**, $\Delta_{mix}G$, is therefore

$$\Delta_{mix}G = n_A RT\ln\frac{p_A}{p} + n_B RT\ln\frac{p_B}{p} \qquad (5.17)°$$

At this point we may replace n_J by $x_J n$, where n is the total amount of A and B, and use the relation between partial pressure and mole fraction (Section 1.2b) to write $p_J/p = x_J$ for each component, which gives

$$\Delta_{mix}G = nRT(x_A \ln x_A + x_B \ln x_B) \qquad (5.18)°$$

Because mole fractions are never greater than 1, the logarithms in this equation are negative, and $\Delta_{mix}G < 0$ (Fig. 5.7). The conclusion that $\Delta_{mix}G$ is negative for all compositions confirms that perfect gases mix spontaneously in all proportions. However, the equation extends common sense by allowing us to discuss the process quantitatively.

Example 5.2 *Calculating a Gibbs energy of mixing*

A container is divided into two equal compartments (Fig. 5.8). One contains 3.0 mol $H_2(g)$ at 25°C; the other contains 1.0 mol $N_2(g)$ at 25°C. Calculate the Gibbs energy of mixing when the partition is removed. Assume perfect behaviour.

Method Equation 5.18 cannot be used directly because the two gases are initially at different pressures. We proceed by calculating the initial Gibbs energy from the chemical potentials. To do so, we need the pressure of each gas. Write the pressure of nitrogen as p; then the pressure of hydrogen as a multiple of p can be found from the gas laws. Next, calculate the Gibbs energy for the system when the partition is removed. The volume occupied by each gas doubles, so its initial partial pressure is halved.

Answer Given that the pressure of nitrogen is p, the pressure of hydrogen is $3p$; therefore, the initial Gibbs energy is

$$G_i = (3.0\ \text{mol})\{\mu^{\ominus}(H_2) + RT\ln 3p\} + (1.0\ \text{mol})\{\mu^{\ominus}(N_2) + RT\ln p\}$$

When the partition is removed and each gas occupies twice the original volume, the partial pressure of nitrogen falls to $\frac{1}{2}p$ and that of hydrogen falls to $\frac{3}{2}p$. Therefore, the Gibbs energy changes to

$$G_f = (3.0\ \text{mol})\{\mu^{\ominus}(H_2) + RT\ln\tfrac{3}{2}p\} + (1.0\ \text{mol})\{\mu^{\ominus}(N_2) + RT\ln\tfrac{1}{2}p\}$$

The Gibbs energy of mixing is the difference of these two quantities:

$$\Delta_{mix}G = (3.0\ \text{mol})RT\ln\left(\frac{\tfrac{3}{2}p}{3p}\right) + (1.0\ \text{mol})RT\ln\left(\frac{\tfrac{1}{2}p}{p}\right)$$

$$= -(3.0\ \text{mol})RT\ln 2 - (1.0\ \text{mol})RT\ln 2$$

$$= -(4.0\ \text{mol})RT\ln 2 = -6.9\ \text{kJ}$$

In this example, the value of $\Delta_{mix}G$ is the sum of two contributions: the mixing itself, and the changes in pressure of the two gases to their final total pressure, $2p$. When 3.0 mol H_2 mixes with 1.0 mol N_2 at the same pressure, with the volumes of the vessels adjusted accordingly, the change of Gibbs energy is −5.6 kJ.

Self-test 5.3 Suppose that 2.0 mol H_2 at 2.0 atm and 25°C and 4.0 mol N_2 at 3.0 atm and 25°C are mixed at constant volume. Calculate $\Delta_{mix}G$. What would be the value of $\Delta_{mix}G$ had the pressures been identical initially?   [−9.7 kJ, −9.5 kJ]

(b) Other thermodynamic mixing functions

Because $(\partial G/\partial T)_{p,n} = -S$, it follows immediately from eqn 5.18 that, for a mixture of perfect gases initially at the same pressure, the entropy of mixing, $\Delta_{mix}S$, is

$$\Delta_{mix}S = \left(\frac{\partial \Delta_{mix}G}{\partial T}\right)_{p,n_A,n_B} = -nR(x_A \ln x_A + x_B \ln x_B) \tag{5.19}°$$

Because $\ln x < 0$, it follows that $\Delta_{mix}S > 0$ for all compositions (Fig. 5.9). For equal amounts of gas, for instance, we set $x_A = x_B = \frac{1}{2}$, and obtain $\Delta_{mix}S = nR \ln 2$, with n the total amount of gas molecules. This increase in entropy is what we expect when one gas disperses into the other and the disorder increases.

We can calculate the isothermal, isobaric (constant pressure) **enthalpy of mixing**, $\Delta_{mix}H$, the enthalpy change accompanying mixing, of two perfect gases from $\Delta G = \Delta H - T\Delta S$. It follows from eqns 5.18 and 5.19 that

$$\Delta_{mix}H = 0 \tag{5.20}°$$

The enthalpy of mixing is zero, as we should expect for a system in which there are no interactions between the molecules forming the gaseous mixture. It follows that the whole of the driving force for mixing comes from the increase in entropy of the system, because the entropy of the surroundings is unchanged.

5.3 The chemical potentials of liquids

To discuss the equilibrium properties of liquid mixtures we need to know how the Gibbs energy of a liquid varies with composition. To calculate its value, we use the fact that, at equilibrium, the chemical potential of a substance present as a vapour must be equal to its chemical potential in the liquid.

(a) Ideal solutions

We shall denote quantities relating to pure substances by a superscript ⋆, so the chemical potential of pure A is written $\mu_A^\star$, and as $\mu_A^\star(l)$ when we need to emphasize that A is a liquid. Because the vapour pressure of the pure liquid is $p_A^\star$, it follows from eqn 5.14 that the chemical potential of A in the vapour (treated as a perfect gas) is $\mu_A^\ominus + RT \ln p_A^\star$ (with p_A to be interpreted as the relative pressure $p_A/p^\ominus$). These two chemical potentials are equal at equilibrium (Fig. 5.10), so we can write

$$\mu_A^\star = \mu_A^\ominus + RT \ln p_A^\star \tag{5.21}$$

If another substance, a solute, is also present in the liquid, the chemical potential of A in the liquid is changed to μ_A and its vapour pressure is changed to p_A. The vapour and solvent are still in equilibrium, so we can write

$$\mu_A = \mu_A^\ominus + RT \ln p_A \tag{5.22}$$

Next, we combine these two equations to eliminate the standard chemical potential of the gas. To do so, we write eqn 5.21 as $\mu_A^\ominus = \mu_A^\star - RT \ln p_A^\star$ and substitute this expression into eqn 5.22 to obtain
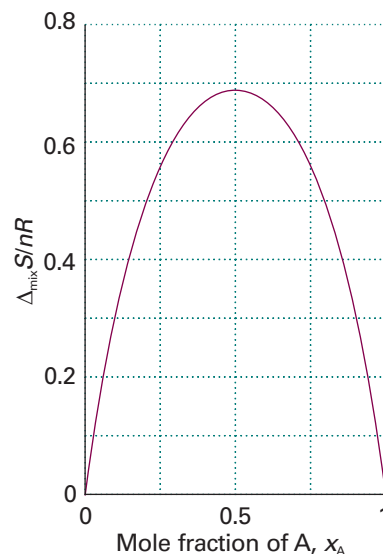
Fig. 5.9 The entropy of mixing of two perfect gases and (as discussed later) of two liquids that form an ideal solution. The entropy increases for all compositions and temperatures, so perfect gases mix spontaneously in all proportions. Because there is no transfer of heat to the surroundings when perfect gases mix, the entropy of the surroundings is unchanged. Hence, the graph also shows the total entropy of the system plus the surroundings when perfect gases mix.
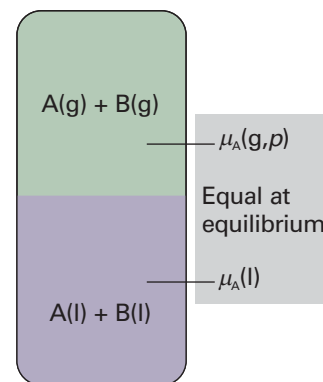
Fig. 5.10 At equilibrium, the chemical potential of the gaseous form of a substance A is equal to the chemical potential of its condensed phase. The equality is preserved if a solute is also present. Because the chemical potential of A in the vapour depends on its partial vapour pressure, it follows that the chemical potential of liquid A can be related to its partial vapour pressure.
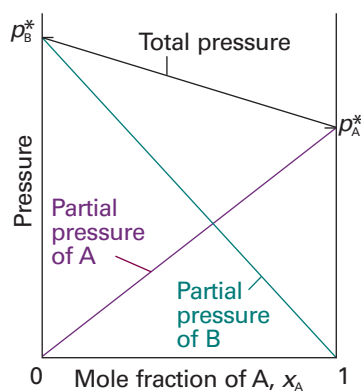
Fig. 5.11 The total vapour pressure and the two partial vapour pressures of an ideal binary mixture are proportional to the mole fractions of the components.

Fig. 5.12 Two similar liquids, in this case benzene and methylbenzene (toluene), behave almost ideally, and the variation of their vapour pressures with composition resembles that for an ideal solution.

$$\mu_A = \mu_A^\star - RT \ln p_A^\star + RT \ln p_A = \mu_A^\star + RT \ln \frac{p_A}{p_A^\star} \tag{5.23}$$

In the final step we draw on additional experimental information about the relation between the ratio of vapour pressures and the composition of the liquid. In a series of experiments on mix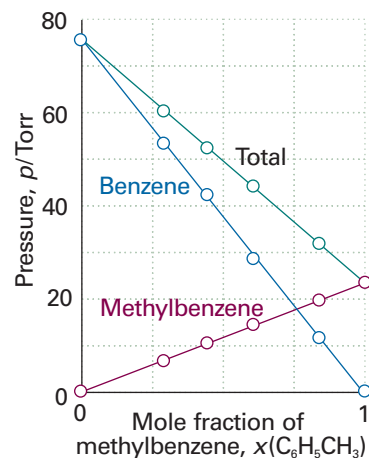tures of closely related liquids (such as benzene and methylbenzene), the French chemist François Raoult found that the ratio of the partial vapour pressure of each component to its vapour pressure as a pure liquid, $p_A/p_A^\star$, is approximately equal to the mole fraction of A in the liquid mixture. That is, he established what we now call **Raoult's law**:

$$p_A = x_A p_A^\star \tag{5.24}°$$

This law is illustrated in Fig. 5.11. Some mixtures obey Raoult's law very well, especially when the components are structurally similar (Fig. 5.12). Mixtures that obey the law throughout the composition range from pure A to pure B are called **ideal solutions**. When we write equations that are valid only for ideal solutions, we shall label them with a superscript °, as in eqn 5.24.

For an ideal solution, it follows from eqns 5.23 and 5.24 that

$$\mu_A = \mu_A^\star + RT \ln x_A \tag{5.25}°$$

This important equation can be used as the *definition* of an ideal solution (so that it implies Raoult's law rather than stemming from it). It is in fact a better definition than eqn 5.24 because it does not assume that the vapour is a perfect gas.
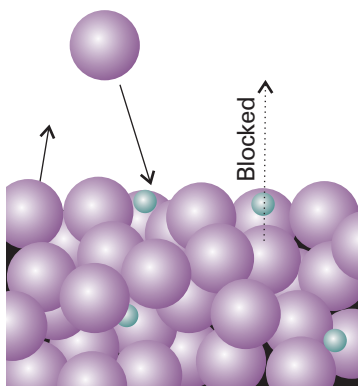
Fig. 5.13 A pictorial representation of the molecular basis of Raoult's law. The large spheres represent solvent molecules at the surface of a solution (the uppermost line of spheres), and the small spheres are solute molecules. The latter hinder the escape of solvent molecules into the vapour, but do not hinder their return.

Molecular interpretation 5.1 *The molecular origin of Raoult's law*

The origin of Raoult's law can be understood in molecular terms by considering the rates at which molecules leave and return to the liquid. The law reflects the fact that the presence of a second component reduces the rate at which A molecules leave the surface of the liquid but does not inhibit the rate at which they return (Fig. 5.13).

The rate at which A molecules leave the surface is proportional to the number of them at the surface, which in turn is proportional to the mole fraction of A:

rate of vaporization $= kx_A$

where k is a constant of proportionality. The rate at which molecules condense is proportional to their concentration in the gas phase, which in turn is proportional to their partial pressure:

rate of condensation $= k'p_A$

At equilibrium, the rates of vaporization and condensation are equal, so $k'p_A = kx_A$. It follows that

$$p_A = \frac{k}{k'} x_A$$

For the pure liquid, $x_A = 1$; so in this special case $p_A^\star = k/k'$. Equation 5.24 then follows by substitution of this relation into the line above.

Some solutions depart significantly from Raoult's law (Fig. 5.14). Nevertheless, even in these cases the law is obeyed increasingly closely for the component in excess (the solvent) as it approaches purity. The law is therefore a good approximation for the properties of the solvent if the solution is dilute.

(b) Ideal-dilute solutions

In ideal solutions the solute, as well as the solvent, obeys Raoult's law. However, the English chemist William Henry found experimentally that, for real solutions at low concentrations, although the vapour pressure of the solute is proportional to its mole fraction, the constant of proportionality is not the vapour pressure of the pure substance (Fig. 5.15). **Henry's law** is:
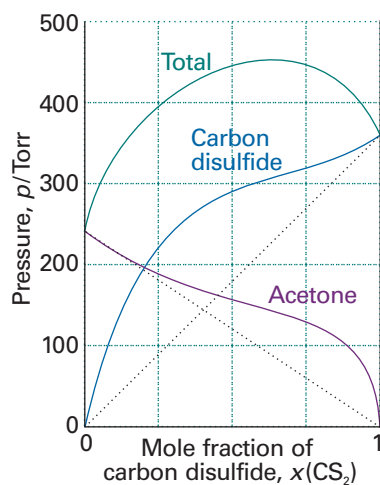
Fig. 5.14 Strong deviations from ideality are shown by dissimilar liquids (in this case carbon disulfide and acetone, propanone).
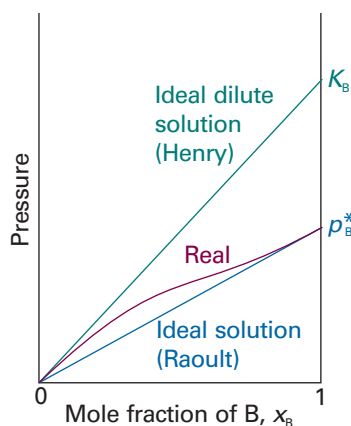
Fig. 5.15 When a component (the solvent) is nearly pure, it has a vapour pressure that is proportional to mole fraction with a slope $p_B^\star$ (Raoult's law). When it is the minor component (the solute) its vapour pressure is still proportional to the mole fraction, but the constant of proportionality is now K_B (Henry's law).
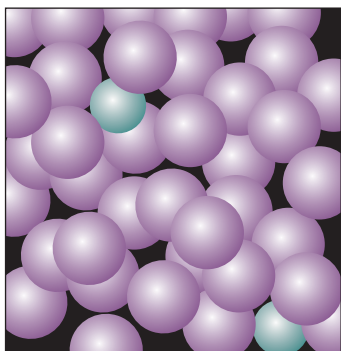
Fig. 5.16 In a dilute solution, the solvent molecules (the purple spheres) are in an environment that differs only slightly from that of the pure solvent. The solute particles, however, are in an environment totally unlike that of the pure solute.
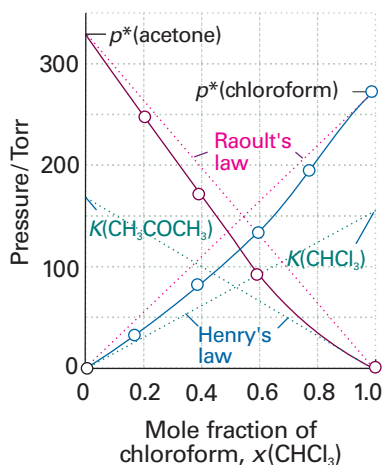
Fig. 5.17 The experimental partial vapour pressures of a mixture of chloroform (trichloromethane) and acetone (propanone) based on the data in *Example 5.3*. The values of K are obtained by extrapolating the dilute solution vapour pressures as explained in the *Example*.

$$p_B = x_B K_B \qquad\qquad (5.26)°$$

In this expression x_B is the mole fraction of the solute and K_B is an empirical constant (with the dimensions of pressure) chosen so that the plot of the vapour pressure of B against its mole fraction is tangent to the experimental curve at $x_B = 0$.

