6

Physical transformations of pure substances

The simplest applications of thermodynamics to chemically significant systems are to the discussion of the phase transitions of pure substances. We shall see that a phase diagram is a map of the pressures and temperatures at which each phase of a substance is the most stable. First, we describe the interpretation of empirically determined phase diagrams for a selection of materials. Then we turn to a consideration of the factors that determine the positions and shapes of the boundaries between the regions on a phase diagram. The practical importance of the expressions we derive is that they show how the vapour pressure of a substance varies with temperature and how the melting point varies with pressure. We shall see that the transitions between phases can be classified by noting how various thermodynamic functions change when the transition occurs. Finally, we consider the thermodynamic discussion of liquid surfaces, such as surface tension and capillary action.

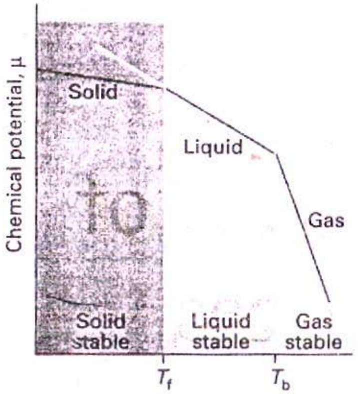
Vaporization, melting, and the conversion of graphite to diamond are all examples of changes of phase without change of chemical composition. In this chapter we describe such processes thermodynamically, using as the guiding principle the tendency of systems at constant temperature and pressure to minimize their Gibbs energy. Because we are dealing with pure substances, the molar Gibbs energy of the system is the same as the chemical potential, μ, so the direction of spontaneous change is in the direction of decreasing chemical potential. Once again we see how the properties of the chemical potential mirror its name: a pure substance with a high chemical potential has a spontaneous tendency to move to a state with lower chemical potential.

Phase diagrams

One of the most succinct ways of presenting the physical changes of state that a substance can undergo is in terms of its phase diagram. We present the concept in this section.

6.1 The stabilities of phases

A **phase** of a substance is a form of matter that is uniform throughout in chemical composition and physical state. Thus, we speak of solid, liquid, and gas phases of a substance, and of its various solid phases, such as the white and black allotropes of phosphorus. A **phase transition**, the spontaneous conversion of one phase into another phase, occurs at a characteristic temperature for a given pressure. Thus, at 1 atm, ice is the stable phase of water below 0°C, but above 0°C liquid water is more stable. This difference indicates that below 0°C the chemical potential of ice is lower than that of liquid water, and that above 0°C the opposite is true (Fig. 6.1). The **transition temperature, T_{trs}**, is the temperature at which the two chemical potentials are equal and the two phases are in equilibrium at the prevailing pressure.

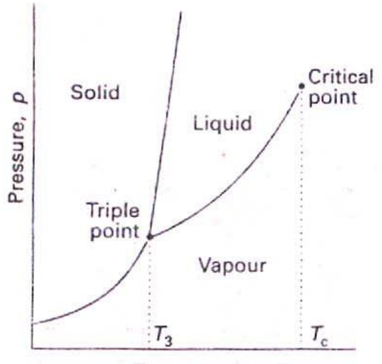


6.1 The schematic temperature dependence of the chemical potential of the solid, liquid, and gas phases of a substance (in practice, the lines are curved). The phase with the lowest chemical potential at a specified temperature is the most stable one at that temperature. The transition temperatures, the melting and boiling temperatures, are the temperatures at which the chemical potentials of two phases are equal.

When considering phase transitions, it is always important to distinguish between the thermodynamic description of the transition and the rate at which the transition actually occurs. A transition that is predicted from thermodynamics to be spontaneous may occur too slowly to be significant in practice. For instance, at normal temperatures and pressures the chemical potential of graphite is lower than that of diamond, so there is a thermodynamic tendency for diamond to change into graphite. However, for this transition to take place, the C atoms must change their locations, which is an immeasurably slow process in a solid except at high temperatures. The rate of attainment of equilibrium is a kinetic problem, and is outside the scope of thermodynamics. In gases and liquids the mobilities of the molecules allow phase transitions to occur rapidly, but in solids thermodynamic instability may be frozen in. Thermodynamically unstable phases that persist because the transition is kinetically hindered are called **metastable phases**. Diamond is a metastable phase of carbon under normal conditions.

6.2 Phase boundaries

The **phase diagram** of a substance shows the regions of pressure and temperature at which its various phases are thermodynamically stable (Fig. 6.2). The lines separating the regions, which are called **phase boundaries**, show the values of p and T at which two phases coexist in equilibrium.

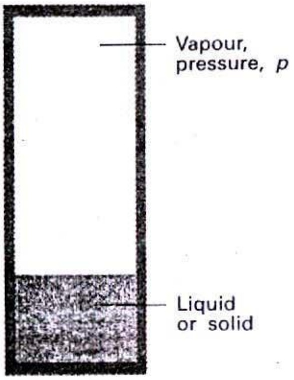


6.2 The general regions of pressure and temperature where solid, liquid, or gas is stable (that is, has lowest chemical potential) are shown on this phase diagram. For example, the solid phase is the most stable phase at low temperatures and high pressures. In the following paragraphs we locate the precise boundaries between the regions.

Consider a liquid sample of a pure substance in a closed vessel. The pressure of a vapour in equilibrium with the liquid is called the **vapour pressure** of the substance (Fig. 6.3). Therefore, the liquid–vapour phase boundary in a phase diagram shows how the vapour pressure of the liquid varies with temperature. Similarly, the solid–vapour phase boundary shows the temperature variation of the **sublimation vapour pressure** of the solid. The vapour pressure of a substance increases with temperature because at higher temperatures the Boltzmann distribution populates more heavily the states of higher energy, corresponding to molecules that have escaped from their neighbours.

(a) Critical points and boiling points

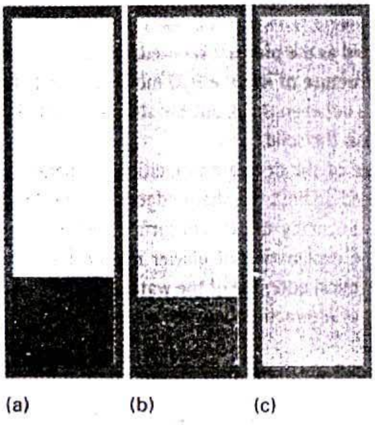
When a liquid is heated in an *open* vessel, the liquid vaporizes from its surface. At the temperature at which its vapour pressure would be equal to the external pressure, vaporization can occur throughout the bulk of the liquid and the vapour can expand freely into the surroundings. The condition of free vaporization throughout the liquid is called **boiling**. The temperature at which the vapour pressure of a liquid is equal to the external pressure is called the **boiling temperature** at that pressure. For the special case of an external pressure of 1 atm, the boiling temperature is called the **normal boiling point, T_b**. With the replacement of 1 atm by 1 bar as standard pressure, there is some advantage in using the **standard boiling point** instead: this is the temperature at which the vapour pressure reaches 1 bar. Because 1 bar is slightly less than 1 atm (1.00 bar = 0.987 atm), the



6.3 The vapour pressure of a liquid or solid is the pressure exerted by the vapour in equilibrium with the condensed phase.

standard boiling point of a liquid is slightly lower than its normal boiling point. The normal boiling point of water is 100.0°C; its standard boiling point is 99.6°C.

Boiling does not occur when a liquid is heated in a *closed* vessel. Instead, the vapour pressure, and hence the density of the vapour, rise continuously as the temperature is raised (Fig. 6.4). At the same time, the density of the liquid decreases slightly as a result of its expansion. There comes a stage when the density of the vapour is equal to that of the remaining liquid and the surface between the two phases disappears. The temperature at which the surface disappears is the **critical temperature,** T_c, of the substance. We first encountered this property in Section 1.4d. The vapour pressure at the critical temperature is called the **critical pressure,** p_c. At and above the critical temperature, a single uniform phase called a **supercritical fluid** fills the container and an interface no longer exists. That is, above the critical temperature, the liquid phase of the substance does not exist.



6.4 (a) A liquid in equilibrium with its vapour. (b) When a liquid is heated in a sealed container, the density of the vapour phase increases and that of the liquid decreases slightly. There comes a stage, (c), at which the two densities are equal and the interface between the fluids disappears. This disappearance occurs at the critical temperature. The container needs to be strong: the critical temperature of water is 374°C and the vapour pressure is then 218 atm.

(b) Melting points and triple points

The temperature at which, under a specified pressure, the liquid and solid phases of a substance coexist in equilibrium is called the **melting temperature.** Because a substance melts at exactly the same temperature as that at which it freezes, the melting temperature of a substance is the same as its freezing temperature. The freezing temperature when the pressure is 1 atm is called the **normal freezing point,** T_f, and its freezing point when the pressure is 1 bar is called the **standard freezing point.** The normal and standard freezing points are negligibly different for most purposes. The normal freezing point is also called the **normal melting point.**

There is a set of conditions under which three different phases of a substance (typically solid, liquid, and vapour) all simultaneously coexist in equilibrium. It is represented by the **triple point,** a point at which the three phase boundaries meet. The temperature at the triple point is denoted T_3. The triple point of a pure substance is outside our control: it occurs at a single definite pressure and temperature characteristic of the substance. The triple point of water lies at 273.16 K and 611 Pa (6.11 mbar, 4.58 Torr), and the three phases of water (ice, liquid water, and water vapour) coexist in equilibrium at no other combination of pressure and temperature. This invariance of the triple point is the basis of its use in the definition of the thermodynamic temperature scale (Section 4.2c).

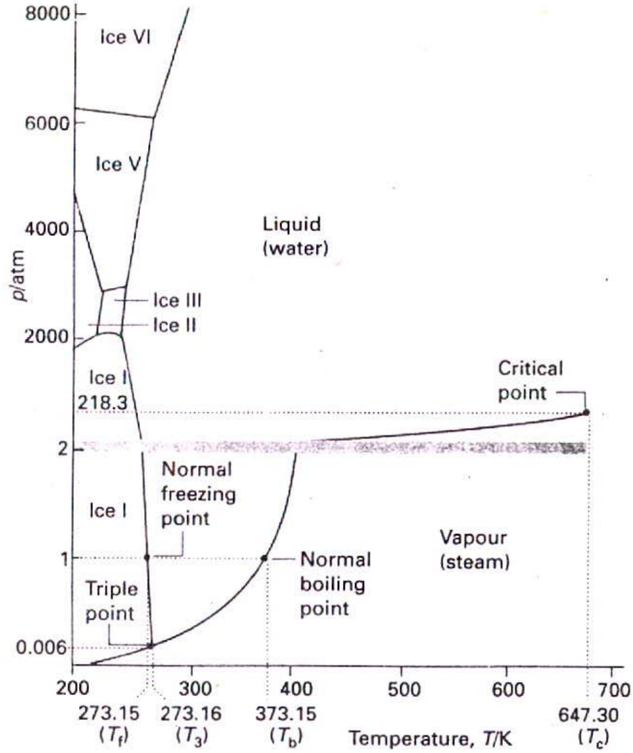
As can be seen from Fig. 6.2, the triple point marks the lowest pressure at which a liquid phase of a substance can exist. If (as is common) the slope of the solid–liquid phase boundary is as shown in the diagram, then the triple point also marks the lowest temperature at which the liquid can exist; the critical temperature is the upper limit.

6.3 Three typical phase diagrams

We shall now illustrate how these general features appear in the phase diagrams of pure substances.

(a) Water

Figure 6.5 is the phase diagram for water. The liquid–vapour boundary in the phase diagram summarizes how the vapour pressure of liquid water varies with temperature. It also summarizes how the boiling temperature varies with pressure: we simply read off the temperature at which the vapour pressure is equal to the prevailing atmospheric pressure. The solid–liquid boundary shows how the melting temperature varies with the pressure. Its very steep slope indicates that enormous pressures are needed to bring about significant changes. Notice that the line has a negative slope up to 2000 atm, which means that the melting temperature falls as the pressure is raised. The reason for this unusual behaviour can be traced to the decrease in volume that occurs on melting, and hence it being more

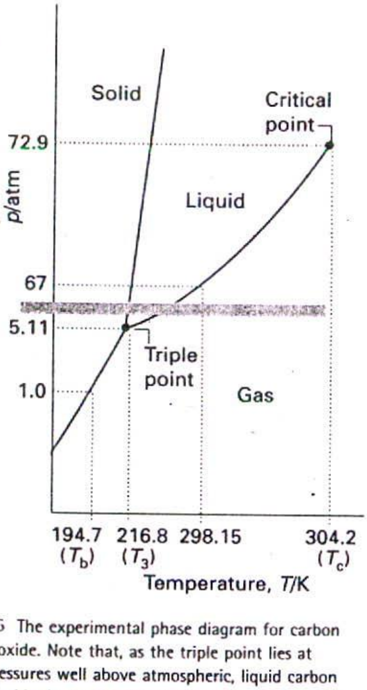


6.5 The experimentally determined phase diagram for water showing the different solid phases. Note the change of vertical scale at 2 atm.

favourable for the solid to transform into the liquid as the pressure is raised. The decrease in volume is a result of the very open molecular structure of ice: the H_2O molecules are held apart (as well as together) by the hydrogen bonds between them, but the structure partially collapses on melting, and the liquid is denser than the solid.

The motion of glaciers may be a consequence of the decrease in melting temperature with pressure: glacial ice melts where it is pressed against the sharp edges of stones and rocks and the glacier inches forwards. However, for many substances surface melting also occurs below the normal melting point, and the explanation of glacier motion (and ice skating) may be more subtle. The reduction in chemical potential of the water below that of the ice may stem from differences in the energy of interaction between water and ice and the rock surface.

At high pressures, different structural forms of ice come into stability as the bonds between molecules are modified by the stress. Some of these phases (which are called ice II, III, V, VI, and VII)[1] melt at high temperatures. Ice VII, for instance, melts at 100°C but exists only above 25 kbar. Note that five more triple points occur in the diagram other than the one where vapour, liquid, and ice I coexist. Each one occurs at a definite pressure and temperature that cannot be changed.



6.6 The experimental phase diagram for carbon dioxide. Note that, as the triple point lies at pressures well above atmospheric, liquid carbon dioxide does not exist under normal conditions (a pressure of at least 5.11 atm must be applied).

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[1] Ice IV was an illusion, or possibly a transient, not thermodynamically stable, state.

(b) Carbon dioxide

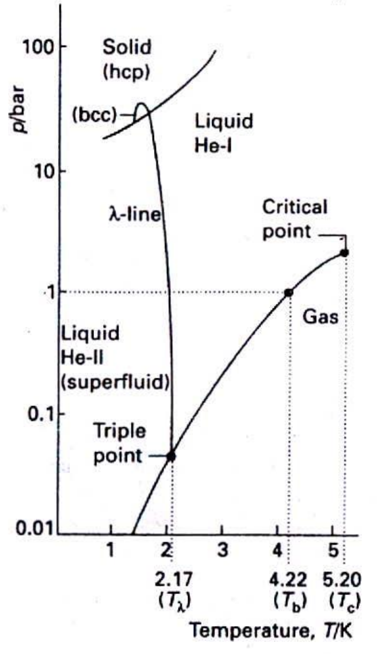
The phase diagram for carbon dioxide is shown in Fig. 6.6. The features to notice include the positive slope of the solid–liquid boundary (the direction of this line is characteristic of most substances), which indicates that the melting temperature of solid carbon dioxide rises as the pressure is increased. Notice also that, as the triple point lies above 1 atm, the liquid cannot exist at normal atmospheric pressures whatever the temperature, and the solid sublimes when left in the open (hence the name 'dry ice'). To obtain the liquid, it is necessary to exert a pressure of at least 5.11 atm. Cylinders of carbon dioxide generally contain the liquid or compressed gas; at a temperature of 25 °C that implies a vapour pressure of 67 atm if both gas and liquid are present in equilibrium. When the gas squirts through the throttle it cools by the Joule–Thomson effect, so when it emerges into a region where the pressure is only 1 atm, it condenses into a finely divided snow-like solid.

Supercritical carbon dioxide (that is, highly compressed carbon dioxide above its critical temperature) is used in **supercritical fluid chromatography** (SFC), a form of chromatography in which the supercritical fluid is used as the mobile phase. The technique can be used to separate lipids and phospholipids and to separate fuel oil into alkanes, alkenes, and arenes. A more mundane application of supercritical carbon dioxide is in the decaffeination of coffee, in which caffeine is extracted from green coffee beans.

(c) Helium

The phase diagram of helium is shown in Fig. 6.7. Helium behaves unusually at low temperatures. For instance, the solid and gas phases are never in equilibrium however low the temperature: the He atoms are so light that they vibrate with a large-amplitude motion even at very low temperatures, and the solid simply shakes itself apart. Solid helium can be obtained, but only by holding the atoms together by applying pressure.

When considering helium at low temperatures it is necessary to distinguish between the isotopes ^{3}He and ^{4}He, because quantum mechanical effects become important and these two isotopes differ not only in mass but also in the spin of their nuclei.[2] As a result of quantum mechanical effects, pure helium-4 has a liquid–liquid phase transition at its **λ-line** (lambda line); the reason for this name is explained in Section 6.7. The liquid phase marked He-I behaves like a normal liquid. The other phase, He-II, is a **superfluid.** It is so called because it flows without viscosity. The phase diagram of helium-3 differs from the phase diagram of helium-4, but it also possesses a superfluid phase. Helium-3 is unusual in that the entropy of the liquid is lower than that of the solid, and melting is exothermic.



6.7 The phase diagram for helium (^{4}He). The λ-line marks the conditions under which the two liquid phases are in equilibrium. Helium-II is the superfluid phase. Note that a pressure of over 20 bar must be exerted before solid helium can be obtained. The labels hcp and bcc denote different solid phases in which the atoms pack together differently: hcp denotes hexagonal close packing and bcc denotes body-centred cubic (see Section 21.1 for a description of these structures).

Phase stability and phase transitions

We shall now see how thermodynamic considerations can account for the features of the phase diagrams we have just described.

6.4 The thermodynamic criterion of equilibrium

We shall base our discussion on the following consequence of the Second Law:

> **At equilibrium, the chemical potential of a substance is the same throughout a sample, regardless of how many phases are present.**

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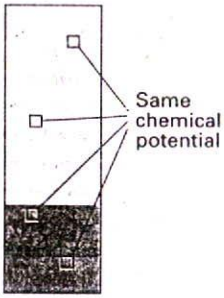
[2] Nuclear spin is a quantum mechanical property that will be encountered in more detail in Part 2. At this stage it can be visualized as a spinning motion of the nucleus. A ^{4}He nucleus has zero spin; a ^{3}He nucleus has nonzero spin.

When the liquid and solid phases of a substance are in equilibrium, the chemical potential of the substance is the same throughout the liquid and throughout the solid, and is the same in the solid as in the liquid (Fig. 6.8).



6.8 When two or more phases are in equilibrium, the chemical potential of a substance (and, in a mixture, a component) is the same in each phase and is the same at all points in each phase.

To see the validity of this remark, consider a system in which the chemical potential of a substance is μ_1 at one location and μ_2 at another location. The locations may be in the same or in different phases. When an amount dn of the substance is transferred from one location to the other, the Gibbs energy of the system changes by $-\mu_1\,dn$ when material is removed from location 1, and it changes by $+\mu_2\,dn$ when that material is added to location 2. The overall change is therefore $dG = (\mu_2 - \mu_1)\,dn$. If the chemical potential at location 1 is higher than that at location 2, the transfer is accompanied by a decrease in G, and so has a spontaneous tendency to occur. Only if $\mu_1 = \mu_2$ is there no change in G, and only then is the system at equilibrium.

Molecular interpretation 6.1 The tendency towards equality of chemical potential is a disguised form of the tendency to greater entropy as expressed by the Second Law. Suppose that in location 1 the molecules experience less favourable attractive forces than in location 2. Then the entropy of the surroundings will increase if molecules migrate from location 1 to location 2 because heat will be released into the surroundings and increase their disorder. However, to judge whether a process is spontaneous, we need to consider the total entropy change, and there may be a difference in molecular disorder between the two locations. If the disorder of the molecules in location 1 is greater than in location 2, the entropy of the system will decrease when molecules migrate from location 1 to location 2. For example, location 1 might be a gas phase and location 2 might be a liquid phase. The transfer of molecules from location 1 (gas) to location 2 (liquid) is spontaneous if the increase in entropy of the surroundings exceeds the decrease in entropy of the system. The opposite transfer, from location 2 (liquid) to location 1 (gas) is spontaneous if the increase in disorder of the system is greater than the decrease in disorder of the surroundings. The change is spontaneous in neither direction if the changes in entropies of the system and its surroundings cancel, which is expressed by setting the chemical potentials of the two phases equal to each other. The chemical potential takes into account the contributions of the enthalpy change to the surroundings and the change in entropy of the molecules themselves.

6.5 The dependence of stability on the conditions

At low temperatures, the solid phase of a substance has the lowest chemical potential and, provided the pressure is not too low, is usually the most stable at low temperatures. However, the chemical potentials of phases change with temperature in different ways, and as the temperature is raised the chemical potential of another phase (perhaps another solid phase, a liquid, or a gas) will fall below that of the solid. When that happens, a phase transition occurs if it is kinetically feasible to do so.

(a) The temperature dependence of phase stability

The temperature dependence of the Gibbs energy is expressed in terms of the entropy of the system by eqn 5.10 ($(\partial G/\partial T)_p = -S$). Because the chemical potential of a pure substance is equal to the molar Gibbs energy of that substance, it follows that

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_{\mathrm{m}} \qquad (1)$$

This relation shows that, as the temperature is raised, the chemical potential of a pure substance decreases: $S_m > 0$ always, so the slope of a plot of μ against T is negative.

Equation 1 implies that the slope of a plot of μ against temperature is steeper for gases than for liquids, because $S_m(g) > S_m(l)$. The slope is also steeper for a liquid than the corresponding solid, because $S_m(l) > S_m(s)$ almost always, on account of the greater disorder of a liquid. These features were illustrated in Fig. 6.1. The steep negative slope of $\mu(l)$ results in its falling below $\mu(s)$ when the temperature is high enough, and then the liquid becomes the stable phase: the solid melts. The chemical potential of the gas phase plunges steeply downwards as the temperature is raised (because the molar entropy of the vapour is so high), and there comes a temperature at which it lies lowest. Then the gas is the stable phase and the liquid vaporizes. When we bring about a phase transition, what we are actually doing is modifying the relative values of the chemical potentials of the phases. The easiest way of doing that is by changing the temperature of the sample.

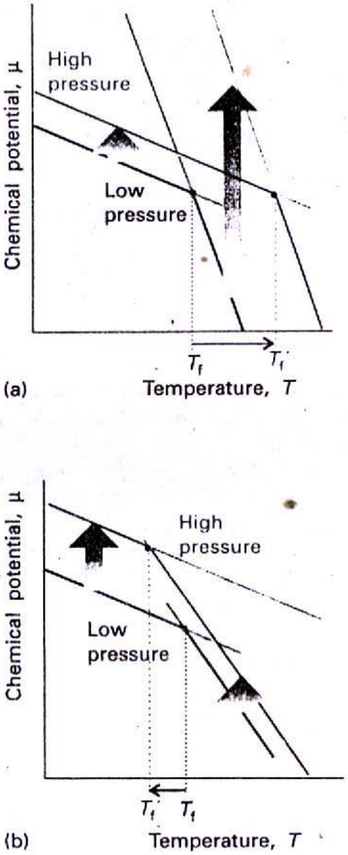
(b) The response of melting to applied pressure

Most substances melt at a higher temperature when subjected to pressure. It is as though the pressure is preventing the formation of the less dense liquid phase. Exceptions to this behaviour include water, for which the liquid is denser than the solid. Application of pressure to water encourages the formation of the liquid phase. That is, water freezes at a lower temperature when it is under pressure.

We can rationalize the response of melting temperatures to pressure as follows. The variation of the chemical potential with pressure is expressed (from eqn. 5.10) by

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m \qquad (2)$$

This equation shows that the slope of a plot of chemical potential against pressure is equal to the molar volume of the substance. An increase in pressure raises the chemical potential of any pure substance (because $V_m > 0$). In most cases, $V_m(l) > V_m(s)$ and the equation predicts that an increase in pressure increases the chemical potential of the liquid more than that of the solid. As shown in Fig. 6.9a, the effect of pressure in such a case is to raise the melting temperature slightly. For water, however, $V_m(l) < V_m(s)$, and an increase in pressure increases the chemical potential of the solid more than that of the liquid. In this case, the melting temperature is lowered slightly (Fig. 6.9b).



6.9 The pressure dependence of the chemical potential of a substance depends on the molar volume of the phase. The lines show schematically the effect of increasing pressure on the chemical potentials of the solid and liquid phases (in practice, the lines are curved), and the corresponding effects on the freezing temperatures. (a) In this case the molar volume of the solid is less than that of the liquid and $\mu(s)$ increases less than $\mu(l)$. As a result, the freezing temperature rises. (b) Here the molar volume is greater for the solid than the liquid (as for water), $\mu(s)$ increases more strongly than $\mu(l)$, and the freezing temperature is lowered.

Example 6.1 Assessing the effect of pressure on the chemical potential

Calculate the effect on the chemical potentials of ice and water of increasing the pressure from 1.00 bar to 2.00 bar at 0°C. The density of ice is 0.917 $\mathrm{g\,cm^{-3}}$ and that of liquid water is 0.999 $\mathrm{g\,cm^{-3}}$ under these conditions.

Method From eqn 2, we know that the change in chemical potential of an incompressible substance when the pressure is changed by Δp is $\Delta\mu = V_m \Delta p$. Therefore, to answer the question, we need to know the molar volumes of the two phases of water. These values are obtained from the mass density, ρ, and the molar mass, M, by using $V_m = M/\rho$. We therefore use the expression

$$\Delta\mu = \frac{M\Delta p}{\rho}$$

Convert all data to SI units, and use 1 $\mathrm{Pa\,m^3}$ = 1 J.

Answer The molar mass of water is 18.02 $\mathrm{g\,mol^{-1}}$ ($1.802\times10^{-2}\ \mathrm{kg\,mol^{-1}}$); therefore,

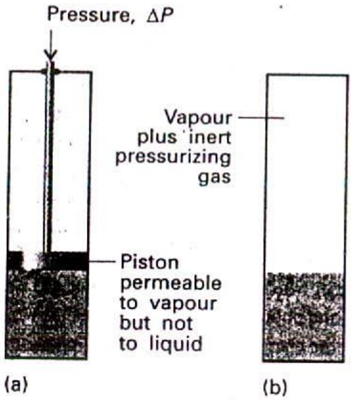
$$\Delta\mu(\text{ice}) = \frac{(1.802\times10^{-2}\ \mathrm{kg\,mol^{-1}})\times(1.00\times10^{5}\ \mathrm{Pa})}{917\ \mathrm{kg\,m^{-3}}} = +1.97\ \mathrm{J\,mol^{-1}}$$

$$\Delta\mu(\text{water}) = \frac{(1.802\times10^{-2}\ \mathrm{kg\,mol^{-1}})\times(1.00\times10^{5}\ \mathrm{Pa})}{999\ \mathrm{kg\,m^{-3}}} = +1.80\ \mathrm{J\,mol^{-1}}$$

Comment The chemical potential of ice rises more sharply than that of water so, if they are initially in equilibrium at 1 bar, there will be a tendency for the ice to melt at 2 bar.

Self-test 6.1 Calculate the effect of an increase in pressure of 1.00 bar on the liquid and solid phases of carbon dioxide (of molar mass 44.0 $\mathrm{g\,mol^{-1}}$) in equilibrium with densities 2.35 $\mathrm{g\,cm^{-3}}$ and 2.50 $\mathrm{g\,cm^{-3}}$, respectively.

[$\Delta\mu(\mathrm{l}) = +1.87\ \mathrm{J\,mol^{-1}}$, $\Delta\mu(\mathrm{s}) = +1.76\ \mathrm{J\,mol^{-1}}$; solid forms]



6.10 Pressure may be applied to a condensed phase either (a) by compressing the condensed phase or (b) by subjecting it to an inert pressurizing gas. When pressure is applied, the vapour pressure of the condensed phase increases.

(c) The effect of applied pressure on vapour pressure

When pressure is applied to a condensed phase, its vapour pressure rises: in effect, molecules are squeezed out of the phase and escape as a gas. Pressure can be exerted on the condensed phase mechanically or by subjecting it to the applied pressure of an inert gas (Fig. 6.10); in the latter case, the vapour pressure is the partial pressure of the vapour in equilibrium with the condensed phase, and we speak of the **partial vapour pressure** of the substance. One complication (which we ignore here) is that, if the condensed phase is a liquid, then the pressurizing gas might dissolve and change its properties. Another complication is that the gas-phase molecules might attract molecules out of the liquid by the process of **gas solvation**, the attachment of molecules to gas-phase species.

The quantitative relation between the vapour pressure, p, when a pressure ΔP is applied and the vapour pressure, p^*, of the liquid in the absence of an additional pressure is

$$p = p^* e^{V_\mathrm{m}\Delta P/RT} \qquad (3)^\circ$$

This equation shows how the vapour pressure increases when the pressure acting on the condensed phase is increased.

Justification 6.1

We calculate the vapour pressure of a pressurized liquid by using the fact that at equilibrium the chemical potentials of the liquid and its vapour are equal: $\mu(\mathrm{l}) = \mu(\mathrm{g})$. It follows that, for any change that preserves equilibrium, the resulting change in $\mu(\mathrm{l})$ must be equal to the change in $\mu(\mathrm{g})$; therefore, we can write $\mathrm{d}\mu(\mathrm{g}) = \mathrm{d}\mu(\mathrm{l})$. When the pressure P on the liquid is increased by $\mathrm{d}P$, the chemical potential of the liquid changes by $\mathrm{d}\mu(\mathrm{l}) = V_\mathrm{m}(\mathrm{l})\,\mathrm{d}P$. The chemical potential of the vapour changes by $\mathrm{d}\mu(\mathrm{g}) = V_\mathrm{m}(\mathrm{g})\,\mathrm{d}p$ where $\mathrm{d}p$ is the change in the vapour pressure we are trying to find. If we treat the vapour as a perfect gas, the molar volume can be replaced by $V_\mathrm{m}(\mathrm{g}) = RT/p$, and we obtain

$$\mathrm{d}\mu(\mathrm{g}) = \frac{RT\,\mathrm{d}p}{p}$$

Next, we equate the changes in chemical potentials of the vapour and the liquid:

$$\frac{RT\,\mathrm{d}p}{p} = V_\mathrm{m}(\mathrm{l})\,\mathrm{d}P$$

This expression can be integrated once we know the limits of integration.

When there is no additional pressure acting on the liquid, P (the pressure experienced by the liquid) is equal to the normal vapour pressure p^*; so, when $P = p^*$, $p = p^*$ too. When there is an additional pressure ΔP on the liquid, with the result that $P = p + \Delta P$, the vapour pressure is p (the value we want to find). The effect of pressure on the vapour pressure is so small that it is a good approximation to replace the p in $p + \Delta P$ by p^* itself, and to set the upper limit of the integral to $p^* + \Delta P$. The integrations required are therefore as follows:

$$RT\int_{p^*}^{p}\frac{\mathrm{d}p}{p} = \int_{p^*}^{p^*+\Delta P} V_\mathrm{m}(\mathrm{l})\,\mathrm{d}P$$

We now assume that the molar volume of the liquid is the same throughout the small range of pressures involved. Then both integrations are straightforward, and lead to

$$RT\ln\left(\frac{p}{p^*}\right) = V_\mathrm{m}(\mathrm{l})\Delta P$$

which rearranges to eqn 3.

Example 6.2 Estimating the effect of pressure on the vapour pressure

Derive an expression from eqn 3 that is valid for small changes in vapour pressure and calculate the fractional increase of the vapour pressure of water for an increase in pressure of 10 bar at 25 °C.

Method The question centres on the approximation of the right-hand side of eqn 3 when the exponent is small. For the approximation, we note that the exponential function e^x is equal to the expansion $1 + x + \frac{1}{2}x^2 + \cdots$; so if $x \ll 1$, a good approximation is $e^x \approx 1 + x$.

Answer If $V_\mathrm{m}\Delta p/RT \ll 1$, the exponential function on the right of eqn 3 may be approximated by $1 + V_\mathrm{m}\Delta p/RT$:

$$p \approx p^*\left(1 + \frac{V_\mathrm{m}\Delta p}{RT}\right)$$

which rearranges to

$$\frac{p - p^*}{p^*} \approx \frac{V_\mathrm{m}\Delta P}{RT}$$

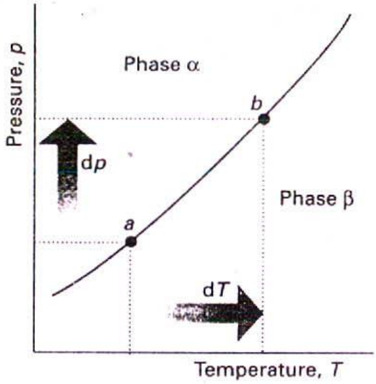
For water (which has density $0.997\ \mathrm{g\,cm^{-3}}$ at 25 °C and therefore molar volume $18.1\ \mathrm{cm^3\,mol^{-1}}$)

$$\frac{V_\mathrm{m}\Delta P}{RT} = \frac{(1.81\times10^{-5}\ \mathrm{m^3\,mol^{-1}})\times(1.0\times10^{6}\ \mathrm{Pa})}{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})\times(298\ \mathrm{K})} = 7.3\times10^{-3}$$

Because $V_\mathrm{m}\Delta P/RT \ll 1$, the approximate formula can be used, and we obtain $(p - p^*)/p^* = 7.3\times10^{-3}$, an increase of 0.73 per cent.

Self-test 6.2 Calculate the effect of an increase in pressure of 100 bar on the vapour pressure of benzene at 25 °C, which has density $0.879\ \mathrm{g\,cm^{-3}}$.

