TOPIC 5A The thermodynamic description of mixtures

➤ Why do you need to know this material?

Chemistry deals with a wide variety of mixtures, including mixtures of substances that can react together. Therefore, it is important to generalize the concepts introduced in Focus 4 to deal with substances that are mingled together.

➤ What is the key idea?

The chemical potential of a substance in a mixture is a logarithmic function of its concentration.

➤ What do you need to know already?

This Topic extends the concept of chemical potential to substances in mixtures by building on the concept introduced in the context of pure substances (Topic 4A). It makes use of the relation between the temperature dependence of the Gibbs energy and entropy (Topic 3E), and the concept of partial pressure (Topic 1A). Throughout this and related Topics various measures of concentration of a solute in a solution are used: they are summarized in *The chemist's toolkit* 11.

The consideration of mixtures of substances that do not react together is a first step towards dealing with chemical reactions (which are treated in Topic 6A). At this stage the discussion centres on **binary mixtures**, which are mixtures of two components, A and B. In Topic 1A it is shown how 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 other analogous 'partial' properties need to be introduced.

5A.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 $18\,cm^3$ and it follows that the molar volume of pure water is $18\,cm^3\,mol^{-1}$. However, upon adding 1 mol H_2O to a huge volume of pure ethanol, the volume is found to increase by only $14\,cm^3$. 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. The network of hydrogen bonds that normally hold H_2O molecules at certain distances from each other in pure water does not form; as a result the H_2O molecules are packed more tightly and so increase the volume by only $14\,cm^3$. The quantity $14\,cm^3\,mol^{-1}$ 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. This changing molecular environment, and the consequential modification of the forces acting between molecules, 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. 5A.1.

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

$$V_J = \left(\frac{\partial V}{\partial n_J}\right)_{p,T,n'} \qquad \text{Partial molar volume [definition]} \qquad (5A.1)$$

where the subscript n' signifies that the amounts of all other substances present are constant. 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. 5A.2). Its value depends on the composition, as seen for water and ethanol.

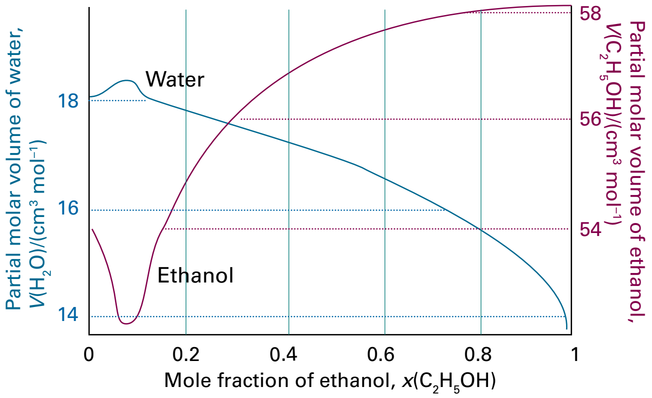

Figure 5A.1 The partial molar volumes of water and ethanol at 25 °C. Note the different scales (water on the left, ethanol on the right).

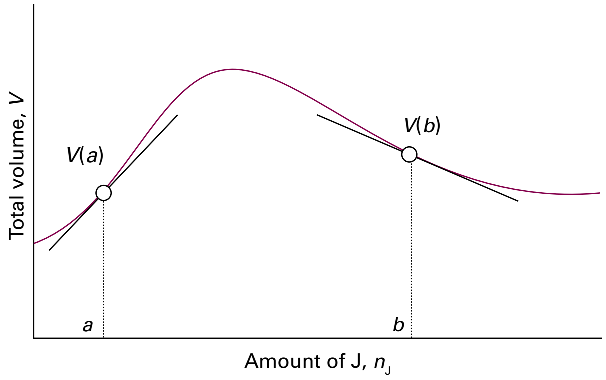

Figure 5A.2 The partial molar volume of a substance is the slope of the variation of the total volume of the sample plotted against the amount of that substance. In general, partial molar quantities vary with the composition, as shown by the different slopes at *a* and *b*. Note that the partial molar volume at *b* is negative: the overall volume of the sample decreases as A is added.

A note on good practice The IUPAC recommendation is to denote a partial molar quantity by $\overline{X}$, but only when there is the possibility of confusion with the quantity X. For instance, to avoid confusion, the partial molar volume of NaCl in water could be written $\overline{V}$(NaCl,aq) to distinguish it from the total volume of the solution, V.

The definition in eqn 5A.1 implies that when the composition of a binary 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

$$\begin{aligned} dV &= \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{p,T,n_A} dn_B \\ &= V_A dn_A + V_B dn_B \end{aligned} \tag{5A.2}$$

This equation can be integrated with respect to n_A and n_B provided that the amounts of A and B are both increased in such a way as to keep their ratio constant. This linkage ensures that the partial molar volumes V_A and V_B are constant and so can be taken outside the integrals:

$$\begin{aligned} V &= \int_0^{n_A} V_A\, dn_A + \int_0^{n_B} V_B\, dn_B = V_A \int_0^{n_A} dn_A + V_B \int_0^{n_B} dn_B \\ &= V_A n_A + V_B n_B \end{aligned} \tag{5A.3}$$

Although the two integrations are linked (in order to preserve constant relative composition), because V is a state function the final result in eqn 5A.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.

Example 5A.1 Determining a 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

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

where $v = V/\text{cm}^3$, $z = n_E/\text{mol}$, and n_E is the amount of CH_3CH_2OH present. Determine the partial molar volume of ethanol.

Collect your thoughts Apply the definition in eqn 5A.1, taking care to convert the derivative with respect to n to a derivative with respect to z and keeping the units intact.

The solution The partial molar volume of ethanol, V_E, is

$$\begin{aligned} V_E &= \left(\frac{\partial V}{\partial n_E}\right)_{p,T,n_W} = \left(\frac{\partial (V/\text{cm}^3)}{\partial (n_E/\text{mol})}\right)_{p,T,n_W} \frac{\text{cm}^3}{\text{mol}} \\ &= \left(\frac{\partial v}{\partial z}\right)_{p,T,n_W} \text{cm}^3\,\text{mol}^{-1} \end{aligned}$$

Then, because

$$\frac{dv}{dz} = 54.6664 - 2(0.363\,94)z + 3(0.028\,256)z^2$$

it follows that

$$V_E/(\text{cm}^3\,\text{mol}^{-1}) = 54.6664 - 0.727\,88z + 0.084\,768z^2$$

Figure 5A.3 shows a graph of this function.

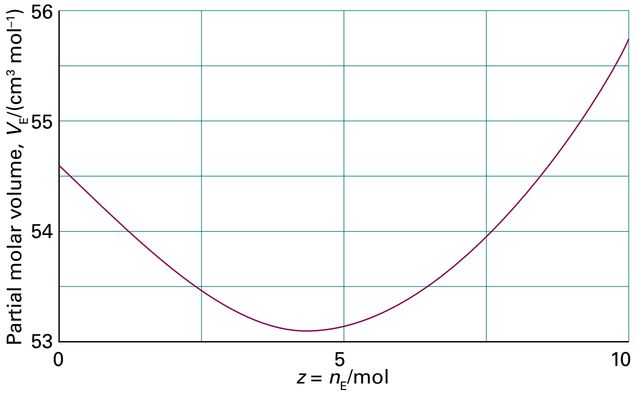

Figure 5A.3 The partial molar volume of ethanol as expressed by the polynomial in *Example* 5A.1.

Self-test 5A.1 At 25 °C, the mass 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?

Answer: 56.4 cm^3 mol^{-1} by using eqn 5A.3; 54.6 cm^3 mol^{-1} by the formula above

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 Mg^{2+} and SO_4^{2-} ions become hydrated, so the structure collapses slightly.

