

7.8 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.

Because $\ln x < 0$, it follows that $\Delta_{\text{mix}}S > 0$ for all compositions (Fig. 7.8). This increase in entropy is what we expect when one gas disperses into the other and the system becomes more disordered. The Gibbs energy of mixing in Example 7.2 was calculated as $-(4.0 \text{ mol})RT \ln 2$, so the corresponding entropy of mixing is $+(4.0 \text{ mol})R \ln 2$, or $+23 \text{ J K}^{-1}$.

We can calculate the isothermal, isobaric (constant pressure) **enthalpy of mixing**, $\Delta_{\text{mix}}H$, the enthalpy change accompanying mixing, of two perfect gases from $\Delta G = \Delta H - T\Delta S$. It follows from eqns 18 and 19 that

$$\Delta_{\text{mix}}H = 0 \quad (7.20)^\circ$$

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.

7.3 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 μ_A^* , and as $\mu_A^*(l)$ when we need to emphasize that A is a liquid. Because the vapour pressure of the pure liquid is p_A^* , it follows from eqn 14 that the chemical potential of A in the vapour is $\mu_A^g + RT \ln p_A^*$ (with p_A to be interpreted as the relative pressure p_A/p^\ominus). These two chemical potentials are equal at equilibrium (Fig. 7.9), so we can write

$$\mu_A^* = \mu_A^g + RT \ln p_A^* \quad (7.21)$$

If another substance, a solute, is also present in the liquid, the chemical potential of A in the liquid is μ_A and its vapour pressure is p_A . In this case

$$\mu_A = \mu_A^g + RT \ln p_A \quad (7.22)$$

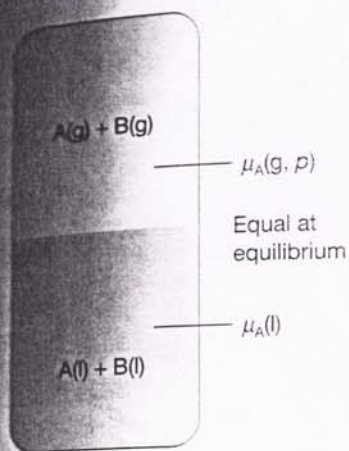
Next, we combine these two equations to eliminate the standard chemical potential of the gas, and obtain

$$\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*} \quad (7.23)$$

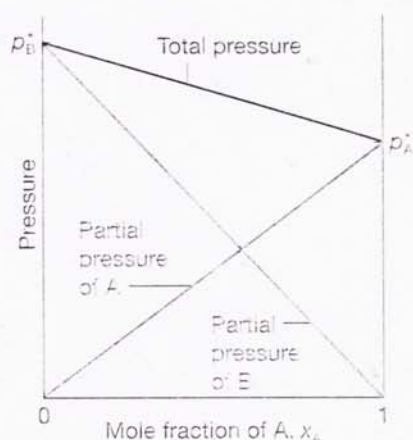
In the final step we draw on additional experimental information about the relation between the ratio of vapour pressures and the composition of the liquid. In a series of experiments on mixtures of closely related liquids (such as benzene and methylbenzene), the French chemist François Raoult found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

$$p_A = x_A p_A^* \quad (7.24)^\circ$$

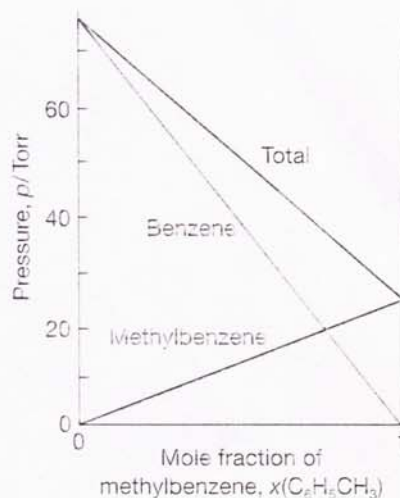
This law is illustrated in Fig. 7.10. Some mixtures obey Raoult's law very well, especially when the components are structurally similar (Fig. 7.11). Mixtures that obey the law throughout the composition range from pure A to pure B are called **ideal**



7.9 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.



7.10 The total vapour pressure and the two partial vapour pressures of an ideal binary mixture are proportional to the mole fractions of the components.