[36 per cent; because the change is so large, use eqn 3]



6.11 When pressure is applied to a system in which two phases are in equilibrium (at *a*), the equilibrium is disturbed. It can be restored by changing the temperature, so moving the state of the system to *b*. It follows that there is a relation between dp and dT that ensures that the system remains in equilibrium as either variable is changed.

6.6 The location of phase boundaries

We can find the precise locations of the phase boundaries—the pressures and temperatures at which two phases can coexist—by making use of the fact that, when two phases are in equilibrium, their chemical potentials must be equal. Therefore, where the phases α and β are in equilibrium,

$$\mu_\alpha(p,T) = \mu_\beta(p,T) \tag{4}$$

By solving this equation for p in terms of T, we get an equation for the phase boundary.

(a) The slopes of the phase boundaries

It turns out to be simplest to discuss the phase boundaries in terms of their slopes, $\mathrm{d}p/\mathrm{d}T$.

Let p and T be changed infinitesimally, but in such a way that the two phases α and β remain in equilibrium. The chemical potentials of the phases are initially equal (the two phases are in equilibrium). They remain equal when the conditions are changed to another point on the phase boundary, where the two phases continue to be in equilibrium (Fig. 6.11). Therefore, the changes in the chemical potentials of the two phases must be equal, and we can write $\mathrm{d}\mu_\alpha = \mathrm{d}\mu_\beta$. Because, from eqn 5.9, we know that

$$\mathrm{d}\mu = -S_\mathrm{m}\,\mathrm{d}T + V_\mathrm{m}\,\mathrm{d}p$$

for each phase, it follows that

$$-S_{\alpha,\mathrm{m}}\,\mathrm{d}T + V_{\alpha,\mathrm{m}}\,\mathrm{d}p = -S_{\beta,\mathrm{m}}\,\mathrm{d}T + V_{\beta,\mathrm{m}}\,\mathrm{d}p$$

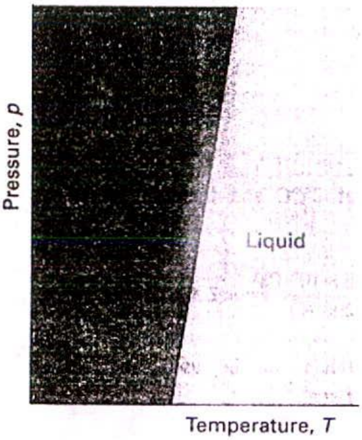
where $S_{\alpha,\mathrm{m}}$ and $S_{\beta,\mathrm{m}}$ are the molar entropies of the phases and $V_{\alpha,\mathrm{m}}$ and $V_{\beta,\mathrm{m}}$ are their molar volumes. Hence

$$(V_{\beta,\mathrm{m}} - V_{\alpha,\mathrm{m}})\,\mathrm{d}p = (S_{\beta,\mathrm{m}} - S_{\alpha,\mathrm{m}})\,\mathrm{d}T \tag{5}$$

which rearranges into the **Clapeyron equation**:

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_\mathrm{trs}S}{\Delta_\mathrm{trs}V} \tag{6}$$

In this expression $\Delta_\mathrm{trs}S = S_{\beta,\mathrm{m}} - S_{\alpha,\mathrm{m}}$ and $\Delta_\mathrm{trs}V = V_{\beta,\mathrm{m}} - V_{\alpha,\mathrm{m}}$ are the entropy and volume of transition. The Clapeyron equation is an exact expression for the slope of the phase boundary and applies to any phase equilibrium of any pure substance.



6.12 A typical solid–liquid phase boundary slopes steeply upwards. This slope implies that, as the pressure is raised, the melting temperature rises. Most substances behave in this way.

(b) The solid–liquid boundary

Melting (fusion) is accompanied by a molar enthalpy change $\Delta_\mathrm{fus}H$ and occurs at a temperature T. The molar entropy of melting at T is therefore $\Delta_\mathrm{fus}H/T$, and the Clapeyron equation becomes

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_\mathrm{fus}H}{T\Delta_\mathrm{fus}V} \tag{7}$$

where $\Delta_\mathrm{fus}V$ is the change in molar volume that occurs on melting. The enthalpy of melting is positive (the only exception is helium-3) and the volume change is usually positive and always small. Consequently, the slope $\mathrm{d}p/\mathrm{d}T$ is steep and usually positive (Fig. 6.12).

The formula for the phase boundary can be obtained by integrating $\mathrm{d}p/\mathrm{d}T$, assuming that $\Delta_\mathrm{fus}H$ and $\Delta_\mathrm{fus}V$ change so little with temperature and pressure that they can be treated as constant. If the melting temperature is T^* when the pressure is p^*, and T when the pressure is p, the integration required is

$$\int_{p^*}^{p} \mathrm{d}p = \frac{\Delta_\mathrm{fus}H}{\Delta_\mathrm{fus}V}\int_{T^*}^{T}\frac{\mathrm{d}T}{T}$$

Therefore, the approximate equation of the solid–liquid boundary is

$$p = p^* + \frac{\Delta_{\text{fus}}H}{\Delta_{\text{fus}}V} \ln\left(\frac{T}{T^*}\right) \tag{8}$$

This equation was originally obtained by yet another Thomson—James, the brother of William, Lord Kelvin. When T is close to T^*, the logarithm can be approximated by using

$$\ln\left(\frac{T}{T^*}\right) = \ln\left(1 + \frac{T - T^*}{T^*}\right) \approx \frac{T - T^*}{T^*}$$

because $\ln(1 + x) \approx x$ when $x \ll 1$; therefore,

$$p \approx p^* + \frac{(T - T^*)\Delta_{\text{fus}}H}{T^*\Delta_{\text{fus}}V} \tag{9}$$

This expression is the equation of a steep straight line when p is plotted against T (as in Fig. 6.12).

(c) The liquid–vapour boundary

The entropy of vaporization at a temperature T is equal to $\Delta_{\text{vap}}H/T$; the Clapeyron equation for the liquid–vapour boundary is therefore

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\text{vap}}H}{T\Delta_{\text{vap}}V} \tag{10}$$

The enthalpy of vaporization is positive; $\Delta_{\text{vap}}V$ is large and positive. Therefore, $\mathrm{d}p/\mathrm{d}T$ is positive, but it is much smaller than for the solid–liquid boundary. It follows that $\mathrm{d}T/\mathrm{d}p$ is large, and hence that the boiling temperature is more responsive to pressure than the freezing temperature.

Example 6.3 Estimating the effect of pressure on the boiling point

Estimate the typical size of the effect of increasing pressure on the boiling point of a liquid.

Method To use eqn 10 we need to estimate the right-hand side. At the boiling point, the term $\Delta_{\text{vap}}H/T$ is Trouton's constant (Section 4.3a). Because the molar volume of a gas is so much greater than the molar volume of a liquid, we can write

$$\Delta_{\text{vap}}V = V_{\text{m}}(\text{g}) - V_{\text{m}}(\text{l}) \approx V_{\text{m}}(\text{g})$$

and take for $V_{\text{m}}(\text{g})$ the molar volume of a perfect gas (at low pressures, at least).

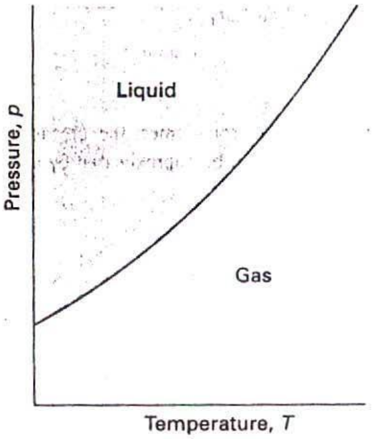
Answer Trouton's constant has the value 85 $\text{J K}^{-1}\,\text{mol}^{-1}$. The molar volume of a perfect gas is about 25 L mol^{-1} at 1 atm and near but above room temperature. Therefore,

$$\frac{\mathrm{d}p}{\mathrm{d}T} \approx \frac{85\ \text{J K}^{-1}\,\text{mol}^{-1}}{25 \times 10^{-3}\ \text{m}^3\,\text{mol}^{-1}} = 3.4 \times 10^3\ \text{Pa K}^{-1}$$

This value corresponds to 0.034 atm K^{-1}, and hence to $\mathrm{d}T/\mathrm{d}p = 30\ \text{K atm}^{-1}$. Therefore, a change of pressure of +0.1 atm can be expected to change a boiling temperature by about +3 K.

Self-test 6.3 Estimate $\mathrm{d}T/\mathrm{d}p$ for water at its normal boiling point using the information in Table 4.2 and $V_{\text{m}}(\text{g}) = RT/p$.

[28 K atm^{-1}]



6.13 A typical liquid–vapour phase boundary. The boundary can be regarded as a plot of the vapour pressure against the temperature. Note that, in some depictions of phase diagrams in which a logarithmic pressure scale is used, the phase boundary has the opposite curvature (see Fig. 6.7). That phase boundary terminates at the critical point (not shown).

Because the molar volume of a gas is so much greater than the molar volume of a liquid, we can write $\Delta_{\text{vap}}V \approx V_{\text{m}}(\text{g})$ (see the example above). Moreover, if the gas behaves perfectly, $V_{\text{m}}(\text{g}) = RT/p$. These two approximations turn the exact Clapeyron equation into

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\text{vap}}H}{T(RT/p)}$$

which rearranges into the Clausius–Clapeyron equation for the variation of vapour pressure with temperature:

$$\frac{\mathrm{d}\ln p}{\mathrm{d}T} = \frac{\Delta_{\text{vap}}H}{RT^2} \qquad (11)^\circ$$

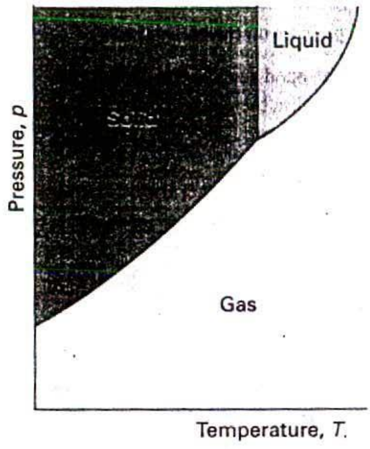
(We have used $\mathrm{d}x/x = \mathrm{d}\ln x$.) If we also assume that the enthalpy of vaporization is independent of temperature, this equation integrates to

$$p = p^* \mathrm{e}^{-\chi} \qquad \chi = \frac{\Delta_{\text{vap}}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right) \qquad (12)^\circ$$

where p^* is the vapour pressure when the temperature is T^* and p the vapour pressure when the temperature is T. Equation 12 is the curve plotted as the liquid–vapour boundary in Fig. 6.13. The line does not extend beyond the critical temperature T_{c}, because above this temperature the liquid does not exist.

(d) The solid–vapour boundary

The only difference between this case and the last is the replacement of the enthalpy of vaporization by the enthalpy of sublimation, $\Delta_{\text{sub}}H$. Because the enthalpy of sublimation is greater than the enthalpy of vaporization, the equation predicts a steeper slope for the sublimation curve than for the vaporization curve at similar temperatures, which is near where they meet (Fig. 6.14).



6.14 Near the point where they coincide (at the triple point), the solid–gas boundary has a steeper slope than the liquid–gas boundary because the enthalpy of sublimation is greater than the enthalpy of vaporization and the temperatures that occur in the Clausius–Clapeyron equation for the slope have similar values.

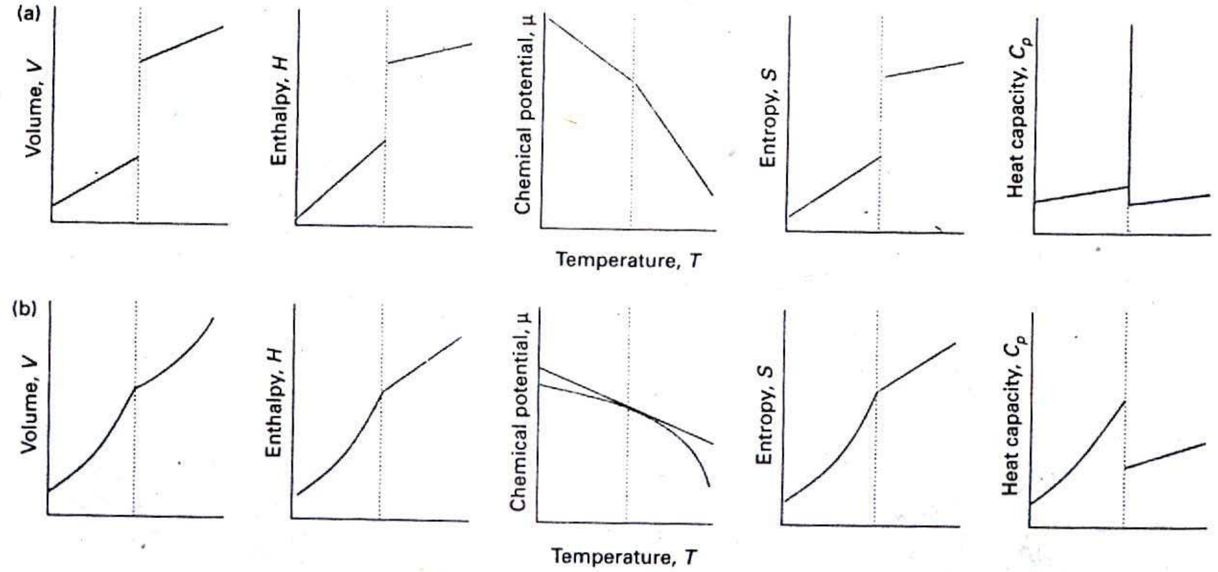
6.7 The Ehrenfest classification of phase transitions

There are many different types of phase transition, including the common examples of fusion and vaporization and the less common examples of solid–solid, conducting–superconducting, and fluid–superfluid transitions. We shall now see that it is possible to use thermodynamic properties of substances, and in particular the behaviour of the chemical potential, to classify phase transitions into different types. The classification scheme was originally proposed by Paul Ehrenfest, and is known as the **Ehrenfest classification**.

Many familiar phase transitions, like fusion and vaporization, are accompanied by changes of enthalpy and volume. These changes have implications for the slopes of the chemical potentials of the phases at either side of the phase transition. Thus, at the transition from a phase α to another phase β,

$$\begin{aligned}\left(\frac{\partial\mu_\beta}{\partial p}\right)_T - \left(\frac{\partial\mu_\alpha}{\partial p}\right)_T &= V_{\beta,\text{m}} - V_{\alpha,\text{m}} = \Delta_{\text{trs}}V \\ \left(\frac{\partial\mu_\beta}{\partial T}\right)_p - \left(\frac{\partial\mu_\alpha}{\partial T}\right)_p &= -S_{\beta,\text{m}} + S_{\alpha,\text{m}} = -\Delta_{\text{trs}}S = -\frac{\Delta_{\text{trs}}H}{T_{\text{trs}}}\end{aligned} \qquad (13)$$

Because $\Delta_{\text{trs}}V$ and $\Delta_{\text{trs}}H$ are nonzero for melting and vaporization, it follows that for such transitions the slopes of the chemical potential plotted against either pressure or temperature are different on either side of the transition (Fig. 6.15a). In other words, the first derivatives of the chemical potentials with respect to pressure and temperature are discontinuous at the transition. A transition for which the first derivative with respect to temperature is discontinuous is classified as a **first-order phase transition**.

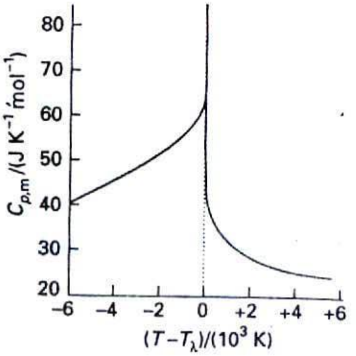


6.15 The changes in thermodynamic properties accompanying (a) first-order and (b) second-order phase transitions.

The constant-pressure heat capacity C_p of a substance is the slope of a plot of the enthalpy with respect to temperature. At a first-order phase transition, H changes by a finite amount for an infinitesimal change of temperature. Therefore, at the transition the heat capacity is infinite. The physical reason is that heating drives the transition rather than raising the temperature. For example, boiling water stays at the same temperature even though heat is being supplied.

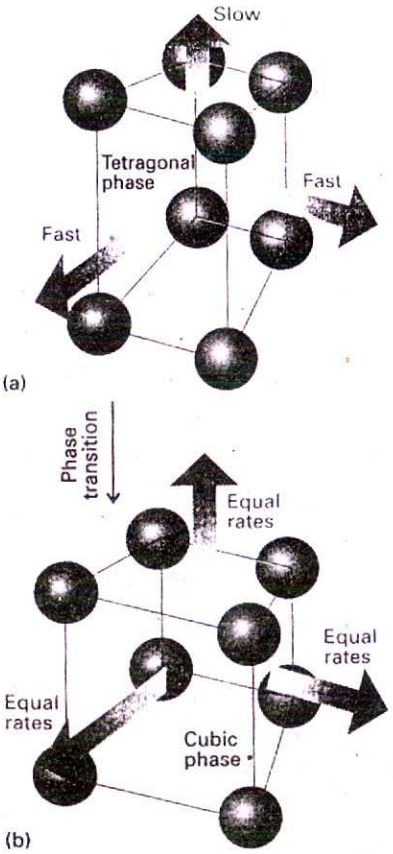
A **second-order phase transition** in the Ehrenfest sense is one in which the first derivative of μ with respect to temperature is continuous but its second derivative is discontinuous. A continuous slope of μ (a graph with the same slope on either side of the transition) implies that the volume and entropy (and hence the enthalpy) do not change at the transition (Fig. 6.15b). The heat capacity is discontinuous at the transition but does not become infinite there. An example of a second-order transition is the conducting–superconducting transition in metals at low temperatures.

The term **λ-transition** is applied to a phase transition that is not first-order yet the heat capacity becomes infinite at the transition temperature. Typically, the heat capacity of a system that shows such a transition begins to increase well before the transition (Fig. 6.16), and the shape of the heat capacity curve resembles the Greek letter lambda. This type of transition includes order–disorder transitions in alloys, the onset of ferromagnetism, and the fluid–superfluid transition of liquid helium.



6.16 The λ-curve for helium, where the heat capacity rises to infinity. The shape of this curve is the origin of the name λ-transition.

Molecular interpretation 6.2 One type of second-order transition is associated with a change in symmetry of the crystal structure of a solid. Thus, suppose the arrangement of atoms in a solid is like that represented in Fig. 6.17a, with one dimension (technically, of the unit cell) longer than the other two, which are equal. Such a crystal structure is classified as tetragonal (see Section 21.1). Moreover, suppose the two shorter dimensions increase more than the long dimension when the temperature is raised. There may come a stage when the three dimensions become equal. At that point the crystal has cubic symmetry (Fig. 6.17b), and at higher temperatures it will expand equally in all three



6.17 One version of a second-order phase transition in which (a) a tetragonal phase expands more rapidly in two directions than a third, and hence becomes a cubic phase, which (b) expands uniformly in three directions as the temperature is raised. There is no rearrangement of atoms at the transition temperature, and hence no enthalpy of transition.

directions (because there is no longer any distinction between them). The tetragonal → cubic phase transition has occurred, but, as it has not involved a discontinuity in the interaction energy between the atoms or the volume they occupy, the transition is not first-order.

The order–disorder transition in β-brass (CuZn) is an example of a λ-transition. The low-temperature phase is an orderly array of alternating Cu and Zn atoms. The high-temperature phase is a random array of the atoms (Fig. 6.18). At $T = 0$ the order is perfect, but islands of disorder appear as the temperature is raised. The islands form because the transition is cooperative in the sense that, once two atoms have exchanged locations, it is easier for their neighbours to exchange their locations. The islands grow in extent, and merge throughout the crystal at the transition temperature (742 K). The heat capacity increases as the transition temperature is approached because the cooperative nature of the transition means that it is increasingly easy for the heat supplied to drive the phase transition rather than to be stored as thermal motion.

The physical liquid surface

So far, we have concentrated on the properties of the boundaries in the phase diagram of a substance. However, the *physical* boundary between phases, such as the surface where solid is in contact with liquid or liquid is in contact with vapour, has interesting properties. In this section we concentrate on the liquid–vapour interface, which is interesting because it is so mobile. Chapter 28 deals with solid surfaces and their important role in catalysis.

6.8 Surface tension

Liquids tend to adopt shapes that minimize their surface area, for then the maximum number of molecules are in the bulk and hence surrounded by and interacting with neighbours. Droplets of liquids therefore tend to be spherical, because a sphere is the shape with the smallest surface-to-volume ratio. However, there may be other forces present that compete against the tendency to form this ideal shape, and in particular gravity may flatten spheres into puddles or oceans.

Surface effects may be expressed in the language of Helmholtz and Gibbs energies. The link between these quantities and the surface area is the work needed to change the area by a given amount, and the fact that dA and dG are equal (under different conditions) to the work done in changing the energy of a system. The work needed to change the surface area, σ, of a sample by an infinitesimal amount dσ is proportional to dσ, and we write

$$\mathrm{d}w = \gamma\,\mathrm{d}\sigma \qquad [14]$$

The constant of proportionality, γ, is called the **surface tension**; its dimensions are energy/area and its units are typically joules per metre squared (J m^{-2}). However, as in Table 6.1, values of γ are usually reported in newtons per metre (N m^{-1}, because 1 J = 1 N m). The work of surface formation at constant volume and temperature can be identified with the change in the Helmholtz energy, and we can write

$$\mathrm{d}A = \gamma\,\mathrm{d}\sigma \qquad (15)$$

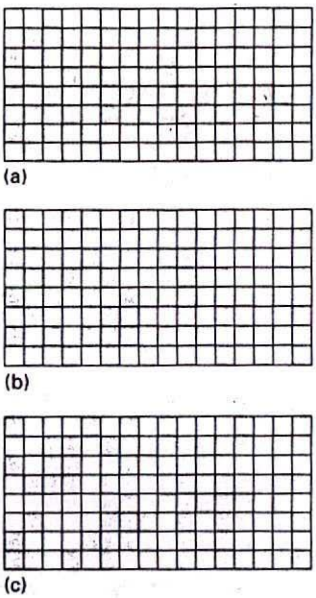
Because the Helmholtz energy decreases (d$A < 0$) if the surface area decreases (d$\sigma < 0$), surfaces have a natural tendency to contract. This is a more formal way of expressing what we have already described.

Table 6.1* Surface tensions of liquids at 293 K

	$\gamma/(\mathrm{mN\,m^{-1}})$†
Benzene	28.88
Mercury	472
Methanol	22.6
Water	72.75

* More values are given in the *Data section* at the end of this volume.

† Note that 1 N m^{-1} = 1 J m^{-2}.



6.18 An order–disorder transition. (a) At $T = 0$, there is perfect order, with different kinds of atoms occupying alternate sites. (b) As the temperature is increased, atoms exchange locations and islands of each kind of atom form in regions of the solid. Some of the original order survives. (c) At and above the transition temperature, the islands occur at random throughout the sample.

Example 6.4 Using the surface tension

Calculate the work needed to raise a wire of length l and to stretch the surface of a liquid through a height h in the arrangement shown in Fig. 6.19. Disregard gravitational potential energy.

Method According to eqn 14, the work required to create a surface area given that the surface tension does not vary as the surface is formed is $w = \gamma\sigma$. Therefore, all we need do is to calculate the surface area of the two-sided rectangle formed as the frame is withdrawn from the liquid.

Answer When the wire of length l is raised through a height h it increases the area of the liquid by twice the area of the rectangle (because there is a surface on each side). The total increase is therefore $2lh$ and the work done is $2\gamma lh$.

Comment The work can be expressed as a force × distance by writing it as $2\gamma l \times h$, and identifying γl as the opposing force on the wire of length l. This is why γ is called a tension and why its units are often chosen to be newtons per metre ($\mathrm{N\,m^{-1}}$, so γl is a force in newtons).

Self-test 6.4 Calculate the work of creating a spherical cavity of radius r in a liquid of surface tension γ.

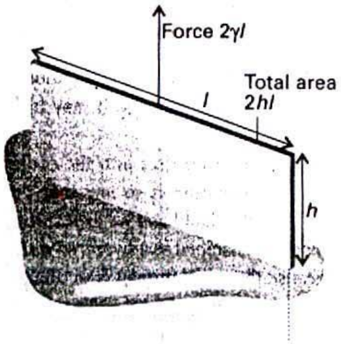
$[4\pi r^2\gamma]$

6.9 Curved surfaces

The minimization of the surface area of a liquid may result in the formation of a curved surface, as in a bubble. We shall now see that there are two consequences of curvature, and hence of the surface tension, that are relevant to the properties of liquids. One is that the vapour pressure of a liquid depends on the curvature of its surface. The other is the capillary rise (or fall) of liquids in narrow tubes.

(a) Bubbles, cavities, and droplets

A **bubble** is a region in which vapour (and possibly air too) is trapped by a thin film; a **cavity** is a vapour-filled hole in a liquid. What are widely called 'bubbles' in liquids are therefore strictly cavities. True bubbles have two surfaces (one on each side of the film); cavities have only one. The treatments of both are similar, but a factor of 2 is required for bubbles to take into account the doubled surface area. A **droplet** is a small volume of liquid at equilibrium surrounded by its vapour (and possibly also air).

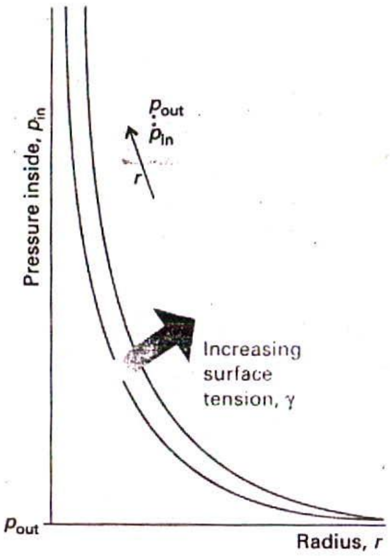


6.19 The model used for calculating the work of forming a liquid film when a wire of length l is raised and pulls the surface with it through a height h.

The pressure on the concave side of an interface, p_{in}, is always greater than the pressure on the convex side, p_{out}. This relation is expressed by the **Laplace equation**, which is derived in the *Justification* below:

$$p_{\text{in}} = p_{\text{out}} + \frac{2\gamma}{r} \qquad (16)$$

The Laplace equation shows that the difference in pressure decreases to zero as the radius of curvature becomes infinite (when the surface is flat, Fig. 6.20). Small cavities have small radii of curvature, and so the pressure difference across their surface is quite large. For instance, a 'bubble' (actually, a cavity) of radius 0.10 mm in champagne implies a pressure difference of 1.5 kPa, which is enough to sustain a column of water of height 15 cm.



6.20 The dependence of the pressure inside a curved surface on the radius of the surface, for two different values of the surface tension.

Justification 6.2

The cavities in a liquid are at equilibrium when the tendency for their surface area to decrease is balanced by the rise of internal pressure which would then result. When the pressure inside a cavity is p_{in} and its radius is r, the outward force is pressure × area $= 4\pi r^2 p_{in}$. The force inwards arises from the external pressure and the surface tension. The former has magnitude $4\pi r^2 p_{out}$. The latter is calculated as follows. The change in surface area when the radius of a sphere changes from r to $r + dr$ is

$$d\sigma = 4\pi(r + dr)^2 - 4\pi r^2 = 8\pi r\, dr$$

(The second-order infinitesimal, $(dr)^2$, is ignored.) The work done when the surface is stretched by this amount is therefore

$$dw = 8\pi\gamma r\, dr$$

As force × distance is work, the force opposing stretching through a distance dr when the radius is r is

$$F = 8\pi\gamma r$$

The total inward force is therefore $4\pi r^2 p_{out} + 8\pi\gamma r$. At equilibrium, the outward and inward forces are balanced, so we can write

$$4\pi r^2 p_{in} = 4\pi r^2 p_{out} + 8\pi\gamma r$$

which rearranges into eqn 16.

We saw in Section 6.5c that the vapour pressure of a liquid depends on the pressure applied to the liquid. Because curving a surface gives rise to a pressure differential of $2\gamma/r$, we can expect the vapour pressure above a curved surface to be different from that above a flat surface. By substituting this value of the pressure difference into eqn 3 we obtain the **Kelvin equation** for the vapour pressure of a liquid when it is dispersed as droplets of radius r:

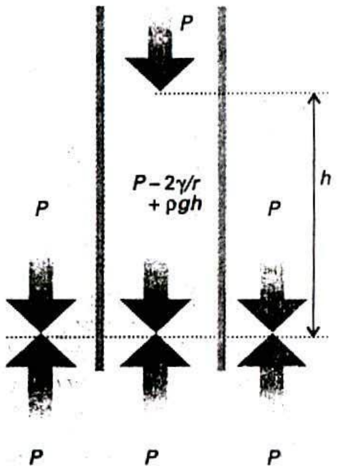
$$p = p^* e^{2\gamma V_m/rRT} \tag{17}$$

The analogous expression for the vapour pressure inside a cavity can be written at once. The pressure of the liquid outside the cavity is less than the pressure inside, so the only change is in the sign of the exponent in the last expression.

(b) Nucleation

For droplets of water of radius 1 μm and 1 nm, the ratios p/p^* at 25 °C are about 1.001 and 3, respectively. The second figure, although quite large, is unreliable because at that radius the droplet is less than about 10 molecules in diameter and the basis of the calculation is suspect. The first figure shows that the effect is usually small; nevertheless it may have important consequences.

Consider, for example, the formation of a cloud. Warm, moist air rises into the cooler regions higher in the atmosphere. At some altitude the temperature is so low that the vapour becomes thermodynamically unstable with respect to the liquid and we expect it to condense into a cloud of liquid droplets. The initial step can be imagined as a swarm of water molecules congregating into a microscopic droplet. Because the initial droplet is so small it has an enhanced vapour pressure. Therefore, instead of growing it evaporates. This effect effectively stabilizes the vapour because an initial tendency to condense is overcome by a heightened tendency to evaporate. The vapour phase is then said to be **supersaturated**. It is thermodynamically unstable with respect to the liquid but not unstable with respect to the small droplets that need to form before the bulk liquid phase can appear, so the formation of the latter by a simple, direct mechanism is hindered.



6.21 When a capillary tube is first stood in a liquid, the latter climbs up the walls, so curving the surface. The pressure just under the meniscus is less than that arising from the atmosphere by $2\gamma/r$. The pressure is equal at equal heights throughout the liquid provided the hydrostatic pressure (which is equal to ρgh) cancels the pressure difference arising from the curvature.

Clouds do form, so there must be a mechanism. Two processes are responsible. The first is that a sufficiently large number of molecules might congregate into a droplet so big that the enhanced evaporative effect is unimportant. The chance of one of these **spontaneous nucleation centres** forming is low, and in rain formation it is not a dominant mechanism. The more important process depends on the presence of minute dust particles or other kinds of foreign matter. These particles **nucleate** the condensation (that is, provide centres at which it can occur) by providing surfaces to which the water molecules can attach.

Liquids may be **superheated** above their boiling temperatures and **supercooled** below their freezing temperatures. In each case the thermodynamically stable phase is not achieved on account of the kinetic stabilization that occurs in the absence of nucleation centres. For example, superheating occurs because the vapour pressure inside a cavity is artificially low, so any cavity that does form tends to collapse. This instability is encountered when an unstirred beaker of water is heated, for its temperature may be raised above its boiling point. Violent bumping often ensues as spontaneous nucleation leads to bubbles big enough to survive. To ensure smooth boiling at the true boiling temperature, nucleation centres, such as small pieces of sharp-edged glass or bubbles (cavities) of air, should be introduced. A *bubble chamber*, a device for tracking elementary particles, depends on the nucleation of the evaporation of superheated liquid hydrogen by ionizing radiation.

6.10 Capillary action

The tendency of liquids to rise up capillary tubes (tubes of narrow bore), which is called **capillary action**, is a consequence of surface tension. Consider what happens when a glass capillary tube is first immersed in water or any liquid that has a tendency to adhere to the walls. The energy is lowest when a thin film covers as much of the glass as possible. As this film creeps up the inside wall it has the effect of curving the surface of the liquid inside the tube. This curvature implies that the pressure just beneath the curving meniscus is less than the atmospheric pressure by approximately $2\gamma/r$, where r is the radius of the tube and we assume a hemispherical surface. The pressure immediately under the flat surface outside the tube is p, the atmospheric pressure, but inside the tube under the curved surface it is only $p - 2\gamma/r$. The excess external pressure presses the liquid up the tube until hydrostatic equilibrium (equal pressures at equal depths) has been reached (Fig. 6.21).

(a) Capillary rise

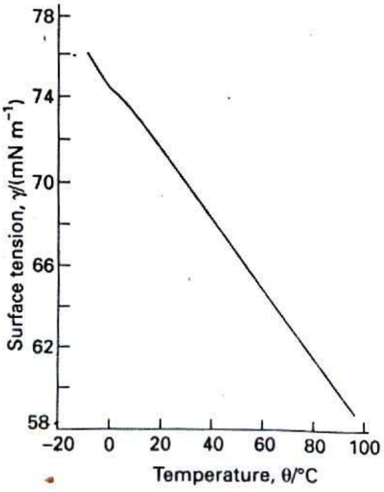
The pressure exerted by a column of liquid of mass density ρ and height h is

$$p = \rho gh \tag{18}$$

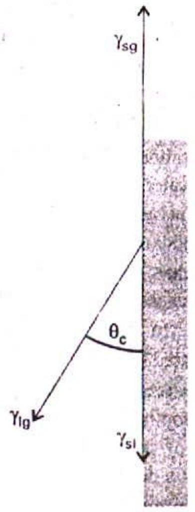
This hydrostatic pressure matches the pressure difference $2\gamma/r$ at equilibrium. Therefore, the height of the column at equilibrium is obtained by equating $2\gamma/r$ and ρgh, which gives

$$h = \frac{2\gamma}{\rho gr} \tag{19}$$

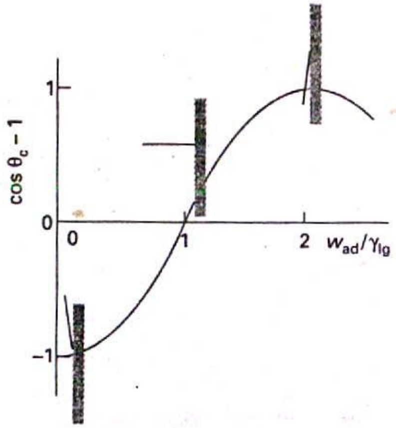
This simple expression provides a reasonably accurate way of measuring the surface tension of liquids. Surface tension decreases with increasing temperature (Fig. 6.22).