(b) Partial molar Gibbs energies

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

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'} \quad \text{Chemical potential [definition]} \quad (5A.4)$$

where n' is used to denote that the amounts of all other components of the mixture are held constant. That is, the chemical potential is the slope of a plot of Gibbs energy against the amount of the component J, with the pressure, temperature, and the amounts of the other substances held constant (Fig. 5A.4). For a pure substance $G = n_J G_{J,m}$, and from eqn 5A.4 it follows that $\mu_J = G_{J,m}$: in this case, the chemical potential is simply the molar Gibbs energy of the substance, as is used in Topic 4A.

By the same argument that led to eqn 5A.3, it follows that the total Gibbs energy of a binary mixture is

$$G = n_A\mu_A + n_B\mu_B \quad (5A.5)$$

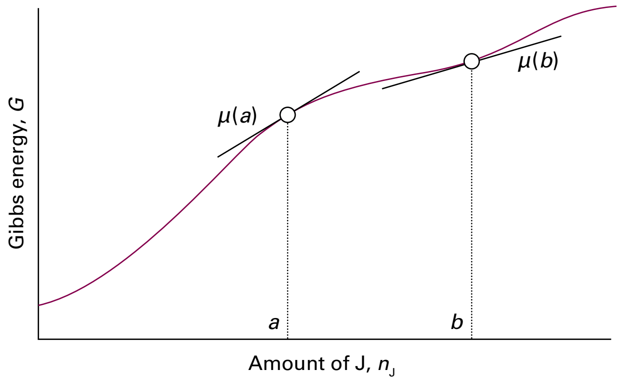

Figure 5A.4 The chemical potential of a substance is the slope of the total Gibbs energy of a mixture with respect to the amount of substance of interest. In general, the chemical potential varies with composition, as shown for the two values at *a* and *b*. In this case, both chemical potentials are positive.

where μ_A and μ_B are the chemical potentials at the composition of the mixture. That is, the chemical potential of a substance, multiplied by the amount of that substance present in the mixture, is its contribution 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, …, eqn 3E.7 ($dG = Vdp - SdT$) for a general change in G becomes

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \cdots \quad \text{Fundamental equation of chemical thermodynamics} \quad (5A.6)$$

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

At constant pressure and temperature, eqn 5A.6 simplifies to

$$dG = \mu_A dn_A + \mu_B dn_B + \cdots \quad (5A.7)$$

As established in Topic 3E, under the same conditions $dG = dw_{add,max}$. Therefore, at constant temperature and pressure,

$$dw_{add,max} = \mu_A dn_A + \mu_B dn_B + \cdots \quad (5A.8)$$

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) and 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 $U = -pV + TS + G$, the general form of an infinitesimal change in U for a system of variable composition is

$$\begin{aligned}\mathrm{d}U &= -p\mathrm{d}V - V\mathrm{d}p + S\mathrm{d}T + T\mathrm{d}S + \mathrm{d}G\\ &= -p\mathrm{d}V - V\mathrm{d}p + S\mathrm{d}T + T\mathrm{d}S\\ &\quad + (V\mathrm{d}p - S\mathrm{d}T + \mu_A\mathrm{d}n_A + \mu_B\mathrm{d}n_B + \cdots)\\ &= -p\mathrm{d}V + T\mathrm{d}S + \mu_A\mathrm{d}n_A + \mu_B\mathrm{d}n_B + \cdots\end{aligned}$$

This expression is the generalization of eqn 3E.1 (that $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$) to systems in which the composition may change. It follows that at constant volume and entropy,

$$\mathrm{d}U = \mu_A\mathrm{d}n_A + \mu_B\mathrm{d}n_B + \cdots \qquad (5A.9)$$

and hence that

$$\mu_J = \left(\frac{\partial U}{\partial n_J}\right)_{S,V,n'} \qquad (5A.10)$$

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 possible to deduce that

$$\text{(a)}\ \mu_J = \left(\frac{\partial H}{\partial n_J}\right)_{S,p,n'} \qquad \text{(b)}\ \mu_J = \left(\frac{\partial A}{\partial n_J}\right)_{T,V,n'} \qquad (5A.11)$$

Thus, 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 5A.5 ($G = n_A\mu_A + n_B\mu_B$), and the chemical potentials depend on the composition, when the compositions are changed infinitesimally the Gibbs energy of a binary system is expected to change by

$$\mathrm{d}G = \mu_A\mathrm{d}n_A + \mu_B\mathrm{d}n_B + n_A\mathrm{d}\mu_A + n_B\mathrm{d}\mu_B$$

However, at constant pressure and temperature the change in Gibbs energy is given by eqn 5A.7. Because G is a state function, these two expressions for dG must be equal, which implies that at constant temperature and pressure

$$n_A\mathrm{d}\mu_A + n_B\mathrm{d}\mu_B = 0 \qquad (5A.12a)$$

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

$$\sum_J n_J\mathrm{d}\mu_J = 0 \qquad \text{Gibbs–Duhem equation} \qquad (5A.12b)$$

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 chemical potential increases, then the other must decrease, with the two changes related by eqn 5A.12a and therefore

$$\mathrm{d}\mu_B = -\frac{n_A}{n_B}\mathrm{d}\mu_A \qquad (5A.13)$$

Brief illustration 5A.1

If the composition of a mixture is such that $n_A = 2n_B$, and a small change in composition results in μ_A changing by $\Delta\mu_A = +1\,\mathrm{J\,mol^{-1}}$, μ_B will change by

$$\Delta\mu_B = -2\times(1\,\mathrm{J\,mol^{-1}}) = -2\,\mathrm{J\,mol^{-1}}$$

The same line of reasoning applies to all partial molar quantities. For instance, changes in the partial molar volumes of the species in a mixture are related by

$$\sum_J n_J\mathrm{d}V_J = 0 \qquad (5A.14a)$$

For a binary mixture,

$$\mathrm{d}V_B = -\frac{n_A}{n_B}\mathrm{d}V_A \qquad (5A.14b)$$

As seen in Fig. 5A.1, where the partial molar volume of water increases, the partial molar volume of ethanol decreases. Moreover, as eqn 5A.14b implies, and as seen from Fig. 5A.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.

Example 5A.2 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

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

where $v_B = V_{K_2SO_4}/(\mathrm{cm^3\,mol^{-1}})$ and z is the numerical value of the molality of K_2SO_4 ($z = b/b^{\ominus}$; see *The chemist's toolkit* 11). 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 $\mathrm{cm^3\,mol^{-1}}$.

Collect your thoughts Let A denote H_2O, the solvent, and B denote K_2SO_4, the solute. Because the Gibbs–Duhem equation for the partial molar volumes of two components implies that $dv_A = -(n_B/n_A)dv_B$, v_A can be found by integration:

$$v_A = v_A^\star - \int_0^{v_B} \frac{n_B}{n_A} dv_B$$

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

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

$$v_A = v_A^\star - 9.108\int_0^{b/b^\ominus} \frac{n_B}{n_A} z^{-1/2} dz$$

The amount of A (H_2O) is $n_A = (1\,\text{kg})/M_A$, where M_A is the molar mass of water, and $n_B/(1\,\text{kg})$, which then occurs in the ratio n_B/n_A, will be recognized as the molality b of B:

$$\frac{n_B}{n_A} \overset{n_A=(1\,\text{kg})/M_A}{=} \frac{n_B}{(1\,\text{kg})/M_A} = \frac{n_B M_A}{1\,\text{kg}} \overset{n_B/(1\,\text{kg})=b}{=} bM_A = zb^\ominus M_A$$

Hence

$$\begin{aligned} v_A &= v_A^\star - 9.108M_A b^\ominus \int_0^{b/b^\ominus} z^{1/2} dz \\ &= v_A^\star - \tfrac{2}{3}(9.108M_A b^\ominus)(b/b^\ominus)^{3/2} \end{aligned}$$

It then follows, by substituting the data (including $M_A = 1.802 \times 10^{-2}\,\text{kg}\,\text{mol}^{-1}$, 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. 5A.5.