7.11 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.

solutions. When we write equations that are valid only for ideal solutions, we shall label them with a superscript \circ , as in eqn 24.

For an ideal solution, it follows from eqns 23 and 24 that

$$u_A = u_A^\circ - RT \ln x_A \quad (7.25)^\circ$$

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 24 because it does not assume that the gas is perfect.

Molecular interpretation 7.1

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. 7.12).

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:

$$\text{rate of vaporization} = kx_A$$

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:

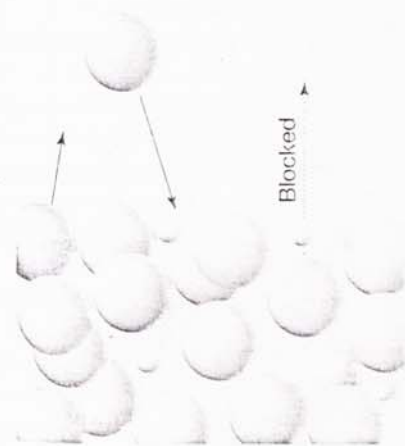
$$\text{rate of condensation} = k'p_A$$

At equilibrium, the rates of vaporization and condensation are equal, so

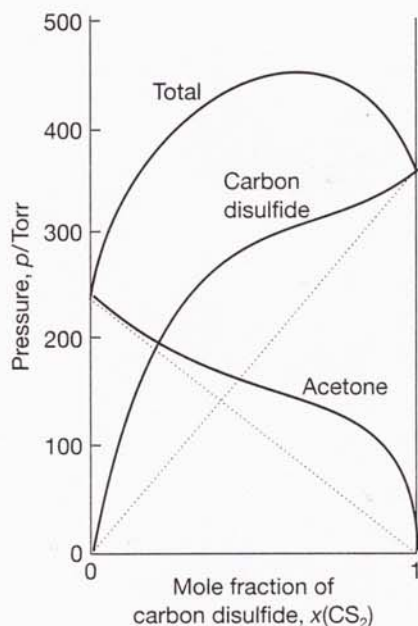
$$k'p_A = kx_A$$

It follows that

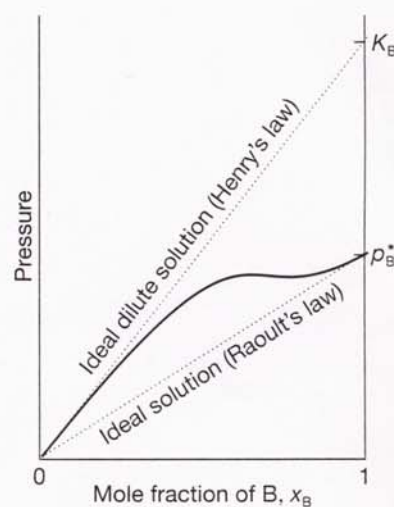
$$p_A = \frac{k}{k'} x_A$$



7.12 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.



7.13 Strong deviations from ideality are shown by dissimilar liquids (in this case carbon disulfide and acetone (propanone)).



7.14 When a component (the solvent) is nearly pure, it has a vapour pressure that is proportional to the mole fraction with a slope p_B^* (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).

For the pure liquid, $x_A = 1$; so

$$p_A^* = \frac{k}{k'}$$

Equation 24 then follows by substitution of this relation into the previous one.

Some solutions depart significantly from Raoult's law (Fig. 7.13). 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. 7.14). Henry's law is:

$$p_B = x_B K_B \quad (7.25)$$

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 \circ when they have been derived from Henry's law.

Molecular interpretation 7.2

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. 7.15). 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 7.3 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/Torr	0	35	82	142	200	273
p_A/Torr	347	250	175	92	37	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. 7.16 together with the Raoult's law lines. Henry's law requires $K = 175$ Torr for propanone and $K = 165$ Torr for trichloromethane.