6.22 The variation of the surface tension of water with temperature.



6.23 The balance of forces that results in a contact angle, θ_c.



6.24 The variation of contact angle (shown by the semaphore-like object) as the ratio w_{ad}/γ_{lg} changes.

Illustration

If water at 25 °C rises through 7.36 cm in a capillary of radius 0.20 mm, its surface tension at that temperature is

$$
\begin{aligned}
\gamma &= \tfrac{1}{2}\rho g h r \\
&= \tfrac{1}{2}\times(997.1\ \mathrm{kg\,m^{-3}})\times(9.81\ \mathrm{m\,s^{-2}})\times(7.36\times10^{-2}\ \mathrm{m}) \\
&\qquad \times(2.0\times10^{-4}\ \mathrm{m}) = 72\ \mathrm{mN\,m^{-1}}
\end{aligned}
$$

When the adhesive forces between the liquid and the material of the capillary wall are weaker than the cohesive forces within the liquid (as for mercury in glass), the liquid in the tube retracts from the walls. This retraction curves the surface with the concave, high-pressure side downwards. To equalize the pressure at the same depth throughout the liquid the surface must fall to compensate for the heightened pressure arising from its curvature. This compensation results in a capillary depression.

(b) The contact angle

In many cases there is a nonzero angle between the edge of the meniscus and the wall. If this contact angle is θ_c, then eqn 19 should be modified by multiplying the right-hand side by $\cos\theta_c$.

The origin of the contact angle can be traced to the balance of forces at the line of contact between the liquid and the solid (Fig. 6.23). If the solid–gas, solid–liquid, and liquid–gas surface tensions (essentially the energy needed to create a unit area of each of the interfaces) are denoted γ_{sg}, γ_{sl}, and γ_{lg}, respectively, the horizontal forces are in balance if

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg}\cos\theta_c \qquad (20)$$

This expression solves to

$$\cos\theta_c = \frac{\gamma_{sg}-\gamma_{sl}}{\gamma_{lg}} \qquad (21)$$

If we note that the work of adhesion of the liquid to the solid (per unit area of contact) is

$$w_{ad} = \gamma_{sg} + \gamma_{lg} - \gamma_{sl} \qquad (22)$$

eqn 21 can be written

$$\cos\theta_c = \frac{w_{ad}}{\gamma_{lg}} - 1 \qquad (23)$$

We now see that the liquid completely 'wets' (spreads over) the surface fully, corresponding to $\theta_c > 0$, when $w_{ad} > 2\gamma_{lg}$ (Fig. 6.24). The liquid does not wet the surface (corresponding to $(\theta_c > 90°)$ when $w_{ad} < \gamma_{lg}$). For mercury in contact with glass, $\theta_c = 140°$, which corresponds to $w_{ad}/\gamma_{lg} = 0.23$, indicating a relatively low work of adhesion of the mercury to glass on account of the strong cohesive forces within mercury.

Checklist of key ideas

Phase diagrams

6.1 The stabilities of phases

- ☐ phase
- ☐ phase transition
- ☐ transition temperature
- ☐ metastable phase

6.2 Phase boundaries

- ☐ phase diagram
- ☐ phase boundary
- ☐ vapour pressure
- ☐ sublimation vapour pressure
- ☐ boiling
- ☐ boiling temperature
- ☐ normal boiling point
- ☐ standard boiling point
- ☐ critical temperature
- ☐ critical pressure
- ☐ supercritical fluid
- ☐ melting temperature
- ☐ normal freezing point
- ☐ standard freezing point
- ☐ normal melting point
- ☐ triple point and its significance

6.3 Three typical phase diagrams

- ☐ the interpretation of the phase diagram for water
- ☐ ice polymorphs
- ☐ the interpretation of the phase diagram for carbon dioxide
- ☐ supercritical fluid chromatography
- ☐ the interpretation of the phase diagram for helium
- ☐ λ-line
- ☐ superfluid helium

Phase stability and phase transitions

6.4 The thermodynamic criterion of equilibrium

- ☐ the uniformity of chemical potential throughout a system at equilibrium

6.5 The dependence of stability on the conditions

- ☐ the variation of chemical potential with temperature (1) and its implications for phase stability
- ☐ the variation of chemical potential with pressure (2) and its implications for phase stability
- ☐ partial vapour pressure
- ☐ gas solvation
- ☐ vapour pressure in the presence of applied pressure (3)

6.6 The location of phase boundaries

- ☐ the Clapeyron equation
- ☐ the slope of the solid–liquid boundary (7) and the corresponding formula for the boundary (8,9)
- ☐ the slope of the liquid–vapour boundary (10)
- ☐ the Clausius–Clapeyron equation (11) and the corresponding formula for the boundary (12)
- ☐ the slope of the solid–vapour boundary

6.7 The Ehrenfest classification of phase transitions

- ☐ the Ehrenfest classification of phase transitions
- ☐ first-order phase transition
- ☐ second-order phase transition
- ☐ λ-transition

The physical liquid surface

6.8 Surface tension

- ☐ work of forming a surface (14)
- ☐ surface tension

6.9 Curved surfaces

- ☐ bubble
- ☐ cavity
- ☐ droplet
- ☐ Laplace equation for the vapour pressure at a curved surface (16)
- ☐ Kelvin equation for the vapour pressure of droplets (17)
- ☐ supersaturated phase
- ☐ spontaneous nucleation centres
- ☐ nucleate
- ☐ superheated
- ☐ supercooled

6.10 Capillary action

- ☐ capillary rise and surface tension (19)
- ☐ contact angle and interfacial tension (21)
- ☐ the criteria for surface wetting

Further reading

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Exercises

6.1 (a) The vapour pressure of dichloromethane at 24.1°C is 400 Torr and its enthalpy of vaporization is 28.7 kJ mol^{-1}. Estimate the temperature at which its vapour pressure is 500 Torr.

6.1 (b) The vapour pressure of a substance at 20.0°C is 58.0 kPa and its enthalpy of vaporization is 32.7 kJ mol^{-1}. Estimate the temperature at which its vapour pressure is 66.0 kPa.

6.2 (a) The molar volume of a certain solid is 161.0 cm^3 mol^{-1} at 1.00 atm and 350.75 K, its melting temperature. The molar volume of the liquid at this temperature and pressure is 163.3 cm^3 mol^{-1}. At 100 atm the melting temperature changes to 351.26 K. Calculate the enthalpy and entropy of fusion of the solid.

6.2 (b) The molar volume of a certain solid is 142.0 cm^3 mol^{-1} at 1.00 atm and 427.15 K, its melting temperature. The molar volume of the liquid at this temperature and pressure is 152.6 cm^3 mol^{-1}. At 1.2 MPa the melting temperature changes to 429.26 K. Calculate the enthalpy and entropy of fusion of the solid.

6.3 (a) The vapour pressure of a liquid in the temperature range 200 K to 260 K was found to fit the expression $\ln(p/\text{Torr}) = 16.255 - 2501.8/(T/\text{K})$. Calculate the enthalpy of vaporization of the liquid.

6.3 (b) The vapour pressure of a liquid in the temperature range 200 K to 260 K was found to fit the expression $\ln(p/\text{Torr}) = 18.361 - 3036.8/(T/\text{K})$. Calculate the enthalpy of vaporization of the liquid.

6.4 (a) The vapour pressure of benzene between 10°C and 30°C fits the expression $\log(p/\text{Torr}) = 7.960 - 1780/(T/\text{K})$. Calculate (a) the enthalpy of vaporization and (b) the normal boiling point of benzene.

6.4 (b) The vapour pressure of a liquid between 15°C and 35°C fits the expression $\log(p/\text{Torr}) = 8.750 - 1625/(T/\text{K})$. Calculate (a) the enthalpy of vaporization and (b) the normal boiling point of the liquid.

6.5 (a) When benzene freezes at 5.5°C its density changes from 0.879 g cm^{-3} to 0.891 g cm^{-3}. Its enthalpy of fusion is 10.59 kJ mol^{-1}. Estimate the freezing point of benzene at 1000 atm.

6.5 (b) When ethanol freezes at −3.65°C its density changes from 0.789 g cm^{-3} to 0.801 g cm^{-3}. Its enthalpy of fusion is 8.68 kJ mol^{-1}. Estimate the freezing point of the liquid at 100 MPa.

6.6 (a) In July in Los Angeles, the incident sunlight at ground level has a power density of 1.2 kW m^{-2} at noon. A swimming pool of area 50 m^2 is directly exposed to the sun. What is the maximum rate of loss of water assuming that all radiation is absorbed?

6.6 (b) Suppose the incident sunlight at ground level has a power density of 0.87 kW m^{-2} at noon. What is the maximum rate of loss of water from a lake of area 1.0 ha? (1 ha = 10^4 m^2.)

6.7 (a) An open vessel containing (a) water, (b) benzene, (c) mercury stands in a laboratory measuring 5.0 m × 5.0 m × 3.0 m at 25°C. What mass of each substance will be found in the air if there is no ventilation? (The vapour pressures are (a) 24 Torr, (b) 98 Torr, (c) 1.7 mTorr.)

6.7 (b) On a cold, dry morning after a frost, the temperature was −5°C and the partial pressure of water in the atmosphere fell to 2.0 Torr. Will the frost sublime? What partial pressure of water would ensure that the frost remained?

6.8 (a) Refer to Fig. 6.5 and describe the changes that would be observed when water vapour at 1.0 atm and 400 K is cooled at constant pressure to 260 K. Suggest the appearance of the cooling curve, a plot of temperature against time.

6.8 (b) Use the phase diagram in Fig. 6.6 to state what would be observed when a sample of carbon dioxide, initially at 1.0 atm and 298 K, is subjected to the following cycle: (a) isobaric (constant-pressure) heating to 320 K, (b) isothermal compression to 100 atm, (c) isobaric cooling to 210 K, (d) isothermal decompression to 1.0 atm, (e) isobaric heating to 298 K.

6.9 (a) Naphthalene, $C_{10}H_8$, melts at 80.2°C. If the vapour pressure of the liquid is 10 Torr at 85.8°C and 40 Torr at 119.3°C, use the Clausius–Clapeyron equation to calculate (a) the enthalpy of vaporization, (b) the normal boiling point, and (c) the enthalpy of vaporization at the boiling point.

6.9 (b) The boiling point of hexane is 69.0°C. Estimate (a) its enthalpy of vaporization and (b) its vapour pressure at 25°C and 60°C.

6.10 (a) Calculate the melting point of ice under a pressure of 50 bar. Assume that the density of ice under these conditions is approximately 0.92 g cm^{-3} and that of liquid water is 1.00 g cm^{-3}.

6.10 (b) Calculate the melting point of ice under a pressure of 10 MPa. Assume that the density of ice under these conditions is approximately 0.915 g cm^{-3} and that of liquid water is 0.998 g cm^{-3}.

6.11 (a) What fraction of the enthalpy of vaporization of water is spent on expanding the water vapour?

6.11 (b) What fraction of the enthalpy of vaporization of ethanol is spent on expanding its vapour?

6.12 (a) Calculate the vapour pressure of a spherical droplet of water of radius 10 nm at 20°C. The vapour pressure of bulk water at that temperature is 2.3 kPa and its density is 0.9982 g cm^{-3}.

6.12 (b) Calculate the vapour pressure of a spherical droplet of water of radius 20.0 nm at 35.0°C. The vapour pressure of bulk water at that temperature is 5.623 kPa and its density is 994.0 kg m^{-3}.

6.13 (a) The contact angle for water on clean glass is close to zero. Calculate the surface tension of water at 20°C given that at that temperature water climbs to a height of 4.96 cm in a clean glass capillary tube of internal radius 0.300 mm. The density of water at 20°C is 998.2 $\mathrm{kg\,m^{-3}}$.

6.13 (b) The contact angle for water on clean glass is close to zero. Calculate the surface tension of water at 30°C given that at that temperature water climbs to a height of 9.11 cm in a clean glass capillary tube of internal diameter 0.320 mm. The density of water at 30°C is 0.9956 $\mathrm{g\,cm^{-3}}$.

6.14 (a) Calculate the pressure differential of water across the surface of a spherical droplet of radius 200 nm at 20°C.

6.14 (b) Calculate the pressure differential of ethanol across the surface of a spherical droplet of radius 220 nm at 20°C. The surface tension of ethanol at that temperature is 22.39 $\mathrm{mN\,m^{-1}}$.

Problems

Numerical problems

6.1 The temperature dependence of the vapour pressure of solid sulfur dioxide can be approximately represented by the relation $\log(p/\mathrm{Torr}) = 10.5916 - 1871.2/(T/\mathrm{K})$ and that of liquid sulfur dioxide by $\log(p/\mathrm{Torr}) = 8.3186 - 1425.7/(T/\mathrm{K})$. Estimate the temperature and pressure of the triple point of sulfur dioxide.

6.2 Prior to the discovery that freon-12 ($\mathrm{CF_2Cl_2}$) was harmful to the Earth's ozone layer, it was frequently used as the dispersing agent in spray cans for hair spray, etc. Its enthalpy of vaporization at its normal boiling point of −29.2°C is 20.25 $\mathrm{kJ\,mol^{-1}}$. Estimate the pressure that a can of hair spray using freon-12 had to withstand at 40°C, the temperature of a can that has been standing in sunlight. Assume that $\Delta_{\mathrm{vap}}H$ is a constant over the temperature range involved and equal to its value at −29.2°C.

6.3 The enthalpy of vaporization of a certain liquid is found to be 14.4 $\mathrm{kJ\,mol^{-1}}$ at 180 K, its normal boiling point. The molar volumes of the liquid and the vapour at the boiling point are 115 $\mathrm{cm^3\,mol^{-1}}$ and 14.5 $\mathrm{dm^3\,mol^{-1}}$, respectively. (a) Estimate dp/dT from the Clapeyron equation and (b) the percentage error in its value if the Clausius–Clapeyron equation is used instead.

6.4 Calculate the difference in slope of the chemical potential against temperature on either side of (a) the normal freezing point of water and (b) the normal boiling point of water. (c) By how much does the chemical potential of water supercooled to −5.0°C exceed that of ice at that temperature?

6.5 Calculate the difference in slope of the chemical potential against pressure on either side of (a) the normal freezing point of water and (b) the normal boiling point of water. The densities of ice and water at 0°C are 0.917 $\mathrm{g\,cm^{-3}}$ and 1.000 $\mathrm{g\,cm^{-3}}$, and those of water and water vapour at 100°C are 0.958 $\mathrm{g\,cm^{-3}}$ and 0.598 $\mathrm{g\,L^{-1}}$, respectively. By how much does the chemical potential of water vapour exceed that of liquid water at 1.2 atm and 100°C?

6.6 The enthalpy of fusion of mercury is 2.292 $\mathrm{kJ\,mol^{-1}}$, and its normal freezing point is 234.3 K with a change in molar volume of +0.517 $\mathrm{cm^{-3}\,mol^{-1}}$ on melting. At what temperature will the bottom of a column of mercury (density 13.6 $\mathrm{g\,cm^{-3}}$) of height 10.0 m be expected to freeze?

6.7 50.0 L of dry air was slowly bubbled through a thermally insulated beaker containing 250 g of water initially at 25°C. Calculate the final temperature. (The vapour pressure of water is approximately constant at 23.8 Torr throughout, and its heat capacity is 75.5 $\mathrm{J\,K^{-1}\,mol^{-1}}$. Assume that the air is not heated or cooled and that water vapour is a perfect gas.)

6.8 The vapour pressure, p, of nitric acid varies with temperature as follows:

$\theta/°\mathrm{C}$	0	20	40	50	70	80	90	100
p/Torr	14.4	47.9	133	208	467	670	937	1282

What are (a) the normal boiling point and (b) the enthalpy of vaporization of nitric acid?

6.9 The vapour pressure of the ketone carvone ($M = 150.2\ \mathrm{g\,mol^{-1}}$), a component of oil of spearmint, is as follows:

$\theta/°\mathrm{C}$	57.4	100.4	133.0	157.3	203.5	227.5
p/Torr	1.00	10.0	40.0	100	400	760

What are (a) the normal boiling point and (b) the enthalpy of vaporization of carvone?

6.10 Construct the phase diagram for benzene near its triple point at 36 Torr and 5.50°C using the following data: $\Delta_{\mathrm{fus}}H = 10.6\ \mathrm{kJ\,mol^{-1}}$, $\Delta_{\mathrm{vap}}H = 30.8\ \mathrm{kJ\,mol^{-1}}$, $\rho(\mathrm{s}) = 0.891\ \mathrm{g\,cm^{-3}}$, $\rho(\mathrm{l}) = 0.879\ \mathrm{g\,cm^{-3}}$.

Theoretical problems

6.11 Show that, for a transition between two incompressible solid phases, ΔG is independent of the pressure.

6.12 The change in enthalpy is given by $dH = C_p\,dT + V\,dp$. The Clapeyron equation relates dp and dT at equilibrium, and so in combination the two equations can be used to find how the enthalpy changes along a phase boundary as the temperature changes and the two phases remain in equilibrium. Show that $d(\Delta H/T) = \Delta C_p\,d\ln T$.

6.13 In the 'gas saturation method' for the measurement of vapour pressure, a volume V of gas (as measured at a temperature T and a pressure P) is bubbled slowly through the liquid that is maintained at the temperature T and a mass loss m is measured. Show that the vapour pressure, p, of the liquid is related to its molar mass, M, by $p = AmP/(1 + Am)$, where $A = RT/MPV$. The vapour pressure of geraniol ($M = 154.2\ \mathrm{g\,mol^{-1}}$), which is a component of oil of roses, was measured at 110°C. It was found that, when 5.00 L of nitrogen at 760 Torr was passed slowly through the heated liquid, the loss of mass was 0.32 g. Calculate the vapour pressure of geraniol.

6.14 Combine the barometric formula (stated in Problem 1.35) for the dependence of the pressure on altitude with the Clausius–Clapeyron equation, and predict how the boiling temperature of a liquid depends on the altitude and the ambient temperature. Take the mean ambient temperature as 20°C and predict the boiling temperature of water at 3000 m.

6.15 Figure 6.1 gives schematic representations of how the chemical potentials of the solid, liquid, and gaseous phases of a substance vary with temperature. All have a negative slope, but it is unlikely that they are truly straight lines as indicated in the illustrations. Derive an expression for the curvatures (specifically, the second derivatives with respect to temperature) of these lines. Is there a restriction on the curvature of these lines? Which state of matter shows the greatest curvature?

6.16 The Clapeyron equation does not apply to second-order phase transitions, but there are two analogous equations, the *Ehrenfest equations*, which do. They are:

$$\frac{\mathrm{d}p}{\mathrm{d}T}=\frac{\alpha_2-\alpha_1}{\kappa_{T,2}-\kappa_{T,1}} \qquad \frac{\mathrm{d}p}{\mathrm{d}T}=\frac{C_{p,\mathrm{m}2}-C_{p,\mathrm{m}1}}{TV(\alpha_2-\alpha_1)}$$

where α is the expansion coefficient, κ_T the isothermal compressibility, and the subscripts 1 and 2 refer to two different phases. Derive these two equations. Why does the Clapeyron equation not apply to second-order transitions?

6.17 For a first-order phase transition, to which the Clapeyron equation does apply, prove the relation

$$C_S=C_p-\frac{\alpha V\Delta_{\mathrm{trs}}H}{\Delta_{\mathrm{trs}}V}$$

where $C_S=(\partial q/\partial T)_S$ is the heat capacity along the coexistence curve of two phases.

Additional problems supplied by Carmen Giunta and Charles Trapp

6.18 A substance as well known as methane still receives research attention. Friend *et al.* have published a review of the thermophysical properties of methane (D.G. Friend, J.F. Ely, and H. Ingham, *J. Phys. Chem. Ref. Data* **18**, 583 (1989)), which included the following data describing the liquid–vapour phase boundary.

T/K	100	108	110	112	114	120
p/MPa	0.034	0.074	0.088	0.104	0.122	0.192
T/K	130	140	150	160	170	190
p/MPa	0.368	0.642	1.041	1.593	2.329	4.521

(a) Plot the liquid–vapour phase boundary. (b) Estimate the standard boiling point of methane. (c) Compute the standard enthalpy of vaporization of methane, given that the molar volumes of the liquid and vapour at the standard boiling point are 3.80×10^{-2} and 8.89 L mol^{-1}, respectively.

6.19 In an investigation of the thermophysical properties of toluene (R.D. Goodwin, *J. Phys. Chem. Ref. Data* **18**, 1565 (1989)), Goodwin presented expressions for two coexistence curves. The solid–liquid coexistence curve is given by:

$$p/\mathrm{bar}=p_3/\mathrm{bar}+1000\times(5.60+11.727x)x$$

where $x=T/T_3-1$ and the triple point pressure and temperature are $p_3=0.4362\ \mu\mathrm{bar}$ and $T_3=178.15$ K, respectively. The liquid–vapour curve is given by:

$$\ln(p/\mathrm{bar})=-10.418/y+21.157-15.996y+14.015y^2-5.0120y^3+4.7224(1-y)^{1.70}$$

where $y=T/T_\mathrm{c}=T/(593.95\ \mathrm{K})$. (a) Plot the solid–liquid and liquid–vapour phase boundaries. (b) Estimate the standard melting point of toluene. (c) Estimate the standard boiling point of toluene. (d) Compute the standard enthalpy of vaporization of toluene, given that the molar volumes of the liquid and vapour at the normal boiling point are 0.12 L mol^{-1} and 30.3 L mol^{-1}, respectively.

6.20 In a study of the vapour pressure of chloromethane (A. Bah and N. Dupont-Pavlovsky, *J. Chem. Eng. Data* **40**, 869 (1995)), Bah and Dupont-Pavlovsky presented data for the vapour pressure over solid chloromethane at low temperatures. Some of that data are shown below.

T/K	145.94	147.96	149.93	151.94	153.97	154.94
p/Pa	13.07	18.49	25.99	36.76	50.86	59.56

Estimate the standard enthalpy of sublimation of chloromethane at 150 K. (Take the molar volume of the vapour to be that of a perfect gas, and that of the solid to be negligible.)

6.21 What pressure is required to convert graphite into diamond at 25°C? The following data apply to 25°C and 100 kPa. Assume the specific volume, V_s, and κ_T are constant with respect to pressure changes.

	Graphite	Diamond
$\Delta_\mathrm{f}G^\ominus/(\mathrm{kJ\,mol^{-1}})$	0	+2.8678
$V_\mathrm{s}/(\mathrm{cm^3\,g^{-1}})$	0.444	0.284
κ_T/kPa	3.04×10^{-8}	0.187×10^{-8}

7

Simple mixtures

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

Chemistry deals with mixtures, including mixtures of substances that can react together. Therefore, we need to generalize the foregoing material to deal with substances that are mingled together. As a first step towards dealing with chemical reactions (which are treated in Chapter 9), here we consider mixtures of substances that do not react together. At this stage we shall deal mainly with binary mixtures (mixtures of two components, A and B). We shall therefore often be able to simplify equations by making use of the relation $x_A + x_B = 1$. Another restriction of this chapter is that we shall consider mainly non-electrolyte solutions, in which the solute is not present as ions.

The thermodynamic description of mixtures

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

7.1 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 we can report that 18 $cm^3\,mol^{-1}$ is the molar volume of pure water. However, when we add 1 mol H_2O to a huge volume of pure ethanol, the volume increases by only 14 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, and the packing of the molecules results in the H_2O molecules increasing 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. It is this changing molecular environment, and the consequential modification of the forces acting between molecules, that results in the variation of the thermodynamic properties of a mixture as its composition is changed. The partial molar volumes of water and ethanol across the full composition range at 25°C are shown in Fig. 7.1.

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

$$V_J = \left(\frac{\partial V}{\partial n_J}\right)_{p,T,n'} \qquad [1]$$

where the subscript n' signifies that the amounts of all other substances present are constant.[1] The partial molar volume is the slope of the plot of the total volume as the amount of J is changed, the pressure, temperature, and amount of the other components being constant (Fig. 7.2). Its value depends on the composition, as we saw for water and ethanol. The definition in eqn 1 implies that, when the composition of the mixture is changed by the addition of dn_A of A and dn_B of B, the total volume of the mixture changes by

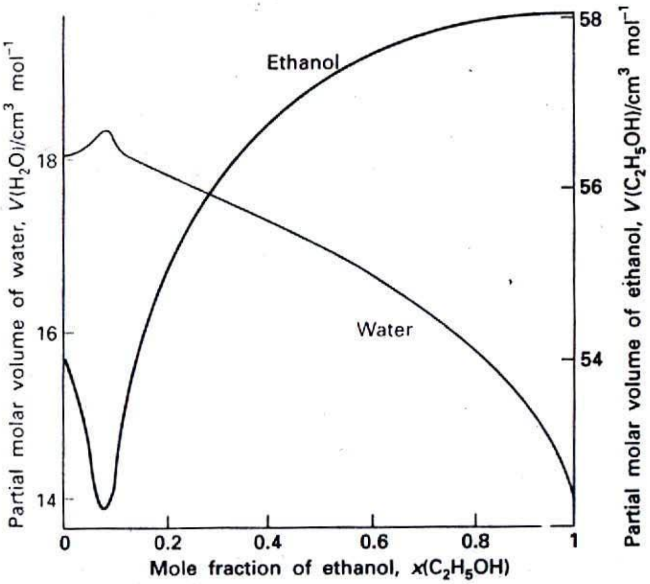
$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{p,T,n_A} dn_B = V_A\,dn_A + V_B\,dn_B \qquad (2)$$

Once the partial molar volumes of the two components of a mixture at the composition (and temperature) of interest are known, we can state the total volume, V, of the mixture by using

$$V = n_A V_A + n_B V_B \qquad (3)$$

---

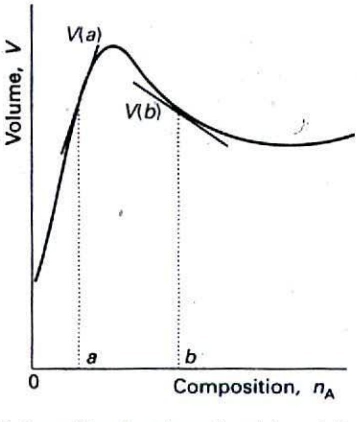
[1] The IUPAC recommendation is to denote a partial molar quantity by $\bar{X}$, but only when there is the possibility of confusion with the quantity X. For instance, the partial molar volume of NaCl in water could be written $\bar{V}(\text{NaCl, aq})$ to distinguish it from the volume of the solution,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



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

Justification 7.1

Consider a very large sample of the mixture of the specified composition. Then, when an amount n_A of A is added to the mixture, the composition remains virtually unchanged, the partial molar volume V_A is constant, and the volume of the sample changes by n_AV_A. When n_B of B is added, the volume changes by n_BV_B, for the same reason. The total change of volume is therefore $n_AV_A + n_BV_B$. The sample now occupies a larger volume, but the proportions of the components are still the same. At this stage, scoop out of the enlarged volume a sample containing n_A of A and n_B of B. Its volume is $n_AV_A + n_BV_B$. Because V is a state function, the same sample could have been prepared simply by mixing the appropriate amounts of A and B. This justifies eqn 3.



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

Partial molar volumes (and partial molar quantities in general) 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 by using a curve-fitting program (that is, by finding the parameters that give a best fit of a particular function to the experimental data). Once the function has been found, its slope can be determined at any composition of interest by differentiation. For instance, if it was found that the volume of a mixture was described by the function

$$V = A + Bn_A + C(n_A^2 - 1)$$

with particular values of the parameters *A*, *B*, and *C*, then the partial molar volume of A at any composition could be obtained from

$$V_A = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} = B + 2Cn_A$$

The partial molar volume of the second component is obtained from eqn 3 arranged into

$$V_B = \frac{V - n_A V_A}{n_B} = \frac{A - (n_A^2 + 1)C}{n_B}$$

Illustration

The total volume of an ethanol solution at 25 °C containing 1.000 kg of water is found to be given by the expression

$$V/\mathrm{mL} = 1002.93 + 54.6664b - 0.36394b^2 + 0.028256b^3$$

where b is the numerical value of the molality. Because the amount of CH_3CH_2OH in moles is equal to the numerical value of the molality in moles per kilogram, we can write the partial molar volume of ethanol, V_E, as

$$V_E/(\mathrm{mL\,mol^{-1}}) = \left(\frac{\partial(V/\mathrm{mL})}{\partial b}\right)_{p,T,n_W} = 54.6664 - 2(0.36394)b + 3(0.028256)b^2$$

Self-test 7.1 At 25 °C, the density of a 50 per cent by mass ethanol/water solution is $0.914\ \mathrm{g\,cm^{-3}}$. Given that the partial molar volume of water in the solution is $17.4\ \mathrm{cm^3\,mol^{-1}}$, what is the partial molar volume of the ethanol?

[$56.3\ \mathrm{cm^3\,mol^{-1}}$]

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

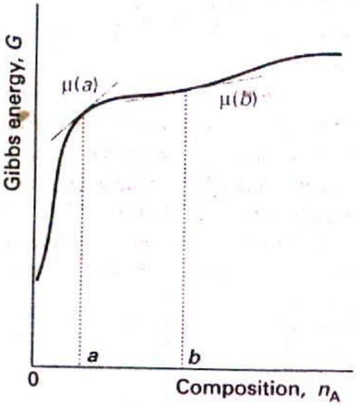
(b) Partial molar Gibbs energies

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

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'} \qquad [4]$$

That is, the chemical potential is the slope of a plot of Gibbs energy against the amount of the component J, with the pressure and temperature (and the amounts of the other substances) held constant (Fig. 7.3). By the same argument that led to eqn 3, it follows that the total Gibbs energy of a binary mixture is

$$G = n_A\mu_A + n_B\mu_B \qquad (5)$$



7.3 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 in a mixture is the contribution of that substance to the total Gibbs energy of the mixture.

In an open system of constant composition, the Gibbs energy depends on the composition, the pressure, and the temperature. Thus, G may change when p, T, and the composition change, and, for a system of components A, B..., the equation $\mathrm{d}G = V\,\mathrm{d}p - S\,\mathrm{d}T$ becomes

$$\mathrm{d}G = V\,\mathrm{d}p - S\,\mathrm{d}T + \mu_\mathrm{A}\,\mathrm{d}n_\mathrm{A} + \mu_\mathrm{B}\,\mathrm{d}n_\mathrm{B} + \cdots \tag{6}$$

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

At constant pressure and temperature, eqn 6 simplifies to

$$\mathrm{d}G = \mu_\mathrm{A}\,\mathrm{d}n_\mathrm{A} + \mu_\mathrm{B}\,\mathrm{d}n_\mathrm{B} + \cdots \tag{7}$$

We saw in Section 4.6c that under the same conditions $\mathrm{d}G = \mathrm{d}w_{\mathrm{e,max}}$. Therefore, at constant temperature and pressure,

$$\mathrm{d}w_{\mathrm{e,max}} = \mu_\mathrm{A}\,\mathrm{d}n_\mathrm{A} + \mu_\mathrm{B}\,\mathrm{d}n_\mathrm{B} + \cdots \tag{8}$$

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

(c) The wider significance of the chemical potential

The chemical potential does more than show how G varies with composition. Because

$$G = U + pV - TS$$

a general infinitesimal change in U for a system of variable composition can be written

$$\begin{aligned}\mathrm{d}U &= -p\,\mathrm{d}V - V\,\mathrm{d}p + S\,\mathrm{d}T + T\,\mathrm{d}S + \mathrm{d}G\\ &= -p\,\mathrm{d}V - V\,\mathrm{d}p + S\,\mathrm{d}T + T\,\mathrm{d}S + (V\,\mathrm{d}p - S\,\mathrm{d}T + \mu_\mathrm{A}\,\mathrm{d}n_\mathrm{A} + \mu_\mathrm{B}\,\mathrm{d}n_\mathrm{B} + \cdots)\\ &= -p\,\mathrm{d}V + T\,\mathrm{d}S + \mu_\mathrm{A}\,\mathrm{d}n_\mathrm{A} + \mu_\mathrm{B}\,\mathrm{d}n_\mathrm{B} + \cdots\end{aligned}$$

This expression is the generalization of eqn 5.2 (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,

$$\mathrm{d}U = \mu_\mathrm{A}\,\mathrm{d}n_\mathrm{A} + \mu_\mathrm{B}\,\mathrm{d}n_\mathrm{B} + \cdots$$

and hence that

$$\mu_\mathrm{J} = \left(\frac{\partial U}{\partial n_\mathrm{J}}\right)_{S,V,n'} \tag{9}$$

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

$$\text{(a)}\quad \mu_\mathrm{J} = \left(\frac{\partial H}{\partial n_\mathrm{J}}\right)_{S,p,n'} \qquad \text{(b)}\quad \mu_\mathrm{J} = \left(\frac{\partial A}{\partial n_\mathrm{J}}\right)_{T,V,n'} \tag{10}$$

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

(d) The Gibbs–Duhem equation

Because the total Gibbs energy of a mixture is given by eqn 5 and the chemical potentials depend on the composition, when the compositions are changed infinitesimally we might expect G of a binary system to change by

$$\mathrm{d}G = \mu_\mathrm{A}\,\mathrm{d}n_\mathrm{A} + \mu_\mathrm{B}\,\mathrm{d}n_\mathrm{B} + n_\mathrm{A}\,\mathrm{d}\mu_\mathrm{A} + n_\mathrm{B}\,\mathrm{d}\mu_\mathrm{B}$$

However, we have seen that at constant pressure and temperature a change in Gibbs energy is given by eqn 7. Because G is a state function, these two equations must be equal to each other, which implies that at constant temperature and pressure

$$n_A\,d\mu_A + n_B\,d\mu_B = 0 \tag{11}$$

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

$$\sum_J n_J\,d\mu_J = 0 \tag{12}$$

The significance of the Gibbs–Duhem equation is that the chemical potential of one component of a mixture cannot change independently of the chemical potentials of the other components: in a binary mixture, if one partial molar quantity increases, the other must decrease:

$$d\mu_B = -\frac{n_A}{n_B}\,d\mu_A \tag{13}$$

The same line of reasoning applies to all partial molar quantities. We can see in Fig. 7.1, for example, that where the partial molar volume of water increases, that of ethanol decreases. Moreover, as eqn 13 shows, and as we can see from Fig 7.1, 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 7.1 Using the Gibbs-Duhem equation

The experimental value of the partial molar volume of $K_2SO_4(aq)$ at 298 K is given by the expression

$$V_{K_2SO_4}/(\text{cm}^3\,\text{mol}^{-1}) = 32.280 + 18.216b^{1/2}$$

where b is the numerical value of the molality of K_2SO_4. 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 $\text{cm}^3\,\text{mol}^{-1}$.