Mixtures for which the solute obeys Henry's law and the solvent obeys Raoult's law are called **ideal-dilute solutions**. We shall also label equations with a superscript ° when they have been derived from Henry's law. The difference in behaviour of the solute and solvent at low concentrations (as expressed by Henry's and Raoult's laws, respectively) arises from the fact that in a dilute solution the solvent molecules are in an environment very much like the one they have in the pure liquid (Fig. 5.16). In contrast, the solute molecules are surrounded by solvent molecules, which is entirely different from their environment when pure. Thus, the solvent behaves like a slightly modified pure liquid, but the solute behaves entirely differently from its pure state unless the solvent and solute molecules happen to be very similar. In the latter case, the solute also obeys Raoult's law.


Example 5.3 *Investigating the validity of Raoult's and Henry's laws*

The vapour pressures of each component in a mixture of propanone (acetone, A) and trichloromethane (chloroform, C) were measured at 35°C with the following results:

x_C	0	0.20	0.40	0.60	0.80	1
p_C/kPa	0	4.7	11	18.9	26.7	36.4
p_A/kPa	46.3	33.3	23.3	12.3	4.9	0

Confirm that the mixture conforms to Raoult's law for the component in large excess and to Henry's law for the minor component. Find the Henry's law constants.

Method Both Raoult's and Henry's laws are statements about the form of the graph of partial vapour pressure against mole fraction. Therefore, plot the partial vapour pressures against mole fraction. Raoult's law is tested by comparing the data with the straight line $p_J = x_J p_J^*$ for each component in the region in which it is in excess (and acting as the solvent). Henry's law is tested by finding a straight line $p_J = x_J K_J$ that is tangent to each partial vapour pressure at low x, where the component can be treated as the solute.

Answer The data are plotted in Fig. 5.17 together with the Raoult's law lines. Henry's law requires $K = 23.3$ kPa for propanone and $K = 22.0$ kPa for trichloromethane. Notice how the system deviates from both Raoult's and Henry's laws even for quite small departures from $x = 1$ and $x = 0$, respectively. We deal with these deviations in Section 5.5.

Self-test 5.4 The vapour pressure of chloromethane at various mole fractions in a mixture at 25°C was found to be as follows:

x	0.005	0.009	0.019	0.024
p/kPa	27.3	48.4	101	126

Estimate Henry's law constant.   [5 MPa]

For practical applications, Henry's law is expressed in terms of the molality, b, of the solute,

$$p_B = b_B K_B$$

Some Henry's law data for this convention are listed in Table 5.1. As well as providing a link between the mole fraction of solute and its partial pressure, the data in the table may also be used to calculate gas solubilities. A knowledge of Henry's law constants for gases in blood and fats is important for the discussion of respiration, especially when the partial pressure of oxygen is abnormal, as in diving and mountaineering, and for the discussion of the action of gaseous anaesthetics.

Synoptic Table 5.1* Henry's law constants for gases in water at 298 K

	$K/(\text{kPa kg mol}^{-1})$
CO_2	3.01×10^3
H_2	1.28×10^5
N_2	1.56×10^5
O_2	7.92×10^4

* More values are given in the *Data section*.

Illustration 5.2 *Using Henry's law*

To estimate the molar solubility of oxygen in water at 25°C and a partial pressure of 21 kPa, its partial pressure in the atmosphere at sea level, we write

$$b_{O_2} = \frac{p_{O_2}}{K_{O_2}} = \frac{21 \text{ kPa}}{7.9 \times 10^4 \text{ kPa kg mol}^{-1}} = 2.9 \times 10^{-4} \text{ mol kg}^{-1}$$

The molality of the saturated solution is therefore 0.29 mmol kg^{-1}. To convert this quantity to a molar concentration, we assume that the mass density of this dilute solution is essentially that of pure water at 25°C, or $\rho_{H_2O} = 0.99709$ kg dm^{-3}. It follows that the molar concentration of oxygen is

$$[O_2] = b_{O_2} \times \rho_{H_2O} = 0.29 \text{ mmol kg}^{-1} \times 0.99709 \text{ kg dm}^{-3} = 0.29 \text{ mmol dm}^{-3}$$

A note on good practice The number of significant figures in the result of a calculation should not exceed the number in the data (only two in this case).

Self-test 5.5 Calculate the molar solubility of nitrogen in water exposed to air at 25°C; partial pressures were calculated in *Example 1.3*.   [0.51 mmol dm^{-3}]

IMPACT ON BIOLOGY
I5.1 Gas solubility and breathing

We inhale about 500 cm^3 of air with each breath we take. The influx of air is a result of changes in volume of the lungs as the diaphragm is depressed and the chest expands, which results in a decrease in pressure of about 100 Pa relative to atmospheric pressure. Expiration occurs as the diaphragm rises and the chest contracts, and gives rise to a differential pressure of about 100 Pa above atmospheric pressure. The total volume of air in the lungs is about 6 dm^3, and the additional volume of air that can be exhaled forcefully after normal expiration is about 1.5 dm^3. Some air remains in the lungs at all times to prevent the collapse of the alveoli.

A knowledge of Henry's law constants for gases in fats and lipids is important for the discussion of respiration. The effect of gas exchange between blood and air inside the alveoli of the lungs means that the composition of the air in the lungs changes throughout the breathing cycle. Alveolar gas is in fact a mixture of newly inhaled air and air about to be exhaled. The concentration of oxygen present in arterial blood is equivalent to a partial pressure of about 40 Torr (5.3 kPa), whereas the partial pressure of freshly inhaled air is about 104 Torr (13.9 kPa). Arterial blood remains in the capillary passing through the wall of an alveolus for about 0.75 s, but such is the steepness of the pressure gradient that it becomes fully saturated with oxygen in about 0.25 s. If the lungs collect fluids (as in pneumonia), then the respiratory membrane thickens, diffusion is greatly slowed, and body tissues begin to suffer from oxygen starvation. Carbon dioxide moves in the opposite direction across the respiratory

Comment 5.2
The web site contains links to online databases of Henry's law constants.

tissue, but the partial pressure gradient is much less, corresponding to about 5 Torr (0.7 kPa) in blood and 40 Torr (5.3 kPa) in air at equilibrium. However, because carbon dioxide is much more soluble in the alveolar fluid than oxygen is, equal amounts of oxygen and carbon dioxide are exchanged in each breath.

A hyperbaric oxygen chamber, in which oxygen is at an elevated partial pressure, is used to treat certain types of disease. Carbon monoxide poisoning can be treated in this way as can the consequences of shock. Diseases that are caused by anaerobic bacteria, such as gas gangrene and tetanus, can also be treated because the bacteria cannot thrive in high oxygen concentrations.

In scuba diving (where *scuba* is an acronym formed from 'self-contained underwater breathing apparatus'), air is supplied at a higher pressure, so that the pressure within the diver's chest matches the pressure exerted by the surrounding water. The latter increases by about 1 atm for each 10 m of descent. One unfortunate consequence of breathing air at high pressures is that nitrogen is much more soluble in fatty tissues than in water, so it tends to dissolve in the central nervous system, bone marrow, and fat reserves. The result is *nitrogen narcosis*, with symptoms like intoxication. If the diver rises too rapidly to the surface, the nitrogen comes out of its lipid solution as bubbles, which causes the painful and sometimes fatal condition known as *the bends*. Many cases of scuba drowning appear to be consequences of arterial embolisms (obstructions in arteries caused by gas bubbles) and loss of consciousness as the air bubbles rise into the head.

The properties of solutions

In this section we consider the thermodynamics of mixing of liquids. First, we consider the simple case of mixtures of liquids that mix to form an ideal solution. In this way, we identify the thermodynamic consequences of molecules of one species mingling randomly with molecules of the second species. The calculation provides a background for discussing the deviations from ideal behaviour exhibited by real solutions.

5.4 Liquid mixtures

Thermodynamics can provide insight into the properties of liquid mixtures, and a few simple ideas can bring the whole field of study together.

(a) Ideal solutions

The Gibbs energy of mixing of two liquids to form an ideal solution is calculated in exactly the same way as for two gases (Section 5.2). The total Gibbs energy before liquids are mixed is

$$G_i = n_A \mu_A^\star + n_B \mu_B^\star$$

When they are mixed, the individual chemical potentials are given by eqn 5.25 and the total Gibbs energy is

$$G_f = n_A\{\mu_A^\star + RT \ln x_A\} + n_B\{\mu_B^\star + RT \ln x_B\}$$

Consequently, the Gibbs energy of mixing is

$$\Delta_{mix}G = nRT\{x_A \ln x_A + x_B \ln x_B\} \tag{5.27}°$$

where $n = n_A + n_B$. As for gases, it follows that the ideal entropy of mixing of two liquids is

$$\Delta_{mix}S = -nR\{x_A \ln x_A + x_B \ln x_B\} \tag{5.28}°$$

and, because $\Delta_{mix}H = \Delta_{mix}G + T\Delta_{mix}S = 0$, the ideal enthalpy of mixing is zero. The ideal volume of mixing, the change in volume on mixing, is also zero because it follows from eqn 3.50 $((\partial G/\partial p)_T = V)$ that $\Delta_{mix}V = (\partial\Delta_{mix}G/\partial p)_T$, but $\Delta_{mix}G$ in eqn 5.27 is independent of pressure, so the derivative with respect to pressure is zero.

Equation 5.27 is the same as that for two perfect gases and all the conclusions drawn there are valid here: the driving force for mixing is the increasing entropy of the system as the molecules mingle and the enthalpy of mixing is zero. It should be noted, however, that solution ideality means something different from gas perfection. In a perfect gas there are no forces acting between molecules. In ideal solutions there are interactions, but the average energy of A—B interactions in the mixture is the same as the average energy of A—A and B—B interactions in the pure liquids.[2] The variation of the Gibbs energy of mixing with composition is the same as that already depicted for gases in Fig. 5.7; the same is true of the entropy of mixing, Fig. 5.9.

Real solutions are composed of particles for which A—A, A—B, and B—B interactions are all different. Not only may there be enthalpy and volume changes when liquids mix, but there may also be an additional contribution to the entropy arising from the way in which the molecules of one type might cluster together instead of mingling freely with the others. If the enthalpy change is large and positive or if the entropy change is adverse (because of a reorganization of the molecules that results in an orderly mixture), then the Gibbs energy might be positive for mixing. In that case, separation is spontaneous and the liquids may be immiscible. Alternatively, the liquids might be **partially miscible**, which means that they are miscible only over a certain range of compositions.

(b) Excess functions and regular solutions

The thermodynamic properties of real solutions are expressed in terms of the **excess functions**, X^E, the difference between the observed thermodynamic function of mixing and the function for an ideal solution. The **excess entropy**, S^E, for example, is defined as

$$S^E = \Delta_{mix}S - \Delta_{mix}S^{ideal} \qquad [5.29]$$

where $\Delta_{mix}S^{ideal}$ is given by eqn 5.28. The excess enthalpy and volume are both equal to the observed enthalpy and volume of mixing, because the ideal values are zero in each case.

Deviations of the excess energies from zero indicate the extent to which the solutions are nonideal. In this connection a useful model system is the **regular solution**, a solution for which $H^E \neq 0$ but $S^E = 0$. We can think of a regular solution as one in which the two kinds of molecules are distributed randomly (as in an ideal solution) but have different energies of interactions with each other. Figure 5.18 shows two examples of the composition dependence of molar excess functions.

We can make this discussion more quantitative by supposing that the excess enthalpy depends on composition as

$$H^E = n\beta RT x_A x_B \qquad (5.30)$$

where β is a dimensionless parameter that is a measure of the energy of AB interactions relative to that of the AA and BB interactions. The function given by eqn 5.30 is plotted in Fig. 5.19, and we see it resembles the experimental curve in Fig. 5.18. If $\beta < 0$, mixing is exothermic and the solute–solvent interactions are more favourable than the solvent–solvent and solute–solute interactions. If $\beta > 0$, then the mixing is
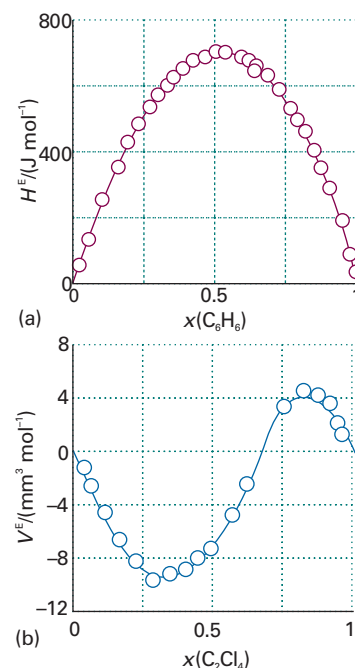
Fig. 5.18 Experimental excess functions at 25°C. (a) H^E for benzene/cyclohexane; this graph shows that the mixing is endothermic (because $\Delta_{mix}H = 0$ for an ideal solution). (b) The excess volume, V^E, for tetrachloroethene/cyclopentane; this graph shows that there is a contraction at low tetrachloroethane mole fractions, but an expansion at high mole fractions (because $\Delta_{mix}V = 0$ for an ideal mixture).

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[2] It is on the basis of this distinction that the term 'perfect gas' is preferable to the more common 'ideal gas'.
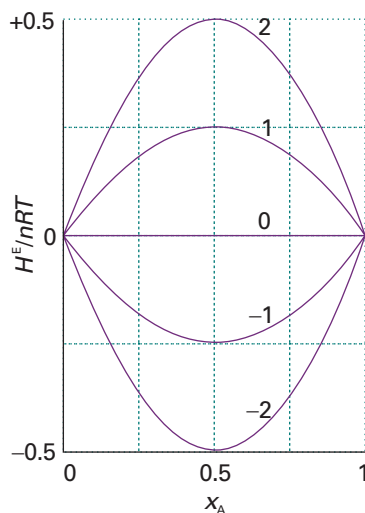
Fig. 5.19 The excess enthalpy according to a model in which it is proportional to $\beta x_A x_B$, for different values of the parameter β.

Exploration Using the graph above, fix β and vary the temperature. For what value of x_A does the excess enthalpy depend on temperature most strongly?
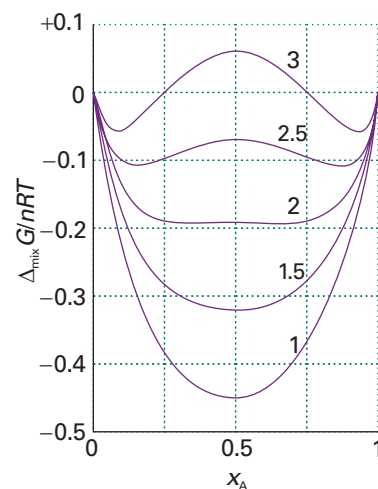
Fig. 5.20 The Gibbs energy of mixing for different values of the parameter β.

Exploration Using the graph above, fix β at 1.5 and vary the temperature. Is there a range of temperatures over which you observe phase separation?

endothermic. Because the entropy of mixing has its ideal value for a regular solution, the excess Gibbs energy is equal to the excess enthalpy, and the Gibbs energy of mixing is

$$\Delta_{mix}G = nRT\{x_A \ln x_A + x_B \ln x_B + \beta x_A x_B\} \tag{5.31}$$

Figure 5.20 shows how $\Delta_{mix}G$ varies with composition for different values of β. The important feature is that for $\beta > 2$ the graph shows two minima separated by a maximum. The implication of this observation is that, provided $\beta > 2$, then the system will separate spontaneously into two phases with compositions corresponding to the two minima, for that separation corresponds to a reduction in Gibbs energy. We develop this point in Sections 5.8 and 6.5.

5.5 Colligative properties

The properties we now consider are the lowering of vapour pressure, the elevation of boiling point, the depression of freezing point, and the osmotic pressure arising from the presence of a solute. In dilute solutions these properties depend only on the number of solute particles present, not their identity. For this reason, they are called **colligative properties** (denoting 'depending on the collection').

We assume throughout the following that the solute is not volatile, so it does not contribute to the vapour. We also assume that the solute does not dissolve in the solid solvent: that is, the pure solid solvent separates when the solution is frozen. The latter assumption is quite drastic, although it is true of many mixtures; it can be avoided at the expense of more algebra, but that introduces no new principles.

(a) The common features of colligative properties

All the colligative properties stem from the reduction of the chemical potential of the liquid solvent as a result of the presence of solute. For an ideal-dilute solution, the

reduction is from $\mu_A^\star$ for the pure solvent to $\mu_A^\star + RT \ln x_A$ when a solute is present ($\ln x_A$ is negative because $x_A < 1$). There is no direct influence of the solute on the chemical potential of the solvent vapour and the solid solvent because the solute appears in neither the vapour nor the solid. As can be seen from Fig. 5.21, the reduction in chemical potential of the solvent implies that the liquid–vapour equilibrium occurs at a higher temperature (the boiling point is raised) and the solid–liquid equilibrium occurs at a lower temperature (the freezing point is lowered).