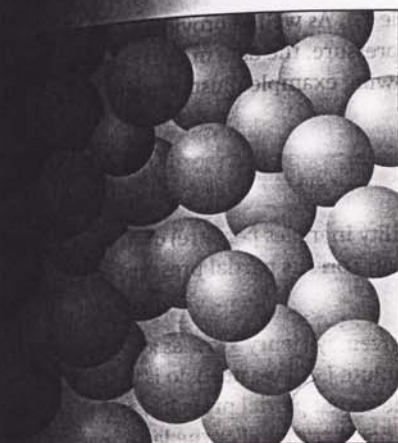
Comment Notice how the system deviates from both Raoult's and Henry's laws even for quite small departures from $x = 1$ and $x = 0$, respectively. We deal with these deviations in Section 7.5.

Self-test 7.4 The vapour pressure of chloromethane at various mole fractions in a mixture at 25°C was found to be as follows:

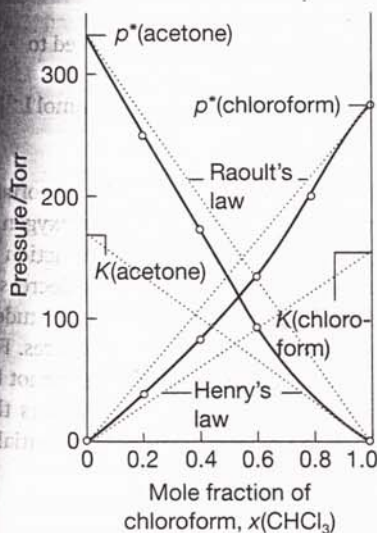
x	0.005	0.009	0.019	0.024
p/Torr	205	363	756	946

Estimate Henry's law constant.

$[4 \times 10^4 \text{ Torr}]$



In a dilute solution, the solvent molecules (the blue 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 liquid.



7.16 The experimental partial vapour pressures of a mixture of chloroform (trichloromethane) and acetone (propanone) based on the data in Example 7.3. The values of K are obtained by extrapolating the dilute solution vapour pressures as explained in the Example.

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

Table 7.1* Henry's law constants for gases in water at 298 K

	K/(10 MPa)	K/Torr
CO ₂	0.167	1.25 × 10 ⁶
H ₂	7.12	5.34 × 10 ⁷
N ₂	8.68	6.51 × 10 ⁷
O ₂	4.40	3.30 × 10 ⁷

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

Some Henry's law data are listed in Table 7.1. 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. The following example illustrates the procedure.

Example 7.4 Using Henry's law

Estimate the molar solubility (the solubility in moles per litre) of oxygen in water at 25°C and a partial pressure of 160 Torr, its partial pressure in the atmosphere at sea level.

Method The mole fraction of solute is given by Henry's law as $x_j = p_j/K_j$, where p_j is the partial pressure of the gaseous solute J. All we need do is to calculate the mole fraction that corresponds to the stated partial pressure, and then interpret that mole fraction as a molar concentration. For the latter part of the calculation, we calculate the amount of O₂ dissolved in 1.00 kg of water (which corresponds to about 1.00 L water). The solution is dilute, so the expressions for the mole fraction can be simplified.

Answer Because the amount of O₂ dissolved is small, its mole fraction is

$$x_{\text{O}_2} = \frac{n_{\text{O}_2}}{n_{\text{O}_2} + n_{\text{H}_2\text{O}}} \approx \frac{n_{\text{O}_2}}{n_{\text{H}_2\text{O}}}$$

Hence,

$$n_{\text{O}_2} \approx x_{\text{O}_2} n_{\text{H}_2\text{O}} = \frac{p_{\text{O}_2} n_{\text{H}_2\text{O}}}{K} \approx \frac{(160 \text{ Torr}) \times (55.5 \text{ mol})}{3.30 \times 10^7 \text{ Torr}} = 2.69 \times 10^{-4} \text{ mol}$$

The molality of the saturated solution is therefore $2.69 \times 10^{-4} \text{ mol kg}^{-1}$, corresponding to a molar concentration of approximately $2.7 \times 10^{-4} \text{ mol L}^{-1}$.

Self-test 7.5 Calculate the molar solubility of nitrogen in water exposed to air at 25°C; partial pressures were calculated in Example 1.5.

[0.51 mmol L⁻¹]

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. For example, the molar solubility of O₂ gas in blood decreases with decreasing atmospheric pressure and this impairs respiration at high altitudes. Conversely, the solubility of air in blood increases with increasing pressures. For this reason, a diver who has been underwater for a long period of time cannot be returned to the surface too rapidly: the sudden decrease in pressure lowers the solubility of gases and forms bubbles (emboli) in the bloodstream, with potentially fatal consequences.