Method Let A denote K_2SO_4 and B denote H_2O, the solvent. The Gibbs–Duhem equation for the partial molar volumes of two components is

$$n_A\,dV_A + n_B\,dV_B = 0$$

This relation implies that

$$dV_B = -\frac{n_A}{n_B}\,dV_A$$

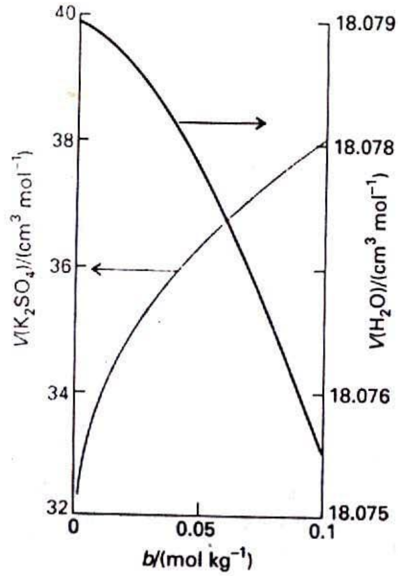
Therefore, V_B can be found by integration:

$$V_B = V_B^* - \int \frac{n_A}{n_B}\,dV_A$$

The first step is to change the variable V_A to the molality b, and then to integrate the right-hand side between $b = 0$ (pure B) and the molality of interest.

Answer It follows from the information in the question, that, with $A = K_2SO_4$,

$$\frac{dV_A}{db} = 9.108b^{-1/2}$$



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

Therefore, the integration required is

$$V_B = V_B^* - 9.108 \int_0^b \frac{n_A}{n_B} b^{-1/2}\,db$$

However, we need to note that the molality is related to the amounts of A and B by

$$b = \frac{n_A}{n_B M_B}$$

where M_B is the molar mass of water (in kilograms per mole). Therefore,

$$\begin{aligned} V_B &= V_B^* - 9.108 M_B \int_0^b b^{1/2}\,db \\ &= V_B^* - \tfrac{2}{3}(9.108 M_B b^{3/2}) \end{aligned}$$

It then follows, by substituting the data, that

$$V_B/(\mathrm{cm^3\,mol^{-1}}) = 18.079 - 0.1094 b^{3/2}$$

The partial molar volumes are plotted in Fig. 7.4.

Self-test 7.2 Repeat the calculation for a salt A for which $V_A/(\mathrm{cm^3\,mol^{-1}}) = 6.218 + 5.146b - 7.147b^2$.

$[V_B/(\mathrm{cm^3\,mol^{-1}}) = 18.079 - 0.0464b^2 + 0.0859b^3]$

7.2 The thermodynamics of mixing

The dependence of the Gibbs energy of a mixture on its composition is given by eqn 5, and we know that at constant temperature and pressure systems tend towards a lower Gibbs energy. This is the link we need in order to apply thermodynamics to the discussion of spontaneous changes of composition, as in the mixing of two substances. One simple example of a spontaneous mixing process is that of two gases introduced into the same container. The mixing is spontaneous, so it must correspond to a decrease in *G*. We shall now see how to express this idea quantitatively.

(a) The Gibbs energy of mixing

Let the amounts of two perfect gases in the two containers be n_A and n_B; both are at a temperature *T* and a pressure *p*. At this stage, the chemical potentials of the two gases have their 'pure' values and the Gibbs energy of the total system is given by eqn 5 as

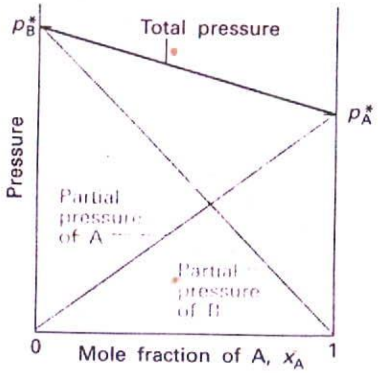
$$\begin{aligned} G_i &= n_A\mu_A + n_B\mu_B \\ &= n_A\left\{\mu_A^\ominus + RT\ln\left(\frac{p}{p^\ominus}\right)\right\} + n_B\left\{\mu_B^\ominus + RT\ln\left(\frac{p}{p^\ominus}\right)\right\} \end{aligned}$$

It will be much simpler notationally if we agree to let *p* denote the pressure *relative* to $p^\ominus$; that is, to replace $p/p^\ominus$ by *p*, for then we can write

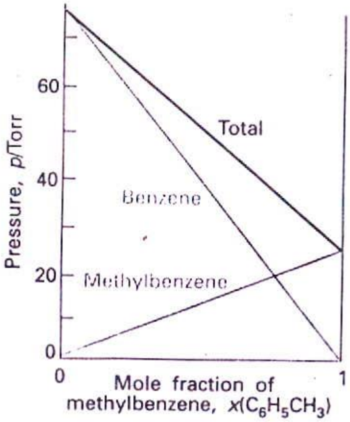
$$G_i = n_A\{\mu_A^\ominus + RT\ln p\} + n_B\{\mu_B^\ominus + RT\ln p\} \qquad \{14\}$$

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

$$G_f = n_A\{\mu_A^\ominus + RT\ln p_A\} + n_B\{\mu_B^\ominus + RT\ln p_A\} \qquad \{15\}$$



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



7.10 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.

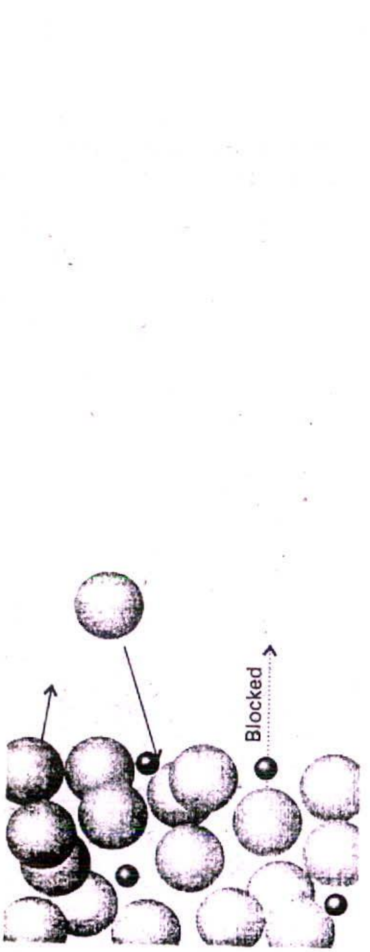
This law is illustrated in Fig. 7.9. Some mixtures obey Raoult's law very well, especially when the components are structurally similar (Fig. 7.10). Mixtures that obey the law throughout the composition range from pure A to pure B are called **ideal solutions.** When we write equations that are valid only for ideal solutions, we shall label them with a superscript °, as in eqn 23.

For an ideal solution, it follows from eqns 22 and 23 that

$$\mu_A = \mu_A^* + RT \ln x_A \qquad (24)^\circ$$

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 23 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. 7.11).



7.11 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.

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:

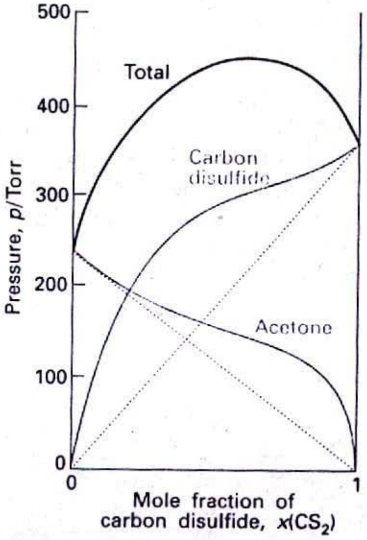
$$\text{rate of condensation} = k'p_A$$

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

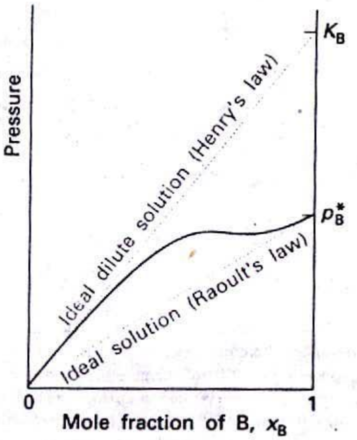
$$k'p_A = kx_A$$

It follows that

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



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



7.13 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 23 then follows by substitution of this relation into the previous one.

Some solutions depart significantly from Raoult's law (Fig. 7.12). 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.

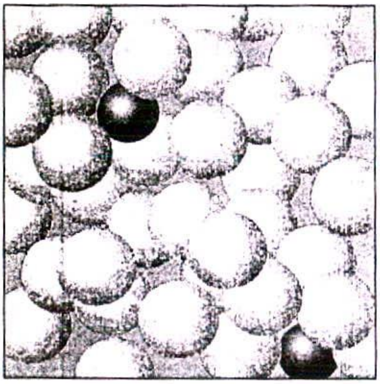
(b) Ideal-dilute solutions

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. 7.13). **Henry's law** is:

$$p_B = x_B K_B \qquad (25)^{\circ}$$

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

Mixtures for which the solute obeys Henry's law and the solvent obeys Raoult's law are called **ideal-dilute solutions**. We shall also label equations with a superscript ° when they have been derived from Henry's law.



7.14 In a dilute solution, the solvent molecules (the green spheres) are in an environment that differs only slightly from that of the pure solvent. The solute particles, however, are in an environment totally unlike that of the pure solute.

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. 7.14). 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	219	293
p_A/Torr	347	270	185	102	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. 7.15 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 7.6.

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.

[4×10^4 Torr]

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.

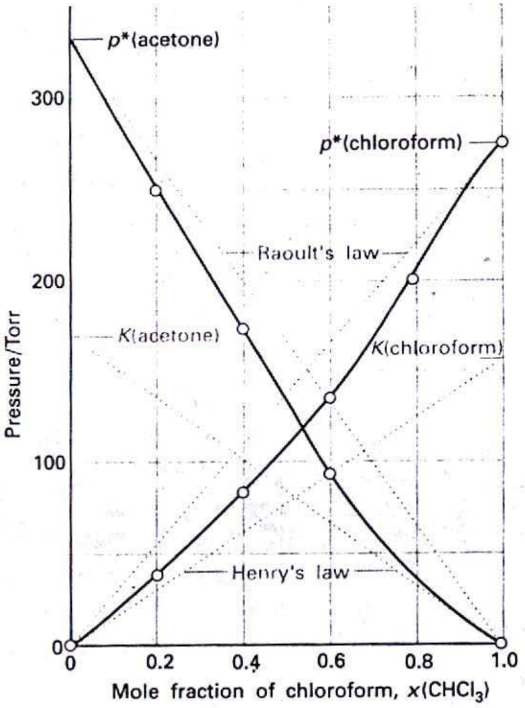
Table 7.1* Henry's law constants for gases in water at 298 K

	K/Torr
CO_2	1.25×10^6
H_2	5.34×10^7
N_2	6.51×10^7
O_2	3.30×10^7

*More values are given in the *Data section* at the end of this volume.

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.



7.15 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.

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 O_2 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 O_2 dissolved is small, its mole fraction is

$$x(O_2) = \frac{n(O_2)}{n(O_2) + n(H_2O)} \approx \frac{n(O_2)}{n(H_2O)}$$

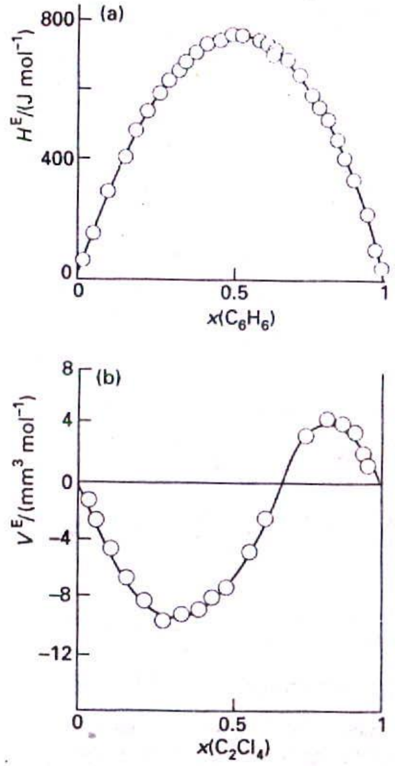
Hence,

$$n(O_2) \approx x(O_2)n(H_2O) = \frac{p(O_2)n(H_2O)}{K}$$

$$\approx \frac{(160\ \text{Torr}) \times (55.5\ \text{mol})}{3.30 \times 10^7\ \text{Torr}} = 2.69 \times 10^{-4}\ \text{mol}$$

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

Comment Knowledge of Henry's law constants for gases in fats and lipids 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.



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

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.

[0.505 mmol L^{-1}]

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

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 7.2a). 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 24 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

$$\Delta_{mix}G = nRT\{x_A \ln x_A + x_B \ln x_B\} \qquad (26)^\circ$$

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

$$\Delta_{mix}S = -nR\{x_A \ln x_A + x_B \ln x_B\} \qquad (27)^\circ$$

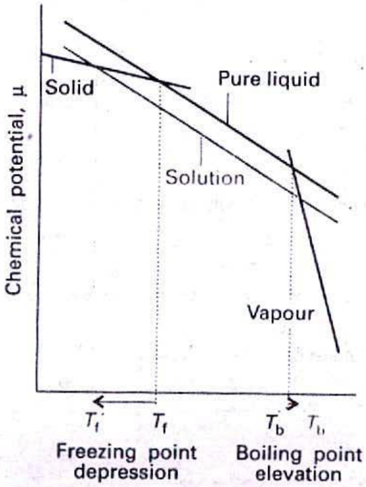
and the ideal enthalpy of mixing is zero.

Equation 26 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. 7.5; the same is true of the entropy of mixing, Fig. 7.7.

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.

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

$$S^E = \Delta_{mix}S - \Delta_{mix}S^{ideal} \qquad [28]$$



7.17 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. 6.1).

where $\Delta_{\text{mix}}S^{\text{ideal}}$ is given by eqn 27. 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 $H^{\text{E}} \neq 0$ but $S^{\text{E}} = 0$. 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 interactions with each other. Two examples of the composition dependence of excess functions are shown in Fig. 7.16.

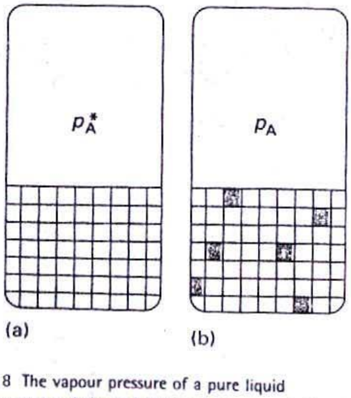
7.5 Colligative properties

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 shall assume throughout the following that the solute is not volatile, so it does not contribute to the vapour. We shall 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. 7.17, 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).



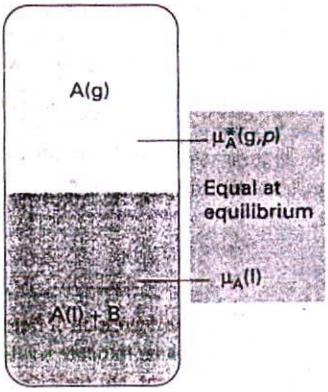
7.18 The vapour pressure of a pure liquid represents a balance between the increased disorder arising from vaporization and the decreased disorder of the surroundings. (a) Here the structure of the liquid is represented highly schematically by the grid of squares. (b) When solute (the dark squares) is 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 ideal solutions (which have zero enthalpy of mixing). If it is not an enthalpy effect, then 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 in the solution is already higher than that of the pure liquid, there is a weaker tendency to form the gas (Fig. 7.18). 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.



7.19 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. 7.19). We denote the solvent by A and the solute by B. The equilibrium is established at a temperature for which

$$\mu_A^*(g) = \mu_A^*(l) + RT \ln x_A \qquad (29)$$

(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

$$\Delta T = Kx_B \qquad K = \frac{RT^{*2}}{\Delta_{vap}H} \qquad (30)^{\circ}$$

Justification 7.2

Equation 29 rearranges into

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

where $\Delta_{vap}G$ 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

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

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

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

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

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

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

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

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

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

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

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

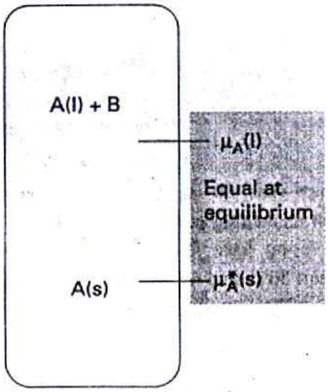
with $\Delta T = T - T^*$. The previous equation then rearranges into eqn 30.

Because eqn 30 makes no reference to the identity of the solute, only to its mole fraction, we conclude that the elevation of boiling point is a colligative property. The value of ΔT does depend on the properties of the solvent, and the biggest changes occur for solvents

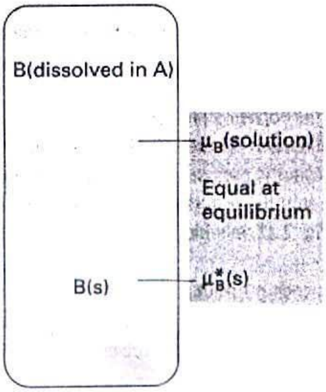
Table 7.2* Cryoscopic and ebullioscopic constants

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

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



7.20 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.



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

with high boiling points.[2] For practical applications of eqn 30, we note that the mole fraction of B is proportional to its molality, *b*, in dilute solutions and write

$$\Delta T = K_b b \qquad (31)$$

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

$$\mu_A^*(s) = \mu_A^*(l) + RT \ln x_A \qquad (32)$$

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 30:

$$\Delta T = K' x_B \qquad K' = \frac{RT^{*2}}{\Delta_{fus}H} \qquad (33)^\circ$$

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

$$\Delta T = K_f b \qquad (34)$$

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. 7.21). Because the latter is

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

we can write

$$\mu_B^*(s) = \mu_B^*(l) + RT \ln x_B \qquad (35)$$

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.

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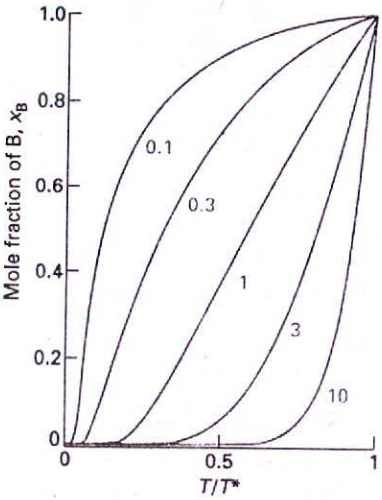
[2] By Trouton's rule (Section 4.3a), $\Delta_{vap}H/T^*$ is a constant, therefore eqn 30 has the form $\Delta T \propto T^*$ and is independent of $\Delta_{vap}H$ itself.



7.22 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

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

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

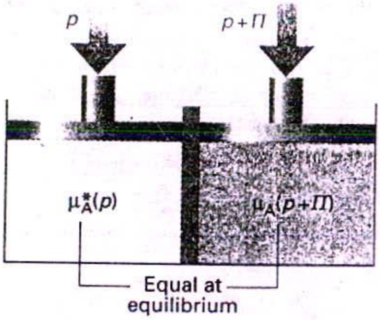
$$\ln x_B = -\frac{\Delta_{\text{fus}}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right) \qquad (36)^\circ$$

Equation 36 is plotted in Fig. 7.22. It shows that the solubility of B decreases exponentially as the temperature is lowered from its melting point, and that solutes with high melting points and large enthalpies of fusion have low solubilities at normal temperatures. However, the detailed content of eqn 36 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. 7.23). The **osmotic pressure**, Π, is the pressure that must be applied to the solution to stop the influx of solvent. One of the most important examples of osmosis is transport of fluids through cell membranes, but it is also the basis of **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. 7.24, 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 complication in 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. 7.23, in which there is no flow and the concentrations remain unchanged.

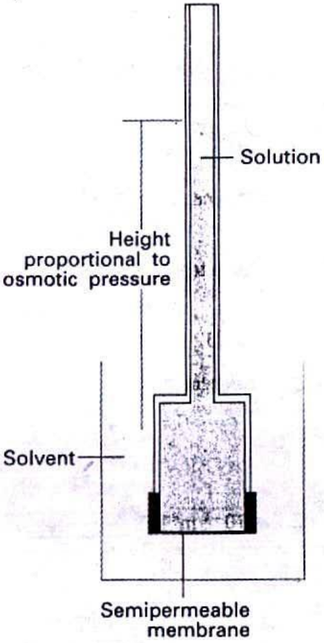


7.23 The equilibrium involved in the calculation of osmotic pressure, Π, is between pure solvent A at a pressure p on one side of the semipermeable membrane and A as a component of the mixture on the other side of the membrane, where the pressure is $p + \Pi$.

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**:

$$\Pi = [\text{B}]RT \qquad (37)^\circ$$

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



7.24 In a simple version of the osmotic pressure experiment, A is at equilibrium on each side of the membrane when enough has passed into the solution to cause a hydrostatic pressure difference.

Justification 7.3

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

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

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

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

We saw in Section 5.2b (eqn 5.14) how to take the effect of pressure into account:

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

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

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

For dilute solutions, $\ln x_A$ may be replaced by $\ln(1 - x_B) \approx -x_B$. We may also assume that the pressure range in the integration is so small that the molar volume of the solvent is a constant. That being so, V_m may be taken outside the integral, giving

$$RTx_B = \Pi V_m$$

When the solution is dilute, $x_B \approx n_B/n_A$. Moreover, because $n_A V_m = V$, the total volume of the solvent, the equation simplifies to eqn 37.

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

$$\Pi = [B]RT\{1 + B[B] + \cdots\} \qquad (38)$$

The additional terms take the nonideality into account; the empirical constant B is called the **osmotic virial coefficient**. The osmotic pressure is measured at a series of mass concentrations, c, and a plot of Π/c against c is used to determine the molar mass of B.

Example 7.5 Using osmometry to determine the molar mass of a macromolecule

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

$c/(\text{g L}^{-1})$	1.00	2.00	4.00	7.00	9.00
h/cm	0.28	0.71	2.01	5.10	8.00

Method We use eqn 38 with $[B] = c/M$, where c is the mass concentration of the polymer and M is its molar mass. The osmotic pressure is related to the hydrostatic pressure by $\Pi = \rho g h$ (Example 1.2) with $g = 9.81\ \mathrm{m\,s^{-2}}$. With these substitutions, eqn 38 becomes

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

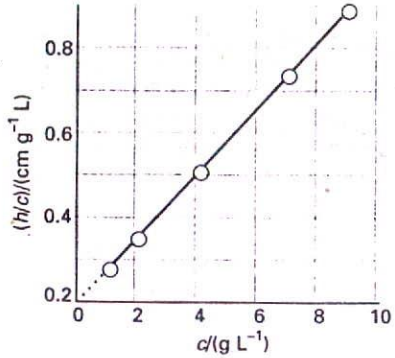
Therefore, to find M, plot h/c against c, and expect a straight line with intercept $RT/\rho g M$ at $c = 0$.

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

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

The points are plotted in Fig. 7.25. The intercept is at 0.21. Therefore,

$$\begin{aligned} M &= \frac{RT}{\rho g} \times \frac{1}{0.21\ \mathrm{cm\,g^{-1}\,L}} \\ &= \frac{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\ \mathrm{K})}{(980\ \mathrm{kg\,m^{-3}}) \times (9.81\ \mathrm{m\,s^{-2}})} \times \frac{1}{2.1 \times 10^{-3}\ \mathrm{m^4\,kg^{-1}}} \\ &= 1.2 \times 10^2\ \mathrm{kg\,mol^{-1}} \end{aligned}$$



7.25 The plot involved in the determination of molar mass by osmometry. The molar mass is calculated from the intercept at $c = 0$; in Chapter 23 we shall see that additional information comes from the slope.

Comment Molar masses of macromolecules are often reported in daltons (Da), with $1\ \mathrm{Da} = 1\ \mathrm{g\,mol^{-1}}$. The macromolecule in this example has a molar mass of about 120 kDa.

Self-test 7.6 Estimate the depression of freezing point of the most concentrated of these solutions, taking K_f as about $10\ \mathrm{K/(mol\,kg^{-1})}$.

[0.8 mK]

Activities

Now we see how to adjust the expressions developed earlier in the chapter to take into account deviations from ideal behaviour. In Section 5.4 we saw how the fugacity was introduced to take into account the effects of gas imperfections in a manner that resulted in the least upset of the form of equations. Here we see how the expressions encountered in the treatment of ideal solutions can also be preserved almost intact by introducing the concept of activity.

7.6 The solvent activity

The general form of the chemical potential of a real or ideal solvent is given by a straightforward modification of eqn 22:

$$\mu_A = \mu_A^* + RT \ln\left(\frac{p_A}{p_A^*}\right) \qquad (39)$$

where p_A^* is the vapour pressure of pure A and p_A is the vapour pressure of A when it is a component of a solution. For an ideal solution, the solvent obeys Raoult's law at all concentrations and we write

$$\mu_A = \mu_A^* + RT \ln x_A \qquad (40)^\circ$$

The standard state of the solvent is the pure liquid (at 1 bar) and is obtained when $x_A = 1$. The form of the last equation can be preserved when the solution does not obey Raoult's law by writing

$$\mu_A = \mu_A^* + RT \ln a_A \qquad [41]$$

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

Because eqn 39 is true for both real and ideal solutions (the only approximation being the use of pressures rather than fugacities), we can conclude by comparing it with eqn 41 that

$$a_A = \frac{p_A}{p_A^*} \qquad (42)$$

We see there is nothing mysterious about the activity of a solvent: it can be determined experimentally simply by measuring the vapour pressure and then using eqn 42.

Illustration

The vapour pressure of 0.500 M $KNO_3(aq)$ at 100 °C is 749.7 Torr, so the activity of water in the solution at this temperature is

$$a_A = \frac{749.7\ \text{Torr}}{760.0\ \text{Torr}} = 0.9864$$

……

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

$$a_A \rightarrow x_A \text{ as } x_A \rightarrow 1 \qquad (43)$$

As in the case of real gases, a convenient way of expressing this convergence is to introduce the **activity coefficient**, γ, by the definition

$$a_A = \gamma_A x_A \qquad \gamma_A \rightarrow 1 \text{ as } x_A \rightarrow 1 \qquad [44]$$

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

$$\mu_A = \mu_A^* + RT \ln x_A + RT \ln \gamma_A \qquad (45)$$

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

7.7 The solute activity

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

(a) Ideal-dilute solutions

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

$$\mu_B = \mu_B^* + RT \ln\left(\frac{p_B}{p_B^*}\right) = \mu_B^* + RT \ln\left(\frac{K_B}{p_B^*}\right) + RT \ln x_B$$

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

$$\mu_B^\dagger = \mu_B^* + RT \ln\left(\frac{K_B}{p_B^*}\right) \qquad [46]$$

It then follows that

$$\mu_B = \mu_B^\dagger + RT \ln x_B \qquad (47)^\circ$$

(b) Real solutes

We now permit deviations from ideal-dilute, Henry's law behaviour. For the solute, we introduce a_B in place of x_B in eqn 47, and obtain

$$\mu_B = \mu_B^\dagger + RT \ln a_B \qquad [48]$$

The standard state remains unchanged in this last stage, and all the deviations from ideality are captured in the activity a_B. The value of the activity at any concentration can be obtained in the same way as for the solvent, but in place of eqn 42 we use

$$a_B = \frac{p_B}{K_B} \qquad (49)$$

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

$$a_B = \gamma_B x_B \qquad [50]$$

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

$$a_B \rightarrow x_B \text{ and } \gamma_B \rightarrow 1 \text{ as } x_B \rightarrow 0 \qquad (51)$$

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

Example 7.6 Measuring activity

Use the information in Example 7.3 to calculate the activity and activity coefficient of chloroform in acetone at 25 °C, treating it first as a solvent and then as a solute.

Method For the activity of chloroform as a solvent (the Raoult's law activity), form $a = p/p^*$ and $\gamma = a/x$. For its activity as a solute (the Henry's law activity), form $a = p/K$ and $\gamma = a/x$.

Answer Because $p^* = 293$ Torr and $K = 165$ Torr, we can construct the following table (with x the mole fraction of chloroform):

x	0	0.20	0.40	0.60	0.80	1.00

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

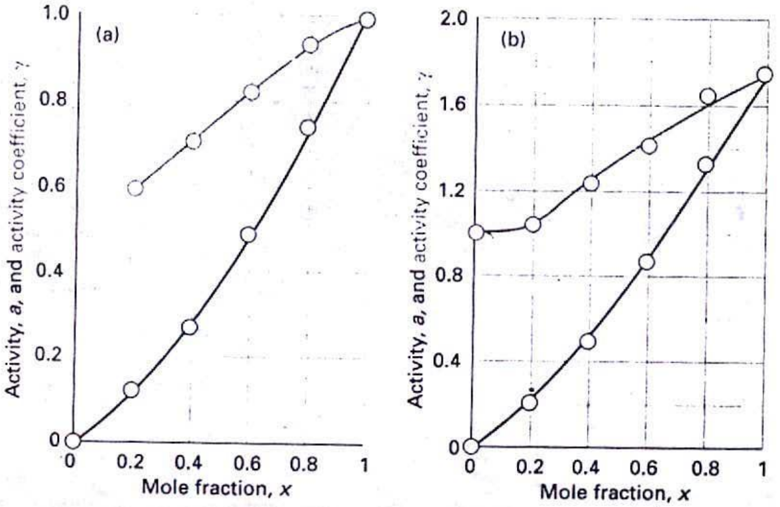
a	0	0.12	0.28	0.49	0.75	1.00
γ		0.60	0.70	0.82	0.94	1.00

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

a	0	0.21	0.50	0.86	1.33	1.78
γ	1	1.05	1.25	1.43	1.66	1.78

These values are plotted in Fig. 7.26.

Comment Notice that $\gamma \rightarrow 1$ as $x \rightarrow 1$ in the Raoult's law case, but that $\gamma \rightarrow 1$ as $x \rightarrow 0$ in the Henry's law case.



7.26 The variation of activity and activity coefficient of chloroform (trichloromethane) and acetone (propanone) with composition according to (a) Raoult's law, (b) Henry's law.

Self-test 7.7 Calculate the activities and activity coefficients for acetone according to the two conventions.

(c) *Activities in terms of molalities*

The compositions of mixtures are often expressed as molalities, *b*, in place of mole fractions. It proves convenient to introduce yet another definition of activity, but one that follows naturally from what we have done so far. First, we note that in dilute solutions the amount of solute is much less than the amount of solvent ($n_B \ll n_A$), so to a good approximation $x_B \approx n_B/n_A$. Because n_B is proportional to the molality b_B, we can write $x_B = \kappa b_B/b^{\ominus}$, where $b^{\ominus} = 1\ \text{mol kg}^{-1}$ and κ is a dimensionless constant. For an ideal-dilute solution it follows that

$$\mu_B = \mu_B^{\dagger} + RT \ln \kappa + RT \ln \left(\frac{b_B}{b^{\ominus}}\right) \qquad (52)$$

As before, it will simplify the notation if we adopt the convention of interpreting *b* as a relative molality (that is, replacing $b/b^{\ominus}$ by *b*; in practice, using for *b* its numerical value in moles per kilogram), and signifying this convention by using the label $\{\cdots\}$ for the equation number. Then eqn 52 is written

$$\mu_B = \mu_B^{\dagger} + RT \ln \kappa + RT \ln b_B \qquad \{53\}$$

We now define a new standard chemical potential, $\mu^{\ominus}$, by combining the first two terms on the right, and hence obtain

$$\mu_B = \mu_B^{\ominus} + RT \ln b_B \qquad \{54\}$$

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

Table 7.3 Standard states

Component	Basis	Standard state	Chemical potential	Limits
Solvent‡	Raoult	Pure solvent	$\mu = \mu^* + RT \ln a$ $a = p/p^*$ and $a = \gamma x$	$\gamma \to 1$ as $x \to 1$ (pure solvent)
Solute	Henry	(1) A hypothetical state of the pure solute	$\mu = \mu^\dagger + RT \ln a$ $a = p/K$ and $a = \gamma x$	$\gamma \to 1$ as $x \to 0$
		(2) A hypothetical state of the solute at molality $b^\ominus$	$\mu = \mu^\ominus + RT \ln a$ $a = \gamma b/b^\ominus$	$\gamma \to 1$ as $b \to 0$

‡ The implication of this entry is that the activity of a pure solid or liquid is 1. The pressure in each case is 1 bar.

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

$$a_B = \gamma_B \frac{b_B}{b^\ominus} \quad \text{where } \gamma_B \to 1 \text{ as } b_B \to 0 \qquad [55]$$

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

$$\mu = \mu^\ominus + RT \ln a \qquad (56)$$

It is important to be aware of the different definitions of standard states and activities, and they are summarized in Table 7.3. We shall put them to work in the next few chapters, when we shall see that using them is much easier than defining them.