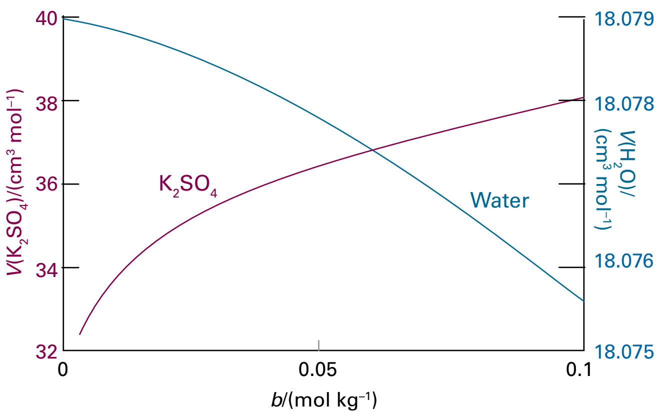

Figure 5A.5 The partial molar volumes of the components of an aqueous solution of potassium sulfate.

Self-test 5A.2 Repeat the calculation for a salt B for which $V_B/(\text{cm}^3\,\text{mol}^{-1}) = 6.218 + 5.146z - 7.147z^2$ with $z = b/b^\ominus$.

Answer: $V_A/(\text{cm}^3\,\text{mol}^{-1}) = 18.079 - 0.0464z^2 + 0.0859z^3$

5A.2 The thermodynamics of mixing

The dependence of the Gibbs energy of a mixture on its composition is given by eqn 5A.5, and, as established in Topic 3E, at constant temperature and pressure systems tend towards lower Gibbs energy. This is the link needed 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.

(a) The Gibbs energy of mixing of perfect gases

Let the amounts of two perfect gases in the two containers before mixing be n_A and n_B; both are at a temperature T and a pressure p (Fig. 5A.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 3E.15 ($G_m(p) = G_m^\ominus + RT\ln(p/p^\ominus)$):

$$\mu = \mu^\ominus + RT\ln\frac{p}{p^\ominus} \qquad \text{(5A.15a)}$$

Variation of chemical potential with pressure [perfect gas]

where $\mu^\ominus$ is the **standard chemical potential**, the chemical potential of the pure gas at 1 bar.

The notation is simplified by replacing $p/p^\ominus$ by p itself, for eqn 5A.15a then becomes

$$\mu = \mu^\ominus + RT\ln p \qquad \text{(5A.15b)}$$

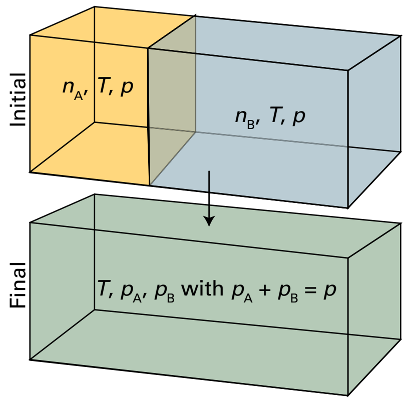

Figure 5A.6 The arrangement for calculating the thermodynamic functions of mixing of two perfect gases.

The chemist's toolkit 11

Measures of concentration

Let A be the solvent and B the solute. The **molar concentration** (informally: 'molarity'), c_B or [B], is the amount of solute molecules (in moles) divided by the volume, V, of the solution:

$$c_B = \frac{n_B}{V}$$

It is commonly reported in moles per cubic decimetre (mol dm^{-3}) or, equivalently, in moles per litre (mol L^{-1}). It is convenient to define its 'standard' value as $c^\ominus = 1\,\text{mol dm}^{-3}$.

The **molality**, b_B, of a solute is the amount of solute species (in moles) in a solution divided by the total mass of the solvent (in kilograms), m_A:

$$b_B = \frac{n_B}{m_A}$$

Both the molality and mole fraction are independent of temperature; in contrast, the molar concentration is not. It is convenient to define the 'standard' value of the molality as $b^\ominus = 1\,\text{mol kg}^{-1}$.

1. The relation between molality and mole fraction

Consider a solution with one solute and having a total amount n of molecules. If the mole fraction of the solute is x_B, the amount of solute molecules is $n_B = x_B n$. The mole fraction of solvent molecules is $x_A = 1 - x_B$, so the amount of solvent molecules is $n_A = x_A n = (1 - x_B)n$. The mass of solvent, of molar mass M_A, present is $m_A = n_A M_A = (1 - x_B)nM_A$. The molality of the solute is therefore

$$b_B = \frac{n_B}{m_A} = \frac{x_B n}{(1-x_B)nM_A} = \frac{x_B}{(1-x_B)M_A}$$

The inverse of this relation, the mole fraction in terms of the molality, is

$$x_B = \frac{b_B M_A}{1 + b_B M_A}$$

2. The relation between molality and molar concentration

The total mass of a volume V of *solution* (not solvent) of mass density ρ is $m = \rho V$. The amount of solute molecules in this volume is $n_B = c_B V$. The mass of solute present is $m_B = n_B M_B = c_B V M_B$. The mass of solvent present is therefore $m_A = m - m_B = \rho V - c_B V M_B = (\rho - c_B M_B)V$. The molality is therefore

$$b_B = \frac{n_B}{m_A} = \frac{c_B V}{(\rho - c_B M_B)V} = \frac{c_B}{\rho - c_B M_B}$$

The inverse of this relation, the molar concentration in terms of the molality, is

$$c_B = \frac{b_B \rho}{1 + b_B M_B}$$

3. The relation between molar concentration and mole fraction

By inserting the expression for b_B in terms of x_B into the expression for c_B, the molar concentration of B in terms of its mole fraction is

$$c_B = \frac{x_B \rho}{x_A M_A + x_B M_B}$$

with $x_A = 1 - x_B$. For a dilute solution in the sense that $x_B M_B \ll x_A M_A$,

$$c_B \approx \left(\frac{\rho}{x_A M_A}\right) x_B$$

If, moreover, $x_B \ll 1$, so $x_A \approx 1$, then

$$c_B \approx \left(\frac{\rho}{M_A}\right) x_B$$

In practice, the replacement of $p/p^\ominus$ by p means using the numerical value of p in bars. The total Gibbs energy of the separated gases is then given by eqn 5A.5 as

$$G_i = n_A \mu_A + n_B \mu_B = n_A(\mu_A^\ominus + RT\ln p) + n_B(\mu_B^\ominus + RT\ln p) \tag{5A.16a}$$

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

$$G_f = n_A(\mu_A^\ominus + RT\ln p_A) + n_B(\mu_B^\ominus + RT\ln p_B) \tag{5A.16b}$$

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

$$\Delta_{\text{mix}}G = n_A RT\ln\frac{p_A}{p} + n_B RT\ln\frac{p_B}{p} \tag{5A.16c}$$

At this point n_J can be replaced by $x_J n$, where n is the total amount of A and B, and the relation between partial pressure and mole fraction (Topic 1A, $p_J = x_J p$) can be used to write $p_J/p = x_J$ for each component. The result is

$$\Delta_{\text{mix}}G = nRT(x_A\ln x_A + x_B\ln x_B) \tag{5A.17}$$

Gibbs energy of mixing [perfect gas]

Because mole fractions are never greater than 1, the logarithms in this equation are negative, and $\Delta_{\text{mix}}G < 0$ (Fig. 5A.7). The conclusion that $\Delta_{\text{mix}}G$ is negative for all compositions confirms that perfect gases mix spontaneously in all proportions.

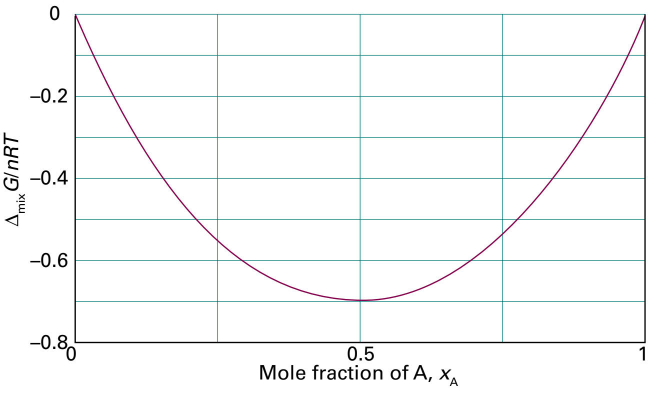

Figure 5A.7 The Gibbs energy of mixing of two perfect gases at constant temperature and pressure, and (as discussed later) of two liquids that form an ideal solution. The Gibbs energy of mixing is negative for all compositions, so perfect gases mix spontaneously in all proportions.