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.

7.4 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 7.2). The total Gibbs energy before liquids are mixed is

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

When they are mixed, the individual chemical potentials are given by eqn 25 and the total Gibbs energy is

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

Consequently, the Gibbs energy of mixing is

$$\Delta_{\text{mix}} G = nRT \{ x_A \ln x_A + x_B \ln x_B \} \quad (7.27)^c$$

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

$$\Delta_{\text{mix}} S = -nR \{ x_A \ln x_A + x_B \ln x_B \} \quad (7.28)^c$$

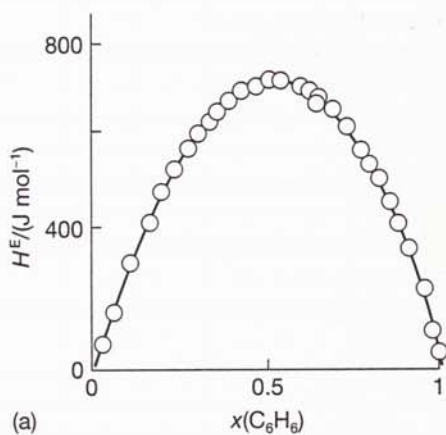
and the ideal enthalpy of mixing is zero.

Equation 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 interactions between molecules. In ideal solutions there are interactions, but the average A-B interactions in the mixture are the same as the average A-A and B-B interactions in the pure liquids. The variation of the Gibbs energy of mixing with composition is the same as that already depicted for gases in Fig. 7.6; the same is true of the entropy of mixing, Fig. 7.8.

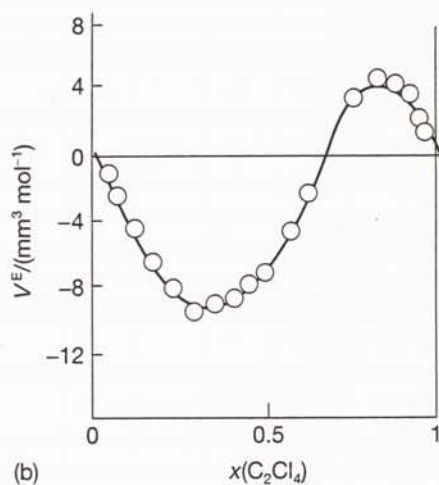
Real solutions are composed of particles for which A-A, A-B, and B-B interactions are all different. Not only may there be an enthalpy change when liquids mix, but there may also be an additional contribution to the entropy arising from the way in which the molecules of one type might cluster together 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



(a)



(b)

7.17 Experimental excess functions at 25°C.

(a) H^E for benzene/cyclohexane; this graph shows that the mixing is endothermic (because $\Delta_{\text{mix}}H = 0$ for an ideal solution).

(b) The excess volume, V^E , for tetrachloroethane/cyclopentane; this graph shows that there is a contraction at low tetrachloroethane mole fractions, but an expansion at high mole fractions (because $\Delta_{\text{mix}}V = 0$ for an ideal mixture).

$$S^E = \Delta_{\text{mix}}S - \Delta_{\text{mix}}S^{\text{ideal}} \quad [7.29]$$

where $\Delta_{\text{mix}}S^{\text{ideal}}$ is given by eqn 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 7.17 shows two examples of the composition dependence of excess functions.

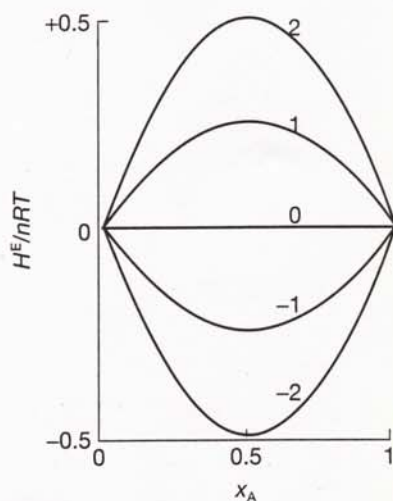
We can make this discussion more quantitative by supposing that the excess enthalpy depends on composition as