Fig. 5.21 The chemical potential of a solvent in the presence of a solute. The lowering of the liquid's chemical potential has a greater effect on the freezing point than on the boiling point because of the angles at which the lines intersect.

Molecular interpretation 5.2 *The lowering of vapour pressure of a solvent in a mixture*

The molecular origin of the lowering of the chemical potential is not the energy of interaction of the solute and solvent particles, because the lowering occurs even in an ideal solution (for which the enthalpy of mixing is zero). If it is not an enthalpy effect, it must be an entropy effect.

The pure liquid solvent has an entropy that reflects the number of microstates available to its molecules. Its vapour pressure reflects the tendency of the solution towards greater entropy, which can be achieved if the liquid vaporizes to form a gas. When a solute is present, there is an additional contribution to the entropy of the liquid, even in an ideal solution. Because the entropy of the liquid is already higher than that of the pure liquid, there is a weaker tendency to form the gas (Fig. 5.22). The effect of the solute appears as a lowered vapour pressure, and hence a higher boiling point.

Similarly, the enhanced molecular randomness of the solution opposes the tendency to freeze. Consequently, a lower temperature must be reached before equilibrium between solid and solution is achieved. Hence, the freezing point is lowered.

The strategy for the quantitative discussion of the elevation of boiling point and the depression of freezing point is to look for the temperature at which, at 1 atm, one phase (the pure solvent vapour or the pure solid solvent) has the same chemical potential as the solvent in the solution. This is the new equilibrium temperature for the phase transition at 1 atm, and hence corresponds to the new boiling point or the new freezing point of the solvent.

(b) The elevation of boiling point

The heterogeneous equilibrium of interest when considering boiling is between the solvent vapour and the solvent in solution at 1 atm (Fig. 5.23). We denote the solvent by A and the solute by B. The equilibrium is established at a temperature for which

$$\mu_A^\star(g) = \mu_A^\star(l) + RT \ln x_A \tag{5.32}°$$

(The pressure of 1 atm is the same throughout, and will not be written explicitly.) We show in the *Justification* below that this equation implies that the presence of a solute at a mole fraction x_B causes an increase in normal boiling point from $T^\star$ to $T^\star + \Delta T$, where

$$\Delta T = K x_B \qquad K = \frac{RT^{\star 2}}{\Delta_{vap} H} \tag{5.33}°$$
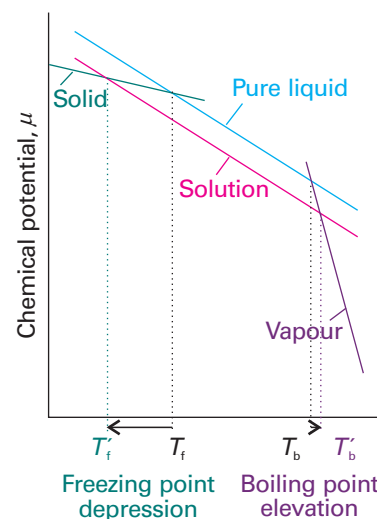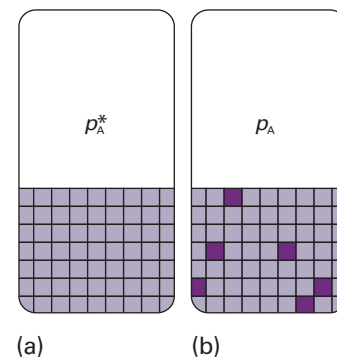
Fig. 5.22 The vapour pressure of a pure liquid represents a balance between the increase in disorder arising from vaporization and the decrease in disorder of the surroundings. (a) Here the structure of the liquid is represented highly schematically by the grid of squares. (b) When solute (the dark squares) is present, the disorder of the condensed phase is higher than that of the pure liquid, and there is a decreased tendency to acquire the disorder characteristic of the vapour.
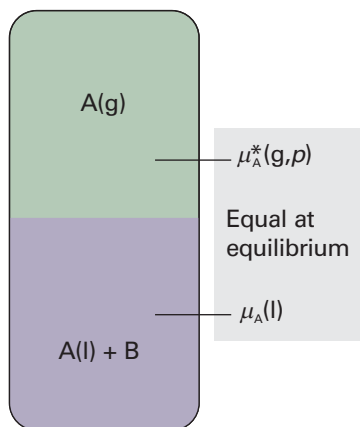
Fig. 5.23 The heterogeneous equilibrium involved in the calculation of the elevation of boiling point is between A in the pure vapour and A in the mixture, A being the solvent and B an involatile solute.

Comment 5.3

The series expansion of a natural logarithm (see *Appendix 2)* is

$$\ln(1-x) = -x - \tfrac{1}{2}x^2 - \tfrac{1}{3}x^3 \cdots$$

provided that $-1 < x < 1$. If $x \ll 1$, then the terms involving x raised to a power greater than 1 are much smaller than x, so $\ln(1-x) \approx -x$.
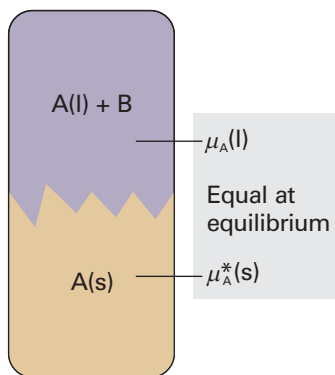
Fig. 5.24 The heterogeneous equilibrium involved in the calculation of the lowering of freezing point is between A in the pure solid and A in the mixture, A being the solvent and B a solute that is insoluble in solid A.

Justification 5.1 *The elevation of the boiling point of a solvent*

Equation 5.32 can be rearranged into

$$\ln x_A = \frac{\mu_A^\star(g) - \mu_A^\star(l)}{RT} = \frac{\Delta_{vap}G}{RT}$$

where $\Delta_{vap}G$ is the Gibbs energy of vaporization of the pure solvent (A). First, to find the relation between a change in composition and the resulting change in boiling temperature, we differentiate both sides with respect to temperature and use the Gibbs–Helmholtz equation (eqn 3.52, $(\partial(G/T)/\partial T)_p = -H/T^2$) to express the term on the right:

$$\frac{d \ln x_A}{dT} = \frac{1}{R}\frac{d(\Delta_{vap}G/T)}{dT} = -\frac{\Delta_{vap}H}{RT^2}$$

Now multiply both sides by dT and integrate from $x_A = 1$, corresponding to $\ln x_A = 0$ (and when $T = T^\star$, the boiling point of pure A) to x_A (when the boiling point is T):

$$\int_0^{\ln x_A} d \ln x_A = -\frac{1}{R}\int_{T^\star}^{T} \frac{\Delta_{vap}H}{T^2} dT$$

The left-hand side integrates to $\ln x_A$, which is equal to $\ln(1 - x_B)$. The right-hand side can be integrated if we assume that the enthalpy of vaporization is a constant over the small range of temperatures involved and can be taken outside the integral. Thus, we obtain

$$\ln(1 - x_B) = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^\star}\right)$$

We now suppose that the amount of solute present is so small that $x_B \ll 1$. We can then write $\ln(1 - x_B) \approx -x_B$ and hence obtain

$$x_B = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T^\star} - \frac{1}{T}\right)$$

Finally, because $T \approx T^\star$, it also follows that

$$\frac{1}{T^\star} - \frac{1}{T} = \frac{T - T^\star}{TT^\star} \approx \frac{\Delta T}{T^{\star 2}}$$

with $\Delta T = T - T^\star$. The previous equation then rearranges into eqn 5.33.

Because eqn 5.33 makes no reference to the identity of the solute, only to its mole fraction, we conclude that the elevation of boiling point is a colligative property. The value of ΔT does depend on the properties of the solvent, and the biggest changes occur for solvents with high boiling points.[3] For practical applications of eqn 5.33, we note that the mole fraction of B is proportional to its molality, b, in the solution, and write

$$\Delta T = K_b b \tag{5.34}$$

where K_b is the empirical **boiling-point constant** of the solvent (Table 5.2).

(c) The depression of freezing point

The heterogeneous equilibrium now of interest is between pure solid solvent A and the solution with solute present at a mole fraction x_B (Fig. 5.24). At the freezing point, the chemical potentials of A in the two phases are equal:

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[3] By Trouton's rule (Section 3.3b), $\Delta_{vap}H/T^\star$ is a constant; therefore eqn 5.33 has the form $\Delta T \propto T^\star$ and is independent of $\Delta_{vap}H$ itself.

Synoptic Table 5.2* Freezing-point and boiling-point constants

	$K_f/(\text{K kg mol}^{-1})$	$K_b/(\text{K kg mol}^{-1})$
Benzene	5.12	2.53
Camphor	40	
Phenol	7.27	3.04
Water	1.86	0.51

* More values are given in the *Data section*.

$$\mu_A^\star(s) = \mu_A^\star(l) + RT \ln x_A \qquad (5.35)°$$

The only difference between this calculation and the last is the appearance of the solid's chemical potential in place of the vapour's. Therefore we can write the result directly from eqn 5.33:

$$\Delta T = K' x_B \qquad K' = \frac{RT^{\star 2}}{\Delta_{fus}H} \qquad (5.36)°$$

where ΔT is the freezing point depression, $T^\star - T$, and $\Delta_{fus}H$ is the enthalpy of fusion of the solvent. Larger depressions are observed in solvents with low enthalpies of fusion and high melting points. When the solution is dilute, the mole fraction is proportional to the molality of the solute, b, and it is common to write the last equation as

$$\Delta T = K_f b \qquad (5.37)$$

where K_f is the empirical **freezing-point constant** (Table 5.2). Once the freezing-point constant of a solvent is known, the depression of freezing point may be used to measure the molar mass of a solute in the method known as **cryoscopy**; however, the technique is of little more than historical interest.

(d) Solubility

Although solubility is not strictly a colligative property (because solubility varies with the identity of the solute), it may be estimated by the same techniques as we have been using. When a solid solute is left in contact with a solvent, it dissolves until the solution is saturated. Saturation is a state of equilibrium, with the undissolved solute in equilibrium with the dissolved solute. Therefore, in a saturated solution the chemical potential of the pure solid solute, $\mu_B^*(s)$, and the chemical potential of B in solution, μ_B, are equal (Fig. 5.25). Because the latter is

$$\mu_B = \mu_B^*(l) + RT \ln x_B$$

we can write

$$\mu_B^*(s) = \mu_B^*(l) + RT \ln x_B \qquad (5.38)°$$

This expression is the same as the starting equation of the last section, except that the quantities refer to the solute B, not the solvent A. We now show in the following *Justification* that

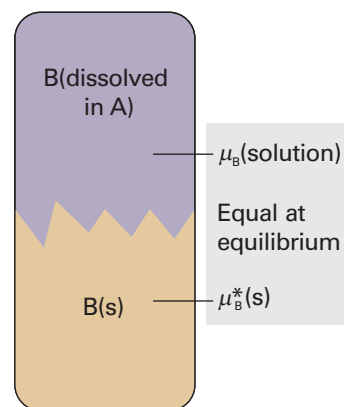$$\ln x_B = \frac{\Delta_{fus}H}{R} \left(\frac{1}{T_f} - \frac{1}{T} \right) \qquad (5.39)°$$

Fig. 5.25 The heterogeneous equilibrium involved in the calculation of the solubility is between pure solid B and B in the mixture.
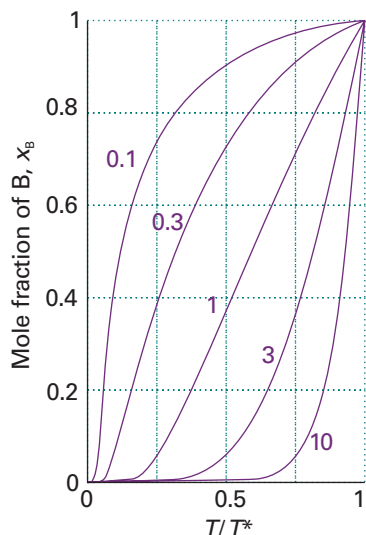
Fig. 5.26 The variation of solubility (the mole fraction of solute in a saturated solution) with temperature ($T^\star$ is the freezing temperature of the solute). Individual curves are labelled with the value of $\Delta_{fus}H/RT^\star$.

Exploration Derive an expression for the temperature coefficient of the solubility, dx_B/dT, and plot it as a function of temperature for several values of the enthalpy of fusion.
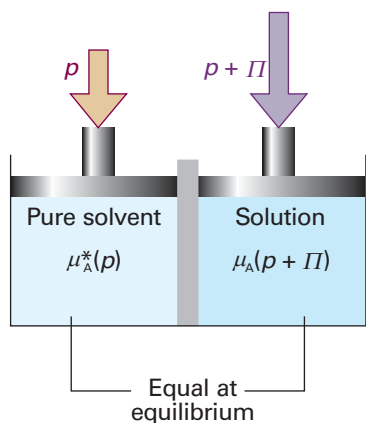

Fig. 5.27 The equilibrium involved in the calculation of osmotic pressure, Π, is between pure solvent A at a pressure p on one side of the semipermeable membrane and A as a component of the mixture on the other side of the membrane, where the pressure is $p + \Pi$.

Justification 5.2 *The solubility of an ideal solute.*

The starting point is the same as in *Justification 5.1* but the aim is different. In the present case, we want to find the mole fraction of B in solution at equilibrium when the temperature is T. Therefore, we start by rearranging eqn 5.38 into

$$\ln x_B = \frac{\mu_B^\star(s) - \mu_B^\star(l)}{RT} = -\frac{\Delta_{fus}G}{RT}$$

As in *Justification 5.1*, we relate the change in composition $d \ln x_B$ to the change in temperature by differentiation and use of the Gibbs–Helmholtz equation. Then we integrate from the melting temperature of B (when $x_B = 1$ and $\ln x_B = 0$) to the *lower* temperature of interest (when x_B has a value between 0 and 1):

$$\int_0^{\ln x_B} d \ln x_B = \frac{1}{R} \int_{T_f}^{T} \frac{\Delta_{fus}H}{T^2} \, dT$$

If we suppose that the enthalpy of fusion of B is constant over the range of temperatures of interest, it can be taken outside the integral, and we obtain eqn 5.39.

Equation 5.39 is plotted in Fig. 5.26. It shows that the solubility of B decreases exponentially as the temperature is lowered from its melting point. The illustration also shows that solutes with high melting points and large enthalpies of melting have low solubilities at normal temperatures. However, the detailed content of eqn 5.39 should not be treated too seriously because it is based on highly questionable approximations, such as the ideality of the solution. One aspect of its approximate character is that it fails to predict that solutes will have different solubilities in different solvents, for no solvent properties appear in the expression.

(e) Osmosis

The phenomenon of **osmosis** (from the Greek word for 'push') is the spontaneous passage of a pure solvent into a solution separated from it by a **semipermeable membrane**, a membrane permeable to the solvent but not to the solute (Fig. 5.27). The **osmotic pressure**, Π, is the pressure that must be applied to the solution to stop the influx of solvent. Important examples of osmosis include transport of fluids through cell membranes, dialysis and **osmometry**, the determination of molar mass by the measurement of osmotic pressure. Osmometry is widely used to determine the molar masses of macromolecules.

In the simple arrangement shown in Fig. 5.28, the opposing pressure arises from the head of solution that the osmosis itself produces. Equilibrium is reached when the hydrostatic pressure of the column of solution matches the osmotic pressure. The complicating feature of this arrangement is that the entry of solvent into the solution results in its dilution, and so it is more difficult to treat than the arrangement in Fig. 5.27, in which there is no flow and the concentrations remain unchanged.

The thermodynamic treatment of osmosis depends on noting that, at equilibrium, the chemical potential of the solvent must be the same on each side of the membrane. The chemical potential of the solvent is lowered by the solute, but is restored to its 'pure' value by the application of pressure. As shown in the *Justification* below, this equality implies that for dilute solutions the osmotic pressure is given by the **van 't Hoff equation**:

$$\Pi = [B]RT \tag{5.40}°$$

where $[B] = n_B/V$ is the molar concentration of the solute.