Example 5A.3 Calculating a Gibbs energy of mixing

A container is divided into two equal compartments (Fig. 5A.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 that the gases are perfect.

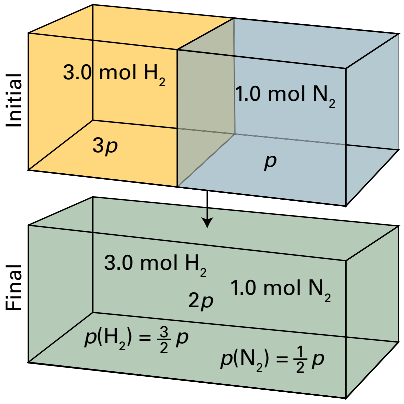

Figure 5A.8 The initial and final states considered in the calculation of the Gibbs energy of mixing of gases at different initial pressures.

Collect your thoughts Equation 5A.17 cannot be used directly because the two gases are initially at different pressures, so proceed by calculating the initial Gibbs energy from the chemical potentials. To do so, calculate 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 final partial pressure is half its initial pressure.

The solution 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 final total pressure is 2p. 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:

$$\begin{aligned}\Delta_{\text{mix}}G &= (3.0\,\text{mol})RT\ln\frac{\frac{3}{2}p}{3p} + (1.0\,\text{mol})RT\ln\frac{\frac{1}{2}p}{p}\\ &= -(3.0\,\text{mol})RT\ln 2 - (1.0\,\text{mol})RT\ln 2\\ &= -(4.0\,\text{mol})RT\ln 2 = -6.9\,\text{kJ}\end{aligned}$$

Comment. In this example, the value of $\Delta_{\text{mix}}G$ is the sum of two contributions: the mixing itself, and the changes in pressure of the two gases to their final total pressure, 2p. Do not be misled into interpreting this negative change in Gibbs energy as a sign of spontaneity: in this case, the pressure changes, and $\Delta G < 0$ is a signpost of spontaneous change only at constant temperature and pressure. 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. Because this value is for a change at constant pressure and temperature, the fact that it is negative does imply spontaneity.

Self-test 5A.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 by removing the partition between them. Calculate $\Delta_{\text{mix}}G$.

Answer: −9.7 kJ

(b) Other thermodynamic mixing functions

In Topic 3E it is shown that $(\partial G/\partial T)_p = -S$. It follows immediately from eqn 5A.17 that, for a mixture of perfect gases initially at the same pressure, the entropy of mixing, $\Delta_{\text{mix}}S$, is

$$\Delta_{\text{mix}}S = -\left(\frac{\partial \Delta_{\text{mix}}G}{\partial T}\right)_p = -nR(x_A\ln x_A + x_B\ln x_B) \qquad (5A.18)$$

Entropy of mixing [perfect gases, constant T and p]

Because $\ln x < 0$, it follows that $\Delta_{\text{mix}}S > 0$ for all compositions (Fig. 5A.9).

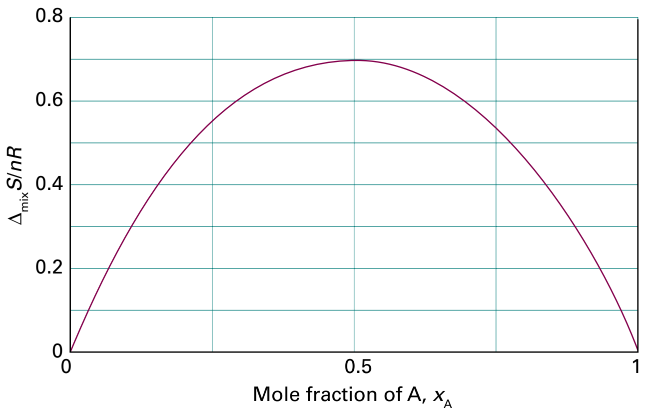

Figure 5A.9 The entropy of mixing of two perfect gases at constant temperature and pressure, and (as discussed later) of two liquids that form an ideal solution. The entropy increases for all compositions, and because there is no transfer of heat to the surroundings when perfect gases mix, the entropy of the surroundings is unchanged. Hence, the graph also shows the total entropy of the system plus the surroundings; because the total entropy of mixing is positive at all compositions, perfect gases mix spontaneously in all proportions.

Brief illustration 5A.2

For equal amounts of perfect gas molecules that are mixed at the same pressure, set $x_A = x_B = \frac{1}{2}$ and obtain

$$\Delta_{mix}S = -nR\{\tfrac{1}{2}\ln\tfrac{1}{2}+\tfrac{1}{2}\ln\tfrac{1}{2}\} = nR\ln 2$$

with n the total amount of gas molecules. For 1 mol of each species, so $n = 2\,\text{mol}$,

$$\Delta_{mix}S = (2\,\text{mol}) \times R\ln 2 = +11.5\,\text{J K}^{-1}$$

An increase in entropy is expected when one gas disperses into the other and the disorder increases.

Under conditions of constant pressure and temperature, the **enthalpy of mixing**, $\Delta_{mix}H$, the enthalpy change accompanying mixing, of two perfect gases can be calculated from $\Delta G = \Delta H - T\Delta S$. It follows from eqns 5A.17 and 5A.18 that

$$\Delta_{mix}H = 0 \qquad (5A.19)$$

Enthalpy of mixing [perfect gases, constant T and p]

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

5A.3 The chemical potentials of liquids

To discuss the equilibrium properties of liquid mixtures it is necessary to know how the Gibbs energy of a liquid varies with composition. The calculation of this dependence uses the fact that, as established in Topic 4A, 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

Quantities relating to pure substances are denoted by a superscript *, so the chemical potential of pure A is written μ_A^* and as $\mu_A^*(\text{l})$ when it is necessary to emphasize that A is a liquid. Because the vapour pressure of the pure liquid is p_A^* it follows from eqn 5A.15b that the chemical potential of A in the vapour (treated as a perfect gas) is $\mu_A^{\ominus} + RT\ln p_A$ (with p_A to be interpreted as $p_A/p^{\ominus}$). These two chemical potentials are equal at equilibrium (Fig. 5A.10), so

$$\overbrace{\mu_A^*(\text{l})}^{\text{liquid}} = \overbrace{\mu_A^{\ominus}(\text{g}) + RT\ln p_A^*}^{\text{vapour}} \qquad (5A.20a)$$

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

$$\mu_A(\text{l}) = \mu_A^{\ominus}(\text{g}) + RT\ln p_A \qquad (5A.20b)$$

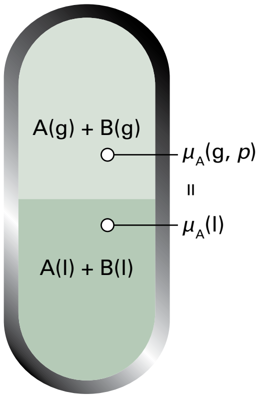

Figure 5A.10 At equilibrium, the chemical potential of the gaseous form of a substance A is equal to the chemical potential of its condensed phase. The equality is preserved if a solute is also present. Because the chemical potential of A in the vapour depends on its partial vapour pressure, it follows that the chemical potential of liquid A can be related to its partial vapour pressure.