$$H^E = n\beta RTx_Ax_B \quad (7.30)$$

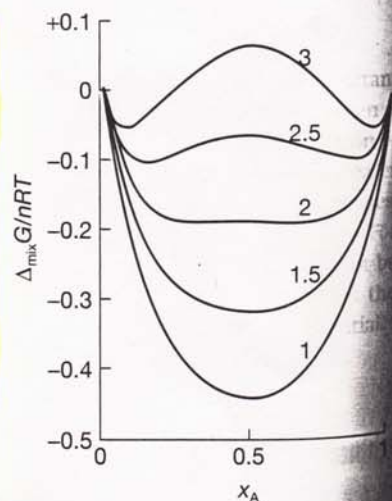
where β is a parameter. We let $\beta = w/RT$, where w is an indication of the energy of AB interactions relative to AA and BB interactions. The function given by eqn 30 is plotted in Fig. 7.18, and we see it resembles the experimental curve in Fig. 7.17. If $\beta < 0$, mixing is exothermic and the solute-solvent interactions are more favourable than the solvent-solvent and solute-solute interactions. If $\beta > 0$, then the mixing is 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

$$\Delta_{\text{mix}}G = nRT(x_A \ln x_A + x_B \ln x_B + \beta x_Ax_B) \quad (7.31)$$

Figure 7.19 shows how $\Delta_{\text{mix}}G$ 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 take up this point in Sections 7.8 and 8.5.



7.18 The excess enthalpy according to a model in which it is proportional to βx_Ax_B , for different values of the parameter β .



7.19 The Gibbs energy of mixing for different values of the parameter β .

7.5 Colligative properties

The properties we now consider are 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. The reduction is from μ_A^* for the pure solvent to $\mu_A^* + RT \ln x_A$ 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. 7.20, 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).

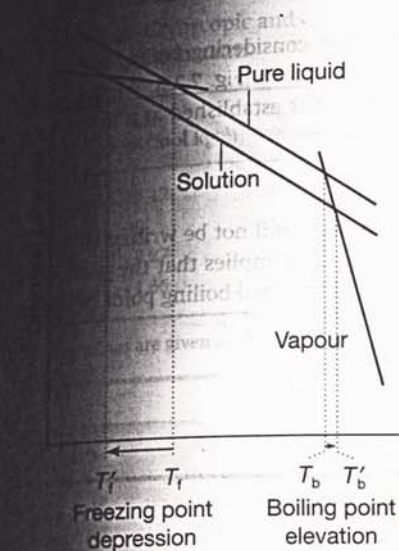
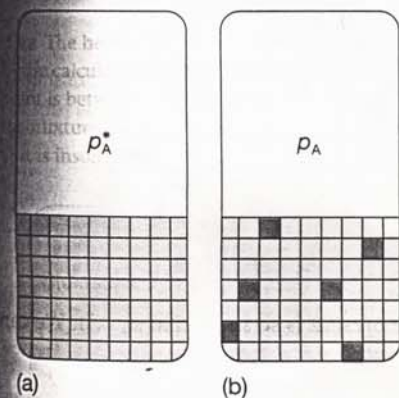


Fig. 7.20 The chemical potential of a solvent in the presence of a solute. The lowering of the liquid's chemical potential has a greater effect on the freezing point than on the boiling point because of the angles at which the lines intersect (which are determined by entropies; recall Fig. 6.8).



7.21 The vapour pressure of a pure liquid represents a balance between the increased disorder arising from vaporization and the decreased 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 relatively higher than that of the pure liquid, and there is a decreased tendency to acquire the disorder characteristic of the vapour.

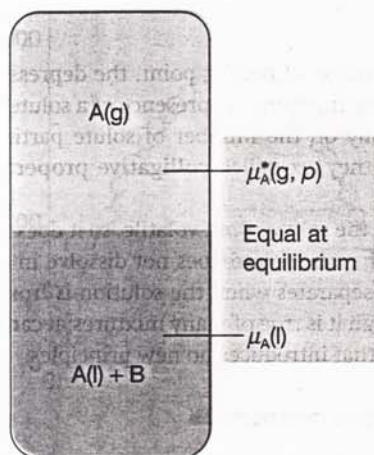
Molecular interpretation 7.3

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 disorder of 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 more disordered 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. 7.21). 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.



7.22 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.