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Justification 5.3 *The van 't Hoff equation*

On the pure solvent side the chemical potential of the solvent, which is at a pressure p, is $\mu_A^\star(p)$. On the solution side, the chemical potential is lowered by the presence of the solute, which reduces the mole fraction of the solvent from 1 to x_A. However, the chemical potential of A is raised on account of the greater pressure, $p + \Pi$, that the solution experiences. At equilibrium the chemical potential of A is the same in both compartments, and we can write

$$\mu_A^\star(p) = \mu_A(x_A, p + \Pi)$$

The presence of solute is taken into account in the normal way:

$$\mu_A(x_A, p + \Pi) = \mu_A^\star(p + \Pi) + RT \ln x_A$$

We saw in Section 3.9c (eqn 3.54) how to take the effect of pressure into account:

$$\mu_A^\star(p + \Pi) = \mu_A^\star(p) + \int_p^{p+\Pi} V_m dp$$

where V_m is the molar volume of the pure solvent A. When these three equations are combined we get

$$-RT \ln x_A = \int_p^{p+\Pi} V_m dp$$

This expression enables us to calculate the additional pressure Π that must be applied to the solution to restore the chemical potential of the solvent to its 'pure' value and thus to restore equilibrium across the semipermeable membrane. For dilute solutions, $\ln x_A$ may be replaced by $\ln (1 - x_B) \approx -x_B$. We may also assume that the pressure range in the integration is so small that the molar volume of the solvent is a constant. That being so, V_m may be taken outside the integral, giving

$$RTx_B = \Pi V_m$$

When the solution is dilute, $x_B \approx n_B/n_A$. Moreover, because $n_A V_m = V$, the total volume of the solvent, the equation simplifies to eqn 5.40.

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Because the effect of osmotic pressure is so readily measurable and large, one of the most common applications of osmometry is to the measurement of molar masses of macromolecules, such as proteins and synthetic polymers. As these huge molecules dissolve to produce solutions that are far from ideal, it is assumed that the van 't Hoff equation is only the first term of a virial-like expansion:[4]

$$\Pi = [J]RT\{1 + B[J] + \cdots\} \tag{5.41}$$

The additional terms take the nonideality into account; the empirical constant B is called the **osmotic virial coefficient**.

Example 5.4 *Using osmometry to determine the molar mass of a macromolecule*

The osmotic pressures of solutions of poly(vinyl chloride), PVC, in cyclohexanone at 298 K are given below. The pressures are expressed in terms of the heights of solution (of mass density $\rho = 0.980$ g cm^{-3}) in balance with the osmotic pressure. Determine the molar mass of the polymer.

$c/(g\ dm^{-3})$	1.00	2.00	4.00	7.00	9.00
h/cm	0.28	0.71	2.01	5.10	8.00

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[4] We have denoted the solute J to avoid too many different Bs in this expression.
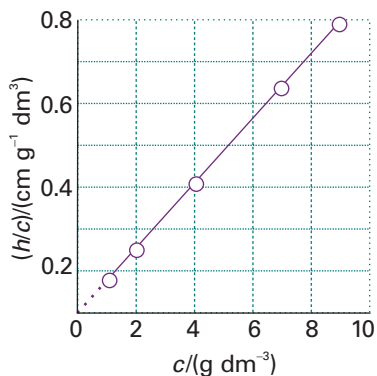
Fig. 5.28 The plot involved in the determination of molar mass by osmometry. The molar mass is calculated from the intercept at $c = 0$; in Chapter 19 we shall see that additional information comes from the slope.

Exploration Calculate the osmotic virial coefficient B from these data.

Method The osmotic pressure is measured at a series of mass concentrations, c, and a plot of Π/c against c is used to determine the molar mass of the polymer. We use eqn 5.41 with $[J] = c/M$ where c is the mass concentration of the polymer and M is its molar mass. The osmotic pressure is related to the hydrostatic pressure by $\Pi = \rho gh$ (Example 1.2) with $g = 9.81$ m s^{-2}. With these substitutions, eqn 5.41 becomes

$$\frac{h}{c} = \frac{RT}{\rho gM}\left(1 + \frac{Bc}{M} + \cdots\right) = \frac{RT}{\rho gM} + \left(\frac{RTB}{\rho gM^2}\right)c + \cdots$$

Therefore, to find M, plot h/c against c, and expect a straight line with intercept $RT/\rho gM$ at $c = 0$.

Answer The data give the following values for the quantities to plot:

$c/(\text{g dm}^{-3})$	1.00	2.00	4.00	7.00	9.00
$(h/c)/(\text{cm g}^{-1}\,\text{dm}^3)$	0.28	0.36	0.503	0.729	0.889

The points are plotted in Fig. 5.28. The intercept is at 0.21. Therefore,

$$M = \frac{RT}{\rho g} \times \frac{1}{0.21 \text{ cm g}^{-1}\,\text{dm}^3}$$

$$= \frac{(8.3145 \text{ J K}^{-1}\,\text{mol}^{-1}) \times (298 \text{ K})}{(980 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2})} \times \frac{1}{2.1 \times 10^{-3} \text{ m}^4\,\text{kg}^{-1}}$$

$$= 1.2 \times 10^2 \text{ kg mol}^{-1}$$

where we have used 1 kg m^2 s^{-2} = 1 J. Molar masses of macromolecules are often reported in daltons (Da), with 1 Da = 1 g mol^{-1}. The macromolecule in this example has a molar mass of about 120 kDa. Modern osmometers give readings of osmotic pressure in pascals, so the analysis of the data is more straightforward and eqn 5.41 can be used directly. As we shall see in Chapter 19, the value obtained from osmometry is the 'number average molar mass'.

Self-test 5.6 Estimate the depression of freezing point of the most concentrated of these solutions, taking K_f as about 10 K/(mol kg^{-1}).   [0.8 mK]
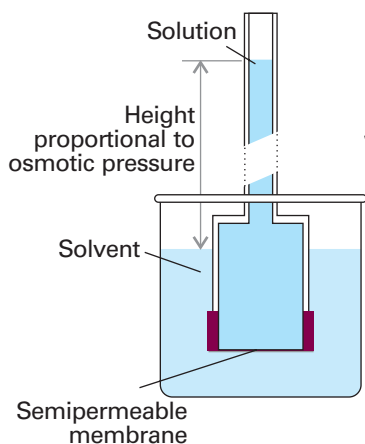
Fig. 5.29 In a simple version of the osmotic pressure experiment, A is at equilibrium on each side of the membrane when enough has passed into the solution to cause a hydrostatic pressure difference.

IMPACT ON BIOLOGY

I5.2 Osmosis in physiology and biochemistry

Osmosis helps biological cells maintain their structure. Cell membranes are semipermeable and allow water, small molecules, and hydrated ions to pass, while blocking the passage of biopolymers synthesized inside the cell. The difference in concentrations of solutes inside and outside the cell gives rise to an osmotic pressure, and water passes into the more concentrated solution in the interior of the cell, carrying small nutrient molecules. The influx of water also keeps the cell swollen, whereas dehydration causes the cell to shrink. These effects are important in everyday medical practice. To maintain the integrity of blood cells, solutions that are injected into the bloodstream for blood transfusions and intravenous feeding must be *isotonic* with the blood, meaning that they must have the same osmotic pressure as blood. If the injected solution is too dilute, or *hypotonic*, the flow of solvent into the cells, required to equalize the osmotic pressure, causes the cells to burst and die by a process called *haemolysis*. If the solution is too concentrated, or *hypertonic*, equalization of the osmotic pressure requires flow of solvent out of the cells, which shrink and die.

Osmosis also forms the basis of *dialysis*, a common technique for the removal of impurities from solutions of biological macromolecules and for the study of binding of small molecules to macromolecules, such as an inhibitor to an enzyme, an antibiotic to DNA, and any other instance of cooperation or inhibition by small molecules attaching to large ones. In a purification experiment, a solution of macromolecules containing impurities, such as ions or small molecules (including small proteins or nucleic acids), is placed in a bag made of a material that acts as a semipermeable membrane and the filled bag is immersed in a solvent. The membrane permits the passage of the small ions and molecules but not the larger macromolecules, so the former migrate through the membrane, leaving the macromolecules behind. In practice, purification of the sample requires several changes of solvent to coax most of the impurities out of the dialysis bag.

In a binding experiment, a solution of macromolecules and smaller ions or molecules is placed in a dialysis bag, which is then immersed in a solvent. Suppose the molar concentration of the macromolecule M is $[M]$ and the total concentration of the small molecule A in the bag is $[A]_{in}$. This total concentration is the sum of the concentrations of free A and bound A, which we write $[A]_{free}$ and $[A]_{bound}$, respectively. At equilibrium, the chemical potential of free A in the macromolecule solution is equal to the chemical potential of A in the solution on the other side of the membrane, where its concentration is $[A]_{out}$. We shall see in Section 5.7 that the equality $\mu_{A,free} = \mu_{A,out}$ implies that $[A]_{free} = [A]_{out}$, provided the activity coefficient of A is the same in both solutions. Therefore, by measuring the concentration of A in the 'outside' solution, we can find the concentration of unbound A in the macromolecule solution and, from the difference $[A]_{in} - [A]_{free}$, which is equal to $[A]_{in} - [A]_{out}$, the concentration of bound A. The average number of A molecules bound to M molecules, v, is then the ratio

$$v = \frac{[A]_{bound}}{[M]} = \frac{[A]_{in} - [A]_{out}}{[M]}$$

The bound and unbound A molecules are in equilibrium, $M + A \rightleftharpoons MA$, so their concentrations are related by an equilibrium constant K, where

$$K = \frac{[MA]}{[M]_{free}[A]_{free}} = \frac{[A]_{bound}}{([M] - [A]_{bound})[A]_{free}}$$

We have used $[MA] = [A]_{bound}$ and $[M]_{free} = [M] - [MA] = [M] - [A]_{bound}$. On division by $[M]$, and replacement of $[A]_{free}$ by $[A]_{out}$, the last expression becomes

$$K = \frac{v}{(1 - v)[A]_{out}}$$

If there are N *identical* and *independent* binding sites on each macromolecule, each macromolecule behaves like N separate smaller macromolecules, with the same value of K for each site. The average number of A molecules per site is v/N, so the last equation becomes

$$K = \frac{v/N}{\left(1 - \dfrac{v}{N}\right)[A]_{out}}$$

It then follows that
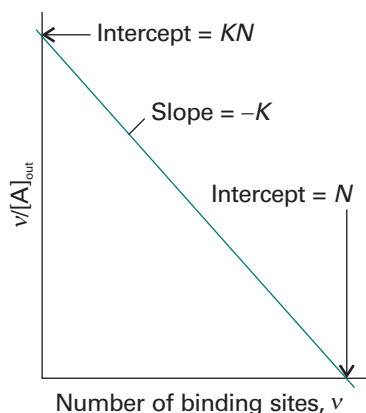
$$\frac{v}{[A]_{out}} = KN - Kv$$

Fig. 5.30 A Scatchard plot of $v/[\text{A}]_{\text{out}}$ against v. The slope is $-K$ and the intercept at $v = 0$ is KN.

Exploration The following tasks will give you an idea of how graphical analysis can distinguish between systems with the same values of K or N. First, display on the same graph several Scatchard plots with varying K values but fixed N. Then repeat the process, this time varying N but fixing K.

This expression is the *Scatchard equation*. It implies that a plot of $v/[\text{A}]_{\text{out}}$ against v should be a straight line of slope $-K$ and intercept KN at $v = 0$ (see Fig. 5.30). From these two quantities, we can find the equilibrium constant for binding and the number of binding sites on each macromolecule. If a straight line is not obtained we can conclude that the binding sites are not equivalent or independent.

Activities

Now we see how to adjust the expressions developed earlier in the chapter to take into account deviations from ideal behaviour. In Chapter 3 (specifically, *Further information 3.2*) we remarked that a quantity called 'fugacity' takes into account the effects of gas imperfections in a manner that resulted in the least upset of the form of equations. Here we see how the expressions encountered in the treatment of ideal solutions can also be preserved almost intact by introducing the concept of 'activity'. It is important to be aware of the different definitions of standard states and activities, and they are summarized in Table 5.3. We shall put them to work in the next few chapters, when we shall see that using them is much easier than defining them.

5.6 The solvent activity

The general form of the chemical potential of a real or ideal solvent is given by a straightforward modification of eqn 5.23 (that $\mu_A = \mu_A^\star + RT \ln(p_A/p_A^\star)$, where $p_A^\star$ is the vapour pressure of pure A and p_A is the vapour pressure of A when it is a component of a solution. For an ideal solution, as we have seen, the solvent obeys Raoult's law at all concentrations and we can express this relation as eqn 5.25 (that is, as $\mu_A = \mu_A^\star + RT \ln x_A$). The form of the this relation can be preserved when the solution does not obey Raoult's law by writing

$$\mu_A = \mu_A^\star + RT \ln a_A \qquad [5.42]$$

The quantity a_A is the **activity** of A, a kind of 'effective' mole fraction, just as the fugacity is an effective pressure.

Because eqn 5.23 is true for both real and ideal solutions (the only approximation being the use of pressures rather than fugacities), we can conclude by comparing it with eqn 5.42 that

$$a_A = \frac{p_A}{p_A^\star} \qquad (5.43)$$

Table 5.3 Standard states

Component	Basis	Standard state	Activity	Limits
Solid or liquid		Pure	$a = 1$	
Solvent	Raoult	Pure solvent	$a = p/p^\star$, $a = \gamma x$	$\gamma \rightarrow 1$ as $x \rightarrow 1$ (pure solvent)
Solute	Henry	(1) A hypothetical state of the pure solute	$a = p/K$, $a = \gamma x$	$\gamma \rightarrow 1$ as $x \rightarrow 0$
		(2) A hypothetical state of the solute at molality $b^\ominus$	$a = \gamma b/b^\ominus$	$\gamma \rightarrow 1$ as $b \rightarrow 0$

In each case, $\mu = \mu^\ominus + RT \ln a$.

We see that there is nothing mysterious about the activity of a solvent: it can be determined experimentally simply by measuring the vapour pressure and then using eqn 5.43.

Illustration 5.3 *Calculating the solvent activity*

The vapour pressure of 0.500 M KNO_3(aq) at 100°C is 99.95 kPa, so the activity of water in the solution at this temperature is

$$a_A = \frac{99.95 \text{ kPa}}{101.325 \text{ kPa}} = 0.9864$$

Because all solvents obey Raoult's law (that $p_A/p_A^* = x_A$) increasingly closely as the concentration of solute approaches zero, the activity of the solvent approaches the mole fraction as $x_A \to 1$:

$$a_A \to x_A \quad \text{as} \quad x_A \to 1 \tag{5.44}$$

A convenient way of expressing this convergence is to introduce the **activity coefficient**, γ, by the definition

$$a_A = \gamma_A x_A \qquad \gamma_A \to 1 \quad \text{as} \quad x_A \to 1 \tag{5.45}$$

at all temperatures and pressures. The chemical potential of the solvent is then

$$\mu_A = \mu_A^* + RT \ln x_A + RT \ln \gamma_A \tag{5.46}$$

The standard state of the solvent, the pure liquid solvent at 1 bar, is established when $x_A = 1$.

5.7 The solute activity

The problem with defining activity coefficients and standard states for solutes is that they approach ideal-dilute (Henry's law) behaviour as $x_B \to 0$, not as $x_B \to 1$ (corresponding to pure solute). We shall show how to set up the definitions for a solute that obeys Henry's law exactly, and then show how to allow for deviations.

(a) Ideal-dilute solutions

A solute B that satisfies Henry's law has a vapour pressure given by $p_B = K_B x_B$, where K_B is an empirical constant. In this case, the chemical potential of B is

$$\mu_B = \mu_B^* + RT \ln \frac{p_B}{p_B^*} = \mu_B^* + RT \ln \frac{K_B}{p_B^*} + RT \ln x_B$$

Both K_B and p_B^* are characteristics of the solute, so the second term may be combined with the first to give a new standard chemical potential:

$$\mu_B^\ominus = \mu_B^* + RT \ln \frac{K_B}{p_B^*} \tag{5.47}$$

It then follows that the chemical potential of a solute in an ideal-dilute solution is related to its mole fraction by

$$\mu_B = \mu_B^\ominus + RT \ln x_B \tag{5.48}°$$

If the solution is ideal, $K_B = p_B^*$ and eqn 5.47 reduces to $\mu_B^\ominus = \mu_B^*$, as we should expect.