Checklist of key ideas

The thermodynamic description of mixtures

7.1 Partial molar quantities

- ☐ partial molar volume (1)
- ☐ the total volume of a mixture (3)
- ☐ partial molar Gibbs energy and the definition of the chemical potential (4)
- ☐ the total Gibbs energy of a mixture (5)
- ☐ the fundamental equation of chemical thermodynamics (6)
- ☐ the chemical potential in terms of U (9), H (10a), and A (10b)
- ☐ the Gibbs–Duhem equation (12)

7.2 The thermodynamics of mixing

- ☐ the Gibbs energy of mixing of two perfect gases ($\Delta_{mix}G$, 17)
- ☐ the entropy of mixing of two perfect gases ($\Delta_{mix}S$, 18)
- ☐ the enthalpy of mixing ($\Delta_{mix}H$, 19)

7.3 The chemical potentials of liquids

- ☐ Raoult's law (23)
- ☐ ideal solution
- ☐ the chemical potential of a component of an ideal solution (24)
- ☐ Henry's law (25)
- ☐ ideal-dilute solution
- ☐ Henry's law and gas solubility

The properties of solutions

7.4 Liquid mixtures

- ☐ the Gibbs energy of mixing of two liquids to give an ideal solution (26) and the entropy of mixing (27)
- ☐ partially miscible liquids
- ☐ excess function (X^E, 28)
- ☐ regular solution

7.5 Colligative properties

- ☐ colligative property
- ☐ the origin of colligative properties: the lowering of chemical potential of the solvent
- ☐ the elevation of boiling point (30)
- ☐ ebullioscopic constant (31)
- ☐ the depression of freezing point (33)
- ☐ cryoscopic constant (34)
- ☐ cryoscopy
- ☐ ideal solubility (36)
- ☐ osmosis
- ☐ semipermeable membrane
- ☐ osmotic pressure
- ☐ osmometry
- ☐ van't Hoff equation for the osmotic pressure (37)

Activities

- ☐ osmotic virial coefficient

7.6 The solvent activity

- ☐ solvent activity and chemical potential (41)
- ☐ the determination of activity from vapour pressure (42)
- ☐ the Raoult's law basis of activity and activity coefficient (44)

7.7 The solute activity

- ☐ the chemical potential of a solute in an ideal-dilute solution (47)
- ☐ the activity of a solute (49) and the Henry's law basis of activity coefficient (50)
- ☐ chemical potential of a solute in terms of its molality (54) and the activity on this basis (55)

Further reading

Articles of general interest

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Exercises

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

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

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

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

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

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

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

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

x_B	0.010	0.015	0.020
p_B/kPa	82.0	122.0	166.1

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

7.4 (a) Predict the partial vapour pressure of HCl above its solution in liquid germanium tetrachloride of molality 0.10 $mol\,kg^{-1}$. For data, see Exercise 7.3a.

7.4 (b) Predict the partial vapour pressure of the component B above its solution in A in Exercise 7.3b when the molality of B is 0.25 $mol\,kg^{-1}$. The molar mass of A is 74.1 $g\,mol^{-1}$.

7.5 (a) Calculate the cryoscopic and ebullioscopic constants of tetrachloromethane.

7.5 (b) Calculate the cryoscopic and ebullioscopic constants of naphthalene.

7.6 (a) The vapour pressure of benzene is 400 Torr at 60.6 °C, but it fell to 386 Torr when 19.0 g of an involatile organic compound was dissolved in 500 g of benzene. Calculate the molar mass of the compound.

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

7.7 (a) The addition of 100 g of a compound to 750 g of CCl_4 lowered the freezing point of the solvent by 10.5 K. Calculate the molar mass of the compound.

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

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

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

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

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

7.10 (a) Air is a mixture with a composition given in Self-test 1.5. Calculate the entropy of mixing when it is prepared from the pure (and perfect) gases.

7.10 (b) Calculate the Gibbs energy, entropy, and enthalpy of mixing when 1.00 mol C_6H_{14} (hexane) is mixed with 1.00 mol C_7H_{16} (heptane) at 298 K; treat the solution as ideal.

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

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

7.12 (a) Use Henry's law and the data in Table 7.1 to calculate the solubility (as a molality) of CO_2 in water at 25 °C when its partial pressure is (a) 0.10 atm, (b) 1.00 atm.

7.12 (b) The mole fractions of N_2 and O_2 in air at sea level are approximately 0.78 and 0.21. Calculate the molalities of the solution formed in an open flask of water at 25 °C.

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

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

7.14 (a) Calculate the freezing point of a glass of water of volume 250 cm^3 sweetened with 7.5 g of sucrose.

7.14 (b) Calculate the freezing point of a glass of water of volume 200 cm^3 in which 10 g of glucose has been dissolved.

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

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

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

$c/(g\,L^{-1})$	2.042	6.613	9.521	12.602
h/cm	0.592	1.910	2.750	3.600

Calculate the molar mass of the polymer.

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

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

Calculate the molar mass of the enzyme.

7.17 (a) Substances A and B are both volatile liquids with $p_{\rm A}^* = 300$ Torr, $p_{\rm B}^* = 250$ Torr, and $K_{\rm B} = 9.00$ Torr (concentration expressed in mole fraction). When $x_{\rm A} = 0.9$, $b_{\rm B} = 2.22\ mol\,kg^{-1}$, $p_{\rm A} = 250$ Torr, and $p_{\rm B} = 25$ Torr. Calculate the activities and activity coefficients of A and B. Use the mole fraction, Raoult's law basis for A and the Henry's law basis (both mole fractions and molalities) for B.

7.17 (b) Given that $p^*(H_2O) = 0.02308$ atm and $p(H_2O) = 0.02239$ atm in a solution in which 0.122 kg of a non-volatile solute ($M = 241\ g\,mol^{-1}$) is dissolved in 0.920 kg water at 293 K, calculate the activity and activity coefficient of water in the solution.

7.18 (a) A dilute solution of bromine in carbon tetrachloride behaves as an ideal-dilute solution. The vapour pressure of pure CCl_4 is 33.85 Torr at 298 K. The Henry's law constant when the concentration of Br_2 is expressed as a mole fraction is 122.36 Torr. Calculate the vapour pressure of each component, the total pressure, and the composition of the vapour phase when the mole fraction of Br_2 is 0.050, on the assumption that the conditions of the ideal-dilute solution are satisfied at this concentration.

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

7.19 (a) By measuring the equilibrium between liquid and vapour phases of an acetone (A)–methanol (M) solution at 57.2°C at 1.00 atm, it was found that $x_A = 0.400$ when $y_A = 0.516$. Calculate the activities and activity coefficients of both components in this solution on the Raoult's law basis. The vapour pressures of the pure components at this temperature are: $p_A^* = 786$ Torr and $p_M^* = 551$ Torr. (x_A is the mole fraction in the liquid and y_A the mole fraction in the vapour.)

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

Problems

Numerical problems

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

x_A	0	0.0898	0.2476	0.3577	0.5194	0.6036	0.7188	0.8019	0.9105	1
y_A	0	0.0410	0.1154	0.1762	0.2772	0.3393	0.4450	0.5435	0.7284	1
p/kPa	36.066	34.121	30.900	28.626	25.239	23.402	20.6984	18.592	15.496	12.295

7.2 The volume of an aqueous solution of NaCl at 25°C was measured at a series of molalities b, and it was found that the volume fitted the expression

$$V/\text{cm}^3 = 1003 + 16.62b + 1.77b^{3/2} + 0.12b^2$$

where V is the volume of a solution formed from 1.000 kg of water and b is to be understood as $b/b^{\ominus}$. Calculate the partial molar volume of the components in a solution of molality 0.100 mol kg^{-1}.

7.3 At 18°C the total volume of a solution formed from $MgSO_4$ and 1.000 kg of water fits the expression

$$V/\text{cm}^3 = 1001.21 + 34.69(b - 0.070)^2$$

where b is to be understood as $b/b^{\ominus}$. Calculate the partial molar volumes of the salt and the solvent when in a solution of molality 0.050 mol kg^{-1}.

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

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

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

7.5 What proportions of ethanol and water should be mixed in order to produce 100 cm^3 of a mixture containing 50 per cent by mass of ethanol? What change in volume is brought about by adding 1.00 cm^3 of ethanol to the mixture? (Use data from Fig. 7.1.)

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

x_I	0	0.0579	0.1095	0.1918	0.2353	0.3718	0.5478	0.6349	0.8253	0.9093	1.0000
p_I/Torr	0	20.0	52.7	87.7	105.4	155.4	213.3	239.1	296.9	322.5	353.4
p_A/Torr	280.4	266.1	252.3	231.4	220.8	187.9	144.2	122.9	66.6	38.2	0

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

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

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

Theoretical problems

7.8 The excess Gibbs energy of a certain binary mixture is equal to $gRTx(1-x)$ where g is a constant and x is the mole fraction of a solute A. Find an expression for the chemical potential of A in the mixture and sketch its dependence on the composition.

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

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

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

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

$$V_{\mathrm{B}} = V_{\mathrm{B}}^{*} + \int_{V_{\mathrm{A}}^{*}}^{V_{\mathrm{A}}} \frac{x_{\mathrm{A}}}{1-x_{\mathrm{A}}}\,\mathrm{d}V_{\mathrm{A}}$$

7.11 Use the Gibbs–Helmholtz equation to find an expression for $\mathrm{d}\ln x_{\mathrm{A}}$ in terms of $\mathrm{d}T$. Integrate $\mathrm{d}\ln x_{\mathrm{A}}$ from $x_{\mathrm{A}} = 0$ to the value of interest, and integrate the right-hand side from the transition temperature for the pure liquid A to the value in the solution. Show that, if the enthalpy of transition is constant, then eqns 30 and 33 are obtained.

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

$$\ln\left(\frac{a_{\mathrm{B}}}{r}\right) = \phi - \phi(0) + \int_0^r \left(\frac{\phi-1}{r}\right)\mathrm{d}r$$

7.13 Show that the osmotic pressure of a real solution is given by

$$\Pi V = -RT\ln a_{\mathrm{A}}$$

Go on to show that, provided the concentration of the solution is low, this expression takes the form

$$\Pi V = \phi RT[\mathrm{B}]$$

and hence that the osmotic coefficient, ϕ (which is defined in Problem 7.12), may be determined from osmometry.

Additional problems supplied by Carmen Giunta and Charles Trapp

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

x_c	0.6965	0.7988	0.9004
$\rho/(\mathrm{g\,cm^{-3}})$	0.7661	0.7674	0.7697

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

7.15 Comelli and Francesconi examined mixtures of propionic acid with various other organic liquids at 313.15 K (F. Comelli and R. Francesconi, *J. Chem. Eng. Data* **41**, 101 (1996)). They report the excess volume of mixing propionic acid with oxane as $V^{\mathrm{E}} = x_1x_2\{a_0 + a_1(x_1 - x_2)\}$, where x_1 is the mole fraction of propionic acid, x_2 that of oxane, $a_0 = -2.4697\ \mathrm{cm^3\,mol^{-1}}$ and $a_1 = 0.0608\ \mathrm{cm^3\,mol^{-1}}$. The density of propionic acid at this temperature is $0.97174\ \mathrm{g\,cm^{-3}}$; that of oxane is $0.86398\ \mathrm{g\,cm^{-3}}$. (a) Derive an expression for the partial molar volume of each component at this temperature. (b) Compute the partial molar volume for each component in an equimolar mixture.

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

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

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

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

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

Determine the Henry's law constant of $\mathrm{CO_2}$ in cyclohexanol, and compute the activity coefficient of $\mathrm{CO_2}$.

7.18 Equation 36 indicates that solubility is an exponential function of temperature. The data in the table below give the solubility, S, of calcium acetate in water as a function of temperature.

$\theta/{}^{\circ}\mathrm{C}$	0	20	40	60	80
$S/(\mathrm{mol\,L^{-1}})$	36.4	34.9	33.7	32.7	31.7

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

8

Phase diagrams

Phase diagrams for pure substances were introduced in Chapter 6. Now we develop their use systematically and show how they are rich summaries of empirical information about a wide range of systems. To set the stage, we introduce the famous phase rule of Gibbs, which shows the extent to which various parameters can be varied yet the equilibrium between phases preserved. With the rule established, we see how it can be used to discuss the phase diagrams that we met in the two preceding chapters. The chapter then introduces systems of gradually increasing complexity. In each case we shall see how the phase diagram for the system summarizes empirical observations on the conditions under which the various phases of the system are stable.

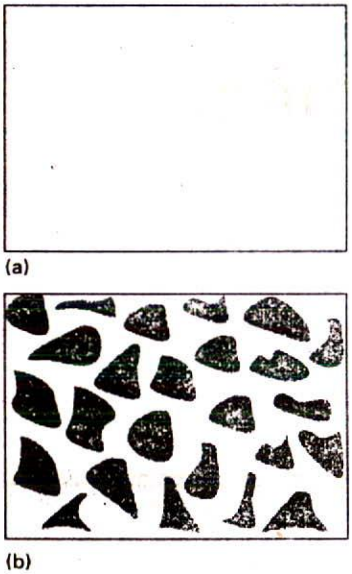
In this chapter we describe a systematic way of discussing the physical changes mixtures undergo when they are heated or cooled and when their compositions are changed. In particular, we shall see how to use phase diagrams to judge whether two substances are mutually miscible, whether an equilibrium can exist over a range of conditions, or whether the system must be brought to a definite pressure, temperature, and composition before equilibrium is established. Phase diagrams are of considerable commercial and industrial significance, particularly for semiconductors, ceramics, steels, and alloys. They are also the basis of separation procedures in the petroleum industry and of the formulation of foods and cosmetic preparations.

Phases, components, and degrees of freedom

All phase diagrams can be discussed in terms of a relationship, the phase rule, derived by J.W. Gibbs. We shall derive this rule first, and then apply it to a wide variety of systems. The phase rule requires a careful use of terms, so we begin by presenting a number of definitions.

8.1 Definitions

The term **phase** was introduced at the start of Chapter 6, where we saw that it signifies a state of matter that is uniform throughout, not only in chemical composition but also in physical state. (The words are Gibbs's.) Thus we speak of the solid, liquid, and gas phases of a substance, and of its various solid phases (as for black phosphorus and white phosphorus). The number of phases in a system is denoted P. A gas, or a gaseous mixture, is a single phase, a crystal is a single phase, and two totally miscible liquids form a single phase. Ice is a single phase ($P = 1$) even though it might be chipped into small fragments. A slurry of ice and water is a two-phase system ($P = 2$) even though it is difficult to map the boundaries between the phases. A system in which calcium carbonate undergoes thermal decomposition consists of two solid phases (one consisting of calcium carbonate and the other of calcium oxide) and one gaseous phase (consisting of carbon dioxide).



8.1 The difference between (a) a single-phase solution, in which the composition is uniform on a microscopic scale, and (b) a dispersion, in which regions of one component are embedded in a matrix of a second component.

An alloy of two metals is a two-phase system ($P = 2$) if the metals are immiscible, but a single-phase system ($P = 1$) if they are miscible. This example shows that it is not always easy to decide whether a system consists of one phase or of two. A solution of solid A in solid B—a homogeneous mixture of the two substances—is uniform on a molecular scale. In a solution, atoms of A are surrounded by atoms of A and B, and any sample cut from the sample, however small, is representative of the composition of the whole.

A dispersion is uniform on a macroscopic scale but not on a microscopic scale, for it consists of grains or droplets of one substance in a matrix of the other. A small sample could come entirely from one of the minute grains of pure A and would not be representative of the whole (Fig. 8.1). Such dispersions are important because, in many advanced materials (including steels), heat treatment cycles are used to achieve the precipitation of a fine dispersion of particles of one phase (such as a carbide phase) within a matrix formed by a saturated solid solution phase. The ability to control this microstructure resulting from phase equilibria makes it possible to tailor the mechanical properties of the materials to a particular application.

By a **constituent** of a system we mean a chemical species (an ion or a molecule) that is present. Thus, a mixture of ethanol and water has two constituents. The term constituent should be carefully distinguished from 'component', which has a more technical meaning. A **component** is a chemically independent constituent of a system. The number of components, C, in a system is the minimum number of independent species necessary to define the composition of *all* the phases present in the system.

When no reaction takes place, the number of components is equal to the number of constituents. Thus, pure water is a one-component system ($C = 1$), because we need only the species H_2O to specify its composition. Similarly, a mixture of ethanol and water is a two-component system ($C = 2$): we need the species H_2O and C_2H_5OH to specify its composition. When a reaction can occur under the conditions prevailing in the system, we need to decide the minimum number of species that, after allowing for reactions in which one species is synthesized from others, can be used to specify the composition of all the phases. Consider, for example, the equilibrium

$$\begin{array}{lll} CaCO_3(s) \rightleftharpoons & CaO(s) + & CO_2(g) \\ \text{Phase 1} & \text{Phase 2} & \text{Phase 3} \end{array}$$

in which there are three phases. To specify the composition of the gas phase we need the species CO_2, and to specify the composition of Phase 2 we need the species CaO. However, we do not need an additional species to specify the composition of the Phase 3 because its identity ($CaCO_3$) can be expressed in terms of the other two constituents by making use of the stoichiometry of the reaction. Hence, the system has three constituents but only two components ($C = 2$).

Example 8.1 Counting components

How many components are present in a system in which ammonium chloride undergoes thermal decomposition?

Method Begin by writing down the chemical equation for the reaction and identifying the constituents of the system (all the species present) and the phases. Then decide whether, under the conditions prevailing in the system, any of the constituents can be prepared from any of the other constituents. The removal of these constituents leaves the number of independent constituents. Finally, identify the minimum number of these independent constituents that are needed to specify the composition of all the phases.

Answer The chemical reaction is

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

There are three constituents and two phases (one solid, one gas). However, NH_3 and HCl are formed in fixed stoichiometric proportions by the reaction. Therefore, the compositions of both phases can be expressed in terms of the single species NH_4Cl. It follows that there is only one component in the system ($C = 1$).

Comment If additional HCl (or NH_3) were supplied to the system, the decomposition of NH_4Cl would not give the correct composition of the gas phase and HCl (or NH_3) would have to be invoked as a second component. A system that consists of hydrogen, oxygen, and water at room temperature has three components, despite it being possible to form H_2O from H_2 and O_2: under the conditions prevailing in the system, hydrogen and oxygen do not react to form water, so they are not in equilibrium and regarded as independent constituents.

Self-test 8.1 Give the number of components in the following systems: (a) water, allowing for its autoprotolysis; (b) aqueous acetic acid; (c) magnesium carbonate in equilibrium with its decomposition products.

[(a) 1; (b) 2; (c) 2]

The **variance**, F, of a system is the number of intensive variables that can be changed independently without disturbing the number of phases in equilibrium. In a single-component, single-phase system ($C = 1$, $P = 1$), the pressure and temperature may be changed independently without changing the number of phases, so $F = 2$. We say that such a system is *bivariant*, or that it has two *degrees of freedom*. On the other hand, if two phases are in equilibrium (a liquid and its vapour, for instance) in a single-component system ($C = 1$, $P = 2$), the temperature (or the pressure) can be changed at will, but the change in temperature (or pressure) demands an accompanying change in pressure (or temperature) to preserve the number of phases in equilibrium. That is, the variance of the system has fallen to 1.

8.2 The phase rule

In one of the most elegant calculations of the whole of chemical thermodynamics, J.W. Gibbs[1] deduced the phase rule, which is a general relation between the variance, F, the

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[1] Josiah Willard Gibbs spent most of his working life at Yale, and may justly be regarded as the originator of chemical thermodynamics. He reflected for years before publishing his conclusions, and then did so in precisely expressed papers in an obscure journal (*The Transactions of the Connecticut Academy of Arts and Sciences*). He needed interpreters before the power of his work was recognized and before it could be applied to industrial processes. He is regarded by many as the first great American theoretical scientist.

number of components, C, and the number of phases at equilibrium, P, for a system of any composition:

$$F = C - P + 2 \tag{1}$$

Justification 8.1

We begin by counting the total number of intensive variables (properties that do not depend on the size of the system). The pressure, p, and temperature, T, count as 2. We can specify the composition of a phase by giving the mole fractions of $C - 1$ components. We need specify only $C - 1$ and not all C mole fractions because $x_1 + x_2 + \cdots + x_C = 1$, and all mole fractions are known if all except one are specified. Because there are P phases, the total number of composition variables is $P(C - 1)$. At this stage, the total number of intensive variables is $P(C - 1) + 2$.

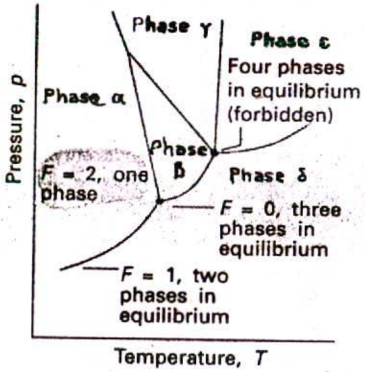
At equilibrium, the chemical potential of a component J must be the same in every phase (Section 6.4):

$$\mu_{J,\alpha} = \mu_{J,\beta} = \cdots \quad \text{for } P \text{ phases}$$

That is, there are $P - 1$ equations of this kind to be satisfied for each component J. As there are C components, the total number of equations is $C(P - 1)$. Each equation reduces our freedom to vary one of the $P(C - 1) + 2$ intensive variables. It follows that the total number of degrees of freedom is

$$F = P(C - 1) + 2 - C(P - 1) = C - P + 2$$

which is eqn 1.



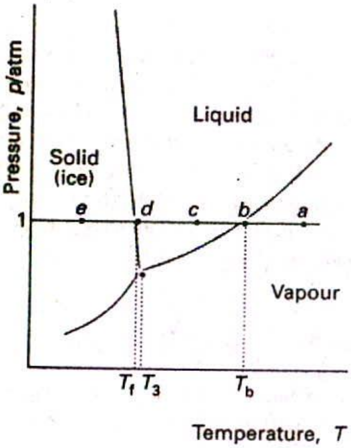
8.2 The typical regions of a one-component phase diagram. The lines represent conditions under which the two adjoining phases are in equilibrium. A point represents the unique set of conditions under which three phases coexist in equilibrium. Four phases cannot mutually coexist in equilibrium.

We shall now go on to see how the phase rule summarizes what we already know about one-component systems and then apply it to more complex cases.

(a) One-component systems

For a one-component system, such as pure water, $F = 3 - P$. When only one phase is present, $F = 2$ and both p and T can be varied independently without changing the number of phases. In other words, a single phase is represented by an *area* on a phase diagram. When two phases are in equilibrium $F = 1$, which implies that pressure is not freely variable if the temperature is set; indeed, at a given temperature, a liquid has a characteristic vapour pressure. It follows that the equilibrium of two phases is represented by a *line* in the phase diagram. Instead of selecting the temperature, we could select the pressure, but having done so the two phases would be in equilibrium at a single definite temperature. Therefore, freezing (or any other phase transition) occurs at a definite temperature at a given pressure.

When three phases are in equilibrium, $F = 0$ and the system is invariant. This special condition can be established only at a definite temperature and pressure that is characteristic of the substance and outside our control. The equilibrium of three phases is therefore represented by a *point*, the triple point, on the phase diagram. Four phases cannot be in equilibrium in a one-component system because F cannot be negative. These features are summarized in Fig. 8.2.



8.3 The phase diagram for water, a simplified version of Fig. 6.5. The label T_3 marks the temperature of the triple point, T_b the normal boiling point, and T_f the normal freezing point.

The features summarized in the illustration can be identified in the experimentally determined phase diagram for water (Fig. 8.3). This diagram summarizes the changes that take place as a sample, such as that at a, is cooled at constant pressure. The sample remains entirely gaseous until the temperature reaches b, when liquid appears. Two phases are now in equilibrium and $F = 1$. Because we have decided to specify the pressure, which uses up the single degree of freedom, the temperature at which this equilibrium occurs is not under our control. Lowering the temperature takes the system to c in the one-phase, liquid region.

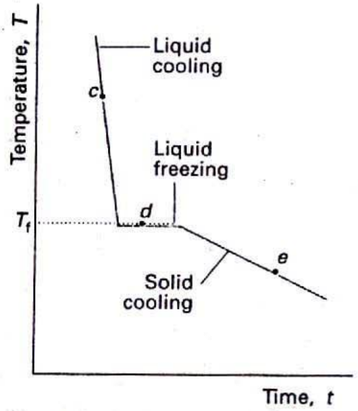
The temperature can now be varied around the point *c* at will, and only when ice appears at *d* does the variance become 1 again.

(b) Experimental procedures

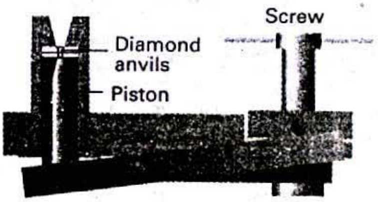
Detecting a phase change is not always as simple as seeing a kettle boil, so special techniques have been developed. One technique is **thermal analysis**, which takes advantage of the effect of the enthalpy change during a first-order transition (Section 6.7). In this method, a sample is allowed to cool and its temperature is monitored. At a first-order transition, heat is evolved and the cooling stops until the transition is complete. The cooling curve along the isobar *cde* in Fig. 8.3 therefore has the shape shown in Fig. 8.4. The transition temperature is obvious, and is used to mark point *d* on the phase diagram. This technique is useful for solid–solid transitions, where simple visual inspection of the sample may be inadequate.

Modern work on phase transitions often deals with systems at very high pressures, and more sophisticated detection procedures must be adopted. Some of the highest pressures currently attainable are produced in a *diamond-anvil cell* like that illustrated in Fig. 8.5. The sample is placed in a minute cavity between two gem-quality diamonds, and then pressure is exerted simply by turning the screw. The advance in design this represents is quite remarkable for, with a turn of the screw, pressures of up to about 1 Mbar can be reached which a few years ago could not be reached with equipment weighing tons.

The pressure is monitored spectroscopically by observing the shift of spectral lines in small pieces of ruby added to the sample, and the properties of the sample itself are observed optically through the diamond anvils. One application of the technique is to study the transition of covalent solids to metallic solids. Iodine, I_2, for instance, becomes metallic at around 200 kbar and makes a transition to a monatomic metallic solid at around 210 kbar. Studies such as these are relevant to the structure of material deep inside the Earth (at the centre of the Earth the pressure is around 5 Mbar) and in the interiors of the giant planets, where even hydrogen may be metallic.



8.4 The cooling curve for the isobar *cde* in Fig. 8.3. The halt marked *d* corresponds to the pause in the fall of temperature while the first-order exothermic transition (freezing) occurs. This pause enables T_f to be located even if the transition cannot be observed visually.



8.5 Ultra-high pressures (up to about 2 Mbar) can be achieved using a diamond anvil. The sample, together with a ruby for pressure measurement and a drop of liquid for pressure transmission, are placed between two gem-quality diamonds. The principle of its action is like a nutcracker: the pressure is exerted by turning the screw by hand.

Two-component systems

When two components are present in a system, $C = 2$ and $F = 4 - P$. If the temperature is constant, the remaining variance is $F' = 3 - P$, which has a maximum value of 2. (The prime on F indicates that one of the degrees of freedom has been discarded, in this case the temperature.) One of these two remaining degrees of freedom is the pressure and the other is the composition (as expressed by the mole fraction of one component). Hence, one form of the phase diagram is a map of pressures and compositions at which each phase is stable. Alternatively, the pressure could be held constant and the phase diagram depicted in terms of temperature and composition. We shall introduce both types of diagram.

8.3 Vapour pressure diagrams

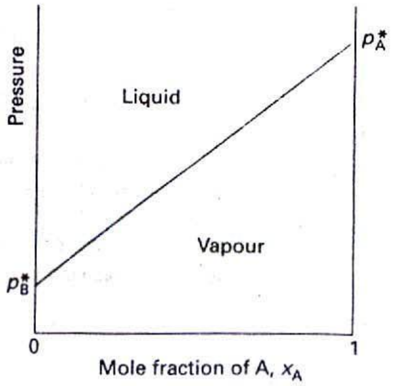
The partial vapour pressures of the components of an ideal solution of two volatile liquids are related to the composition of the liquid mixture by Raoult's law (Section 7.3a):

$$p_A = x_A p_A^* \qquad p_B = x_B p_B^* \qquad (2)^\circ$$

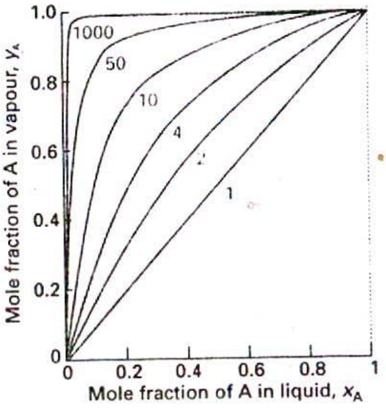
where p_A^* is the vapour pressure of pure A and p_B^* that of pure B. The total vapour pressure p of the mixture is therefore

$$p = p_A + p_B = x_A p_A^* + x_B p_B^* = p_B^* + (p_A^* - p_B^*)x_A \qquad (3)^\circ$$

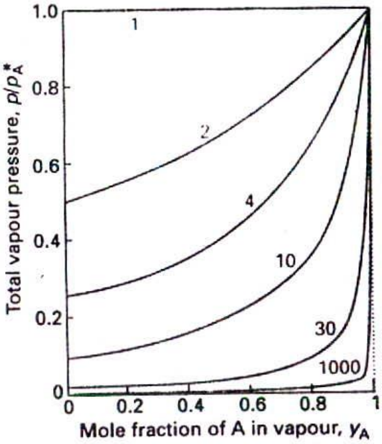
This expression shows that the total vapour pressure (at some fixed temperature) changes linearly with the composition from p_B^* to p_A^* as x_A changes from 0 to 1 (Fig. 8.6).



8.6 The variation of the total vapour pressure of a binary mixture with the mole fraction of A in the liquid when Raoult's law is obeyed.



8.7 The mole fraction of A in the vapour of a binary ideal solution expressed in terms of its mole fraction in the liquid, calculated using eqn 5 for various values of p_A^*/p_B^* (the label on each curve) with A more volatile than B. In all cases the vapour is richer than the liquid in A.



8.8 The dependence of the vapour pressure of the same system as in Fig. 8.7, but expressed in terms of the mole fraction of A in the vapour by using eqn 6. Individual curves are labelled with the value of p_A^*/p_B^*.

(a) The composition of the vapour

The compositions of the liquid and vapour that are in mutual equilibrium are not necessarily the same, and common sense suggests that the vapour should be richer in the more volatile component. This expectation can be confirmed as follows. The partial pressures of the components are given by eqn 2. It follows from Dalton's law that the mole fractions in the gas, y_A and y_B, are

$$y_A = \frac{p_A}{p} \qquad y_B = \frac{p_B}{p} \tag{4}$$

Provided the mixture is ideal, the partial pressures and the total pressure may be expressed in terms of the mole fractions in the liquid by using eqn 2 for p_J and eqn 3 for the total vapour pressure p, which gives

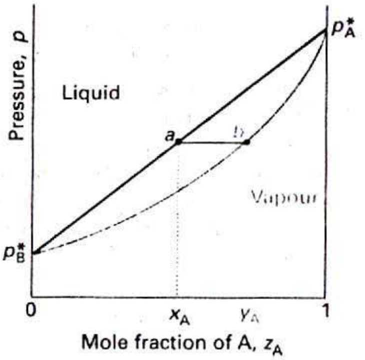
$$y_A = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*)x_A} \qquad y_B = 1 - y_A \tag{5}^\circ$$

Figure 8.7 shows the composition of the vapour plotted against the composition of the liquid for various values of $p_A^*/p_B^* > 1$. We see that in all cases $y_A > x_A$, that is, the vapour is richer than the liquid in the more volatile component. Note that if B is non-volatile, so that $p_B^* = 0$ at the temperature of interest, then it makes no contribution to the vapour ($y_B = 0$).

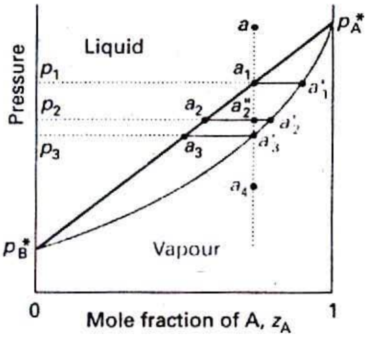
Equation 3 shows how the total vapour pressure of the mixture varies with the composition of the liquid. Because we can relate the composition of the liquid to the composition of the vapour through eqn 5, we can now also relate the total vapour pressure to the composition of the vapour:

$$p = \frac{p_A^* p_B^*}{p_A^* + (p_B^* - p_A^*)y_A} \tag{6}^\circ$$

This expression is plotted in Fig. 8.8.



8.9 The dependence of the total vapour pressure of an ideal solution on the mole fraction of A in the entire system. A point between the two lines corresponds to both liquid and vapour being present; outside that region there is only one phase present. The mole fraction of A is denoted z_A, as explained in the text.



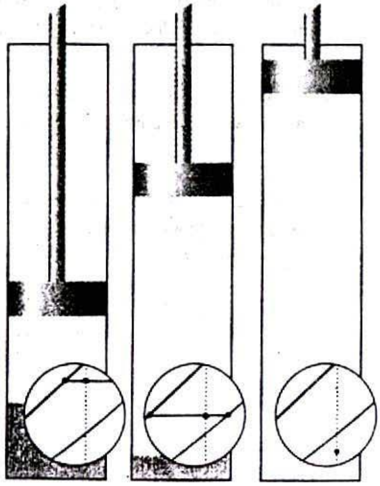
8.10 The points of the pressure-composition diagram discussed in the text. The vertical line through a is an isopleth, a line of constant composition of the entire system.