(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. 7.22). We denote the solvent by A and the solute by B. The equilibrium is established at a temperature for which

$$\mu_A^*(g) = \mu_A^*(l) + RT \ln x_A \quad (7.32)$$

(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^* to $T^* + \Delta T$, where

$$\Delta T = K x_B \quad K = \frac{RT^{*2}}{\Delta_{\text{vap}}H} \quad (7.33)$$

Justification 7.2

Equation 32 rearranges into

$$\ln(1 - x_B) = \frac{\mu_A^*(g) - \mu_A^*(l)}{RT} = \frac{\Delta_{\text{vap}}G}{RT}$$

where $\Delta_{\text{vap}}G$ is the Gibbs energy of vaporization of the pure solvent (A) and x_B is the mole fraction of the solute; we have used $x_A + x_B = 1$. We now write

$$\Delta_{\text{vap}}G = \Delta_{\text{vap}}H - T\Delta_{\text{vap}}S$$

and ignore the small temperature dependence of $\Delta_{\text{vap}}H$ and $\Delta_{\text{vap}}S$. Then,

$$\ln(1 - x_B) = \frac{\Delta_{\text{vap}}H}{RT} - \frac{\Delta_{\text{vap}}S}{R}$$

When $x_B = 0$, the boiling point is that of pure liquid A, T^* , and

$$\ln 1 = \frac{\Delta_{\text{vap}}H}{RT^*} - \frac{\Delta_{\text{vap}}S}{R}$$

Because $\ln 1 = 0$, the difference of the two equations is

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

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

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

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

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

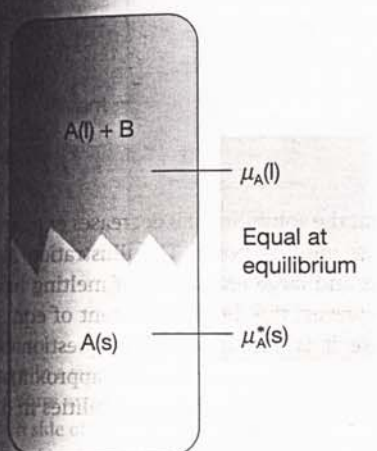
with $\Delta T = T - T^*$. The previous equation then rearranges into eqn 33.

Because eqn 33 makes no reference to the identity of the solute, only to its fraction, we conclude that the elevation of boiling point is a colligative property.

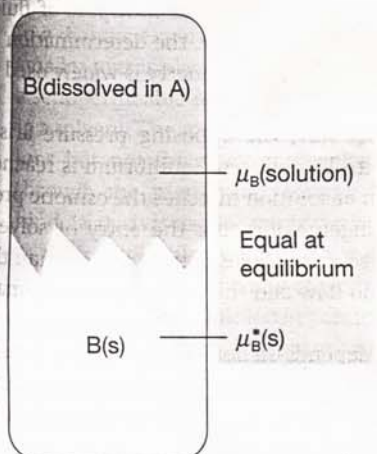
7.2 Cryoscopic and ebullioscopic constants

	$K_f/$ (K/(mol kg ⁻¹))	$K_b/$ (K/(mol kg ⁻¹))
Water	1.86	0.51
Acetic acid	1.86	0.51
Benzene	5.12	2.53
Chloroform	4.0	3.04
Carbon tetrachloride	7.27	3.04

Values are given in the Data section.



7.23 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.



7.24 The heterogeneous equilibrium involved in the calculation of the solubility is between pure solid B and B in the mixture.

value of ΔT does depend on the properties of the solvent, and the biggest changes occur for solvents with high boiling points.² For practical applications of eqn 33, we note that the mole fraction of B is proportional to its molality, b , in the solution, and write

$$\Delta T = K_b b \quad (7.34)$$

where K_b is the empirical ebullioscopic constant of the solvent (Table 7.2).