(b) Real solutes

We now permit deviations from ideal-dilute, Henry's law behaviour. For the solute, we introduce a_B in place of x_B in eqn 5.48, and obtain

$$\mu_B = \mu_B^\ominus + RT \ln a_B \qquad [5.49]$$

The standard state remains unchanged in this last stage, and all the deviations from ideality are captured in the activity a_B. The value of the activity at any concentration can be obtained in the same way as for the solvent, but in place of eqn 5.43 we use

$$a_B = \frac{p_B}{K_B} \qquad (5.50)$$

As for the solvent, it is sensible to introduce an activity coefficient through

$$a_B = \gamma_B x_B \qquad [5.51]$$

Now all the deviations from ideality are captured in the activity coefficient γ_B. Because the solute obeys Henry's law as its concentration goes to zero, it follows that

$$a_B \to x_B \quad \text{and} \quad \gamma_B \to 1 \quad \text{as} \quad x_B \to 0 \qquad (5.52)$$

at all temperatures and pressures. Deviations of the solute from ideality disappear as zero concentration is approached.

Example 5.5 *Measuring activity*

Use the information in Example 5.3 to calculate the activity and activity coefficient of chloroform in acetone at 25°C, treating it first as a solvent and then as a solute. For convenience, the data are repeated here:

x_C	0	0.20	0.40	0.60	0.80	1
p_C/kPa	0	4.7	11	18.9	26.7	36.4
p_A/kPa	46.3	33.3	23.3	12.3	4.9	0

Method For the activity of chloroform as a solvent (the Raoult's law activity), form $a_C = p_C/p_C^\star$ and $\gamma_C = a_C/x_C$. For its activity as a solute (the Henry's law activity), form $a_C = p_C/K_C$ and $\gamma_C = a_C/x_C$.

Answer Because $p_C^\star = 36.4$ kPa and $K_C = 22.0$ kPa, we can construct the following tables. For instance, at $x_C = 0.20$, in the Raoult's law case we find $a_C = (4.7$ kPa$)/(36.4$ kPa$) = 0.13$ and $\gamma_C = 0.13/0.20 = 0.65$; likewise, in the Henry's law case, $a_C = (4.7$ kPa$)/(22.0$ kPa$) = 0.21$ and $\gamma_C = 0.21/0.20 = 1.05$.

From Raoult's law (chloroform regarded as the solvent):

a_C	0	0.13	0.30	0.52	0.73	1.00
γ_C		0.65	0.75	0.87	0.91	1.00

From Henry's law (chloroform regarded as the solute):

a_C	0	0.21	0.50	0.86	1.21	1.65
γ_C	1	1.05	1.25	1.43	1.51	1.65

These values are plotted in Fig. 5.31. Notice that $\gamma_C \to 1$ as $x_C \to 1$ in the Raoult's law case, but that $\gamma_C \to 1$ as $x_C \to 0$ in the Henry's law case.

Self-test 5.7 Calculate the activities and activity coefficients for acetone according to the two conventions.

[At $x_A = 0.60$, for instance $a_R = 0.50$; $\gamma_R = 0.83$; $a_H = 1.00$, $\gamma_H = 1.67$]
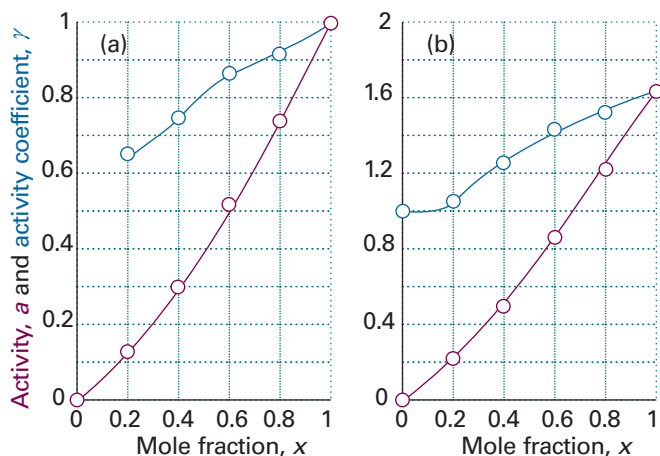
Fig. 5.31 The variation of activity and activity coefficient of chloroform (trichloromethane) and acetone (propanone) with composition according to (a) Raoult's law, (b) Henry's law.

(c) Activities in terms of molalities

The selection of a standard state is entirely arbitrary, so we are free to choose one that best suits our purpose and the description of the composition of the system. In chemistry, compositions are often expressed as molalities, b, in place of mole fractions. It therefore proves convenient to write

$$\mu_B = \mu_B^{\ominus} + RT \ln b_B \qquad \{5.53\}^{\circ}$$

where $\mu^{\ominus}$ has a different value from the standard values introduced earlier. According to this definition, the chemical potential of the solute has its standard value $\mu^{\ominus}$ when the molality of B is equal to $b^{\ominus}$ (that is, at 1 mol kg^{-1}). Note that as $b_B \to 0$, $\mu_B \to -\infty$; that is, as the solution becomes diluted, so the solute becomes increasingly stabilized. The practical consequence of this result is that it is very difficult to remove the last traces of a solute from a solution.

Now, as before, we incorporate deviations from ideality by introducing a dimensionless activity a_B, a dimensionless activity coefficient γ_B, and writing

$$a_B = \gamma_B \frac{b_B}{b^{\ominus}} \qquad \text{where} \quad \gamma_B \to 1 \quad \text{as} \quad b_B \to 0 \qquad [5.54]$$

at all temperatures and pressures. The standard state remains unchanged in this last stage and, as before, all the deviations from ideality are captured in the activity coefficient γ_B. We then arrive at the following succinct expression for the chemical potential of a real solute at any molality:

$$\mu = \mu^{\ominus} + RT \ln a \qquad (5.55)$$

(d) The biological standard state

One important illustration of the ability to choose a standard state to suit the circumstances arises in biological applications. The conventional standard state of hydrogen ions (unit activity, corresponding to pH = 0)[5] is not appropriate to normal biological conditions. Therefore, in biochemistry it is common to adopt the **biological standard state**, in which pH = 7 (an activity of 10^{-7}, neutral solution) and to label the corresponding standard thermodynamic functions as $G^{\oplus}$, $H^{\oplus}$, $\mu^{\oplus}$, and $S^{\oplus}$ (some texts use $X^{\ominus\prime}$).

[5] Recall from introductory chemistry courses that pH = $-\log a_{H_3O^+}$.

To find the relation between the thermodynamic and biological standard values of the chemical potential of hydrogen ions we need to note from eqn 5.55 that

$$\mu_{H^+} = \mu_{H^+}^{\ominus} + RT \ln a_{H^+} = \mu_{H^+}^{\ominus} - (RT \ln 10) \times pH$$

It follows that

$$\mu_{H^+}^{\oplus} = \mu_{H^+}^{\ominus} - 7RT \ln 10 \tag{5.56}$$

At 298 K, $7RT \ln 10 = 39.96$ kJ mol^{-1}, so the two standard values differ by about 40 kJ mol^{-1}.

5.8 The activities of regular solutions

The material on regular solutions presented in Section 5.4 gives further insight into the origin of deviations from Raoult's law and its relation to activity coefficients. The starting point is the expression for the Gibbs energy of mixing for a regular solution (eqn 5.31). We show in the following *Justification* that eqn 5.31 implies that the activity coefficients are given by expressions of the form

$$\ln \gamma_A = \beta x_B^2 \qquad \ln \gamma_B = \beta x_A^2 \tag{5.57}$$

These relations are called the **Margules equations**.

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Justification 5.4 *The Margules equations*

The Gibbs energy of mixing to form a nonideal solution is

$$\Delta_{mix}G = nRT\{x_A \ln a_A + x_B \ln a_B\}$$

This relation follows from the derivation of eqn 5.31 with activities in place of mole fractions. If each activity is replaced by γx, this expression becomes

$$\Delta_{mix}G = nRT\{x_A \ln x_A + x_B \ln x_B + x_A \ln \gamma_A + x_B \ln \gamma_B\}$$

Now we introduce the two expressions in eqn 5.57, and use $x_A + x_B = 1$, which gives

$$\begin{aligned}\Delta_{mix}G &= nRT\{x_A \ln x_A + x_B \ln x_B + \beta x_A x_B^2 + \beta x_B x_A^2\} \\ &= nRT\{x_A \ln x_A + x_B \ln x_B + \beta x_A x_B (x_A + x_B)\} \\ &= nRT\{x_A \ln x_A + x_B \ln x_B + \beta x_A x_B\}\end{aligned}$$

as required by eqn 5.31. Note, moreover, that the activity coefficients behave correctly for dilute solutions: $\gamma_A \to 1$ as $x_B \to 0$ and $\gamma_B \to 1$ as $x_A \to 0$.

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At this point we can use the Margules equations to write the activity of A as

$$a_A = \gamma_A x_A = x_A e^{\beta x_B^2} = x_A e^{\beta(1-x_A)^2} \tag{5.58}$$

with a similar expression for a_B. The activity of A, though, is just the ratio of the vapour pressure of A in the solution to the vapour pressure of pure A (eqn 5.43), so we can write

$$p_A = \{x_A e^{\beta(1-x_A)^2}\}p_A^\star \tag{5.59}$$

This function is plotted in Fig. 5.32. We see that $\beta = 0$, corresponding to an ideal solution, gives a straight line, in accord with Raoult's law (indeed, when $\beta = 0$, eqn 5.59 becomes $p_A = x_A p_A^\star$, which is Raoult's law). Positive values of β (endothermic mixing, unfavourable solute–solvent interactions) give vapour pressures higher than ideal. Negative values of β (exothermic mixing, favourable solute–solvent interactions) give a lower vapour pressure. All the curves approach linearity and coincide with the Raoult's law line as $x_A \to 1$ and the exponential function in eqn 5.59 approaches 1. When $x_A \ll 1$, eqn 5.59 approaches

Fig. 5.32 The vapour pressure of a mixture based on a model in which the excess enthalpy is proportional to $\beta x_A x_B$. An ideal solution corresponds to $\beta = 0$ and gives a straight line, in accord with Raoult's law. Positive values of β give vapour pressures higher than ideal. Negative values of β give a lower vapour pressure.

Exploration Plot $p_A/p_A^\star$ against x_A with $\beta = 2.5$ by using eqn 5.24 and then eqn 5.59. Above what value of x_A do the values of $p_A/p_A^\star$ given by these equations differ by more than 10 per cent?

$$p_A = x_A e^\beta p_A^\star \qquad (5.60)$$

This expression has the form of Henry's law once we identify K with $e^\beta p_A^\star$, which is different for each solute–solvent system.

5.9 **The activities of ions in solution**

Interactions between ions are so strong that the approximation of replacing activities by molalities is valid only in very dilute solutions (less than 10^{-3} mol kg^{-1} in total ion concentration) and in precise work activities themselves must be used. We need, therefore, to pay special attention to the activities of ions in solution, especially in preparation for the discussion of electrochemical phenomena.

(a) Mean activity coefficients

If the chemical potential of a univalent cation M^+ is denoted μ_+ and that of a univalent anion X^- is denoted μ_-, the total molar Gibbs energy of the ions in the electrically neutral solution is the sum of these partial molar quantities. The molar Gibbs energy of an *ideal* solution is

$$G_m^{ideal} = \mu_+^{ideal} + \mu_-^{ideal} \qquad (5.61)°$$

However, for a *real* solution of M^+ and X^- of the same molality,

$$G_m = \mu_+ + \mu_- = \mu_+^{ideal} + \mu_-^{ideal} + RT \ln \gamma_+ + RT \ln \gamma_- = G_m^{ideal} + RT \ln \gamma_+ \gamma_- \qquad (5.62)$$

All the deviations from ideality are contained in the last term.

There is no experimental way of separating the product $\gamma_+ \gamma_-$ into contributions from the cations and the anions. The best we can do experimentally is to assign responsibility for the nonideality equally to both kinds of ion. Therefore, for a 1,1-electrolyte, we introduce the **mean activity coefficient** as the geometric mean of the individual coefficients:

$$\gamma_\pm = (\gamma_+ \gamma_-)^{1/2} \qquad [5.63]$$

and express the individual chemical potentials of the ions as

$$\mu_+ = \mu_+^{ideal} + RT \ln \gamma_\pm \qquad \mu_- = \mu_-^{ideal} + RT \ln \gamma_\pm \qquad (5.64)$$

The sum of these two chemical potentials is the same as before, eqn 5.62, but now the nonideality is shared equally.

We can generalize this approach to the case of a compound $M_p X_q$ that dissolves to give a solution of p cations and q anions from each formula unit. The molar Gibbs energy of the ions is the sum of their partial molar Gibbs energies:

$$G_m = p\mu_+ + q\mu_- = G_m^{ideal} + pRT \ln \gamma_+ + qRT \ln \gamma_- \qquad (5.65)$$

If we introduce the mean activity coefficient

$$\gamma_\pm = (\gamma_+^p \gamma_-^q)^{1/s} \qquad s = p + q \qquad [5.66]$$

and write the chemical potential of each ion as

$$\mu_i = \mu_i^{ideal} + RT \ln \gamma_\pm \qquad (5.67)$$

we get the same expression as in eqn 5.62 for G_m when we write

$$G = p\mu_+ + q\mu_- \qquad (5.68)$$

However, both types of ion now share equal responsibility for the nonideality.

(b) The Debye–Hückel limiting law

The long range and strength of the Coulombic interaction between ions means that it is likely to be primarily responsible for the departures from ideality in ionic solutions

Comment 5.4

The geometric mean of x^p and y^q is $(x^p y^q)^{1/(p+q)}$. For example, the geometric mean of x^2 and y^{-3} is $(x^2 y^{-3})^{-1}$.
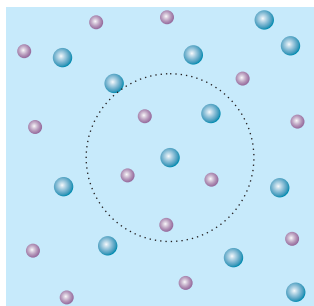
Fig. 5.33 The picture underlying the Debye–Hückel theory is of a tendency for anions to be found around cations, and of cations to be found around anions (one such local clustering region is shown by the circle). The ions are in ceaseless motion, and the diagram represents a snapshot of their motion. The solutions to which the theory applies are far less concentrated than shown here.

and to dominate all the other contributions to nonideality. This domination is the basis of the **Debye–Hückel theory** of ionic solutions, which was devised by Peter Debye and Erich Hückel in 1923. We give here a qualitative account of the theory and its principal conclusions. The calculation itself, which is a profound example of how a seemingly intractable problem can be formulated and then resolved by drawing on physical insight, is described in *Further information 5.1*.

Oppositely charged ions attract one another. As a result, anions are more likely to be found near cations in solution, and vice versa (Fig. 5.33). Overall, the solution is electrically neutral, but near any given ion there is an excess of counter ions (ions of opposite charge). Averaged over time, counter ions are more likely to be found near any given ion. This time-averaged, spherical haze around the central ion, in which counter ions outnumber ions of the same charge as the central ion, has a net charge equal in magnitude but opposite in sign to that on the central ion, and is called its **ionic atmosphere**. The energy, and therefore the chemical potential, of any given central ion is lowered as a result of its electrostatic interaction with its ionic atmosphere. This lowering of energy appears as the difference between the molar Gibbs energy G_m and the ideal value G_m^{ideal} of the solute, and hence can be identified with $RT \ln \gamma_\pm$. The stabilization of ions by their interaction with their ionic atmospheres is part of the explanation why chemists commonly use dilute solutions, in which the stabilization is less important, to achieve precipitation of ions from electrolyte solutions.

The model leads to the result that at very low concentrations the activity coefficient can be calculated from the **Debye–Hückel limiting law**

$$\log \gamma_\pm = -|z_+ z_-| A I^{1/2} \tag{5.69}$$

where $A = 0.509$ for an aqueous solution at 25°C and I is the dimensionless **ionic strength** of the solution:

$$I = \tfrac{1}{2} \sum_i z_i^2 (b_i/b^\ominus) \tag{5.70}$$

In this expression z_i is the charge number of an ion i (positive for cations and negative for anions) and b_i is its molality. The ionic strength occurs widely wherever ionic solutions are discussed, as we shall see. The sum extends over all the ions present in the solution. For solutions consisting of two types of ion at molalities b_+ and b_-,

$$I = \tfrac{1}{2}(b_+ z_+^2 + b_- z_-^2)/b^\ominus \tag{5.71}$$

The ionic strength emphasizes the charges of the ions because the charge numbers occur as their squares. Table 5.4 summarizes the relation of ionic strength and molality in an easily usable form.

Table 5.4 Ionic strength and molality, $I = kb/b^\ominus$

k	X^-	X^{2-}	X^{3-}	X^{4-}
M^+	1	3	6	10
M^{2+}	3	4	15	12
M^{3+}	6	15	9	42
M^{4+}	10	12	42	16

For example, the ionic strength of an M_2X_3 solution of molality b, which is understood to give M^{3+} and X^{2-} ions in solution is $15b/b^\ominus$.