(b) The interpretation of the diagrams

If we are interested in distillation, both the vapour and the liquid compositions are of equal interest. It is therefore sensible to combine the two preceding diagrams into one. The result is summarized in Fig. 8.9. The point a indicates the vapour pressure of a mixture of composition x_A, and the point b indicates the composition of the vapour that is in equilibrium with the liquid at that pressure. Note that, when two phases are in equilibrium, $P = 2$ so $F' = 1$ (as usual, the prime indicating that one degree of freedom, the temperature, has already been discarded). That is, if the composition is specified (so using up the only remaining degree of freedom), the pressure at which the two phases are in equilibrium is fixed.

A richer interpretation of the phase diagram is obtained if we interpret the horizontal axis as showing the *overall* composition, z_A, of the system. If the horizontal axis of the vapour pressure diagram is labelled with z_A, then all the points down to the solid diagonal line in the graph correspond to a system which is under such high pressure that it contains only a liquid phase (the applied pressure is higher than the vapour pressure), so $z_A = x_A$, the composition of the liquid. On the other hand, all points below the lower curve correspond to a system which is under such low pressure that it contains only a vapour phase (the applied pressure is lower than the vapour pressure), so $z_A = y_A$.

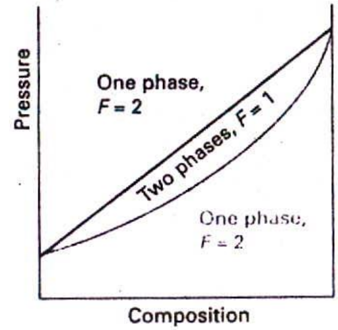
Points that lie *between* the two lines correspond to a system in which there are two phases present, one a liquid and the other a vapour. To see this interpretation, consider lowering the pressure on a liquid mixture of overall composition a in Fig. 8.10. The lowering of pressure can be achieved by drawing out a piston (Fig. 8.11). This degree of freedom is permitted by the phase rule because $F' = 2$ when $P = 1$, and even if the composition is selected one degree of freedom remains. The changes to the system do not affect the overall composition, so the state of the system moves down the vertical line that passes through a. This vertical line is called an isopleth, from the Greek words for 'equal abundance'. Until the point a_1 is reached (when the pressure has been reduced to p_1), the sample consists of a single liquid phase. At a_1 the liquid can exist in equilibrium with its vapour. As we have seen, the composition of the vapour phase is given by point a'_1. The horizontal line joining the two points is called a tie line. The composition of the liquid is the same as initially (a_1 lies on the


(a) (b) (c)

8.11 (a) A liquid in a container exists in equilibrium with its vapour. The superimposed fragment of the phase diagram shows the compositions of the two phases and their abundances (by the lever rule).
(b) When the pressure is changed by drawing out a piston, the compositions of the phases adjust as shown by the tie line in the phase diagram.
(c) When the piston is pulled so far out that all the liquid has vaporized and only the vapour is present, the pressure falls as the piston is withdrawn and the point on the phase diagram moves into the one-phase region.

isopleth through a), so we have to conclude that at this pressure there is virtually no vapour present; however, the tiny amount of vapour that is present has the composition a_1'.

Now consider the effect of lowering the pressure to p_2, so taking the system to a pressure and overall composition represented by the point a_2''. This new pressure is below the vapour pressure of the original liquid, so it vaporizes until the vapour pressure of the remaining liquid falls to p_2. Now we know that the composition of such a liquid must be a_2. Moreover, the composition of the vapour in equilibrium with that liquid must be given by the point a_2' at the other end of the tie line. Note that two phases are now in equilibrium, so $F' = 1$ for all points between the two lines; hence, for a given pressure (such as at p_2) the variance is zero, and the vapour and liquid phases have fixed compositions (Fig. 8.12). If the pressure is reduced to p_3, a similar readjustment in composition takes place, and now the compositions of the liquid and vapour are represented by the points a_3 and a_3', respectively. The latter point corresponds to a system in which the composition of the vapour is the same as the overall composition, so we have to conclude that the amount of liquid present is now virtually zero, but the tiny amount of liquid that is present has the composition a_3. A further decrease in pressure takes the system to the point a_4; at this stage, only vapour is present and its composition is the same as the initial overall composition of the system (the composition of the original liquid).



8.12 The general scheme of interpretation of a pressure-composition diagram (a vapour pressure diagram).

(c) The lever rule

A point in the two-phase region of a phase diagram indicates not only qualitatively that both liquid and vapour are present, but represents quantitatively the relative amounts of each. To find the relative amounts of two phases α and β that are in equilibrium, we measure the distances l_α and l_β along the horizontal tie line, and then use the lever rule (Fig. 8.13):

$$n_\alpha l_\alpha = n_\beta l_\beta \tag{7}$$

where n_α is the amount of phase α and n_β the amount of phase β. In the case illustrated in Fig. 8.13, because $l_\beta \approx 2l_\alpha$, the amount of phase α is about twice the amount of phase β.

Justification 8.2

To prove the lever rule we write $n = n_\alpha + n_\beta$ and the overall amount of A as nz_A. The overall amount of A is also the sum of its amounts in the two phases:

$$nz_A = n_\alpha x_A + n_\beta y_A$$

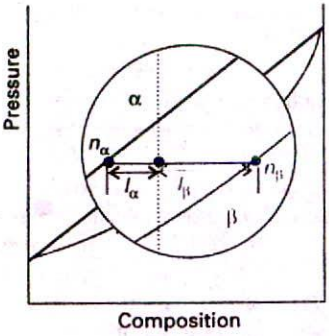
Since also

$$nz_A = n_\alpha z_A + n_\beta z_A$$

by equating these two expressions it follows that

$$n_\alpha(x_A - z_A) = n_\beta(z_A - y_A)$$

which corresponds to eqn 7.



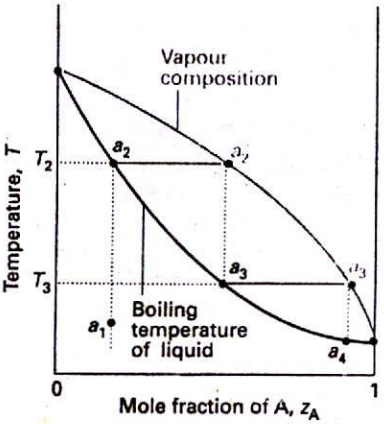
8.13 The lever rule. The distances l_α and l_β are used to find the proportions of the amounts of phases α (such as vapour) and β (for example, liquid) present at equilibrium. The lever rule is so called because a similar rule relates the masses at two ends of a lever to their distances from a pivot ($m_\alpha l_\alpha = m_\beta l_\beta$ for balance).

Illustration

At p_1 in Fig. 8.10, the ratio $l_{\text{vap}}/l_{\text{liq}}$ is almost infinite for this tie line, so $n_{\text{liq}}/n_{\text{vap}}$ is also almost infinite, and there is only a trace of vapour present. When the pressure is reduced to p_2, the value of $l_{\text{vap}}/l_{\text{liq}}$ is about 0.3, so $n_{\text{liq}}/n_{\text{vap}} \approx 0.3$ and the amount of liquid is about 0.3 times the amount of vapour. When the pressure has been reduced to p_3, the sample is almost completely gaseous and, because $l_{\text{vap}}/l_{\text{liq}} \approx 0$, we conclude that there is only a trace of liquid present.

8.4 Temperature–composition diagrams

To discuss distillation we need a **temperature–composition diagram**, a phase diagram in which the boundaries show the compositions of the phases that are in equilibrium at various temperatures (and a given pressure, typically 1 atm). An example is shown in Fig. 8.14. Note that the liquid phase now lies in the lower part of the diagram.



8.14 The temperature-composition diagram corresponding to an ideal mixture with the component A more volatile than component B. Successive boilings and condensations of a liquid originally of composition a_1 lead to a condensate that is pure A. The separation technique is called fractional distillation.

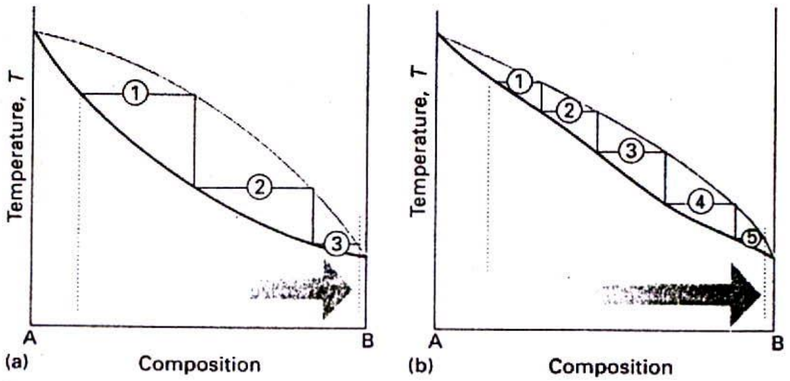
(a) The distillation of mixtures

The region between the lines in Fig. 8.14 is a two-phase region where $F' = 1$ (as usual, the prime indicates that one degree of freedom has been discarded; in this case, the pressure is being kept fixed), and hence at a given temperature the compositions of the phases in equilibrium are fixed. The regions outside the phase lines correspond to a single phase, so $F' = 2$, and the temperature and composition are both independently variable.

Consider what happens when a liquid of composition a_1 is heated. It boils when the temperature reaches T_2. Then the liquid has composition a_2 (the same as a_1) and the vapour (which is present only as a trace) has composition a_2'. The vapour is richer in the more volatile component A (the component with the lower boiling point). From the location of a_2, we can state the vapour's composition at the boiling point, and from the location of the tie line joining a_2 and a_2' we can read off the boiling temperature (T_2) of the original liquid mixture.

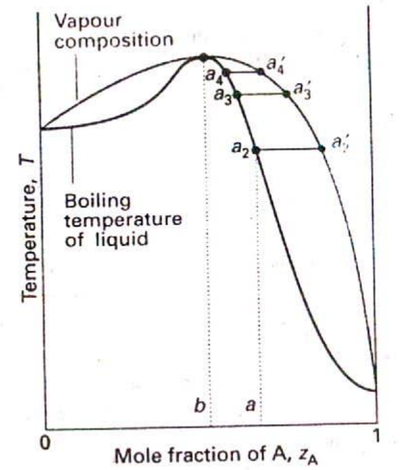
In a simple distillation, the vapour is withdrawn and condensed. If the vapour in this example is drawn off and completely condensed, the first drop gives a liquid of composition a_3, which is richer in the more volatile component, A, than the original liquid. In **fractional distillation**, the boiling and condensation cycle is repeated successively. We can follow the changes that occur by seeing what happens when the condensate of composition a_3 is reheated. The phase diagram shows that this mixture boils at T_3 and yields a vapour of composition a_3', which is even richer in the more volatile component. That vapour is drawn off, and the first drop condenses to a liquid of composition a_4. The cycle can then be repeated until in due course almost pure A is obtained.

The efficiency of a fractionating column is expressed in terms of the number of **theoretical plates**, the number of effective vaporization and condensation steps that are required to achieve a condensate of given composition from a given distillate. Thus, to achieve the degree of separation shown by the dotted lines in Fig. 8.15a, the fractionating column must correspond to 3 theoretical plates. To achieve the same separation for the system shown in



8.15 The number of theoretical plates is the number of steps needed to bring about a specified degree of separation of two components in a mixture. The two systems shown correspond to (a) 3, (b) 5 theoretical plates.

Fig 8.15b, in which the components have more similar partial vapour pressures, the fractionating column must be designed to correspond to five theoretical plates.



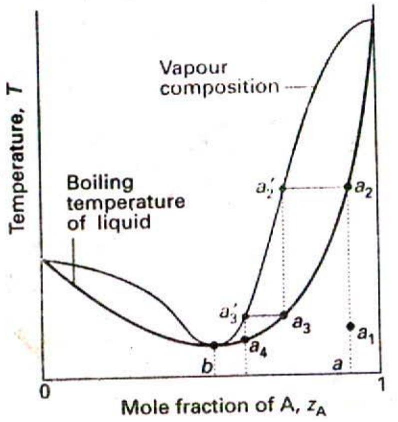
8.16 A high-boiling azeotrope. When the liquid of composition a is distilled, the composition of the remaining liquid changes towards b but no further.

(b) Azeotropes

Although many liquids have temperature–composition phase diagrams resembling the ideal version in Fig. 8.14, in a number of important cases there are marked deviations. A maximum in the phase diagram (Fig. 8.16) may occur when the favourable interactions between A and B molecules reduce the vapour pressure of the mixture below the ideal value: in effect, the A–B interactions stabilize the liquid. In such cases the excess Gibbs energy, G^E (Section 7.4), is negative (more favourable to mixing than ideal). Examples of this behaviour include trichloromethane/propanone and nitric acid/water mixtures. Phase diagrams showing a minimum (Fig. 8.17) indicate that the mixture is destabilized relative to the ideal solution, the A–B interactions then being unfavourable. For such mixtures G^E is positive (less favourable to mixing than ideal), and there may be contributions from both enthalpy and entropy effects. Examples include dioxane/water and ethanol/water mixtures.

Deviations from ideality are not always so strong as to lead to a maximum or minimum in the phase diagram, but when they do there are important consequences for distillation. Consider a liquid of composition a on the right of the maximum in Fig. 8.16. The vapour (at a_2') of the boiling mixture (at a_2) is richer in A. If that vapour is removed (and condensed elsewhere), then the remaining liquid will move to a composition that is richer in B, such as that represented by a_3, and the vapour in equilibrium with this mixture will have composition a_3'. As that vapour is removed, the composition of the boiling liquid shifts to a point such as a_4, and the composition of the vapour shifts to a_4'. Hence, as evaporation proceeds, the composition of the remaining liquid shifts towards B as A is drawn off. The boiling point of the liquid rises, and the vapour becomes richer in B. When so much A has been evaporated that the liquid has reached the composition b, the vapour has the same composition as the liquid. Evaporation then occurs without change of composition. The mixture is said to form an **azeotrope** (which comes from the Greek words for 'boiling without changing'). When the azeotropic composition has been reached, distillation cannot separate the two liquids because the condensate has the same composition as the azeotropic liquid. One example of azeotrope formation is hydrochloric acid/water, which is azeotropic at 80 per cent by mass of water and boils unchanged at 108.6°C.

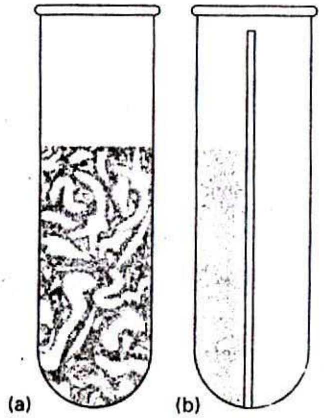
The system shown in Fig. 8.17 is also azeotropic, but shows its azeotropy in a different way. Suppose we start with a mixture of composition a_1, and follow the changes in the composition of the vapour that rises through a fractionating column (essentially a vertical glass tube packed with glass rings to give a large surface area). The mixture boils at a_2 to give a vapour of composition a_2'. This vapour condenses in the column to a liquid of the same composition (now marked a_3). That liquid reaches equilibrium with its vapour at a_3', which condenses higher up the tube to give a liquid of the same composition, which we now call a_4. The fractionation therefore shifts the vapour towards the azeotropic composition at b, but not beyond, and the azeotropic vapour emerges from the top of the column. An example is ethanol/water, which boils unchanged when the water content is 4 per cent by mass and the temperature is 78°C.



8.17 A low-boiling azeotrope. When the mixture at a is fractionally distilled, the vapour in equilibrium in the fractionating column moves towards b and then remains unchanged.

(c) Immiscible liquids

Finally we consider the distillation of two immiscible liquids, such as octane and water. At equilibrium, there is a tiny amount of A dissolved in B, and similarly a tiny amount of B dissolved in A: both liquids are saturated with the other component (Fig. 8.18a). As a result, the total vapour pressure of the mixture is close to $p = p_A^* + p_B^*$. If the temperature is raised to the value at which this total vapour pressure is equal to the atmospheric pressure, boiling



8.18 The distillation of (a) two immiscible liquids can be regarded as (b) the joint distillation of the separated components, and boiling occurs when the sum of the partial pressures equals the external pressure.

commences and the dissolved substances are purged from their solution. However, this boiling results in a vigorous agitation of the mixture, so each component is kept saturated in the other component, and the purging continues as the very dilute solutions are replenished. This intimate contact is essential: two immiscible liquids heated in a container like that shown in Fig. 8.18b would not boil at the same temperature. The presence of the saturated solutions means that the 'mixture' boils at a lower temperature than either component would alone because boiling begins when the total vapour pressure reaches 1 atm, not when either vapour pressure reaches 1 atm. This distinction is the basis of **steam distillation**, which enables some heat-sensitive, water-insoluble organic compounds to be distilled at a lower temperature than their normal boiling point. The only snag is that the composition of the condensate is in proportion to the vapour pressures of the components, so oils of low volatility distil in low abundance.

8.5 Liquid–liquid phase diagrams

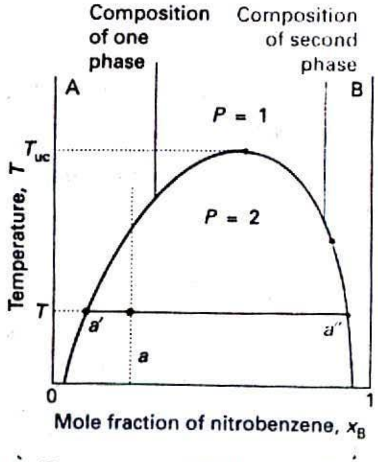
Now we consider temperature–composition diagrams for systems that consist of pairs of **partially miscible liquids**, which are liquids that do not mix in all proportions at all temperatures. An example is hexane and nitrobenzene. The same principles of interpretation apply as to liquid–vapour diagrams. When $P = 2$, $F' = 1$ (the prime denoting the adoption of constant pressure), and the selection of a temperature implies that the compositions of the immiscible liquid phases are fixed. When $P = 1$ (corresponding to a system in which the two liquids are fully mixed), both the temperature and the composition may be adjusted.

(a) Phase separation

Suppose a small amount of a liquid B is added to a sample of another liquid A at a temperature T'. It dissolves completely, and the binary system remains a single phase. As more B is added, a stage comes at which no more dissolves. The sample now consists of two phases in equilibrium with each other ($P = 2$), the most abundant one consisting of A saturated with B, the minor one a trace of B saturated with A. In the temperature–composition diagram drawn in Fig. 8.19, the composition of the former is represented by the point a' and that of the latter by the point a''. The relative abundances of the two phases are given by the lever rule.

When more B is added, A dissolves in it slightly. The compositions of the two phases in equilibrium remain a' and a'' (because $P = 2$ implies that $F' = 0$, and hence that the compositions of the phases are invariant at a fixed temperature and pressure), but the amount of one phase increases at the expense of the other. A stage is reached when so much B is present that it can dissolve all the A, and the system reverts to a single phase. The addition of more B now simply dilutes the solution, and from then on it remains a single phase.

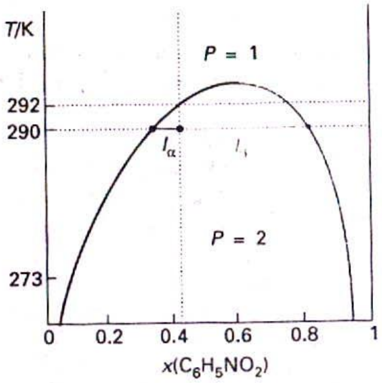
The compositions of the two phases at equilibrium vary with the temperature. For hexane and nitrobenzene, raising the temperature increases their miscibility. The two-phase system therefore becomes less extensive, because each phase in equilibrium is richer in its minor component: the A-rich phase is richer in B and the B-rich phase is richer in A. The entire phase diagram can be constructed by repeating the observations at different temperatures and drawing the envelope of the two-phase region.



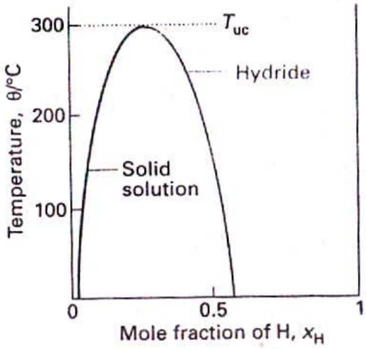
8.19 The temperature–composition diagram for hexane and nitrobenzene at 1 atm. The region below the curve corresponds to the compositions and temperatures at which the liquids form two phases. The upper critical temperature, T_{uc}, is the temperature above which the two liquids are miscible in all proportions.

Example 8.2 Interpreting a liquid–liquid phase diagram

A mixture of 50 g of hexane (0.59 mol C_6H_{14}) and 50 g nitrobenzene (0.41 mol $C_6H_5NO_2$) was prepared at 290 K. What are the compositions of the phases, and in what proportions



8.20 The temperature-composition diagram for hexane and nitrobenzene at 1 atm again, with the points and lengths discussed in the text.



8.21 The phase diagram for palladium and palladium hydride, which has an upper critical temperature at 300°C.

do they occur? To what temperature must the sample be heated in order to obtain a single phase?

Method The compositions of phases in equilibrium are given by the points where the tie line through the point representing the temperature and overall composition of the system intersects the phase boundary. Their proportions are given by the lever rule (eqn 7). The temperature at which the components are completely miscible is found by following the isopleth upwards and noting the temperature at which it enters the one-phase region of the phase diagram.

Answer We denote hexane by H and nitrobenzene by N; refer to Fig. 8.20, which is a simplified version of Fig. 8.19. The point $x_N = 0.41$, $T = 290$ K occurs in the two-phase region of the phase diagram. The horizontal tie line cuts the phase boundary at $x_N = 0.35$ and $x_N = 0.83$, so those are the compositions of the two phases. The ratio of the amounts of each phase is equal to the ratio of the distances l_α and l_β:

$$\frac{n_\alpha}{n_\beta}=\frac{l_\beta}{l_\alpha}=\frac{0.83-0.41}{0.41-0.35}=\frac{0.42}{0.06}=7$$

That is, there is about 7 times more nitrobenzene-rich phase than hexane-rich phase. Heating the sample to 292 K takes it into the single-phase region.

Comment Because the phase diagram has been constructed experimentally, these conclusions are not based on any assumptions about ideality. They would be modified if the system were subjected to a different pressure.

Self-test 8.2 Repeat the problem for 50 g of hexane and 100 g of nitrobenzene at 273 K.
[$x_N = 0.09$ and 0.95 in ratio 1:1.3; 294 K]

(b) Critical solution temperatures

The **upper critical solution temperature**, T_{uc}, is the highest temperature at which phase separation occurs.[2] Above the upper critical temperature the two components are fully miscible. This temperature exists because the greater thermal motion overcomes any

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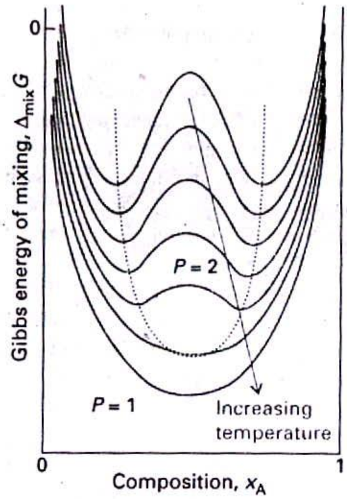
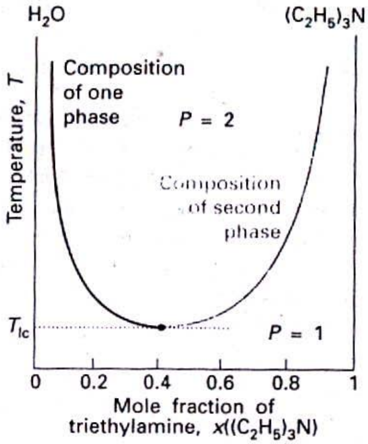
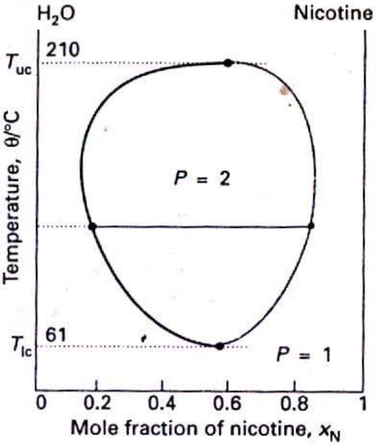
[2] The upper critical solution temperature is also called the 'upper consolute temperature'.



8.22 The temperature variation of the Gibbs energy of mixing of a system that is partially miscible at low temperatures. A system of composition in the region $P = 2$ forms two phases with compositions corresponding to the two local minima of the curve.



8.23 The temperature–composition diagram for water and triethylamine. This system shows a lower critical temperature at 292 K. The labels indicate the interpretation of the boundaries.



8.24 The temperature–composition diagram for water and nicotine, which has both upper and lower critical temperatures. Note the high temperatures for the liquid (especially the water): the diagram corresponds to a sample under pressure.

potential energy advantage in molecules of one type being close together. One example is the nitrobenzene/hexane system shown in Fig. 8.19; an example of a solid solution is the palladium/hydrogen system, which shows two phases, one a solid solution of hydrogen in palladium and the other a palladium hydride, up to 300 °C but which forms a single phase at higher temperatures (Fig. 8.21).

The thermodynamic interpretation of the upper critical solution temperature focuses on the Gibbs energy of mixing and its variation with temperature. The Gibbs energy of mixing of a partially miscible system behaves as shown in Fig. 8.22. The double minima in the curves indicate the compositions of the partially miscible phases. As the temperature rises, the two minima blend together and merge into a single minimum at the upper critical solution temperature.

Some systems show a **lower critical solution temperature,** T_{lc}, below which they mix in all proportions and above which they form two phases.[3] An example is water and triethylamine (Fig. 8.23). In this case, at low temperatures the two components are more miscible because they form a weak complex; at higher temperatures the complexes break up and the two components are less miscible.

Some systems have both upper and lower critical solution temperatures. They occur because, after the weak complexes have been disrupted, leading to partial miscibility, the thermal motion at higher temperatures homogenizes the mixture again, just as in the case of ordinary partially miscible liquids. The most famous example is nicotine and water, which are partially miscible between 61 °C and 210 °C (Fig. 8.24).

(c) The distillation of partially miscible liquids

Consider a pair of liquids that are partially miscible and form a low-boiling azeotrope. This combination is quite common because both properties reflect the tendency of the two kinds

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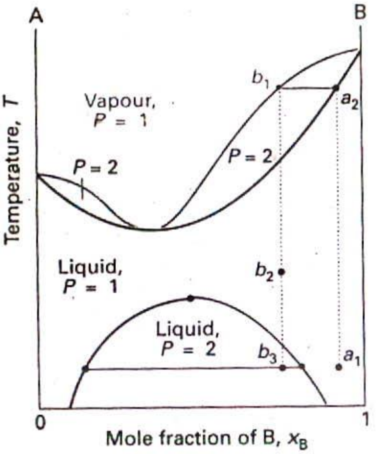
[3] The lower critical solution temperature is also called the 'lower consolute temperature'.



8.25 The temperature–composition diagram for a binary system in which the upper critical temperature is less than the boiling point at all compositions. The mixture forms a low-boiling azeotrope.

of molecule to avoid each other. There are two possibilities: one in which the liquids become fully miscible before they boil, the other in which boiling occurs before mixing is complete.

Figure 8.25 shows the phase diagram for two components that become fully miscible before they boil. Distillation of a mixture of composition a_1 leads to a vapour of composition b_1, which condenses to the completely miscible single-phase solution at b_2. Phase separation occurs only when this distillate is cooled to a point in the two-phase liquid region, such as b_3. This description applies only to the first drop of distillate. If distillation continues, the composition of the remaining liquid changes. In the end, when the whole sample has evaporated and condensed, the composition is back to a_1.

Figure 8.26 shows the second possibility, in which there is no upper critical solution temperature. The distillate obtained from a liquid initially of composition a_1 has composition b_3 and is a two-phase mixture. One phase has composition b_3' and the other has composition b_3''.

The behaviour of a system of composition represented by the isopleth e in Fig. 8.26 is interesting. A system at e_1 forms two phases, which persist (but with changing proportions) up to the boiling point at e_2. The vapour of this mixture has the same composition as the liquid (the liquid is an azeotrope). Similarly, condensing a vapour of composition e_3 gives a two-phase liquid of the same overall composition. At a fixed temperature, the mixture vaporizes and condenses like a single substance.

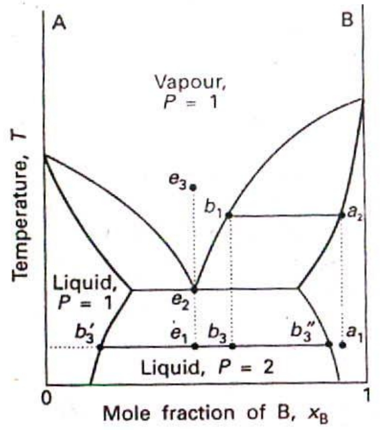
Example 8.3 Interpreting a phase diagram

State the changes that occur when a mixture of composition $x_B = 0.95$ (a_1) in Fig. 8.27 is boiled and the vapour condensed.

Method The area in which the point lies gives the number of phases; the compositions of the phases are given by the points at the intersections of the horizontal tie line with the phase boundaries; the relative abundances are given by the lever rule (eqn 7).

Answer The initial point is in the one-phase region. When heated it boils at 350 K (a_2) giving a vapour of composition $x_B = 0.66$ (b_1). The liquid gets richer in B, and the last drop (of pure B) evaporates at 392 K. The boiling range of the liquid is therefore 350 to 392 K. If the initial vapour is drawn off, it has a composition $x_B = 0.66$. This composition would be maintained if the sample were very large, but for a finite sample it shifts to higher values and ultimately to $x_B = 0.95$. Cooling the distillate corresponds to moving down the $x_B = 0.66$ isopleth. At 330 K, for instance, the liquid phase has composition $x_B = 0.87$, the vapour $x_B = 0.49$; their relative proportions are 1:3. At 320 K the sample is entirely liquid, and consists of three phases: the vapour and two liquids. One liquid phase has composition $x_B = 0.30$; the other has composition $x_B = 0.80$ in the ratio 0.62:1. Further cooling moves the system into the two-phase region, and at 298 K the compositions are 0.20 and 0.90 in the ratio 0.82:1. As further distillate boils over, the overall composition of the distillate becomes richer in B. When the last drop has been condensed, the phase composition is the same as at the beginning.

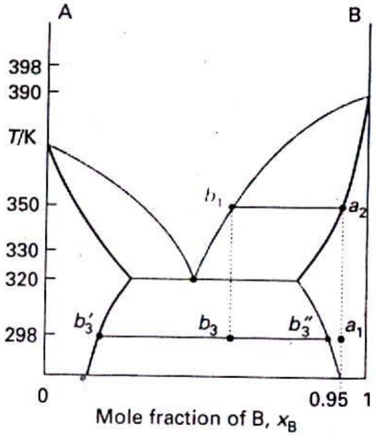
Self-test 8.3 Repeat the discussion, beginning at the point $x_B = 0.4$, $T = 298$ K.



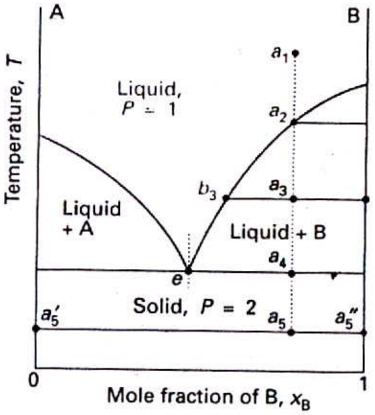
8.26 The temperature–composition diagram for a binary system in which boiling occurs before the two liquids are fully miscible.

8.6 Liquid–solid phase diagrams

Solid and liquid phases may both be present in a system at temperatures below the boiling point. An example is a pair of metals that are almost completely immiscible right up to their melting points (such as antimony and bismuth).



8.27 The points of the phase diagram in Fig. 8.26 that are discussed in Example 8.3.



8.28 The temperature-composition phase diagram for two almost immiscible solids and their completely miscible liquids. Note the similarity to Fig. 8.26. The isopleth through *e* corresponds to the eutectic composition, the mixture with lowest melting point.

Consider the two-component liquid of composition a_1 in Fig. 8.28. The changes that occur may be expressed as follows.

(1) $a_1 \rightarrow a_2$. The system enters the two-phase region labelled 'Liquid + B'. Pure solid B begins to come out of solution and the remaining liquid becomes richer in A.

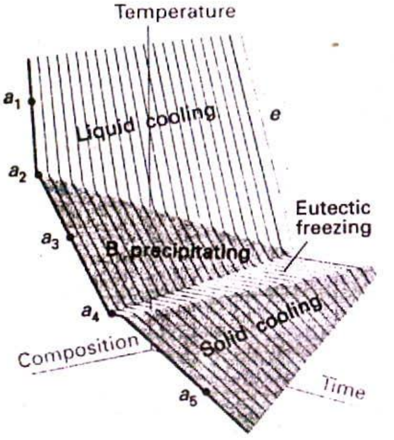
(2) $a_2 \rightarrow a_3$. More of the solid forms, and the relative amounts of the solid and liquid (which are in equilibrium) are given by the lever rule. At this stage there are roughly equal amounts of each. The liquid phase is richer in A than before (its composition is given by b_3) because some B has been deposited.

(3) $a_3 \rightarrow a_4$. At the end of this step, there is less liquid than at a_3, and its composition is given by *e*. This liquid now freezes to give a two-phase system of pure B and pure A.

(a) Eutectics

The isopleth at *e* in Fig. 8.28 corresponds to the **eutectic composition**, the name coming from the Greek words for 'easily melted'. A liquid with the eutectic composition freezes at a single temperature, without previously depositing solid A or B. A solid with the eutectic composition melts, without change of composition, at the lowest temperature of any mixture. Solutions of composition to the right of *e* deposit B as they cool, and solutions to the left deposit A: only the eutectic mixture (apart from pure A or pure B) solidifies at a single definite temperature ($F' = 0$ when $C = 2$ and $P = 3$) without gradually unloading one or other of the components from the liquid.