(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. 7.23). At the freezing point, the chemical potentials of A in the two phases are equal:

$$\mu_A^*(s) = \mu_A^*(l) + RT \ln x_A \quad (7.35)$$

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 33:

$$\Delta T = K' x_B \quad K' = \frac{RT^{*2}}{\Delta_{\text{fus}}H} \quad (7.36)^\circ$$

where ΔT is the freezing point depression, $T^* - T$, and $\Delta_{\text{fus}}H$ 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

$$\Delta T = K_f b \quad (7.37)$$

where K_f is the empirical cryoscopic constant (Table 7.2). Once the cryoscopic 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 it is not strictly a colligative property, the solubility of a solute 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. 7.24). Because the latter is

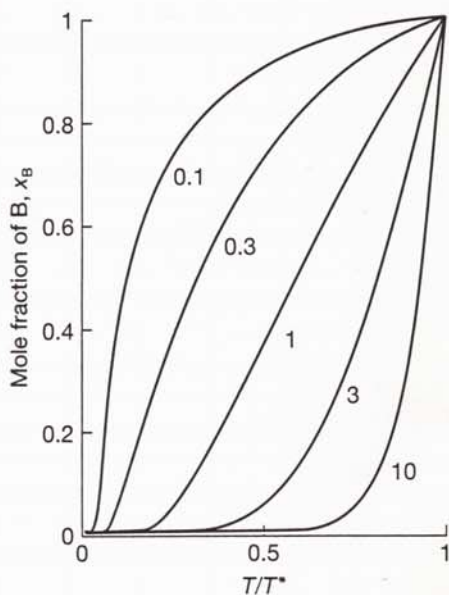
$$\mu_B = \mu_B^*(l) + RT \ln x_B$$

we can write

$$\mu_B^*(s) = \mu_B^*(l) + RT \ln x_B \quad (7.38)$$

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.

2. By Trouton's rule (Section 4.3a), $\Delta_{\text{vap}}H/T^*$ is a constant; therefore eqn 33 has the form $\Delta T \propto T^*$ and is independent of $\Delta_{\text{vap}}H$ itself.



7.25 The variation of solubility (the mole fraction of solute in a saturated solution) with temperature (T^* is the freezing temperature of the solute). Individual curves are labelled with the value of $\Delta_{\text{fus}}H/RT^*$.

The starting point is the same 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 the last equation into

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

$$= -\frac{\Delta_{\text{fus}}H}{RT} + \frac{\Delta_{\text{fus}}S}{R}$$

At the melting point of the solute, T^* , we know that $\Delta_{\text{fus}}G = 0$, so $\Delta_{\text{fus}}G/RT^* = 0$ too; consequently, this term may be added to the right-hand side to give

$$\ln x_B = -\frac{\Delta_{\text{fus}}H}{RT} + \frac{\Delta_{\text{fus}}S}{R} + \frac{\Delta_{\text{fus}}H}{RT^*} - \frac{\Delta_{\text{fus}}S}{R}$$

$$= -\frac{\Delta_{\text{fus}}H}{RT} + \frac{\Delta_{\text{fus}}H}{RT^*}$$

It then follows that

$$\ln x_B = \frac{\Delta_{\text{fus}}H}{R} \left(\frac{1}{T^*} - \frac{1}{T} \right) \quad (7.39)^\circ$$

Equation 39 is plotted in Fig. 7.25. 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 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

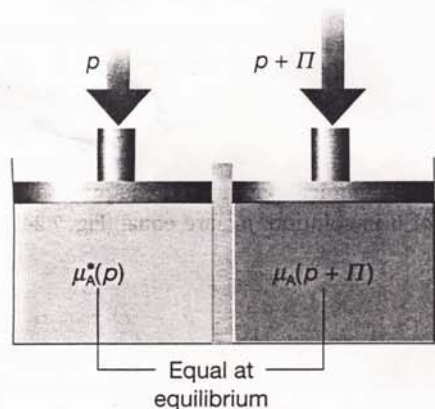
The phenomenon of **osmosis** (from the Greek word for 'push') is the spontaneous passage of a pure solvent into a solution separated from it by a **semipermeable membrane**, a membrane permeable to the solvent but not to the solute (Fig. 7.26). The **osmotic pressure**, Π , is the pressure that must be applied to the solution to stop the influx of solvent. Important examples of osmosis include transport of fluids through cell membranes, dialysis (Box 7.1), 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. 7.27, 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. 7.26, 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. As shown in the *Justification* below, this equality implies that for dilute solutions the osmotic pressure is given by the **van 't Hoff equation**:

$$\Pi = [B]RT$$

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



7.26 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 $p + \Pi$.