Illustration 5.4 *Using the Debye–Hückel limiting law*

The mean activity coefficient of 5.0×10^{-3} mol kg^{-1} KCl(aq) at 25°C is calculated by writing

$$I = \tfrac{1}{2}(b_+ + b_-)/b^\ominus = b/b^\ominus$$

where b is the molality of the solution (and $b_+ = b_- = b$). Then, from eqn 5.69,

$$\log \gamma_\pm = -0.509 \times (5.0 \times 10^{-3})^{1/2} = -0.036$$

Hence, $\gamma_\pm = 0.92$. The experimental value is 0.927.

Self-test 5.8 Calculate the ionic strength and the mean activity coefficient of 1.00 mmol kg^{-1} CaCl$_2$(aq) at 25°C.   [3.00 mmol kg^{-1}, 0.880]

The name 'limiting law' is applied to eqn 5.69 because ionic solutions of moderate molalities may have activity coefficients that differ from the values given by this expression, yet all solutions are expected to conform as $b \to 0$. Table 5.5 lists some experimental values of activity coefficients for salts of various valence types. Figure 5.34 shows some of these values plotted against $I^{1/2}$, and compares them with the theoretical straight lines calculated from eqn 5.69. The agreement at very low molalities (less than about 1 mmol kg^{-1}, depending on charge type) is impressive, and convincing evidence in support of the model. Nevertheless, the departures from the theoretical curves above these molalities are large, and show that the approximations are valid only at very low concentrations.

(c) The extended Debye–Hückel law

When the ionic strength of the solution is too high for the limiting law to be valid, the activity coefficient may be estimated from the **extended Debye–Hückel law**:

$$\log \gamma_\pm = -\frac{A\,|z_+ z_-|\,I^{1/2}}{1 + BI^{1/2}} + CI \qquad (5.72)$$

where B and C are dimensionless constants. Although B can be interpreted as a measure of the closest approach of the ions, it (like C) is best regarded as an adjustable empirical parameter. A curve drawn in this way is shown in Fig. 5.35. It is clear that

Synoptic Table 5.5* Mean activity coefficients in water at 298 K

$b/b^{\ominus}$	KCl	CaCl$_2$
0.001	0.966	0.888
0.01	0.902	0.732
0.1	0.770	0.524
1.0	0.607	0.725

* More values are given in the *Data section*.
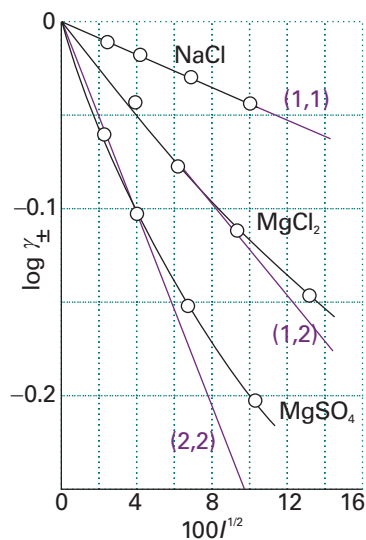
Fig. 5.34 An experimental test of the Debye–Hückel limiting law. Although there are marked deviations for moderate ionic strengths, the limiting slopes as $I \to 0$ are in good agreement with the theory, so the law can be used for extrapolating data to very low molalities.
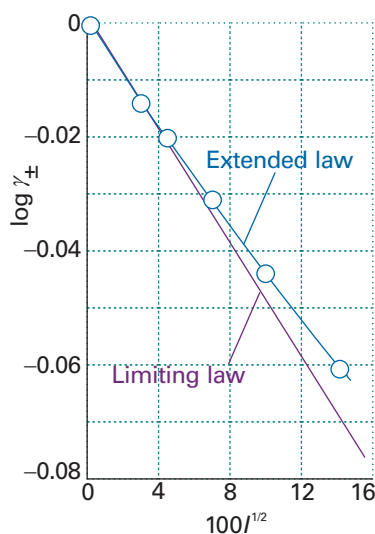
Fig. 5.35 The extended Debye–Hückel law gives agreement with experiment over a wider range of molalities (as shown here for a 1,1-electrolyte), but it fails at higher molalities.

Exploration Consider the plot of $\log \gamma_\pm$ against $I^{1/2}$ with $B = 1.50$ and $C = 0$ as a representation of experimental data for a certain 1,1-electrolyte. Over what range of ionic strengths does the application of the limiting law lead to an error in the value of the activity coefficient of less than 10 per cent of the value predicted by the extended law?

eqn 5.72 accounts for some activity coefficients over a moderate range of dilute solutions (up to about 0.1 mol kg^{-1}); nevertheless it remains very poor near 1 mol kg^{-1}.

Current theories of activity coefficients for ionic solutes take an indirect route. They set up a theory for the dependence of the activity coefficient of the solvent on the concentration of the solute, and then use the Gibbs–Duhem equation (eqn 5.12) to estimate the activity coefficient of the solute. The results are reasonably reliable for solutions with molalities greater than about 0.1 mol kg^{-1} and are valuable for the discussion of mixed salt solutions, such as sea water.

Checklist of key ideas

1. The partial molar volume is the change in volume per mole of A added to a large volume of the mixture: $V_J = (\partial V/\partial n_J)_{p,T,n'}$. The total volume of a mixture is $V = n_A V_A + n_B V_B$.

2. The chemical potential can be defined in terms of the partial molar Gibbs energy, $\mu_J = (\partial G/\partial n_J)_{p,T,n'}$. The total Gibbs energy of a mixture is $G = n_A \mu_A + n_B \mu_B$.

3. The fundamental equation of chemical thermodynamics relates the change in Gibbs energy to changes in pressure, temperature, and composition: $dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \cdots$.

4. The Gibbs–Duhem equation is $\sum_J n_J d\mu_J = 0$.

5. The chemical potential of a perfect gas is $\mu = \mu^\ominus + RT \ln(p/p^\ominus)$, where $\mu^\ominus$ is the standard chemical potential, the chemical potential of the pure gas at 1 bar.

6. The Gibbs energy of mixing of two perfect gases is given by $\Delta_{mix}G = nRT(x_A \ln x_A + x_B \ln x_B)$.

7. The entropy of mixing of two perfect gases is given by $\Delta_{mix}S = -nR(x_A \ln x_A + x_B \ln x_B)$.

8. The enthalpy of mixing is $\Delta_{mix}H = 0$ for perfect gases.

9. An ideal solution is a solution in which all components obeys Raoult's law ($p_A = x_A p_A^\star$) throughout the composition range.

10. The chemical potential of a component of an ideal solution is given by $\mu_A = \mu_A^\star + RT \ln x_A$.

11. An ideal-dilute solution is a solution for which the solute obeys Henry's law ($p_B = x_B K_B^\star$) and the solvent obeys Raoult's law.

12. The Gibbs energy of mixing of two liquids that form an ideal solution is given by $\Delta_{mix}G = nRT(x_A \ln x_A + x_B \ln x_B)$.

13. The entropy of mixing of two liquids that form an ideal solution is given by $\Delta_{mix}S = -nR(x_A \ln x_A + x_B \ln x_B)$.

14. An excess function (X^E) is the difference between the observed thermodynamic function of mixing and the function for an ideal solution.

15. A regular solution is a solution for which $H^E \neq 0$ but $S^E = 0$.

16. A colligative property is a property that depends only on the number of solute particles present, not their identity.

17. The elevation of boiling point is given by $\Delta T = K_b b$, where K_b is the ebullioscopic constant. The depression of freezing point is given by $\Delta T = K_f b$, where K_f is the cryoscopic constant.

18. Osmosis is the spontaneous passage of a pure solvent into a solution separated from it by a semipermeable membrane, a membrane permeable to the solvent but not to the solute.

19. The osmotic pressure is the pressure that must be applied to the solution to stop the influx of solvent.

20. The van 't Hoff equation for the osmotic pressure is $\Pi = [B]RT$.

21. The activity is defined as $a_A = p_A/p_A^\star$.

22. The solvent activity is related to its chemical potential by $\mu_A = \mu_A^\star + RT \ln a_A$. The activity may be written in terms of the activity coefficient $\gamma_A = a_A/x_A$.

23. The chemical potential of a solute in an ideal-dilute solution is given by $\mu_B = \mu_B^\ominus + RT \ln a_B$. The activity may be written in terms of the activity coefficient $\gamma_B = a_B/x_B$.

24. The biological standard state (pH = 7) is related to the thermodynamic standard state by $\mu_{H^+}^\oplus = \mu_{H^+}^\ominus - 7RT \ln 10$.

25. The mean activity coefficient is the geometric mean of the individual coefficients: $\gamma_\pm = (\gamma_+^p \gamma_-^q)^{1/(p+q)}$.

26. The Debye–Hückel theory of activity coefficients of electrolyte solutions is based on the assumption that Coulombic interactions between ions are dominant; a key idea of the theory is that of an ionic atmosphere.

27. The Debye–Hückel limiting law is log $\gamma_\pm = -|z_+ z_-|AI^{1/2}$ where I is the ionic strength, $I = \frac{1}{2}\sum_i z_i^2(b_i/b^\ominus)$.

28. The extended Debye–Hückel law is ln $\gamma_\pm = -|z_+ z_-|AI^{1/2}/(1 + BI^{1/2}) + CI$.

Further reading

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Further information

Further information 5.1 *The Debye–Hückel theory of ionic solutions*

Imagine a solution in which all the ions have their actual positions, but in which their Coulombic interactions have been turned off. The difference in molar Gibbs energy between the ideal and real solutions is equal to w_e, the electrical work of charging the system in this arrangement. For a salt M_pX_q, we write

$$w_e = \overbrace{(p\mu_+ + q\mu_-)}^{G_m} - \overbrace{(p\mu_+^{ideal} + q\mu_-^{ideal})}^{G_m^{ideal}}$$
$$= p(\mu_+ - \mu_+^{ideal}) + q(\mu_- - \mu_-^{ideal})$$

From eqn 5.64 we write

$$\mu_+ - \mu_+^{ideal} = \mu_- - \mu_-^{ideal} = RT \ln \gamma_\pm$$

So it follows that

$$\ln \gamma_\pm = \frac{w_e}{sRT} \qquad s = p + q \qquad (5.73)$$

This equation tells us that we must first find the final distribution of the ions and then the work of charging them in that distribution.

The Coulomb potential at a distance r from an isolated ion of charge $z_i e$ in a medium of permittivity ε is

$$\phi_i = \frac{Z_i}{r} \qquad Z_i = \frac{z_i e}{4\pi\varepsilon} \qquad (5.74)$$

The ionic atmosphere causes the potential to decay with distance more sharply than this expression implies. Such shielding is a familiar problem in electrostatics, and its effect is taken into account by replacing the Coulomb potential by the **shielded Coulomb potential**, an expression of the form

$$\phi_i = \frac{Z_i}{r} e^{-r/r_D} \qquad (5.75)$$

where r_D is called the **Debye length**. When r_D is large, the shielded potential is virtually the same as the unshielded potential. When it is small, the shielded potential is much smaller than the unshielded potential, even for short distances (Fig. 5.36).
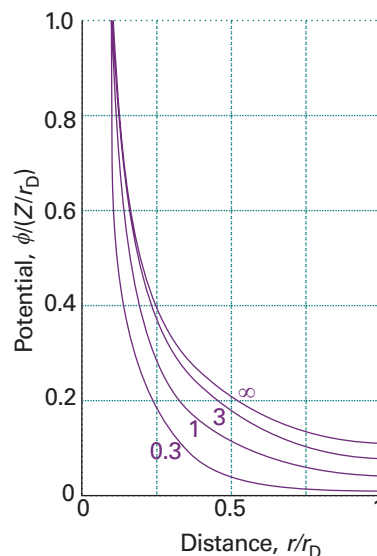
Fig. 5.36 The variation of the shielded Coulomb potential with distance for different values of the Debye length, r_D/a. The smaller the Debye length, the more sharply the potential decays to zero. In each case, a is an arbitrary unit of length.

Exploration Write an expression for the difference between the unshielded and shielded Coulomb potentials evaluated at r_D. Then plot this expression against r_D and provide a physical interpretation for the shape of the plot.

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[6] See *Further reading* in Chapter 2 for additional texts on chemical thermodynamics.

To calculate r_D, we need to know how the **charge density**, ρ_i, of the ionic atmosphere, the charge in a small region divided by the volume of the region, varies with distance from the ion. This step draws on another standard result of electrostatics, in which charge density and potential are related by **Poisson's equation** (see *Appendix 3*):

$$\nabla^2 \phi = -\frac{\rho}{\varepsilon} \tag{5.76}$$

where $\nabla^2 = (\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2)$ is called the *laplacian*. Because we are considering only a spherical ionic atmosphere, we can use a simplified form of this equation in which the charge density varies only with distance from the central ion:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d\phi_i}{dr}\right) = -\frac{\rho_i}{\varepsilon}$$

Comment 5.5

For systems with spherical symmetry, it is best to work in spherical polar coordinates r, θ, and ϕ (see the illustration): $x = r \sin\theta \cos\phi$, $y = r \sin\theta \sin\phi$, and $z = r \cos\theta$. The laplacian in spherical polar coordinates is

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial \theta^2}$$

When a function depends only on r, the derivatives in the second and third terms evaluate to zero and the laplacian takes the form

$$\nabla^2 = \frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d}{dr}\right)$$

Substitution of the expression for the shielded potential, eqn 5.75, results in

$$r_D^2 = -\frac{\varepsilon\phi_i}{\rho_i} \tag{5.77}$$

To solve this equation we need to relate ρ_i and ϕ_i.
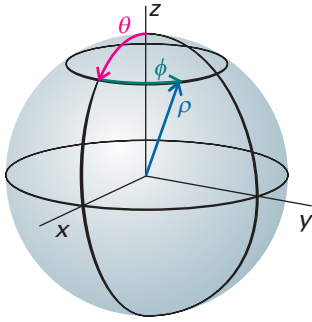
For the next step we draw on the fact that the energy of an ion depends on its closeness to the central ion, and then use the Boltzmann distribution (see Section 16.1) to work out the probability that an ion will be found at each distance. The energy of an ion of charge $z_j e$ at a distance where it experiences the potential ϕ_i of the central ion i relative to its energy when it is far away in the bulk solution is its charge times the potential:

$$E = z_j e \phi_i$$

Therefore, according to the Boltzmann distribution, the ratio of the molar concentration, c_j, of ions at a distance r and the molar concentration in the bulk, c_j°, where the energy is zero, is:

$$\frac{c_j}{c_j^\circ} = e^{-E/kT}$$

The charge density, ρ_i, at a distance r from the ion i is the molar concentration of each type of ion multiplied by the charge per mole of ions, $z_i e N_A$. The quantity $e N_A$, the magnitude of the charge per mole of electrons, is Faraday's constant, $F = 96.48$ kC mol^{-1}. It follows that

$$\rho_i = c_+ z_+ F + c_- z_- F = c_+^\circ z_+ F e^{-z_+ e\phi_i/kT} + c_-^\circ z_- F e^{-z_- e\phi_i/kT} \tag{5.78}$$

At this stage we need to simplify the expression to avoid the awkward exponential terms. Because the average electrostatic interaction energy is small compared with kT we may write eqn 5.78 as

$$\rho_i = c_+^\circ z_+ F\left(1 - \frac{z_+ e\phi_i}{kT} + \cdots\right) + c_-^\circ z_- F\left(1 - \frac{z_- e\phi_i}{kT} + \cdots\right)$$

$$= (c_+^\circ z_+ + c_-^\circ z_-)F - (c_+^\circ z_+^2 + c_-^\circ z_-^2)F\frac{e\phi_i}{kT} + \cdots$$

Comment 5.6

The expansion of an exponential function used here is $e^{-x} = 1 - x + \frac{1}{2}x^2 - \cdots$. If $x \ll 1$, then $e^{-x} \approx 1 - x$.