One technologically important eutectic is solder, which has mass composition of about 67 per cent tin and 33 per cent lead and melts at 183 °C. The eutectic formed by 23 per cent NaCl and 77 per cent H_2O by mass melts at −21.1 °C. When salt is added to ice under isothermal conditions (for example, when spread on an icy road) the mixture melts if the temperature is above −21.1 °C (and the eutectic composition has been achieved). When salt is added to ice under adiabatic conditions (for example, when added to ice in a vacuum flask) the ice melts, but in doing so it absorbs heat from the rest of the mixture. The temperature of the system falls and, if enough salt is added, cooling continues down to the eutectic temperature. Eutectic formation occurs in the great majority of binary alloy systems, and is



8.29 The cooling curves for the system shown in Fig. 8.28. For isopleth a, the rate of cooling slows at a_2 because solid B deposits from solution. There is a complete halt at a_4 while the eutectic solidifies. This halt is longest for the eutectic isopleth, e. The eutectic halt shortens again for compositions beyond e (richer in A). Cooling curves are used to construct the phase diagram.

of great importance for the microstructure of solid materials. Although a eutectic solid is a two-phase system, it crystallizes out in a nearly homogeneous mixture of microcrystals. The two microcrystalline phases can be distinguished by microscopy and structural techniques such as X-ray diffraction.

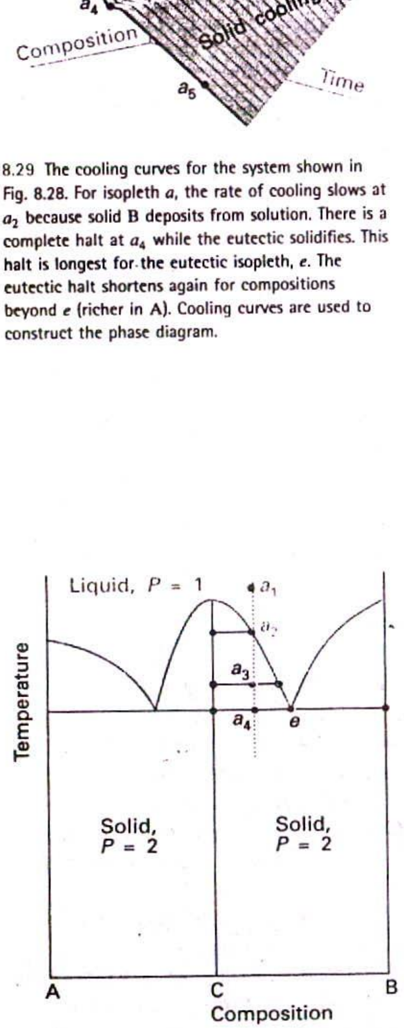
Thermal analysis is a very useful practical way of detecting eutectics. We can see how it is used by considering the rate of cooling down the isopleth through a_1 in Fig. 8.28. The liquid cools steadily until it reaches a_2, when B begins to be deposited (Fig. 8.29). Cooling is now slower because the solidification of B is exothermic and retards the cooling. When the remaining liquid reaches the eutectic composition, the temperature remains constant ($F' = 0$) until the whole sample has solidified: this region of constant temperature is the eutectic halt. If the liquid has the eutectic composition e initially, the liquid cools steadily down to the freezing temperature of the eutectic, when there is a long eutectic halt as the entire sample solidifies (like the freezing of a pure liquid).

Monitoring the cooling curves at different overall compositions gives a clear indication of the structure of the phase diagram. The solid–liquid boundary is given by the points at which the rate of cooling changes. The longest eutectic halt gives the location of the eutectic composition and its melting temperature.

(b) Reacting systems

Many binary mixtures react to produce compounds, and technologically important examples of this behaviour include the III/V semiconductors, such as the gallium arsenide system, which forms the compound GaAs. Although three constituents are present, there are only two components because GaAs is formed from the reaction Ga + As $\rightleftharpoons$ GaAs. We shall illustrate some of the principles involved with a system that forms a compound C which also forms eutectic mixtures with the species A and B (Fig. 8.30).

A system prepared by mixing an excess of B with A consists of C and unreacted B. This is a binary B, C system, which we suppose forms a eutectic. The principal change from the eutectic phase diagram in Fig. 8.28 is that the whole of the phase diagram is squeezed into the range of compositions lying between equal amounts of A and B ($x_B = 0.5$, marked C in Fig. 8.30) and pure B. The interpretation of the information in the diagram is obtained in the same way as for Fig. 8.28. The solid deposited on cooling along the isopleth a is the compound C. At temperatures below a_4 there are two solid phases, one consisting of C and the other of B.



8.30 The phase diagram for a system in which A and B react to form a compound C = AB. This diagram resembles two versions of Fig. 8.28 in each half of the diagram. The constituent C is a true compound, not just an equimolar mixture.

(c) Incongruent melting

In some cases the compound C is not stable as a liquid. An example is the alloy Na_2K, which survives only as a solid (Fig. 8.31). Consider what happens as a liquid at a_1 is cooled:

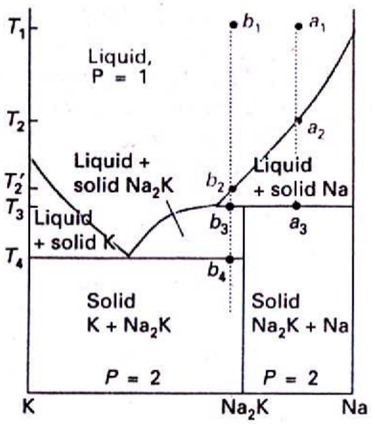
(1) $a_1 \rightarrow a_2$. Some solid Na is deposited, and the remaining liquid is richer in K.
(2) $a_2 \rightarrow$ just below a_3. The sample is now entirely solid, and consists of solid Na and solid Na_2K.

Now consider the isopleth through b_1:

(1) $b_1 \rightarrow b_2$. No obvious change occurs until the phase boundary is reached at b_2 when solid Na begins to deposit.
(2) $b_2 \rightarrow b_3$. Solid Na deposits, but at b_3 a reaction occurs to form Na_2K: this compound is formed by the K atoms diffusing into the solid Na.

At this stage the liquid Na/K mixture is in equilibrium with a little solid Na_2K, but there is still no liquid compound.

(3) $b_3 \rightarrow b_4$. As cooling continues, the amount of solid compound increases until at b_4 the liquid reaches its eutectic composition. It then solidifies to give a two-phase solid consisting of solid K and solid Na_2K.



8.31 The phase diagram for an actual system (sodium and potassium) like that shown in Fig. 8.30, but with two differences. One is that the compound is Na_2K, corresponding to A_2B and not AB as in that illustration. The second is that the compound exists only as the solid, not as the liquid. The transformation of the compound at its melting point is an example of incongruent melting.

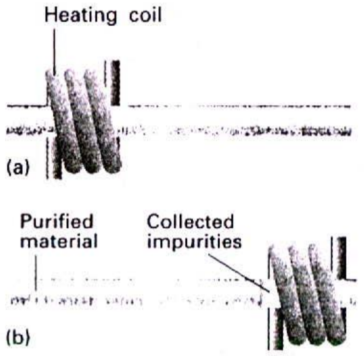
If the solid is reheated, the sequence of events is reversed. No liquid Na_2K forms at any stage because it is too unstable to exist as a liquid. This behaviour is an example of **incongruent melting**, in which a compound melts into its components and does not itself form a liquid phase.

8.7 Ultrapurity and controlled impurity

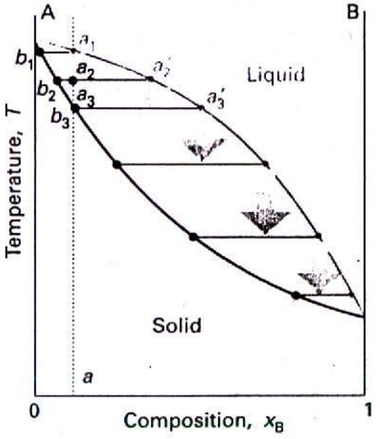
Advances in technology have called for materials of extreme purity. For example, semiconductor devices consist of almost perfectly pure silicon or germanium doped to a precisely controlled extent. For these materials to operate successfully, the impurity level must be kept down to less than 1 ppb (1 part in 10^9, which corresponds to a small grain of salt in 5 tons of sugar).

In the technique of zone refining the sample is in the form of a narrow cylinder. This cylinder is heated in a thin disk-like zone which is swept from one end of the sample to the other. The advancing liquid zone accumulates the impurities as it passes. In practice, a train of hot and cold zones is swept repeatedly from one end to the other (Fig. 8.32). The zone at the end of the sample is the impurity dump: when the heater has gone by, it cools to a dirty solid which can be discarded.

The technique makes use of the non-equilibrium properties of the system. It relies on the impurities being more soluble in the molten sample than in the solid, and sweeps them up by passing a molten zone repeatedly from one end to the other along a sample. The phase diagram in Fig. 8.33 gives some insight into the process. Consider a liquid (this represents the molten zone) on the isopleth through a_1, and let it cool without the entire sample coming to overall equilibrium. If the temperature falls to a_2 a solid of composition b_2 is deposited and the remaining liquid (the zone where the heater has moved on) is at a_2'. Cooling that liquid down an isopleth passing through a_2' deposits solid of composition b_3 and leaves liquid at a_3'. The process continues until the last drop of liquid to solidify is heavily contaminated with B. There is plenty of everyday evidence that impure liquids freeze in this way. For example, an ice cube is clear near the surface but misty in the core: the water used to make ice normally contains dissolved air; freezing proceeds from the outside, and air is accumulated in the



8.32 The procedure for zone refining. (a) Initially, impurities are distributed uniformly along the sample. (b) After a molten zone is passed along the rod, the impurities are more concentrated at the right. In practice, a series of molten zones is passed along the rod from left to right.



8.33 A binary temperature-composition diagram can be used to discuss zone refining, as explained in the text.

retreating liquid phase. It cannot escape from the interior of the cube, and so when that freezes it occludes the air in a mist of tiny bubbles.

A modification of zone refining is zone **levelling**. It is used to introduce controlled amounts of impurity (for example, of indium into germanium). A sample rich in the required dopant is put at the head of the main sample, and made molten. The zone is then dragged repeatedly in alternate directions through the sample, where it deposits a uniform distribution of the impurity.

Checklist of key ideas

Phases, components, and degrees of freedom

8.1 Definitions
- ☐ phase
- ☐ constituent
- ☐ component
- ☐ variance
- ☐ degree of freedom

8.2 The phase rule
- ☐ phase rule (1)
- ☐ application of the phase rule to one-component systems
- ☐ thermal analysis
- ☐ high-pressure studies

Two-component systems

8.3 Vapour pressure diagrams
- ☐ the vapour pressure of a mixture (2,3)
- ☐ the composition of the vapour (5)
- ☐ the total vapour pressure of a mixture (6)
- ☐ the overall composition and the interpretation of phase diagrams
- ☐ isopleth
- ☐ tie line
- ☐ the lever rule (7)

8.4 Temperature–composition diagrams
- ☐ temperature–composition diagram
- ☐ fractional distillation
- ☐ theoretical plate
- ☐ azeotropes and the effect on distillation
- ☐ the behaviour of immiscible liquids
- ☐ steam distillation

8.5 Liquid–liquid phase diagrams
- ☐ partially miscible liquids
- ☐ phase separation and the interpretation of a liquid–liquid phase diagram
- ☐ upper critical solution temperature
- ☐ lower critical solution temperature
- ☐ the interpretation of distillation of partially miscible liquids in terms of phase diagrams

8.6 Liquid–solid phase diagrams
- ☐ the interpretation of solid–liquid phase diagrams
- ☐ eutectic composition
- ☐ eutectic halt
- ☐ cooling curve
- ☐ the effect of reactions on the appearance of phase diagrams
- ☐ incongruent melting

8.7 Ultrapurity and controlled impurity
- ☐ zone refining
- ☐ zone levelling

Further reading

Articles of general interest

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Exercises

8.1 (a) At 90°C, the vapour pressure of methylbenzene is 400 Torr and that of 1,2-dimethylbenzene is 150 Torr. What is the composition of a liquid mixture that boils at 90°C when the pressure is 0.50 atm? What is the composition of the vapour produced?

8.1 (b) At 90°C, the vapour pressure of 1,2-dimethylbenzene is 20 kPa and that of 1,3-dimethylbenzene is 18 kPa. What is the composition of a liquid mixture that boils at 90°C when the pressure is 19 kPa? What is the composition of the vapour produced?

8.2 (a) The vapour pressure of pure liquid A at 300 K is 575 Torr and that of pure liquid B is 390 Torr. These two compounds form ideal liquid and gaseous mixtures. Consider the equilibrium composition of a mixture in which the mole fraction of A in the vapour is 0.350. Calculate the total pressure of the vapour and the composition of the liquid mixture.

8.2 (b) The vapour pressure of pure liquid A at 293 K is 68.8 kPa and that of pure liquid B is 82.1 kPa. These two compounds form ideal liquid and gaseous mixtures. Consider the equilibrium composition of a mixture in which the mole fraction of A in the vapour is 0.612. Calculate the total pressure of the vapour and the composition of the liquid mixture.

8.3 (a) It is found that the boiling point of a binary solution of A and B with $x_A = 0.6589$ is 88°C. At this temperature the vapour pressures of pure A and B are 957.0 Torr and 379.5 Torr, respectively. (a) Is this solution ideal? (b) What is the initial composition of the vapour above the solution?

8.3 (b) It is found that the boiling point of a binary solution of A and B with $x_A = 0.4217$ is 96°C. At this temperature the vapour pressures of pure A and B are 110.1 kPa and 94.93 kPa, respectively. (a) Is this solution ideal? (b) What is the initial composition of the vapour above the solution?

8.4 (a) Dibromoethene (DE, $p^*_{DE} = 172$ Torr at 358 K) and dibromopropene (DP, $p^*_{DP} = 128$ Torr at 358 K) form a nearly ideal solution. If $z_{DE} = 0.60$, what is (a) p_{total} when the system is all liquid, (b) the composition of the vapour when the system is still almost all liquid?

8.4 (b) Benzene and toluene form nearly ideal solutions. At 20°C the vapour pressures of pure benzene and toluene are 74 Torr and 22 Torr, respectively. A solution consisting of 1.00 mol of each component is boiled by reducing the external pressure below the vapour pressure. Calculate (a) the pressure when boiling begins, (b) the composition of each component in the vapour, and (c) the vapour pressure when only a few drops of liquid remain. Assume that the rate of vaporization is low enough for the temperature to remain constant at 20°C.

8.5 (a) The following temperature/composition data were obtained for a mixture of octane (O) and methylbenzene (M) at 760 Torr, where x is the mole fraction in the liquid and y the mole fraction in the vapour at equilibrium.

$\theta/°C$	110.9	112.0	114.0	115.8	117.3	119.0	121.1	123.0
x_M	0.908	0.795	0.615	0.527	0.408	0.300	0.203	0.097
y_M	0.923	0.836	0.698	0.624	0.527	0.410	0.297	0.164

The boiling points are 110.6°C and 125.6°C for M and O, respectively. Plot the temperature/composition diagram for the mixture. What is the composition of the vapour in equilibrium with the liquid of composition (a) $x_M = 0.250$ and (b) $x_O = 0.250$?

8.5 (b) The following temperature/composition data were obtained for a mixture of two liquids A and B at 1.00 atm, where x is the mole fraction in the liquid and y the mole fraction in the vapour at equilibrium.

$\theta/°C$	125	130	135	140	145	150
x_A	0.91	0.65	0.45	0.30	0.18	0.098
y_A	0.99	0.91	0.77	0.61	0.45	0.25

The boiling points are 124°C for A and 155°C for B. Plot the temperature/composition diagram for the mixture. What is the composition of the vapour in equilibrium with the liquid of composition (a) $x_A = 0.50$ and (b) $x_B = 0.33$?

8.6 (a) State the number of components in the following systems. (a) NaH_2PO_4 in water at equilibrium with water vapour but disregarding the fact that the salt is ionized. (b) The same, but taking into account the ionization of the salt.

8.6 (b) State the number of components for a system in which $AlCl_3$ is dissolved in water, noting that hydrolysis and precipitation of $Al(OH)_3$ occur.

8.7 (a) Blue $CuSO_4 \cdot 5H_2O$ crystals release their water of hydration when heated. How many phases and components are present in an otherwise empty heated container?

8.7 (b) Ammonium chloride, NH_4Cl, decomposes when it is heated. (a) How many components and phases are present when the salt is heated in an otherwise empty container? (b) Now suppose that additional ammonia is also present. How many components and phases are present?

8.8 (a) A saturated solution of Na_2SO_4, with excess of the solid, is present at equilibrium with its vapour in a closed vessel. (a) How many phases and components are present? (b) What is the variance (the number of degrees of freedom) of the system? Identify the independent variables.

8.8 (b) Suppose that the solution referred to in Exercise 8.8a is not saturated. (a) How many phases and components are present? (b) What is the variance (the number of degrees of freedom) of the system? Identify the independent variables.

8.9 (a) Draw phase diagrams for the following types of systems. Label the regions and intersections of the diagrams, stating what materials (possibly compounds or azeotropes) are present and whether they are solid, liquid, or gas. (a) One-component, pressure–temperature diagram; liquid density greater than that of solid. (b) Two-component, temperature–composition, solid–liquid diagram; one compound AB formed that melts congruently; negligible solid–solid solubility.

8.9 (b) Draw phase diagrams for the following types of systems. Label the regions and intersections of the diagrams, stating what materials (possibly compounds or azeotropes) are present and whether they are solid, liquid, or gas. (a) Two-component, temperature–composition, solid–liquid diagram; one compound of formula AB_2 that melts incongruently; negligible solid–solid solubility. (b) Two-component, temperature–composition, liquid–vapour diagram; formation of an azeotrope at $x_B = 0.333$; complete miscibility.

8.10 (a) Label the regions of the phase diagram in Fig. 8.34. State what substances (if compounds, give their formulas) exist in each region. Label each substance in each region as solid, liquid, or gas.

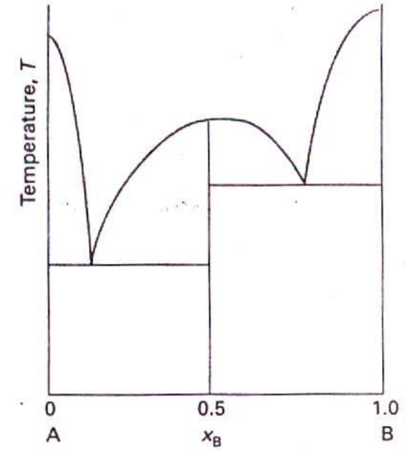


Fig. 8.34

8.10 (b) Label the regions of the phase diagram in Fig. 8.35. State what substances (if compounds, give their formulas) exist in each region. Label each substance in each region as solid, liquid, or gas.

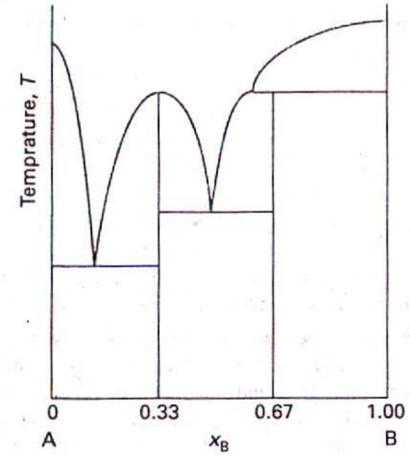


Fig. 8.35

8.11 (a) Methylethyl ether (A) and diborane, B_2H_6 (B), form a compound which melts congruently at 133 K. The system exhibits two eutectics, one at 25 mole per cent B and 123 K and a second at 90 mole per cent B and 104 K. The melting points of pure A and B are 131 K and 110 K, respectively. Sketch the phase diagram for this system. Assume negligible solid–solid solubility.

8.11 (b) Sketch the phase diagram of the system NH_3/N_2H_4 given that the two substances do not form a compound with each other, that NH_3 freezes at −78°C and N_2H_4 freezes at +2°C, and that a eutectic is formed when the mole fraction of N_2H_4 is 0.07 and that the eutectic melts at −80°C.

8.12 (a) Figure 8.36 shows the phase diagram for two partially miscible liquids, which can be taken to be that for water (A) and 2-methyl-1-propanol (B). Describe what will be observed when a mixture of composition $x_B = 0.8$ is heated, at each stage giving the number, composition, and relative amounts of the phases present.

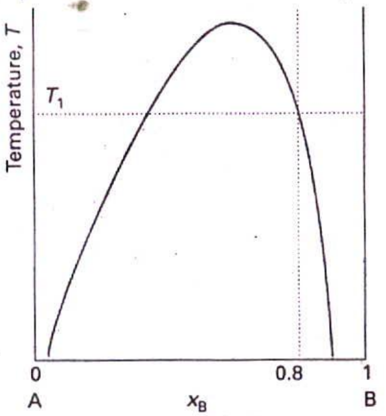


Fig. 8.36

8.12 (b) Figure 8.37 is the phase diagram for silver and tin. Label the regions, and describe what will be observed when liquids of compositions *a* and *b* are cooled to 200 K.

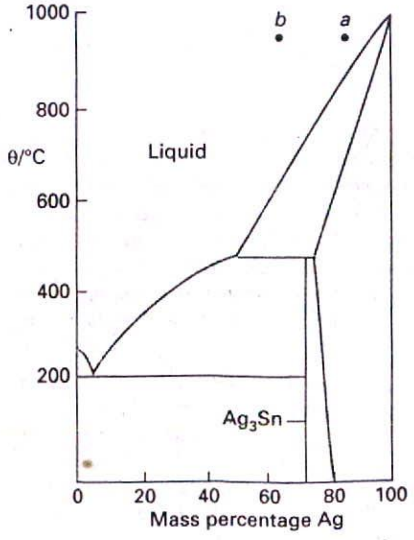


Fig. 8.37

8.13 (a) Indicate on the phase diagram in Fig. 8.38 the feature that denotes incongruent melting. What is the composition of the eutectic mixture and at what temperature does it melt?

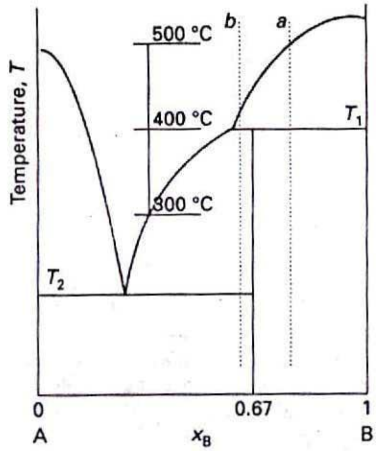


Fig. 8.38

8.13 (b) Indicate on the phase diagram in Fig. 8.39 the feature that denotes incongruent melting. What is the composition of the eutectic mixture and at what temperature does it melt?

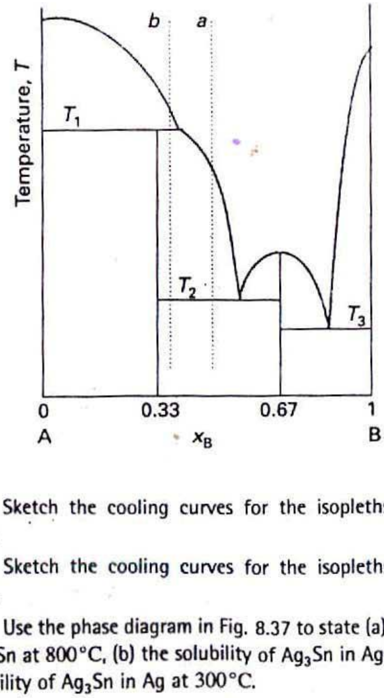


Fig. 8.39

8.14 (a) Sketch the cooling curves for the isopleths *a* and *b* in Fig. 8.38.

8.14 (b) Sketch the cooling curves for the isopleths *a* and *b* in Fig. 8.39.

8.15 (a) Use the phase diagram in Fig. 8.37 to state (a) the solubility of Ag in Sn at 800°C, (b) the solubility of Ag_3Sn in Ag at 460°C, (c) the solubility of Ag_3Sn in Ag at 300°C.

8.15 (b) Use the phase diagram in Fig. 8.38 to state (a) the solubility of B in A at 500°C, (b) the solubility of AB_2 in A at 390°C, (c) the solubility of AB_2 in B at 300°C.

8.16 (a) Figure 8.40 shows the experimentally determined phase diagrams for the nearly ideal solution of hexane and heptane. (a) Label the regions of the diagrams to which phases are present. (b) For a solution containing 1 mol each of hexane and heptane, estimate the vapour pressure at 70°C when vaporization on reduction of the external pressure just begins. (c) What is the vapour pressure of the solution at 70°C when just one drop of liquid remains? (d) Estimate from the figures the mole fraction of hexane in the liquid and vapour phases for the conditions of part b. (e) What are the mole fractions for the conditions of part c? (f) At 85°C and 760 Torr, what are the amounts of substance in the liquid and vapour phases when $z_{\text{Heptane}} = 0.40$?

8.16 (b) Uranium tetrafluoride and zirconium tetrafluoride melt at 1035°C and 912°C, respectively. They form a continuous series of solid solutions with a minimum melting temperature of 765°C and composition $x(ZrF_4) = 0.77$. At 900°C, the liquid solution of composition $x(ZrF_4) = 0.28$ is in equilibrium with a solid solution of composition $x(ZrF_4) = 0.14$. At 850°C the two compositions are 0.87 and 0.90, respectively. Sketch the phase diagram for this system and state what is observed when a liquid of composition $x(ZrF_4) = 0.40$ is cooled slowly from 900°C to 500°C.

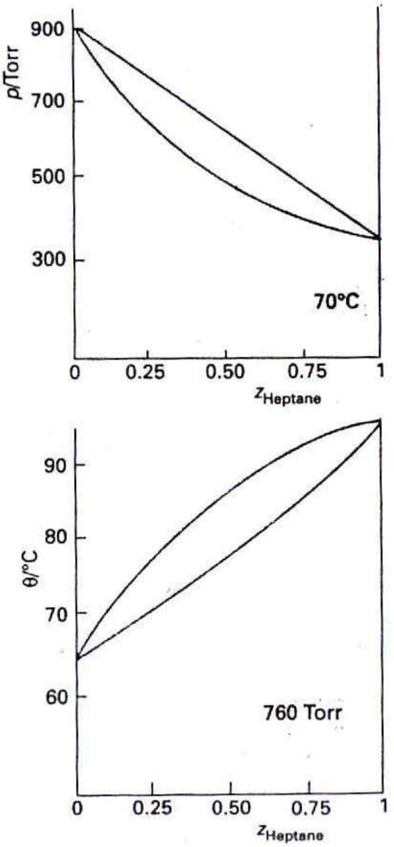


Fig. 8.40

8.17 (a) Methane (melting point 91 K) and tetrafluoromethane (melting point 89 K) do not form solid solutions with each other, and as liquids they are only partially miscible. The upper critical temperature of the liquid mixture is 94 K at $x(CF_4) = 0.43$ and the eutectic temperature is 84 K at $x(CF_4) = 0.88$. At 86 K, the phase in equilibrium with the tetrafluoromethane-rich solution changes from solid methane to a methane-rich liquid. At that temperature, the two liquid solutions that are in mutual equilibrium have the compositions $x(CF_4) = 0.10$ and $x(CF_4) = 0.80$. Sketch the phase diagram.

8.17 (b) Describe the phase changes that take place when a liquid mixture of 4.0 mol B_2H_6 (melting point 131 K) and 1.0 mol CH_3OCH_3 (melting point 135 K) is cooled from 140 K to 90 K. These substances form a compound $(CH_3)_2OB_2H_6$ that melts congruently at 133 K. The system exhibits one eutectic at $x(B_2H_6) = 0.25$ and 123 K and another at $x(B_2H_6) = 0.90$ and 104 K.

8.18 (a) Refer to the information in Exercise 8.17b and sketch the cooling curves for liquid mixtures in which $x(B_2H_6)$ is (a) 0.10, (b) 0.30, (c) 0.50, (d) 0.80, and (e) 0.95.

8.18 (b) Refer to the information in Exercise 8.17a and sketch the cooling curves for liquid mixtures in which $x(CF_4)$ is (a) 0.10, (b) 0.30, (c) 0.50, (d) 0.80, and (e) 0.95.

8.19 (a) Hexane and perfluorohexane show partial miscibility below 22.70°C. The critical concentration at the upper critical temperature is $x = 0.355$, where x is the mole fraction of C_6F_{14}. At 22.0°C the two solutions in equilibrium have $x = 0.24$ and $x = 0.48$, respectively, and at 21.5°C the mole fractions are 0.22 and 0.51. Sketch the phase diagram. Describe the phase changes that occur when perfluorohexane is added to a fixed amount of hexane at (a) 23°C, (b) 22°C.

8.19 (b) Two liquids, A and B, show partial miscibility below 52.4°C. The critical concentration at the upper critical temperature is $x = 0.459$, where x is the mole fraction of A. At 40.0°C the two solutions in equilibrium have $x = 0.22$ and $x = 0.60$, respectively, and at 42.5°C the mole fractions are 0.24 and 0.48. Sketch the phase diagram. Describe the phase changes that occur when B is added to a fixed amount of A at (a) 48°C, (b) 52.4°C.

Problems

Numerical problems

8.1 The compound *p*-azoxyanisole forms a liquid crystal. 5.0 g of the solid was placed in a tube, which was then evacuated and sealed. Use the phase rule to prove that the solid will melt at a definite temperature and that the liquid crystal phase will make a transition to a normal liquid phase at a definite temperature.

8.2 Magnesium oxide and nickel oxide withstand high temperatures. However, they do melt when the temperature is high enough and the behaviour of mixtures of the two is of considerable interest to the ceramics industry. Draw the temperature–composition diagram for the system using the data below, where x is the mole fraction of MgO in the solid and y its mole fraction in the liquid.

$\theta/°C$	1960	2200	2400	2600	2800
x	0	0.35	0.60	0.83	1.00
y	0	0.18	0.38	0.65	1.00

State (a) the melting point of a mixture with $x = 0.30$, (b) the composition and proportion of the phases present when a solid of composition $x = 0.30$ is heated to 2200°C, (c) the temperature at which a liquid of composition $y = 0.70$ will begin to solidify.

8.3 The bismuth–cadmium phase diagram is of interest in metallurgy, and its general form can be estimated from expressions for the depression of freezing point. Construct the diagram using the following data: $T_f(\text{Bi}) = 544.5$ K, $T_f(\text{Cd}) = 594$ K, $\Delta_{\text{fus}}H(\text{Bi}) = 10.88\ \text{kJ mol}^{-1}$, $\Delta_{\text{fus}}H(\text{Cd}) = 6.07\ \text{kJ mol}^{-1}$. The metals are mutually insoluble as solids. Use the phase diagram to state what would be observed when a liquid of composition $x(\text{Bi}) = 0.70$ is cooled slowly from 550 K. What are the relative abundances of the liquid and solid at (a) 460 K and (b) 350 K? Sketch the cooling curve for the mixture.

8.4 Phosphorus and sulfur form a series of binary compounds. The best characterized are P_4S_3, P_4S_7, and P_4S_{10}, all of which melt congruently. Assuming that only these three binary compounds of the two elements exist, (a) draw schematically the P/S phase diagram. Label each region of the diagram with the substance that exists in that region and indicate its phase. Label the horizontal axis as x_S and give the numerical values of x_S that correspond to the compounds. The melting point of pure phosphorus is 44°C and that of pure sulfur is 119°C. (b) Draw, schematically, the cooling curve for a mixture of composition $x_S = 0.28$. Assume that a eutectic occurs at $x_S = 0.2$ and assume negligible solid–solid solubility.

8.5 The table below gives the break and halt temperatures found in the cooling curves of two metals A and B. Construct a phase diagram consistent with the data of these curves. Label the regions of the diagram, stating what phases and substances are present. Give the probable formulas of any compounds that form.

$100x_B$	$\theta_{\text{break}}/°\text{C}$	$\theta_{\text{halt},1}/°\text{C}$	$\theta_{\text{halt},2}/°\text{C}$
0		1100	
10.0	1060	700	
20.0	1000	700	
30.0	940	700	400
40.0	850	700	400
50.0	750	700	400
60.0	670	400	
70.0	550	400	
80.0		400	
90.0	450	400	
100.0		500	

8.6 Consider the phase diagram in Fig. 8.41, which represents a solid–liquid equilibrium. Label all regions of the diagram according to the chemical species that exist in that region and their phases. Indicate the number of species and phases present at the points labelled *b, d, e, f, g,* and *k*. Sketch cooling curves for compositions $x_B = 0.16$, 0.23, 0.57, 0.67, and 0.84.

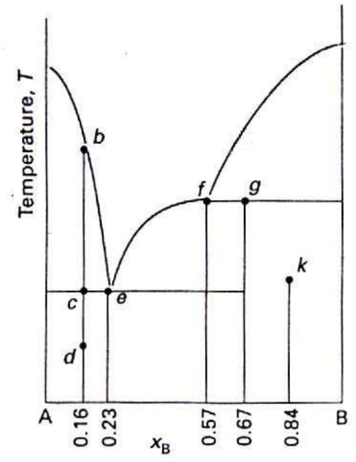


Fig. 8.41

8.7 Solutions of 3-methylphenylamine (MP) were made up in glycerol and then warmed from room temperature. The mixture became turbid at θ_1 and then cleared at θ_2. Plot the phase diagram using the data below, and find the upper and lower critical temperatures.

Mass%	18	20	40	60	80	85
$\theta_1/°\text{C}$	48	18	8	10	19	25
$\theta_2/°\text{C}$	53	90	120	118	83	53

Mass% denotes the mass percentage composition of MP. State what happens as MP is added dropwise to glycerol at 60°C. State the number of phases present at each composition and their relative amounts.