The next step is the combination of these two equations to eliminate the standard chemical potential of the gas, $\mu_A^\ominus(g)$. To do so, write eqn 5A.20a as $\mu_A^\ominus(g) = \mu_A^\star(l) - RT\ln p_A^\star$ and substitute this expression into eqn 5A.20b to obtain

$$\mu_A(l) = \overbrace{\mu_A^\star(l) - RT\ln p_A^\star}^{\mu_A^\ominus(g)} + RT\ln p_A^\star = \mu_A^\star(l) + RT\ln\frac{p_A}{p_A^\star} \quad (5A.21)$$

The final step draws 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), François Raoult found that the ratio of the partial vapour pressure of each component to its vapour pressure when present as the 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 is now called **Raoult's law**:

$$p_A = x_A p_A^\star \quad \text{Raoult's law [ideal solution]} \quad (5A.22)$$

This law is illustrated in Fig. 5A.11. Some mixtures obey Raoult's law very well, especially when the components are structurally similar (Fig. 5A.12). Mixtures that obey the law throughout the composition range from pure A to pure B are called **ideal solutions**.

Brief illustration 5A.3

The vapour pressure of pure benzene at 20 °C is 75 Torr and that of pure methylbenzene is 25 Torr at the same temperature. In an equimolar mixture $x_{\text{benzene}} = x_{\text{methylbenzene}} = \frac{1}{2}$ so the partial vapour pressure of each one in the mixture is

$$p_{\text{benzene}} = \tfrac{1}{2} \times 80\,\text{Torr} = 40\,\text{Torr}$$

$$p_{\text{methylbenzene}} = \tfrac{1}{2} \times 25\,\text{Torr} = 12.5\,\text{Torr}$$

The total vapour pressure of the mixture is 48 Torr. Given the two partial vapour pressures, it follows from the definition of partial pressure (Topic 1A) that the mole fractions in the vapour are

$$x_{\text{vap,benzene}} = (40\,\text{Torr})/(48\,\text{Torr}) = 0.83$$

and

$$x_{\text{vap,methylbenzene}} = (12.5\,\text{Torr})/(48\,\text{Torr}) = 0.26$$

The vapour is richer in the more volatile component (benzene).

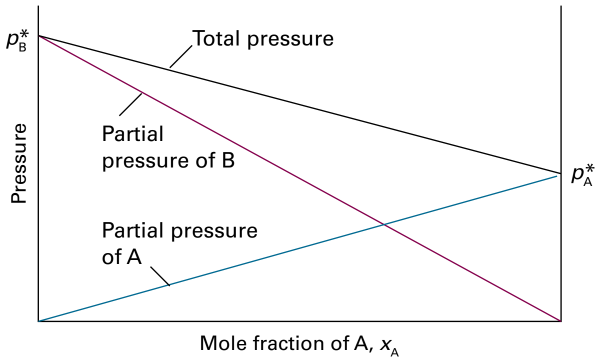

Figure 5A.11 The partial vapour pressures of the two components of an ideal binary mixture are proportional to the mole fractions of the components, in accord with Raoult's law. The total pressure is also linear in the mole fraction of either component.

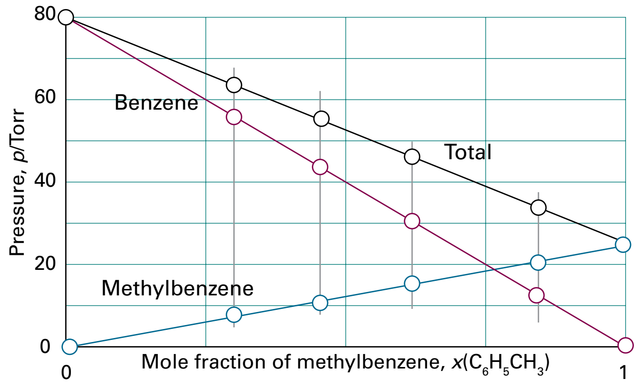

Figure 5A.12 Two similar liquids, in this case benzene and methylbenzene (toluene), behave almost ideally, and the variation of their vapour pressures with composition resembles that for an ideal solution.

For an ideal solution, it follows from eqns 5A.21 and 5A.22 that

$$\mu_A(l) = \mu_A^\star(l) + RT\ln x_A \quad \text{Chemical potential [ideal solution]} \quad (5A.23)$$

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 5A.22 because it does not assume that the vapour is a perfect gas.

The molecular origin of Raoult's law is the effect of the solute on the entropy of the solution. In the pure solvent, the molecules have a certain disorder and a corresponding entropy; the vapour pressure then represents the tendency of the system and its surroundings to reach a higher entropy. When a solute is present, the solution has a greater disorder than the pure solvent because a molecule chosen at random might or might not be a solvent molecule. Because the entropy of the solution is higher than that of the pure solvent, the solution

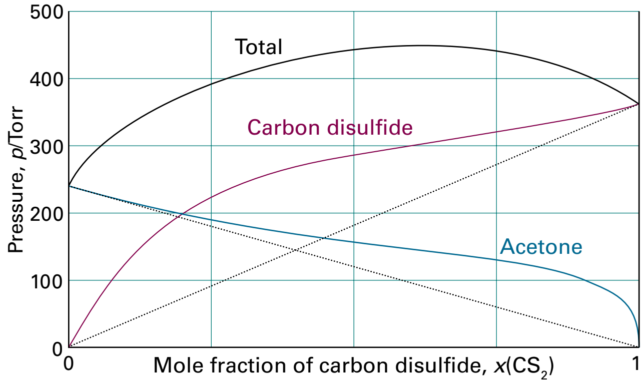

Figure 5A.13 Strong deviations from ideality are shown by dissimilar liquids (in this case carbon disulfide and acetone (propanone)). The dotted lines show the values expected from Raoult's law.

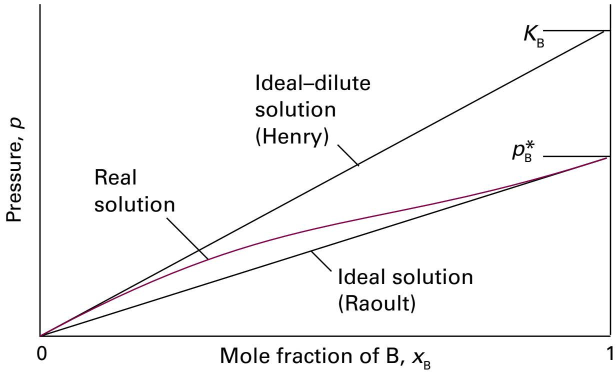

Figure 5A.14 When a component (the solvent) is nearly pure, it has a vapour pressure that is proportional to the mole fraction with a slope p_B^* (Raoult's law). When it is the minor component (the solute) its vapour pressure is still proportional to the mole fraction, but the constant of proportionality is now K_B (Henry's law).

has a lower tendency to acquire an even higher entropy by the solvent vaporizing. In other words, the vapour pressure of the solvent in the solution is lower than that of the pure solvent.

Some solutions depart significantly from Raoult's law (Fig. 5A.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 another example of a limiting law (in this case, achieving reliability as $x_A \to 1$) and is 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, 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. 5A.14). **Henry's law** is:

$$p_B = x_B K_B \qquad (5A.24)$$

Henry's law
[ideal–dilute solution]

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 $x_B = 0$. Henry's law is therefore also a limiting law, achieving reliability as $x_B \to 0$.

Mixtures for which the solute B obeys Henry's law and the solvent A obeys Raoult's law are called **ideal–dilute solutions**. 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. 5A.15). In contrast, the solute molecules are surrounded by solvent molecules, which is entirely different from their environment when it is in its pure form. 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.

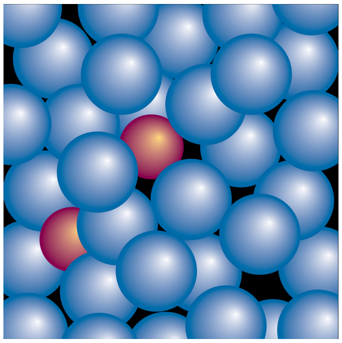

Figure 5A.15 In a dilute solution, the solvent molecules (the blue spheres) are in an environment that differs only slightly from that of the pure solvent. The solute particles (the red spheres), however, are in an environment totally unlike that of the pure solute.

Example 5A.4 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.

Collect your thoughts 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 curve at low x, where the component can be treated as the solute.