Replacing e by F/N_A and $N_A k$ by R results in the following expression:

$$\rho_i = (c_+^\circ z_+ + c_-^\circ z_-)F - (c_+^\circ z_+^2 + c_-^\circ z_-^2)\frac{F^2 \phi_i}{RT} + \cdots \tag{5.79}$$

The first term in the expansion is zero because it is the charge density in the bulk, uniform solution, and the solution is electrically neutral. The unwritten terms are assumed to be too small to be significant. The one remaining term can be expressed in terms of the ionic strength, eqn 5.70, by noting that in the dilute aqueous solutions we are considering there is little difference between molality and molar concentration, and $c \approx b\rho$, where ρ is the mass density of the solvent

$$c_+^\circ z_+^2 + c_-^\circ z_-^2 \approx (b_+^\circ z_+^2 + b_-^\circ z_-^2)\rho = 2Ib^\ominus \rho$$

With these approximations, eqn 5.78 becomes

$$\rho_i = -\frac{2\rho F^2 I b^\ominus \phi_i}{RT}$$

We can now solve eqn 5.77 for r_D:

$$r_D = \left(\frac{\varepsilon RT}{2\rho F^2 I b^\ominus}\right)^{1/2} \tag{5.80}$$

To calculate the activity coefficient we need to find the electrical work of charging the central ion when it is surrounded by its atmosphere. To do so, we need to know the potential at the ion due to its atmosphere, ϕ_{atmos}. This potential is the difference between the total potential, given by eqn 5.75, and the potential due to the central ion itself:

$$\phi_{atmos} = \phi - \phi_{central\ ion} = Z_i\left(\frac{e^{-r/r_D}}{r} - \frac{1}{r}\right)$$

The potential at the central ion (at $r = 0$) is obtained by taking the limit of this expression as $r \to 0$ and is

$$\phi_{atmos}(0) = \frac{Z_i}{r_D}$$

This expression shows us that the potential of the ionic atmosphere is equivalent to the potential arising from a single charge of equal magnitude but opposite sign to that of the central ion and located at a distance r_D from the ion. If the charge of the central ion were q and not $z_i e$, then the potential due to its atmosphere would be

$$\phi_{atmos}(0) = -\frac{q}{4\pi\varepsilon r_D}$$

The work of adding a charge dq to a region where the electrical potential is $\phi_{atmos}(0)$ is

$$dw_e = \phi_{atmos}(0)dq$$

Therefore, the total molar work of fully charging the ions is

$$w_e = N_A \int_0^{z_i e} \phi_{atmos}(0)\, dq = -\frac{N_A}{4\pi\varepsilon r_D}\int_0^{z_i e} q\, dq$$

$$= -\frac{N_A z_i^2 e^2}{8\pi\varepsilon r_D} = -\frac{z_i^2 F^2}{8\pi\varepsilon N_A r_D}$$

where in the last step we have used $F = N_A e$. It follows from eqn 5.73 that the mean activity coefficient of the ions is

$$\ln\gamma_\pm = \frac{pw_{e,+} + qw_{e,-}}{sRT} = -\frac{(pz_+^2 + qz_-^2)F^2}{8\pi\varepsilon sN_A RT r_D}$$

However, for neutrality $pz_+ + qz_- = 0$; therefore

$$\ln\gamma_\pm = -\frac{|z_+ z_-|F^2}{8\pi\varepsilon N_A RT r_D}$$

Replacing r_D with the expression in eqn 5.79 gives

$$\ln\gamma_\pm = -\frac{|z_+ z_-|F^2}{8\pi\varepsilon N_A RT}\left(\frac{2\rho F^2 Ib^{\ominus}}{\varepsilon RT}\right)^{1/2}$$

$$= -|z_+ z_-|\left\{\frac{F^3}{4\pi N_A}\left(\frac{\rho b^{\ominus}}{2\varepsilon^3 R^3 T^3}\right)^{1/2}\right\}I^{1/2}$$

where we have grouped terms in such a way as to show that this expression is beginning to take the form of eqn 5.69. Indeed, conversion to common logarithms (by using $\ln x = \ln 10 \times \log x$) gives

$$\log\gamma_\pm = -|z_+ z_-|\left\{\frac{F^3}{4\pi N_A \ln 10}\left(\frac{\rho b^{\ominus}}{2\varepsilon^3 R^3 T^3}\right)^{1/2}\right\}I^{1/2}$$

which is eqn 5.69 ($\log\gamma_\pm = -|z_+ z_-|AI^{1/2}$) with

$$A = \frac{F^3}{4\pi N_A \ln 10}\left(\frac{\rho b^{\ominus}}{2\varepsilon^3 R^3 T^3}\right)^{1/2} \tag{5.81}$$

Discussion questions

5.1 State and justify the thermodynamic criterion for solution–vapour equilibrium.

5.2 How is Raoult's law modified so as to describe the vapour pressure of real solutions?

5.3 Explain how colligative properties are used to determine molar mass.

5.4 Explain the origin of colligative properties.

5.5 Explain what is meant by a regular solution.

5.6 Describe the general features of the Debye–Hückel theory of electrolyte solutions.

Exercises

5.1(a) The partial molar volumes of acetone (propanone) and chloroform (trichloromethane) in a mixture in which the mole fraction of $CHCl_3$ is 0.4693 are 74.166 $cm^3\ mol^{-1}$ and 80.235 $cm^3\ mol^{-1}$, respectively. What is the volume of a solution of mass 1.000 kg?

5.1(b) The partial molar volumes of two liquids A and B in a mixture in which the mole fraction of A is 0.3713 are 188.2 $cm^3\ mol^{-1}$ and 176.14 $cm^3\ mol^{-1}$, respectively. The molar masses of A and B are 241.1 $g\ mol^{-1}$ and 198.2 $g\ mol^{-1}$. What is the volume of a solution of mass 1.000 kg?

5.2(a) At 25°C, the density of a 50 per cent by mass ethanol–water solution is 0.914 $g\ cm^{-3}$. Given that the partial molar volume of water in the solution is 17.4 $cm^3\ mol^{-1}$, calculate the partial molar volume of the ethanol.

5.2(b) At 20°C, the density of a 20 per cent by mass ethanol–water solution is 968.7 $kg\ m^{-3}$. Given that the partial molar volume of ethanol in the solution is 52.2 $cm^3\ mol^{-1}$, calculate the partial molar volume of the water.

5.3(a) At 300 K, the partial vapour pressures of HCl (that is, the partial pressure of the HCl vapour) in liquid $GeCl_4$ are as follows:

x_{HCl}	0.005	0.012	0.019
p_{HCl}/kPa	32.0	76.9	121.8

Show that the solution obeys Henry's law in this range of mole fractions, and calculate Henry's law constant at 300 K.

5.3(b) At 310 K, the partial vapour pressures of a substance B dissolved in a liquid A are as follows:

x_B	0.010	0.015	0.020
p_B/kPa	82.0	122.0	166.1

Show that the solution obeys Henry's law in this range of mole fractions, and calculate Henry's law constant at 310 K.

5.4(a) Predict the partial vapour pressure of HCl above its solution in liquid germanium tetrachloride of molality 0.10 mol kg^{-1}. For data, see Exercise 5.3a.

5.4(b) Predict the partial vapour pressure of the component B above its solution in A in Exercise 5.3b when the molality of B is 0.25 mol kg^{-1}. The molar mass of A is 74.1 g mol^{-1}.

5.5(a) The vapour pressure of benzene is 53.3 kPa at 60.6°C, but it fell to 51.5 kPa when 19.0 g of an involatile organic compound was dissolved in 500 g of benzene. Calculate the molar mass of the compound.

5.5(b) The vapour pressure of 2-propanol is 50.00 kPa at 338.8°C, but it fell to 49.62 kPa when 8.69 g of an involatile organic compound was dissolved in 250 g of 2-propanol. Calculate the molar mass of the compound.

5.6(a) The addition of 100 g of a compound to 750 g of CCl$_4$ lowered the freezing point of the solvent by 10.5 K. Calculate the molar mass of the compound.

5.6(b) The addition of 5.00 g of a compound to 250 g of naphthalene lowered the freezing point of the solvent by 0.780 K. Calculate the molar mass of the compound.

5.7(a) The osmotic pressure of an aqueous solution at 300 K is 120 kPa. Calculate the freezing point of the solution.

5.7(b) The osmotic pressure of an aqueous solution at 288 K is 99.0 kPa. Calculate the freezing point of the solution.

5.8(a) Consider a container of volume 5.0 dm^3 that is divided into two compartments of equal size. In the left compartment there is nitrogen at 1.0 atm and 25°C; in the right compartment there is hydrogen at the same temperature and pressure. Calculate the entropy and Gibbs energy of mixing when the partition is removed. Assume that the gases are perfect.

5.8(b) Consider a container of volume 250 cm^3 that is divided into two compartments of equal size. In the left compartment there is argon at 100 kPa and 0°C; in the right compartment there is neon at the same temperature and pressure. Calculate the entropy and Gibbs energy of mixing when the partition is removed. Assume that the gases are perfect.

5.9(a) Air is a mixture with a composition given in *Self-test 1.4*. Calculate the entropy of mixing when it is prepared from the pure (and perfect) gases.

5.9(b) Calculate the Gibbs energy, entropy, and enthalpy of mixing when 1.00 mol C$_6$H$_{14}$ (hexane) is mixed with 1.00 mol C$_7$H$_{16}$ (heptane) at 298 K; treat the solution as ideal.

5.10(a) What proportions of hexane and heptane should be mixed (a) by mole fraction, (b) by mass in order to achieve the greatest entropy of mixing?

5.10(b) What proportions of benzene and ethylbenzene should be mixed (a) by mole fraction, (b) by mass in order to achieve the greatest entropy of mixing?

5.11(a) Use Henry's law and the data in Table 5.1 to calculate the solubility (as a molality) of CO$_2$ in water at 25°C when its partial pressure is (a) 0.10 atm, (b) 1.00 atm.

5.11(b) The mole fractions of N$_2$ and O$_2$ in air at sea level are approximately 0.78 and 0.21. Calculate the molalities of the solution formed in an open flask of water at 25°C.

5.12(a) A water carbonating plant is available for use in the home and operates by providing carbon dioxide at 5.0 atm. Estimate the molar concentration of the soda water it produces.

5.12(b) After some weeks of use, the pressure in the water carbonating plant mentioned in the previous exercise has fallen to 2.0 atm. Estimate the molar concentration of the soda water it produces at this stage.

5.13(a) The enthalpy of fusion of anthracene is 28.8 kJ mol^{-1} and its melting point is 217°C. Calculate its ideal solubility in benzene at 25°C.

5.13(b) Predict the ideal solubility of lead in bismuth at 280°C given that its melting point is 327°C and its enthalpy of fusion is 5.2 kJ mol^{-1}.

5.14(a) The osmotic pressure of solutions of polystyrene in toluene were measured at 25°C and the pressure was expressed in terms of the height of the solvent of density 1.004 g cm^{-3}:

$c/(\text{g dm}^{-3})$	2.042	6.613	9.521	12.602
h/cm	0.592	1.910	2.750	3.600

Calculate the molar mass of the polymer.

5.14(b) The molar mass of an enzyme was determined by dissolving it in water, measuring the osmotic pressure at 20°C, and extrapolating the data to zero concentration. The following data were obtained:

$c/(\text{mg cm}^{-3})$	3.221	4.618	5.112	6.722
h/cm	5.746	8.238	9.119	11.990

Calculate the molar mass of the enzyme.

5.15(a) Substances A and B are both volatile liquids with $p_A^\star = 300$ Torr, $p_B^\star = 250$ Torr, and $K_B = 200$ Torr (concentration expressed in mole fraction). When $x_A = 0.9$, $b_B = 2.22$ mol kg^{-1}, $p_A = 250$ Torr, and $p_B = 25$ Torr. Calculate the activities and activity coefficients of A and B. Use the mole fraction, Raoult's law basis system for A and the Henry's law basis system (both mole fractions and molalities) for B.

5.15(b) Given that $p^\star(\text{H}_2\text{O}) = 0.02308$ atm and $p(\text{H}_2\text{O}) = 0.02239$ atm in a solution in which 0.122 kg of a non-volatile solute ($M = 241$ g mol^{-1}) is dissolved in 0.920 kg water at 293 K, calculate the activity and activity coefficient of water in the solution.

5.16(a) A dilute solution of bromine in carbon tetrachloride behaves as an ideal-dilute solution. The vapour pressure of pure CCl$_4$ is 33.85 Torr at 298 K. The Henry's law constant when the concentration of Br$_2$ is expressed as a mole fraction is 122.36 Torr. Calculate the vapour pressure of each component, the total pressure, and the composition of the vapour phase when the mole fraction of Br$_2$ is 0.050, on the assumption that the conditions of the ideal-dilute solution are satisfied at this concentration.

5.16(b) Benzene and toluene form nearly ideal solutions. The boiling point of pure benzene is 80.1°C. Calculate the chemical potential of benzene relative to that of pure benzene when $x_{\text{benzene}} = 0.30$ at its boiling point. If the activity coefficient of benzene in this solution were actually 0.93 rather than 1.00, what would be its vapour pressure?

5.17(a) By measuring the equilibrium between liquid and vapour phases of an acetone (A)–methanol (M) solution at 57.2°C at 1.00 atm, it was found that $x_A = 0.400$ when $y_A = 0.516$. Calculate the activities and activity coefficients of both components in this solution on the Raoult's law basis. The vapour pressures of the pure components at this temperature are: $p_A^\star = 105$ kPa and $p_M^\star = 73.5$ kPa. (x_A is the mole fraction in the liquid and y_A the mole fraction in the vapour.)

5.17(b) By measuring the equilibrium between liquid and vapour phases of a solution at 30°C at 1.00 atm, it was found that $x_A = 0.220$ when $y_A = 0.314$. Calculate the activities and activity coefficients of both components in this solution on the Raoult's law basis. The vapour pressures of the pure components at this temperature are: $p_A^\star = 73.0$ kPa and $p_B^\star = 92.1$ kPa. (x_A is the mole fraction in the liquid and y_A the mole fraction in the vapour.)

5.18(a) Calculate the ionic strength of a solution that is 0.10 mol kg^{-1} in KCl(aq) and 0.20 mol kg^{-1} in CuSO$_4$(aq).

5.18(b) Calculate the ionic strength of a solution that is 0.040 mol kg^{-1} in K$_3$[Fe(CN)$_6$](aq), 0.030 mol kg^{-1} in KCl(aq), and 0.050 mol kg^{-1} in NaBr(aq).

5.19(a) Calculate the masses of (a) $Ca(NO_3)_2$ and, separately, (b) NaCl to add to a 0.150 mol kg^{-1} solution of $KNO_3(aq)$ containing 500 g of solvent to raise its ionic strength to 0.250.

5.19(b) Calculate the masses of (a) KNO_3 and, separately, (b) $Ba(NO_3)_2$ to add to a 0.110 mol kg^{-1} solution of $KNO_3(aq)$ containing 500 g of solvent to raise its ionic strength to 1.00.

5.20(a) Estimate the mean ionic activity coefficient and activity of a solution that is 0.010 mol kg^{-1} $CaCl_2(aq)$ and 0.030 mol kg^{-1} NaF(aq).

5.20(b) Estimate the mean ionic activity coefficient and activity of a solution that is 0.020 mol kg^{-1} NaCl(aq) and 0.035 mol kg^{-1} $Ca(NO_3)_2(aq)$.

5.21(a) The mean activity coefficients of HBr in three dilute aqueous solutions at 25°C are 0.930 (at 5.0 mmol kg^{-1}), 0.907 (at 10.0 mmol kg^{-1}), and 0.879 (at 20.0 mmol kg^{-1}). Estimate the value of B in the extended Debye–Hückel law.

5.21(b) The mean activity coefficients of KCl in three dilute aqueous solutions at 25°C are 0.927 (at 5.0 mmol kg^{-1}), 0.902 (at 10.0 mmol kg^{-1}), and 0.816 (at 50.0 mmol kg^{-1}). Estimate the value of B in the extended Debye–Hückel law.

Problems*

Numerical problems

5.1 The following table gives the mole fraction of methylbenzene (A) in liquid and gaseous mixtures with butanone at equilibrium at 303.15 K and the total pressure p. Take the vapour to be perfect and calculate the partial pressures of the two components. Plot them against their respective mole fractions in the liquid mixture and find the Henry's law constants for the two components.

x_A	0	0.0898	0.2476	0.3577	0.5194	0.6036
y_A	0	0.0410	0.1154	0.1762	0.2772	0.3393
p/kPa	36.066	34.121	30.900	28.626	25.239	23.402

x_A	0.7188	0.8019	0.9105	1
y_A	0.4450	0.5435	0.7284	1
p/kPa	20.6984	18.592	15.496	12.295

5.2 The volume of an aqueous solution of NaCl at 25°C was measured at a series of molalities b, and it was found that the volume fitted the expression $v = 1003 + 16.62x + 1.77x^{3/2} + 0.12x^2$ where $v = V/cm^3$, V is the volume of a solution formed from 1.000 kg of water, and $x = b/b^\oplus$. Calculate the partial molar volume of the components in a solution of molality 0.100 mol kg^{-1}.

5.3 At 18°C the total volume V of a solution formed from $MgSO_4$ and 1.000 kg of water fits the expression $v = 1001.21 + 34.69(x - 0.070)^2$, where $v = V/cm^3$ and $x = b/b^\oplus$. Calculate the partial molar volumes of the salt and the solvent when in a solution of molality 0.050 mol kg^{-1}.

5.4 The densities of aqueous solutions of copper(II) sulfate at 20°C were measured as set out below. Determine and plot the partial molar volume of $CuSO_4$ in the range of the measurements.

$m(CuSO_4)$/g	5	10	15	20
ρ/(g cm^{-3})	1.051	1.107	1.167	1.230

where $m(CuSO_4)$ is the mass of $CuSO_4$ dissolved in 100 g of solution.

5.5 What proportions of ethanol and water should be mixed in order to produce 100 cm^3 of a mixture containing 50 per cent by mass of ethanol? What change in volume is brought about by adding 1.00 cm^3 of ethanol to the mixture? (Use data from Fig. 5.1.)

5.6 Potassium fluoride is very soluble in glacial acetic acid and the solutions have a number of unusual properties. In an attempt to understand them, freezing point depression data were obtained by taking a solution of known molality and then diluting it several times (J. Emsley, *J. Chem. Soc. A*, 2702 (1971)). The following data were obtained:

b/(mol kg^{-1})	0.015	0.037	0.077	0.295	0.602
ΔT/K	0.115	0.295	0.470	1.381	2.67

Calculate the apparent molar mass of the solute and suggest an interpretation. Use $\Delta_{fus}H = 11.4$ kJ mol^{-1} and $T_f^* = 290$ K.

5.7 In a study of the properties of an aqueous solution of $Th(NO_3)_4$ (by A. Apelblat, D. Azoulay, and A. Sahar, *J. Chem. Soc. Faraday Trans., I*, 1618, (1973)), a freezing point depression of 0.0703 K was observed for an aqueous solution of molality 9.6 mmol kg^{-1}. What is the apparent number of ions per formula unit?

5.8 The table below lists the vapour pressures of mixtures of iodoethane (I) and ethyl acetate (A) at 50°C. Find the activity coefficients of both components on (a) the Raoult's law basis, (b) the Henry's law basis with iodoethane as solute.

x_I	0	0.0579	0.1095	0.1918	0.2353	0.3718
p_I/kPa	0	3.73	7.03	11.7	14.05	20.72
p_A/kPa	37.38	35.48	33.64	30.85	29.44	25.05

x_I	0.5478	0.6349	0.8253	0.9093	1.0000
p_I/kPa	28.44	31.88	39.58	43.00	47.12
p_A/kPa	19.23	16.39	8.88	5.09	0

5.9 Plot the vapour pressure data for a mixture of benzene (B) and acetic acid (A) given below and plot the vapour pressure/composition curve for the mixture at 50°C. Then confirm that Raoult's and Henry's laws are obeyed in the appropriate regions. Deduce the activities and activity coefficients of the components on the Raoult's law basis and then, taking B as the solute, its activity and activity coefficient on a Henry's law basis. Finally, evaluate the excess Gibbs energy of the mixture over the composition range spanned by the data.

x_A	0.0160	0.0439	0.0835	0.1138	0.1714
p_A/kPa	0.484	0.967	1.535	1.89	2.45
p_B/kPa	35.05	34.29	33.28	32.64	30.90

x_A	0.2973	0.3696	0.5834	0.6604	0.8437	0.9931
p_A/kPa	3.31	3.83	4.84	5.36	6.76	7.29
p_B/kPa	28.16	26.08	20.42	18.01	10.0	0.47

5.10‡ Aminabhavi *et al.* examined mixtures of cyclohexane with various long-chain alkanes (T.M. Aminabhavi, V.B. Patil, M.I, Aralaguppi, J.D. Ortego, and K.C. Hansen, *J. Chem. Eng. Data* **41**, 526 (1996)). Among their data are the following measurements of the density of a mixture of cyclohexane and pentadecane as a function of mole fraction of cyclohexane (x_c) at 298.15 K:

x_c	0.6965	0.7988	0.9004
ρ/(g cm^{-3})	0.7661	0.7674	0.7697

* Problems denoted with the symbol ‡ were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.

Compute the partial molar volume for each component in a mixture that has a mole fraction cyclohexane of 0.7988.

5.11‡ Comelli and Francesconi examined mixtures of propionic acid with various other organic liquids at 313.15 K (F. Comelli and R. Francesconi, *J. Chem. Eng. Data* **41**, 101 (1996)). They report the excess volume of mixing propionic acid with oxane as $V^E = x_1 x_2\{a_0 + a_1(x_1 - x_2)\}$, where x_1 is the mole fraction of propionic acid, x_2 that of oxane, $a_0 = -2.4697$ cm^3 mol^{-1} and $a_1 = 0.0608$ cm^3 mol^{-1}. The density of propionic acid at this temperature is 0.97174 g cm^{-3}; that of oxane is 0.86398 g cm^{-3}. (a) Derive an expression for the partial molar volume of each component at this temperature. (b) Compute the partial molar volume for each component in an equimolar mixture.

5.12‡ Francesconi *et al.* studied the liquid–vapour equilibria of trichloromethane and 1,2-epoxybutane at several temperatures (R. Francesconi, B. Lunelli, and F. Comelli, *J. Chem. Eng. Data* **41**, 310 (1996)). Among their data are the following measurements of the mole fractions of trichloromethane in the liquid phase (x_T) and the vapour phase (y_T) at 298.15 K as a function of pressure.

p/kPa	23.40	21.75	20.25	18.75	18.15	20.25	22.50	26.30
x	0	0.129	0.228	0.353	0.511	0.700	0.810	1
y	0	0.065	0.145	0.285	0.535	0.805	0.915	1

Compute the activity coefficients of both components on the basis of Raoult's law.

5.13‡ Chen and Lee studied the liquid–vapour equilibria of cyclohexanol with several gases at elevated pressures (J.-T. Chen and M.-J. Lee, *J. Chem. Eng. Data* **41**, 339 (1996)). Among their data are the following measurements of the mole fractions of cyclohexanol in the vapour phase (y) and the liquid phase (x) at 393.15 K as a function of pressure.

p/bar	10.0	20.0	30.0	40.0	60.0	80.0
y_{cyc}	0.0267	0.0149	0.0112	0.00947	0.00835	0.00921
x_{cyc}	0.9741	0.9464	0.9204	0.892	0.836	0.773

Determine the Henry's law constant of CO_2 in cyclohexanol, and compute the activity coefficient of CO_2.

5.14‡ Equation 5.39 indicates that solubility is an exponential function of temperature. The data in the table below gives the solubility, S, of calcium acetate in water as a function of temperature.

θ/°C	0	20	40	60	80
S/(mol dm^{-3})	36.4	34.9	33.7	32.7	31.7

Determine the extent to which the data fit the exponential $S = S_0 e^{\tau/T}$ and obtain values for S_0 and τ. Express these constants in terms of properties of the solute.

5.15 The excess Gibbs energy of solutions of methylcyclohexane (MCH) and tetrahydrofuran (THF) at 303.15 K was found to fit the expression

$$G^E = RTx(1-x)\{0.4857 - 0.1077(2x-1) + 0.0191(2x-1)^2\}$$

where x is the mole fraction of the methylcyclohexane. Calculate the Gibbs energy of mixing when a mixture of 1.00 mol of MCH and 3.00 mol of THF is prepared.

5.16 The mean activity coefficients for aqueous solutions of NaCl at 25°C are given below. Confirm that they support the Debye–Hückel limiting law and that an improved fit is obtained with the extended law.

b/(mmol kg^{-1})	1.0	2.0	5.0	10.0	20.0
$\gamma_{\pm}$	0.9649	0.9519	0.9275	0.9024	0.8712

Theoretical problems

5.17 The excess Gibbs energy of a certain binary mixture is equal to $gRTx(1-x)$ where g is a constant and x is the mole fraction of a solute A.

Find an expression for the chemical potential of A in the mixture and sketch its dependence on the composition.

5.18 Use the Gibbs–Duhem equation to derive the Gibbs–Duhem–Margules equation

$$\left(\frac{\partial \ln f_A}{\partial \ln x_A}\right)_{p,T} = \left(\frac{\partial \ln f_B}{\partial \ln x_B}\right)_{p,T}$$

where f is the fugacity. Use the relation to show that, when the fugacities are replaced by pressures, if Raoult's law applies to one component in a mixture it must also apply to the other.

5.19 Use the Gibbs–Duhem equation to show that the partial molar volume (or any partial molar property) of a component B can be obtained if the partial molar volume (or other property) of A is known for all compositions up to the one of interest. Do this by proving that

$$V_B = V_B^{\star} - \int_{V_A^{\star}}^{V_A} \frac{x_A}{1 - x_A}\, dV_A$$

Use the following data (which are for 298 K) to evaluate the integral graphically to find the partial molar volume of acetone at $x = 0.500$.

$x(CHCl_3)$	0	0.194	0.385	0.559	0.788	0.889	1.000
V_m/(cm^3 mol^{-1})	73.99	75.29	76.50	77.55	79.08	79.82	80.67

5.20 Use the Gibbs–Helmholtz equation to find an expression for d ln x_A in terms of dT. Integrate d ln x_A from $x_A = 0$ to the value of interest, and integrate the right–hand side from the transition temperature for the pure liquid A to the value in the solution. Show that, if the enthalpy of transition is constant, then eqns 5.33 and 5.36 are obtained.

5.21 The 'osmotic coefficient', ϕ, is defined as $\phi = -(x_A/x_B) \ln a_A$. By writing $r = x_B/x_A$, and using the Gibbs–Duhem equation, show that we can calculate the activity of B from the activities of A over a composition range by using the formula

$$\ln\left(\frac{a_B}{r}\right) = \phi - \phi(0) + \int_0^r \left(\frac{\phi - 1}{r}\right) dr$$

5.22 Show that the osmotic pressure of a real solution is given by $\Pi V = -RT \ln a_A$. Go on to show that, provided the concentration of the solution is low, this expression takes the form $\Pi V = \phi RT[B]$ and hence that the osmotic coefficient, ϕ, (which is defined in Problem 5.21) may be determined from osmometry.

5.23 Show that the freezing-point depression of a real solution in which the solvent of molar mass M has activity a_A obeys

$$\frac{d \ln a_A}{d(\Delta T)} = -\frac{M}{K_f}$$

and use the Gibbs–Duhem equation to show that

$$\frac{d \ln a_B}{d(\Delta T)} = -\frac{1}{b_B K_f}$$

where a_B is the solute activity and b_B is its molality. Use the Debye–Hückel limiting law to show that the osmotic coefficient (ϕ, Problem 5.21) is given by $\phi = 1 - \frac{1}{3}A'I$ with $A' = 2.303A$ and $I = b/b^{\ominus}$.

Applications: to biology and polymer science

5.24 Haemoglobin, the red blood protein responsible for oxygen transport, binds about 1.34 cm^3 of oxygen per gram. Normal blood has a haemoglobin concentration of 150 g dm^{-3}. Haemoglobin in the lungs is about 97 per cent saturated with oxygen, but in the capillary is only about 75 per cent saturated.

What volume of oxygen is given up by 100 cm³ of blood flowing from the lungs in the capillary?

5.25 For the calculation of the solubility c of a gas in a solvent, it is often convenient to use the expression $c = Kp$, where K is the Henry's law constant. Breathing air at high pressures, such as in scuba diving, results in an increased concentration of dissolved nitrogen. The Henry's law constant for the solubility of nitrogen is 0.18 µg/(g H₂O atm). What mass of nitrogen is dissolved in 100 g of water saturated with air at 4.0 atm and 20°C? Compare your answer to that for 100 g of water saturated with air at 1.0 atm. (Air is 78.08 mole per cent N₂.) If nitrogen is four times as soluble in fatty tissues as in water, what is the increase in nitrogen concentration in fatty tissue in going from 1 atm to 4 atm?

5.26 Ethidium bromide binds to DNA by a process called *intercalation*, in which the aromatic ethidium cation fits between two adjacent DNA base pairs. An equilibrium dialysis experiment was used to study the binding of ethidium bromide (EB) to a short piece of DNA. A 1.00 µmol dm⁻³ aqueous solution of the DNA sample was dialysed against an excess of EB. The following data were obtained for the total concentration of EB:

[EB]/(µmol dm⁻³)

Side without DNA	0.042	0.092	0.204	0.526	1.150
Side with DNA	0.292	0.590	1.204	2.531	4.150

From these data, make a Scatchard plot and evaluate the intrinsic equilibrium constant, K, and total number of sites per DNA molecule. Is the identical and independent sites model for binding applicable?

5.27 The form of the Scatchard equation given in *Impact I5.2* applies only when the macromolecule has identical and independent binding sites. For non-identical independent binding sites, the Scatchard equation is

$$\frac{\nu}{[A]_{out}} = \sum_i \frac{N_i K_i}{1 + K_i[A]_{out}}$$

Plot $\nu/[A]$ for the following cases. (a) There are four independent sites on an enzyme molecule and the intrinsic binding constant is $K = 1.0 \times 10^7$. (b) There are a total of six sites per polymer. Four of the sites are identical and have an intrinsic binding constant of 1×10^5. The binding constants for the other two sites are 2×10^6.

5.28 The addition of a small amount of a salt, such as $(NH_4)_2SO_4$, to a solution containing a charged protein increases the solubility of the protein in water. This observation is called the *salting-in effect*. However, the addition of large amounts of salt can decrease the solubility of the protein to such an extent that the protein precipitates from solution. This observation is called the *salting-out effect* and is used widely by biochemists to isolate and purify proteins. Consider the equilibrium $PX_\nu(s) \rightleftharpoons P^{\nu+}(aq) + \nu X^-(aq)$, where $P^{\nu+}$ is a polycationic protein of charge $+\nu$ and X^- is its counter ion. Use Le Chatelier's principle and the physical principles behind the Debye–Hückel theory to provide a molecular interpretation for the salting-in and salting-out effects.

5.29‡ Polymer scientists often report their data in rather strange units. For example, in the determination of molar masses of polymers in solution by osmometry, osmotic pressures are often reported in grams per square centimetre (g cm⁻²) and concentrations in grams per cubic centimetre (g cm⁻³). (a) With these choices of units, what would be the units of R in the van't Hoff equation? (b) The data in the table below on the concentration dependence of the osmotic pressure of polyisobutene in chlorobenzene at 25°C have been adapted from J. Leonard and H. Daoust (*J. Polymer Sci.* **57**, 53 (1962)). From these data, determine the molar mass of polyisobutene by plotting Π/c against c. (c) Theta solvents are solvents for which the second osmotic coefficient is zero; for 'poor' solvents the plot is linear and for good solvents the plot is nonlinear. From your plot, how would you classify chlorobenzene as a solvent for polyisobutene? Rationalize the result in terms of the molecular structure of the polymer and solvent. (d) Determine the second and third osmotic virial coefficients by fitting the curve to the virial form of the osmotic pressure equation. (e) Experimentally, it is often found that the virial expansion can be represented as

$$\Pi/c = RT/M \, (1 + B'c + gB'^2 c'^2 + \cdots)$$

and in good solvents, the parameter g is often about 0.25. With terms beyond the second power ignored, obtain an equation for $(\Pi/c)^{1/2}$ and plot this quantity against c. Determine the second and third virial coefficients from the plot and compare to the values from the first plot. Does this plot confirm the assumed value of g?

$10^{-2}(\Pi/c)/(\text{g cm}^{-2}/\text{g cm}^{-3})$	2.6	2.9	3.6	4.3	6.0	12.0
$c/(\text{g cm}^{-3})$		0.0050	0.010	0.020	0.033	0.057	0.10
$10^{-2}(\Pi/c)/(\text{g cm}^{-2}/\text{g cm}^{-3})$	19.0	31.0	38.0	52	63	
$c/(\text{g cm}^{-3})$	0.145	0.195	0.245	0.27	0.29	

5.30‡ K. Sato, F.R. Eirich, and J.E. Mark (*J. Polymer Sci.*, *Polym. Phys.* **14**, 619 (1976)) have reported the data in the table below for the osmotic pressures of polychloroprene ($\rho = 1.25$ g cm⁻³) in toluene ($\rho = 0.858$ g cm⁻³) at 30°C. Determine the molar mass of polychloroprene and its second osmotic virial coefficient.

$c/(\text{mg cm}^{-3})$	1.33	2.10	4.52	7.18	9.87
$\Pi/(\text{N m}^{-2})$	30	51	132	246	390