The solution The data are plotted in Fig. 5A.16 together with the Raoult's law lines. Henry's law requires $K_A = 24.5\,\text{kPa}$ for acetone and $K_C = 23.5\,\text{kPa}$ for chloroform.

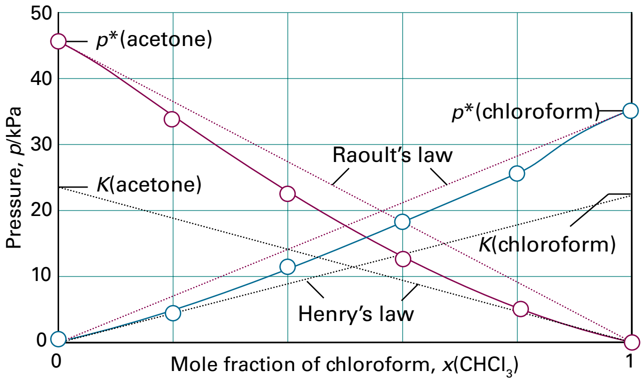

Figure 5A.16 The experimental partial vapour pressures of a mixture of chloroform (trichloromethane) and acetone (propanone) based on the data in *Example* 5A.4. The values of *K* are obtained by extrapolating the dilute solution vapour pressures, as explained in the *Example*.

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. These deviations are discussed in Topic 5E.

Self-test 5A.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 the Henry's law constant for chloromethane.

Answer: 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 5A.1. As well as providing a link between the mole fraction of the solute and its partial pressure, the data in the table may also be used to calculate gas solubilities. 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.

Table 5A.1 Henry's law constants for gases in water at 298 K*

	K/(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 *Resource section*.

Brief illustration 5A.4

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, write

$$b_{O_2} = \frac{p_{O_2}}{K_{O_2}} = \frac{21\,\text{kPa}}{7.9\times10^4\,\text{kPa kg mol}^{-1}} = 2.9\times10^{-4}\,\text{mol kg}^{-1}$$

The molality of the saturated solution is therefore 0.29 mmol kg^{-1}. To convert this quantity to a molar concentration, assume that the mass density of this dilute solution is essentially that of pure water at 25 °C, or $\rho = 0.997\,\text{kg dm}^{-3}$. It follows that the molar concentration of oxygen is

$$\begin{aligned}[O_2] &= b_{O_2}\rho = (2.9\times10^{-4}\,\text{mol kg}^{-1})\times(0.997\,\text{kg dm}^{-3})\\ &= 0.29\,\text{mmol dm}^{-3}\end{aligned}$$

Checklist of concepts

☐ 1. The **partial molar volume** of a substance is the contribution to the volume that a substance makes when it is part of a mixture.

☐ 2. The **chemical potential** is the partial molar Gibbs energy and is the contribution to the total Gibbs energy that a substance makes when it is part of a mixture.

☐ 3. The chemical potential also expresses how, under a variety of different conditions, the thermodynamic functions vary with composition.

☐ 4. The **Gibbs–Duhem equation** shows how the changes in chemical potentials (and, by extension, of other partial molar quantities) of the components of a mixture are related.

☐ 5. The **Gibbs energy of mixing** is negative for perfect gases at the same pressure and temperature.

☐ 6. The **entropy of mixing** of perfect gases initially at the same pressure is positive and the **enthalpy of mixing** is zero.

☐ 7. **Raoult's law** provides a relation between the vapour pressure of a substance and its mole fraction in a mixture.

☐ 8. An **ideal solution** is a solution that obeys Raoult's law over its entire range of compositions; for real solutions it is a limiting law valid as the mole fraction of the species approaches 1.

☐ 9. **Henry's law** provides a relation between the vapour pressure of a solute and its mole fraction in a mixture; it is the basis of the definition of an ideal–dilute solution.

☐ 10. An **ideal–dilute solution** is a solution that obeys Henry's law at low concentrations of the solute, and for which the solvent obeys Raoult's law.

Checklist of equations

Property	Equation	Comment	Equation number
Partial molar volume	$V_\mathrm{J} = (\partial V/\partial n_\mathrm{J})_{p,T,n'}$	Definition	5A.1
Chemical potential	$\mu_\mathrm{J} = (\partial G/\partial n_\mathrm{J})_{p,T,n'}$	Definition	5A.4
Total Gibbs energy	$G = n_\mathrm{A}\mu_\mathrm{A} + n_\mathrm{B}\mu_\mathrm{B}$	Binary mixture	5A.5
Fundamental equation of chemical thermodynamics	$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T + \mu_\mathrm{A}\mathrm{d}n_\mathrm{A} + \mu_\mathrm{B}\mathrm{d}n_\mathrm{B} + \cdots$		5A.6
Gibbs–Duhem equation	$\sum_\mathrm{J} n_\mathrm{J}\mathrm{d}\mu_\mathrm{J} = 0$		5A.12b
Chemical potential of a gas	$\mu = \mu^\ominus + RT\ln(p/p^\ominus)$	Perfect gas	5A.15a
Gibbs energy of mixing	$\Delta_\mathrm{mix}G = nRT(x_\mathrm{A}\ln x_\mathrm{A} + x_\mathrm{B}\ln x_\mathrm{B})$	Perfect gases and ideal solutions	5A.17
Entropy of mixing	$\Delta_\mathrm{mix}S = -nR(x_\mathrm{A}\ln x_\mathrm{A} + x_\mathrm{B}\ln x_\mathrm{B})$	Perfect gases and ideal solutions	5A.18
Enthalpy of mixing	$\Delta_\mathrm{mix}H = 0$	Perfect gases and ideal solutions	5A.19
Raoult's law	$p_\mathrm{A} = x_\mathrm{A}p_\mathrm{A}^*$	True for ideal solutions; limiting law as $x_\mathrm{A} \to 1$	5A.22
Chemical potential of component	$\mu_\mathrm{A}(\mathrm{l}) = \mu_\mathrm{A}^*(\mathrm{l}) + RT\ln x_\mathrm{A}$	Ideal solution	5A.23
Henry's law	$p_\mathrm{B} = x_\mathrm{B}K_\mathrm{B}$	True for ideal–dilute solutions; limiting law as $x_\mathrm{B} \to 0$	5A.24

TOPIC 5B The properties of solutions

➤ Why do you need to know this material?

Mixtures and solutions play a central role in chemistry, and so it is important to understand how their compositions affect their thermodynamic properties, such as their boiling and freezing points. One very important physical property of a solution is its osmotic pressure, which is used, for example, to determine the molar masses of macromolecules.

➤ What is the key idea?

The chemical potential of a substance in a mixture is the same in every phase in which it occurs.

➤ What do you need to know already?

This Topic is based on the expression derived from Raoult's law (Topic 5A) in which chemical potential is related to mole fraction. The derivations make use of the Gibbs–Helmholtz equation (Topic 3E) and the effect of pressure on chemical potential (Topic 5A). Some of the derivations are the same as those used in the discussion of the mixing of perfect gases (Topic 5A).

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

5B.1 Liquid mixtures

The development here is based on the relation derived in Topic 5A between the chemical potential of a component (which here is called J, with J = A or B in a binary mixture) in an ideal mixture or solution, μ_J, its value when pure, μ_J^*, and its mole fraction in the mixture, x_J:

$$\mu_J = \mu_J^* + RT\ln x_J \tag{5B.1}$$

Chemical potential [ideal solution]

(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 (Topic 5A). The total Gibbs energy before the liquids are mixed is

$$G_i = n_A\mu_A^* + n_B\mu_B^* \tag{5B.2a}$$

where the * denotes the pure liquid. When they are mixed, the individual chemical potentials are given by eqn 5B.1 and the total Gibbs energy is

$$G_f = n_A(\mu_A^* + RT\ln x_A) + n_B(\mu_B^* + RT\ln x_B) \tag{5B.2b}$$

Consequently, the Gibbs energy of mixing, the difference of these two quantities, is

$$\Delta_{mix}G = nRT(x_A\ln x_A + x_B\ln x_B) \tag{5B.3}$$

Gibbs energy of mixing [ideal solution]

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

$$\Delta_{mix}S = -nR(x_A\ln x_A + x_B\ln x_B) \tag{5B.4}$$

Entropy of mixing [ideal solution]

Then from $\Delta_{mix}G = \Delta_{mix}H - T\Delta_{mix}S$ it follows that the ideal enthalpy of mixing is zero, $\Delta_{mix}H = 0$. The ideal volume of mixing, the change in volume on mixing, is also zero. To see why, consider that, because $(\partial G/\partial p)_T = V$ (eqn 3E.8), $\Delta_{mix}V = (\partial\Delta_{mix}G/\partial p)_T$. But $\Delta_{mix}G$ in eqn 5B.3 is independent of pressure, so the derivative with respect to pressure is zero, and therefore $\Delta_{mix}V = 0$.

Equations 5B.3 and 5B.4 are the same as those for the mixing of two perfect gases and all the conclusions drawn there are valid here: because the enthalpy of mixing is zero there is no change in the entropy of the surroundings so the driving force for mixing is the increasing entropy of the system as the molecules mingle. It should be noted, however, that solution ideality means something different from gas perfection. In a perfect gas there are no interactions between the 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. The variation of the Gibbs energy and entropy of mixing with composition is the same as that for gases (Figs. 5A.7 and 5A.9); both graphs are repeated here (as Figs. 5B.1 and 5B.2).

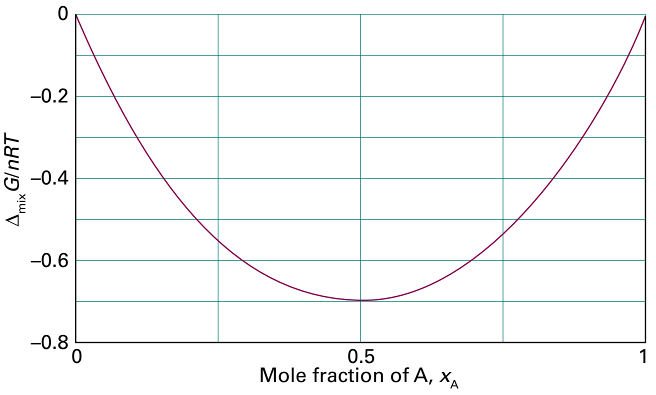

Figure 5B.1 The Gibbs energy of mixing of two liquids that form an ideal solution.

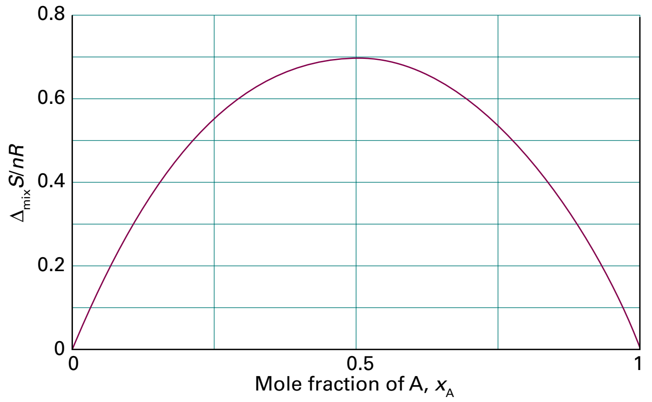

Figure 5B.2 The entropy of mixing of two liquids that form an ideal solution.

A note on good practice It is on the basis of this distinction that the term 'perfect gas' is preferable to the more common 'ideal gas'. In an ideal solution there are interactions, but they are effectively the same between the various species. In a perfect gas, not only are the interactions the same, but they are also zero. Few people, however, trouble to make this valuable distinction.

Brief illustration 5B.1

Consider a mixture of benzene and methylbenzene, which form an approximately ideal solution, and suppose 1.0 mol $C_6H_6(l)$ is mixed with 2.0 mol $C_6H_5CH_3(l)$. For the mixture, $x_{benzene} = 0.33$ and $x_{methylbenzene} = 0.67$. The Gibbs energy and entropy of mixing at 25 °C, when $RT = 2.48\,\mathrm{kJ\,mol^{-1}}$, are

$$\Delta_{mix}G/n = (2.48\,\mathrm{kJ\,mol^{-1}}) \times (0.33\ln 0.33 + 0.67\ln 0.67) = -1.6\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta_{mix}S/n = -(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (0.33\ln 0.33 + 0.67\ln 0.67) = +5.3\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

The enthalpy of mixing is zero (presuming that the solution is ideal).

Real solutions are composed of molecules for which the A–A, A–B, and B–B interactions are all different. Not only may there be enthalpy and volume changes when such 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 negative (because of a reorganization of the molecules that results in an orderly mixture), the Gibbs energy of mixing might be positive. In that case, separation is spontaneous and the liquids are 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:

$$X^E = \Delta_{mix}X - \Delta_{mix}X^{ideal} \qquad \text{Excess function [definition]} \qquad (5B.5)$$

The **excess entropy**, S^E, for example, is calculated by using the value of $\Delta_{mix}S^{ideal}$ given by eqn 5B.4. 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.

Figure 5B.3 shows two examples of the composition dependence of excess functions. Figure 5B.3(a) shows data for

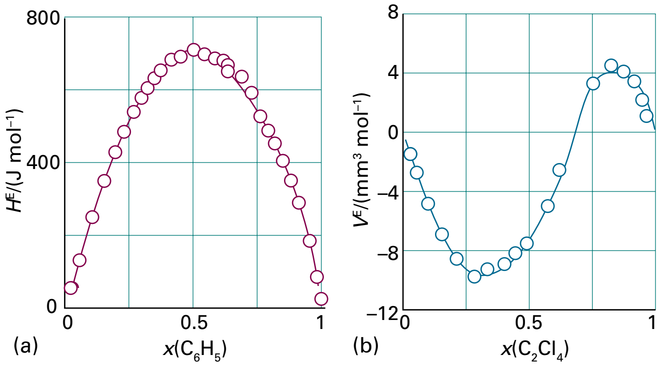

Figure 5B.3 Experimental excess functions at 25 °C. (a) H^E for benzene/cyclohexane; this graph shows that the mixing is endothermic (because $\Delta_{mix}H = 0$ for an ideal solution). (b) The excess volume, V^E, for tetrachloroethene/cyclopentane; this graph shows that there is a contraction at low tetrachloroethene mole fractions, but an expansion at high mole fractions (because $\Delta_{mix}V = 0$ for an ideal mixture).

a benzene/cyclohexane mixture: the positive values of H^{E}, which implies that $\Delta_{\mathrm{mix}}H > 0$, indicate that the A–B interactions in the mixture are less attractive than the A–A and B–B interactions in the pure liquids. The symmetrical shape of the curve reflects the similar strengths of the A–A and B–B interactions. Figure 5B.3(b) shows the composition dependence of the excess volume, V^{E}, of a mixture of tetrachloroethene and cyclopentane. At high mole fractions of cyclopentane, the solution contracts as tetrachloroethene is added because the ring structure of cyclopentane results in inefficient packing of the molecules, but as tetrachloroethene is added, the molecules in the mixture pack together more tightly. Similarly, at high mole fractions of tetrachloroethene, the solution expands as cyclopentane is added because tetrachloroethene molecules are nearly flat and pack efficiently in the pure liquid, but become disrupted as the bulky ring cyclopentane is added.

Deviations of the excess enthalpy from zero indicate the extent to which the solutions are non-ideal. In this connection a useful model system is the **regular solution**, a solution for which $H^{\mathrm{E}} \neq 0$ but $S^{\mathrm{E}} = 0$. A regular solution can be thought of as one in which the two kinds of molecules are distributed randomly (as in an ideal solution) but have different energies of interaction with each other. To express this concept more quantitatively, suppose that the excess enthalpy depends on composition as

$$H^{\mathrm{E}} = n\xi RTx_{\mathrm{A}}x_{\mathrm{B}} \qquad (5\mathrm{B}.6)$$

where ξ (xi) is a dimensionless parameter that is a measure of the energy of A–B interactions relative to that of the A–A and B–B interactions. (For H^{E} expressed as a molar quantity, discard the n.) The function given by eqn 5B.6 is plotted in Fig. 5B.4; it resembles the experimental curve in Fig. 5B.3a. If $\xi < 0$, then mixing is exothermic and the A–B interactions are more favourable than the A–A and B–B interactions. If $\xi > 0$, then the mixing is endothermic. Because the entropy of mixing has its ideal value for a regular solution, the Gibbs energy of mixing is

$$\Delta_{\mathrm{mix}}G = \overbrace{n\xi RTx_{\mathrm{A}}x_{\mathrm{B}}}^{\Delta_{\mathrm{mix}}H} - T\overbrace{[-nR(x_{\mathrm{A}}\ln x_{\mathrm{A}} + x_{\mathrm{B}}\ln x_{\mathrm{B}})]}^{\Delta_{\mathrm{mix}}S} \qquad (5\mathrm{B}.7)$$
$$= nRT(x_{\mathrm{A}}\ln x_{\mathrm{A}} + x_{\mathrm{B}}\ln x_{\mathrm{B}} + \xi x_{\mathrm{A}}x_{\mathrm{B}})$$

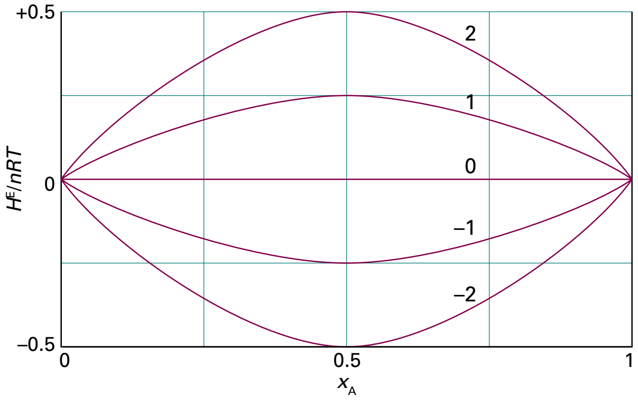

Figure 5B.4 The excess enthalpy according to a model in which it is proportional to $\xi x_{\mathrm{A}}x_{\mathrm{B}}$, for different values of the parameter ξ.

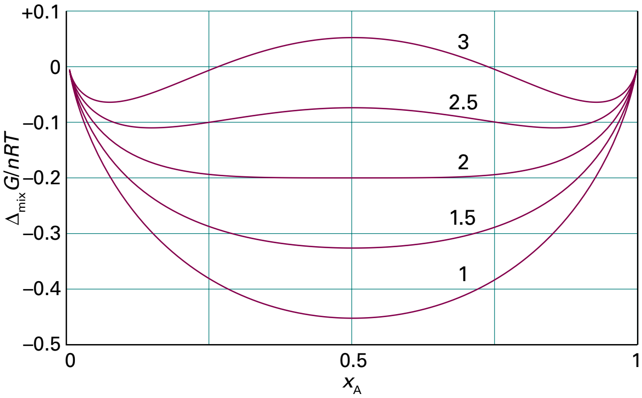

Figure 5B.5 The Gibbs energy of mixing for different values of the parameter ξ.

Figure 5B.5 shows how $\Delta_{\mathrm{mix}}G$ varies with composition for different values of ξ. The important feature is that for $\xi > 2$ the graph shows two minima separated by a maximum. The implication of this observation is that, provided $\xi > 2$, the system will separate spontaneously into two phases with compositions corresponding to the two minima, because such a separation corresponds to a reduction in Gibbs energy. This point is developed in Topic 5C.

Example 5B.1 Identifying the parameter for a regular solution

Identify the value of the parameter ξ that would be appropriate to model a mixture of benzene and cyclohexane at 25 °C, and estimate the Gibbs energy of mixing for an equimolar mixture.

Collect your thoughts Refer to Fig. 5B.3a and identify the value of the maximum in the curve; then relate it to eqn 5B.6 written as a molar quantity ($H^{\mathrm{E}} = \xi RTx_{\mathrm{A}}x_{\mathrm{B}}$). For the second part, assume that the solution is regular and that the Gibbs energy of mixing is given by eqn 5B.7.

The solution In the experimental data the maximum occurs close to $x_{\mathrm{A}} = x_{\mathrm{B}} = \frac{1}{2}$ and its value is close to 701 J mol^{-1}. It follows that

$$\xi = \frac{H^{\mathrm{E}}}{RTx_{\mathrm{A}}x_{\mathrm{B}}} = \frac{701\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})\times\frac{1}{2}\times\frac{1}{2}}$$
$$= 1.13$$

The total Gibbs energy of mixing to achieve the stated composition (provided the solution is regular) is therefore

$$\begin{aligned}\Delta_{\mathrm{mix}}G/n &= \tfrac{1}{2}RT\ln\tfrac{1}{2} + \tfrac{1}{2}RT\ln\tfrac{1}{2} + 701\,\mathrm{J\,mol^{-1}}\\ &= -RT\ln 2 + 701\,\mathrm{J\,mol^{-1}}\\ &= -1.72\,\mathrm{kJ\,mol^{-1}} + 0.701\,\mathrm{kJ\,mol^{-1}} = -1.02\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

Self-test 5B.1 The graph in Fig. 5B.3a suggests the following values:

x	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$H^{\mathrm{E}}/(\mathrm{J\,mol^{-1}})$	150	350	550	680	700	690	600	500	280

Use a curve-fitting procedure to fit these data to an expression of the form in eqn 5B.6 written as $H^{\mathrm{E}}/n = Ax(1-x)$.

Answer: The best fit is with $A = 690\,\mathrm{J\,mol^{-1}}$

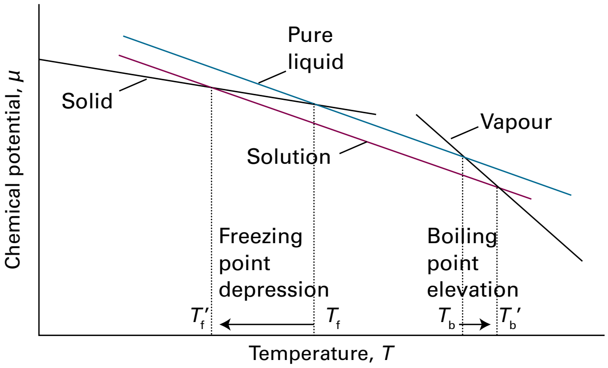

Figure 5B.6 The chemical potential of the liquid solvent in a solution is lower than that of the pure liquid. As a result, the temperature at which the chemical potential of the solvent is equal to that of the solid solvent (the freezing point) is lowered, and the temperature at which it is equal to the vapour (the boiling point) is raised. 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.

5B.2 Colligative properties

A **colligative property** is a physical property that depends on the relative number of solute particles present but not their chemical identity ('colligative' denotes 'depending on the collection'). They include 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.

In this development, the solvent is denoted by A and the solute by B. There are two assumptions. First, the solute is not volatile, so it does not contribute to the vapour. Second, 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 solution (one that obeys Raoult's law, Topic 5A; $p_{\mathrm{A}} = x_{\mathrm{A}}p_{\mathrm{A}}^{\star}$), the reduction is from $\mu_{\mathrm{A}}^{\star}$ for the pure solvent to $\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^{\star} + RT\ln x_{\mathrm{A}}$ when a solute is present ($\ln x_{\mathrm{A}}$ is negative because $x_{\mathrm{A}} < 1$). 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. 5B.6, 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).

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.[1] When a solute is present, there is an additional contribution to the entropy of the solvent which results is a weaker tendency to form the vapour (Fig. 5B.7). This weakening of the tendency to form a vapour lowers the vapour pressure and hence raises the 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.

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[1] More precisely, if it is not an enthalpy effect (that is, an effect arising from changes in the entropy of the surroundings due to the transfer of energy as heat into or from them), then it must be an effect arising from the entropy of the system.