8.8 Sketch the phase diagram for the Mg/Cu system using the following information: $\theta_f(\text{Mg}) = 648\,°\text{C}$, $\theta_f(\text{Cu}) = 1085\,°\text{C}$; two intermetallic compounds are formed with $\theta_f(\text{MgCu}_2) = 800\,°\text{C}$ and $\theta_f(\text{Mg}_2\text{Cu}) = 580\,°\text{C}$; eutectics of mass percentage Mg composition and melting points 10 per cent (690°C), 33 per cent (560°C), and 65 per cent (380°C). A sample of Mg/Cu alloy containing 25 per cent Mg by mass was prepared in a crucible heated to 800°C in an inert atmosphere. Describe what will be observed if the melt is cooled slowly to room temperature. Specify the composition and relative abundances of the phases and sketch the cooling curve.

8.9 Iron(II) chloride (melting point 677°C) and potassium chloride (melting point 776°C) form the compounds KFeCl_3 and K_2FeCl_4 at elevated temperatures. KFeCl_3 melts congruently at 380°C and K_2FeCl_4 melts incongruently at 399°C. Eutectics are formed with compositions $x = 0.38$ (melting point 351°C) and $x = 0.54$ (melting point 393°C), where x is the mole fraction of FeCl_2. The KCl solubility curve intersects the K_2FeCl_4 curve at $x = 0.34$. Sketch the phase diagram. State the phases that are in equilibrium when a mixture of composition $x = 0.36$ is cooled from 400°C to 300°C.

Theoretical problems

8.10 Show that two phases are in thermal equilibrium only if their temperatures are the same.

8.11 Show that two phases are in mechanical equilibrium only if their pressures are equal.

Additional problems supplied by Carmen Giunta and Charles Trapp

8.12 1-Butanol and chlorobenzene form a minimum-boiling azeotropic system. The mole fraction of 1-butanol in the liquid (x) and vapour (y) phases at 1.000 atm is given below for a variety of boiling temperatures (H. Artigas, C. Lafuente, P. Cea, F.M. Royo, and J.S. Urieta, *J. Chem. Eng. Data* **42**, 132 (1997)).

T/K	396.57	393.94	391.60	390.15	389.03	388.66	388.57
x	0.1065	0.1700	0.2646	0.3687	0.5017	0.6091	0.7171
y	0.2859	0.3691	0.4505	0.5138	0.5840	0.6409	0.7070

Pure chlorobenzene boils at 404.86 K. (a) Construct the chlorobenzene-rich portion of the phase diagram from the data. (b) Estimate the temperature at which a solution whose mole fraction of 1-butanol is 0.300 begins to boil. (c) State the compositions and relative proportions of the two phases present after a solution initially 0.300 1-butanol is heated to 393.94 K.

8.13 Carbon dioxide at high pressure is used to separate various compounds in citrus oil. The mole fraction of CO_2 in the liquid (x) and vapour (y) at 323.2 K is given below for a variety of pressures (Y. Iwai, T. Morotomi, K. Sakamoto, Y. Koga, and Y. Arai, *J. Chem. Eng. Data* **41**, 951 (1996)).

p/MPa	3.94	6.02	7.97	8.94	9.27
x	0.2873	0.4541	0.6650	0.7744	0.8338
y	0.9982	0.9980	0.9973	0.9958	0.9922

(a) Plot the portion of the phase diagram represented by these data. (b) State the compositions and relative proportions of the two phases present after an equimolar gas mixture is compressed to 6.02 MPa at 323.2 K.

8.14 An *et al.* investigated the liquid–liquid coexistence curve of *N,N*-dimethylacetamide and heptane (X. An, H. Zhao, F. Fuguo, and W. Shen, *J. Chem. Thermodynamics* **28**, 1221 (1996)). Mole fractions of *N,N*-dimethylacetamide in the upper (x_1) and lower (x_2) phases of a two-phase region are given below as a function of temperature.

T/K	309.820	309.422	309.031	308.006	306.686	304.553	301.803	299.097	296.000	294.534
x_1	0.473	0.400	0.371	0.326	0.293	0.255	0.218	0.193	0.168	0.157
x_2	0.529	0.601	0.625	0.657	0.690	0.724	0.758	0.783	0.804	0.814

(a) Plot the phase diagram. (b) State the proportions and compositions of the two phases that form from mixing 0.750 mol of *N,N*-dimethylacetamide with 0.250 mol of heptane at 296.0 K. To what temperature must the mixture be heated to form a single-phase mixture?

8.15 The following data have been obtained for the liquid–vapour equilibrium compositions of mixtures of nitrogen and oxygen at 100 kPa.

T/K	77.3	78	80	82	84	86	88	90.2
$x(O_2)$	0	10	34	54	70	82	92	100
$y(O_2)$	0	2	11	22	35	52	73	100
$p^*(O_2)$/Torr	154	171	225	294	377	479	601	760

Plot the data on a temperature–composition diagram and determine the extent to which it fits the predictions for an ideal solution by calculating the activity coefficients of O_2 at each composition.

9 Chemical equilibrium

This chapter develops the concept of chemical potential and shows how it can be used to account for the equilibrium composition of chemical reactions. The equilibrium composition corresponds to a minimum in the Gibbs energy plotted against the extent of reaction, and by locating this minimum we establish the relation between the equilibrium constant and the standard Gibbs energy of reaction. The thermodynamic formulation of equilibrium enables us to establish the quantitative effects of changes in pressure and temperature. The final section of the chapter applies the information to three important types of equilibria.

Chemical reactions move towards a dynamic equilibrium in which both reactants and products are present but have no further tendency to undergo net change. In some cases, the concentration of products in the equilibrium mixture is so much greater than the concentration of unchanged reactants that for all practical purposes the reaction is 'complete'. However, in many important cases the equilibrium mixture has significant concentrations of both reactants and products. In this chapter we see how to use thermodynamics to predict the equilibrium composition under any reaction conditions.

Spontaneous chemical reactions

We have seen that the direction of spontaneous change at constant temperature and pressure is towards lower values of the Gibbs energy, G. The idea is entirely general, and in this chapter we apply it to the discussion of reactions.

8.1 The Gibbs energy minimum

We locate the equilibrium composition of a reaction mixture by calculating the Gibbs energy of the reaction mixture and identifying the composition that corresponds to minimum G.

(a) The reaction Gibbs energy

We begin with the simplest possible chemical equilibrium: $A \rightleftharpoons B$. Even though this reaction looks trivial, there are many examples of it, such as the isomerization of pentane to 2-methylbutane and the conversion of L-alanine to D-alanine. Suppose an infinitesimal amount $d\xi$ of A turns into B, then the change in the amount of A present is $dn_A = -d\xi$ and the change in the amount of B present is $dn_B = +d\xi$. The quantity ξ is called the **extent of reaction**; it has the dimensions of amount of substance, and is reported in moles. When the extent of reaction changes by a finite amount $\Delta\xi$, the amount of A present changes from $n_{A,0}$ to $n_{A,0} - \Delta\xi$ and the amount of B changes from $n_{B,0}$ to $n_{B,0} + \Delta\xi$. So, if initially 2.0 mol A is present and we wait until $\Delta\xi = 1.5$ mol, the amount of A remaining will be 0.5 mol.

The reaction Gibbs energy, $\Delta_r G$, is defined as the slope of the graph of the Gibbs energy plotted against the extent of reaction:

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} \qquad [1]$$

Although Δ normally signifies a *difference* in values, Δ_r signifies a *derivative*, the slope of G with respect to ξ. However, to see that there is a close relationship with the normal usage, suppose the reaction advances by $d\xi$. The corresponding change in Gibbs energy is

$$dG = \mu_A \, dn_A + \mu_B \, dn_B = -\mu_A \, d\xi + \mu_B \, d\xi = (\mu_B - \mu_A)\, d\xi$$

This equation can be reorganized into

$$\left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \mu_B - \mu_A$$

That is,

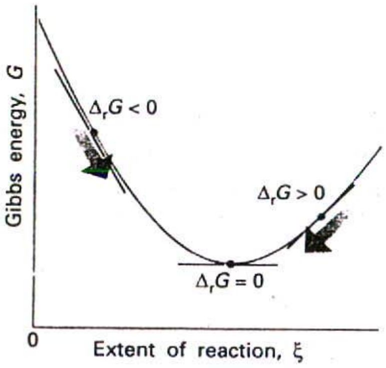
$$\Delta_r G = \mu_B - \mu_A \qquad (2)$$

We see that $\Delta_r G$ can be interpreted as the difference between the chemical potentials of the reactants and products *at the composition of the reaction mixture*.

Because the chemical potentials vary with composition, the slope of the plot of Gibbs energy against extent of reaction changes as the reaction proceeds. Moreover, because the reaction runs in the direction of decreasing G (that is, down the slope of G versus ξ), we see from eqn 2 that the reaction $A \rightarrow B$ is spontaneous when $\mu_A > \mu_B$, whereas the reverse reaction is spontaneous when $\mu_B > \mu_A$. The slope is zero, and the reaction is spontaneous in neither direction, when

$$\Delta_r G = 0 \qquad (3)$$

This condition occurs when $\mu_B = \mu_A$ (Fig. 9.1). It follows that, if we can find the composition of the reaction mixture that ensures $\mu_B = \mu_A$, then we can identify the composition of the reaction mixture at equilibrium.



9.1 As the reaction advances (represented by motion from left to right along the horizontal axis) the slope of the Gibbs energy changes. Equilibrium corresponds to zero slope, at the foot of the valley.

(b) Exergonic and endergonic reactions

The spontaneity of a reaction at constant temperature and pressure is expressed by the reaction Gibbs energy:

If $\Delta_r G < 0$, the forward reaction is spontaneous.
If $\Delta_r G > 0$, the reverse reaction is spontaneous.
If $\Delta_r G = 0$, the reaction is at equilibrium.

Reactions for which $\Delta_r G < 0$ are called **exergonic** (from the Greek words for work-producing). The name signifies that, because they are spontaneous, they can be used to drive other processes, such as other reactions, or used to do non-expansion work. Reactions for which $\Delta_r G > 0$ are called endergonic (signifying work-consuming). They can be made to occur only by doing work on them (like electrolysing water to reverse its spontaneous formation reaction). Reactions at equilibrium are spontaneous in neither direction: they are neither exergonic nor endergonic.

(c) Perfect gas equilibria

When A and B are perfect gases we can use eqn 5.20 ($\mu = \mu^{\ominus} + RT \ln p$, with p interpreted as $p/p^{\ominus}$) to write

$$\begin{aligned}\Delta_r G &= \mu_B - \mu_A \\ &= (\mu_B^{\ominus} + RT \ln p_B) - (\mu_A^{\ominus} + RT \ln p_A) \\ &= \Delta_r G^{\ominus} + RT \ln \left(\frac{p_B}{p_A}\right)\end{aligned} \tag{4}$$

If we denote the ratio of partial pressures by Q, we obtain

$$\Delta_r G = \Delta_r G^{\ominus} + RT \ln Q \qquad Q = \frac{p_B}{p_A} \tag{5}$$

The ratio Q is an example of a **reaction quotient.** It ranges from 0 (pure A) to infinity (pure B). The **standard reaction Gibbs energy, $\Delta_r G^{\ominus}$,** is defined (like the standard reaction enthalpy) as the difference in the standard molar Gibbs energies of the reactants and products. For our reaction

$$\Delta_r G^{\ominus} = G^{\ominus}_{B,m} - G^{\ominus}_{A,m} \tag{6}$$

In Section 4.7 we saw that the difference in standard molar Gibbs energies of the products and reactants is equal to the difference in their standard Gibbs energies of formation, so in practice we calculate $\Delta_r G^{\ominus}$ from

$$\Delta_r G^{\ominus} = \Delta_f G^{\ominus}(B) - \Delta_f G^{\ominus}(A) \tag{7}^{\circ}$$

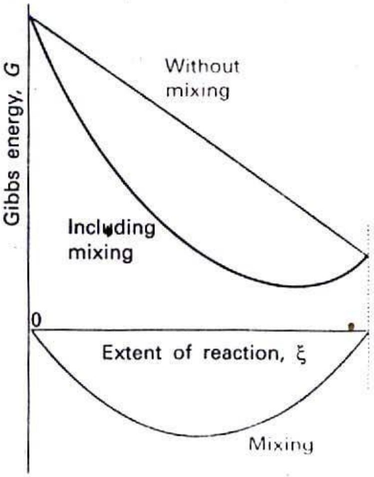
At equilibrium $\Delta_r G = 0$. The ratio of partial pressures at equilibrium is denoted K, and eqn 5 becomes

$$0 = \Delta_r G^{\ominus} + RT \ln K$$

which rearranges to

$$RT \ln K = -\Delta_r G^{\ominus} \qquad K = \left(\frac{p_B}{p_A}\right)_{\text{equilibrium}} \tag{8}^{\circ}$$

This relation is a special case of one of the most important equations in chemical thermodynamics: it is the link between tables of thermodynamic data, such as those in the *Data section* at the end of this volume, and the chemically important equilibrium constant, K.



9.2 If the mixing of reactants and products is ignored, the Gibbs energy changes linearly from its initial value (pure reactants) to its final value (pure products) and the slope of the line is $\Delta_r G^{\ominus}$. However, as products are produced, there is a further contribution to the Gibbs energy arising from their mixing (lowest curve). The sum of the two contributions has a minimum. That minimum corresponds to the equilibrium composition of the system.

Molecular interpretation 9.1 In molecular terms, the minimum in the Gibbs energy, which corresponds to $\Delta_r G = 0$, stems from the Gibbs energy of mixing of the two gases. Hence, an important contribution to the position of chemical equilibrium is the mixing of the products with the reactants as the products are formed.

Consider the hypothetical reaction in which the A molecules change to B molecules without mingling together. Then the Gibbs energy of the system would change from $G^{\ominus}(A)$ to $G^{\ominus}(B)$ in proportion to the amount of B that had been formed, and the slope of the plot of G against the extent of reaction would be constant and equal to $\Delta_r G^{\ominus}$ at all stages of the reaction (Fig. 9.2). However, in fact the newly produced B molecules mix with the surviving

A molecules. We have seen that the contribution of a mixing process to the change in Gibbs energy (eqn 7.17) is

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

This expression makes a U-shaped contribution to the total change in Gibbs energy. As can be seen from the illustration, there is now a minimum in the Gibbs energy, and its position corresponds to the equilibrium composition of the reaction mixture.

We see from eqn 8 that, when $\Delta_r G^\ominus > 0$, $K < 1$. Therefore, at equilibrium the partial pressure of A exceeds that of B, which means that the reactant A is favoured in the equilibrium. When $\Delta_r G^\ominus < 0$, $K > 1$, so at equilibrium the partial pressure of B exceeds that of A. Now the product B is favoured in the equilibrium.

(d) The general case of a reaction

The argument that led to eqn 8 can easily be extended to a general reaction. First, we need to generalize the concept of extent of reaction. We define ξ so that, if the change in it is $\Delta\xi$, then the change in the amount of any species J is $\nu_J\Delta\xi$, where ν_J is the stoichiometric number of J in the chemical equation.[1]

Illustration

Consider the reaction

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \tag{9}$$

The stoichiometric numbers are $\nu_{N_2} = -1$, $\nu_{H_2} = -3$, and $\nu_{NH_3} = +2$. Therefore, if initially there is 10 mol N_2 present, then, when the extent of reaction changes from $\xi = 0$ to $\xi = 1$ mol so that $\Delta\xi = +1$ mol, the amount of N_2 changes from 10 mol to 9 mol. All the N_2 has been consumed when $\xi = 10$ mol. When $\Delta\xi = 1$ mol, the amount of H_2 changes by $-3 \times (1\text{ mol}) = -3$ mol and the amount of NH_3 changes by $+2 \times (1\text{ mol}) = +2$ mol.

The reaction Gibbs energy, $\Delta_r G$, is defined in the same way as before, eqn 1. In the *Justification* below, we show that the Gibbs energy of reaction can always be written

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q \tag{10}$$

with the standard reaction Gibbs energy calculated from

$$\Delta_r G^\ominus = \sum_{\text{Products}} \nu\Delta_f G^\ominus - \sum_{\text{Reactants}} \nu\Delta_f G^\ominus \tag{11}$$

or, more formally,

$$\Delta_r G^\ominus = \sum_J \nu_J \Delta_f G^\ominus(J) \tag{12}$$

The reaction quotient, Q, has the form

$$Q = \frac{\text{activities of products}}{\text{activities of reactants}} \tag{13}$$

with each species raised to the power given by its stoichiometric coefficient. More formally, to write the general expression for Q we introduce the symbol $\prod$ to denote the product of what follows it (just as $\sum$ denotes the sum), and write

$$Q = \prod_J a_J^{\nu_J} \tag*{[14]}$$

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[1] Recall that stoichiometric numbers are positive for products and negative for reactants.

Because reactants have negative stoichiometric numbers, they automatically appear as the denominator when the product is written out explicitly. Recall from Table 7.3 that, for pure solids and liquids, the activity is 1, so such substances make no contribution to Q even though they may appear in the chemical equation. For a gas, $a_J = f_J/p^\ominus$, where f_J is its fugacity. For a perfect gas, $f_J = p_J$, the partial pressure of J.

Justification 9.1

Consider the reaction

$$2\mathrm{A} + 3\mathrm{B} \longrightarrow \mathrm{C} + 2\mathrm{D}$$

When the reaction advances by $d\xi$, the amounts of reactants and products change as follows:

$$dn_\mathrm{A} = -2d\xi \qquad dn_\mathrm{B} = -3d\xi \qquad dn_\mathrm{C} = +d\xi \qquad dn_\mathrm{D} = +2d\xi$$

and in general $dn_J = \nu_J\, d\xi$. The resulting infinitesimal change in the Gibbs energy at constant temperature and pressure is

$$\begin{aligned} dG &= \mu_\mathrm{C}\, dn_\mathrm{C} + \mu_\mathrm{D}\, dn_\mathrm{D} + \mu_\mathrm{A}\, dn_\mathrm{A} + \mu_\mathrm{B}\, dn_\mathrm{B} \\ &= (\mu_\mathrm{C} + 2\mu_\mathrm{D} - 2\mu_\mathrm{A} - 3\mu_\mathrm{B})\, d\xi \end{aligned}$$

The general form of this expression is

$$dG = \left(\sum_J \nu_J \mu_J\right) d\xi \qquad (15)$$

It follows that

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} = -2\mu_\mathrm{A} - 3\mu_\mathrm{B} + \mu_\mathrm{C} + 2\mu_\mathrm{D} \qquad (16)$$

To make further progress, we note that the chemical potential of a species J is related to its activity by

$$\mu_J = \mu_J^\ominus + RT \ln a_J$$

When this expression is substituted into eqn 16 we obtain eqn 10 with

$$Q = \frac{a_\mathrm{C} a_\mathrm{D}^2}{a_\mathrm{A}^2 a_\mathrm{B}^3}$$

which is a special case of eqn 14.

Now we conclude the argument based on eqn 10. At equilibrium, the slope of G is zero: $\Delta_r G = 0$. The activities then have their equilibrium values, and we can write

$$K = \left(\frac{a_\mathrm{C} a_\mathrm{D}^2}{a_\mathrm{A}^2 a_\mathrm{B}^3}\right)_{\text{equilibrium}}$$

and in general

$$K = \left(\prod_J a_J^{\nu_J}\right)_{\text{equilibrium}} \qquad [17]$$

These expressions have the same form as Q, eqn 14, but are evaluated using equilibrium activities. From now on, we shall not write the 'equilibrium' subscript explicitly, and will rely on the context to make it clear that for K we use equilibrium values and for Q we use the values at the specified stage of the reaction.

An equilibrium constant K expressed in terms of activities (or fugacities) is called a **thermodynamic equilibrium constant.** Note that, because activities are dimensionless numbers, the thermodynamic equilibrium constant is also dimensionless. In elementary applications, the activities that occur in eqn 17 are often replaced by the numerical values of molalities or molar concentrations, and fugacities are replaced by partial pressures. In either case, the resulting expressions are only approximations. The approximation is particularly severe for electrolyte solutions, for in them activity coefficients differ from 1 even in very dilute solutions.

At this point we set $\Delta_r G = 0$ in eqn 10 and replace Q by K. We immediately obtain

$$RT \ln K = -\Delta_r G^{\ominus} \tag{18}$$

This is an exact and highly important thermodynamic relation, for it enables us to predict the equilibrium constant of any reaction from tables of thermodynamic data, and hence to predict the equilibrium composition of the reaction mixture.[2]

Example 9.1 Calculating an equilibrium constant

Calculate the equilibrium constant for the ammonia synthesis reaction, eqn 9, at 298 K and show how K is related to the partial pressures of the species at equilibrium when the overall pressure is low enough for the gases to be treated as perfect.

Method Calculate the standard reaction Gibbs energy from eqn 11 and convert it to the value of the equilibrium constant by using eqn 18. The expression for the equilibrium constant is obtained from eqn 17 (or via eqn 13) and, because the gases are taken to be perfect, we replace each fugacity by a partial pressure.

Answer The standard Gibbs energy of the reaction is

$$\begin{aligned}\Delta_r G^{\ominus} &= 2\Delta_f G^{\ominus}(\mathrm{NH_3, g}) - \{\Delta_f G^{\ominus}(\mathrm{N_2, g}) + 3\Delta_f G^{\ominus}(\mathrm{H_2, g})\}\\ &= 2\Delta_f G^{\ominus}(\mathrm{NH_3, g}) = 2\times(-16.5\ \mathrm{kJ\,mol^{-1}})\end{aligned}$$

Then, because $RT = 2.48\ \mathrm{kJ\,mol^{-1}}$,

$$\ln K = -\frac{2\times(-16.5\ \mathrm{kJ\,mol^{-1}})}{2.48\ \mathrm{kJ\,mol^{-1}}} = 13.3$$

Hence, $K = 6.0\times 10^5$. This result is thermodynamically exact. The thermodynamic equilibrium constant for the reaction is

$$K = \frac{a_{\mathrm{NH_3}}^2}{a_{\mathrm{N_2}}a_{\mathrm{H_2}}^3} = \frac{f_{\mathrm{NH_3}}^2 p^{\ominus 2}}{f_{\mathrm{N_2}}f_{\mathrm{H_2}}^3}$$

and this ratio has exactly the value we have just calculated. However, at low overall pressures, when fugacities can be replaced by partial pressures, an approximate form of the equilibrium constant is

$$K = \frac{p_{\mathrm{NH_3}}^2 p^{\ominus 2}}{p_{\mathrm{N_2}}p_{\mathrm{H_2}}^3}$$

Self-test 9.1 Evaluate the equilibrium constant for $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ at 298 K.

[$K = 0.15$]

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[2] In Chapter 20 we shall see that the right-hand side may be expressed in terms of spectroscopic data; so this expression also provides a link between spectroscopy and equilibrium composition.

Example 9.2 Estimating the degree of dissociation at equilibrium

The standard Gibbs energy of reaction for the decomposition $H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$ is $+118.08\ \mathrm{kJ\,mol^{-1}}$ at 2300 K. What is the degree of dissociation of H_2O at 2300 K and 1.00 bar?

Method The equilibrium constant is obtained from the standard Gibbs energy of reaction by using eqn 18, so the task is to relate the degree of dissociation, α, to K and then to find its numerical value. Proceed by expressing the equilibrium compositions in terms of α, and solve for α in terms of K. Because the standard Gibbs energy of reaction is large and positive, we can anticipate that K will be small, and hence that $\alpha \ll 1$, which opens the way to making approximations to obtain its numerical value.

Answer The equilibrium constant is obtained from eqn 18 in the form

$$\ln K = -\frac{\Delta_r G^\ominus}{RT} = -\frac{118.08 \times 10^3\ \mathrm{J\,mol^{-1}}}{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (2300\ \mathrm{K})} = -6.175$$

It follows that $K = 2.08 \times 10^{-3}$. The equilibrium composition can be expressed in terms of α by drawing up the following table:

	H_2O	H_2	O_2
Initial amount	n	0	0
Change to reach equilibrium	$-\alpha n$	$+\alpha n$	$+\frac{1}{2}\alpha n$
Amount at equilibrium	$(1-\alpha)n$	αn	$\frac{1}{2}\alpha n$
Mole fraction	$\frac{1-\alpha}{1+\frac{1}{2}\alpha}$	$\frac{\alpha}{1+\frac{1}{2}\alpha}$	$\frac{\frac{1}{2}\alpha}{1+\frac{1}{2}\alpha}$
Partial pressure	$\frac{(1-\alpha)p}{1+\frac{1}{2}\alpha}$	$\frac{\alpha p}{1+\frac{1}{2}\alpha}$	$\frac{\frac{1}{2}\alpha p}{1+\frac{1}{2}\alpha}$

The equilibrium constant is therefore

$$K = \frac{p_{H_2}p_{O_2}^{1/2}}{p_{H_2O}} = \frac{\alpha^{3/2}p^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$$

In this expression, we have written p in place of $p/p^\ominus$, to keep the notation simple. Now make the approximation that $\alpha \ll 1$, and hence obtain

$$K \approx \frac{\alpha^{3/2}p^{1/2}}{\sqrt{2}}$$

Under the stated conditions, $p = 1.00$ (that is, $p/p^\ominus = 1.00$), so

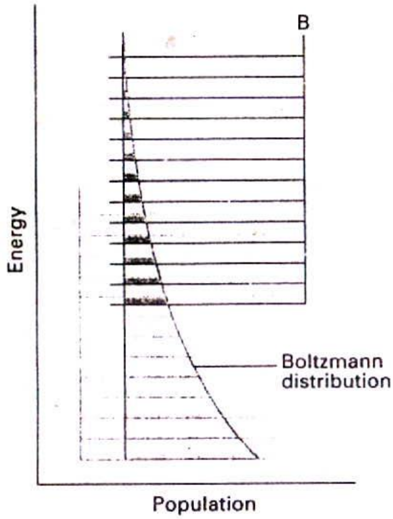
$$\alpha \approx (\sqrt{2}K)^{2/3} = 0.0205$$

That is, about 2 per cent of the water has decomposed.

Comment Always check that the approximation is consistent with the final answer. In this case $\alpha \ll 1$, in accord with the original assumption.

Self-test 9.2 Given that the standard Gibbs energy of reaction at 2000 K is $+135.2\ \mathrm{kJ\,mol^{-1}}$ for the same reaction, suppose that steam at 200 kPa is passed through a furnace tube at that temperature. Calculate the mole fraction of O_2 present in the output gas stream.

[0.00221]



9.3 The Boltzmann distribution of populations over the energy levels of two species A and B with similar densities of energy levels; the reaction A → B is endothermic in this example. The bulk of the population is associated with the species A, so that species is dominant at equilibrium.

(e) The relation between equilibrium constants

The only remaining problem is to express the thermodynamic equilibrium constant in terms of the mole fractions, x_J, or molalities, b_J, of the species. To do so, we need to know the activity coefficients, and then to use $a_J = \gamma_J x_J$ or $a_J = \gamma_J b_J/b^{\ominus}$ (recalling that the activity coefficients depend on the choice). For example, in the latter case, for an equilibrium of the form $A + B \rightleftharpoons C + D$, where all four species are solutes, we write

$$K = \frac{a_C a_D}{a_A a_B} = \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \times \frac{b_C b_D}{b_A b_B} = K_\gamma K_b \qquad (19)$$

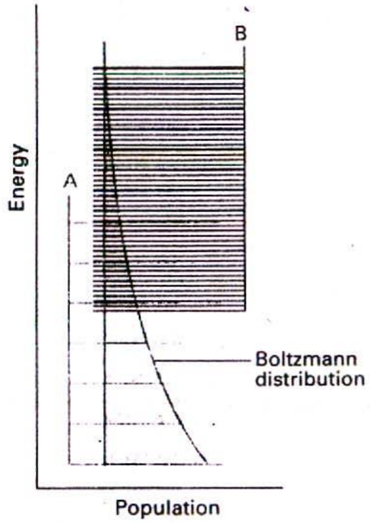
The activity coefficients must be evaluated at the equilibrium composition of the mixture, which may involve a complicated calculation, because the latter is known only if the equilibrium composition is already known. In elementary applications, and to begin the iterative calculation of the concentrations in a real example, the assumption is often made that the activity coefficients are all so close to 1 or they cancel so that $K_\gamma = 1$. Then we obtain the result widely used in elementary chemistry that $K \approx K_b$, and equilibria are discussed in terms of molalities (or molar concentrations) themselves. In Chapter 10 we shall see a way of making better estimates of activity coefficients for equilibria involving ions.

Molecular interpretation 9.2 A deeper insight into the origin and significance of the equilibrium constant can be obtained by considering the Boltzmann distribution of molecules over the available states of a system composed of reactants and products. When atoms can exchange partners, as in a reaction, the available states of the system include arrangements in which the atoms are present in the form of reactants and in the form of products: these arrangements have their characteristic sets of energy levels, but the Boltzmann distribution does not distinguish between their identities, only their energies. The atoms distribute themselves over both sets of energy levels in accord with the Boltzmann distribution (Fig. 9.3). At a given temperature, there will be a specific distribution of populations, and hence a specific composition of the reaction mixture.

It can be appreciated from the illustration that, if the reactants and products both have similar arrays of molecular energy levels, then the dominant species in a reaction mixture at equilibrium will be the species with the lower set of energy levels. However, the fact that the Gibbs energy occurs in the expression is a signal that entropy plays a role as well as energy. Its role can be appreciated by referring to Fig. 9.4. We see that, although the B energy levels lie higher than the A energy levels, in this instance they are much more closely spaced. As a result, their total population may be considerable and B could even dominate in the reaction mixture at equilibrium. Closely spaced energy levels correlate with a high entropy, so in this case we see that entropy effects dominate adverse energy effects. This competition is mirrored in eqn 18, as can be seen most clearly by using $\Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$ and writing it in the form

$$K = e^{-\Delta_r H^{\ominus}/RT} e^{\Delta_r S^{\ominus}/R} \qquad (20)$$

Note that a positive reaction enthalpy results in a lowering of the equilibrium constant (that is, an endothermic reaction can be expected to have an equilibrium composition that favours the reactants). However, if there is positive reaction entropy, then the equilibrium composition may favour products, despite the endothermic character of the reaction.



9.4 Even though the reaction A → B is endothermic, the density of energy levels in B is so much greater than that in A that the population associated with B is greater than that associated with A, so B is dominant at equilibrium.

The response of equilibria to the conditions

There is one type of response that can be dismissed quickly: the equilibrium constant for a reaction is unaffected by the presence of a catalyst or an enzyme (a biological catalyst).

Catalysts increase the rate at which equilibrium is attained but do not affect its position. However, it is important to note that in industry reactions rarely reach equilibrium, partly on account of the rates at which reactants mix. Under these non-equilibrium conditions, catalysts can have some unexpected effects and may change the composition of the reaction mixture.

9.2 How equilibria respond to pressure

The equilibrium constant depends on the value of $\Delta_r G^\ominus$, which is defined at a single, standard pressure. The value of $\Delta_r G^\ominus$, and hence of K, is therefore independent of the pressure at which the equilibrium is actually established. Formally we may express this independence as

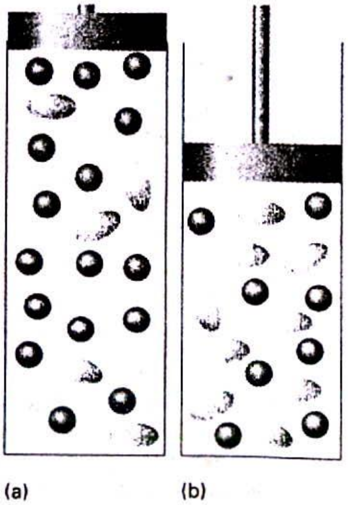
$$\left(\frac{\partial K}{\partial p}\right)_T = 0 \qquad (21)$$

The conclusion that K is independent of pressure does not necessarily mean that the equilibrium composition is independent of the pressure. However, before considering the consequences of pressure, we need to distinguish between the two ways in which pressure may be applied. The pressure within a reaction vessel can be increased by injecting an inert gas into it. Provided the gases are perfect, this addition of gas leaves all the partial pressures of the reacting gases unchanged: the partial pressure of a perfect gas is the pressure it would exert if it were alone in the container, so the presence of another gas has no effect. Put another way, the addition of an inert gas leaves the molar concentrations of the original gases unchanged, as they continue to occupy the same volume. It follows that pressurization by the addition of an inert gas has no effect on the equilibrium composition of the system (provided the gases are perfect). Alternatively, the pressure of the system may be increased by confining the gases to a smaller volume (that is, by compression). Now the partial pressures are changed. Put another way, their molar concentrations are modified because the volume the gases occupy is reduced.

We need to consider the role of compression and understand how changes in partial pressures can be consistent with the general result expressed in eqn 21 that the equilibrium constant itself is independent of the pressure. We shall see that compression can adjust the individual partial pressures of the reactants and products in such a way that, although each one changes, their ratio (as it appears in the equilibrium constant) remains the same. Consider, for instance, the perfect gas equilibrium $A \rightleftharpoons 2B$, for which the equilibrium constant is

$$K = \frac{p_B^2}{p_A p^\ominus} \qquad (22)$$

The right-hand side of this expression remains constant only if an increase in p_A cancels an increase in the *square* of p_B. This relatively steep increase of p_A compared to p_B will occur if the equilibrium composition shifts in favour of A at the expense of B. Then the number of A molecules will increase as the volume of the container is decreased and its partial pressure will rise more rapidly than can be ascribed to a simple change in volume alone (Fig. 9.5).

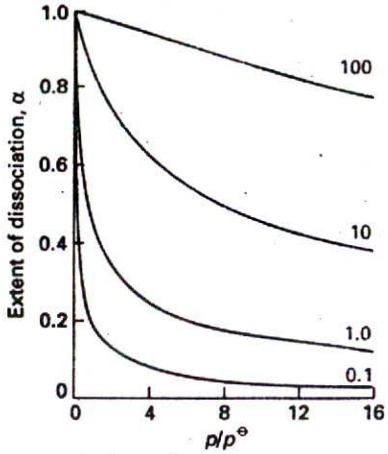


9.5 When a reaction at equilibrium is compressed (from a to b), the reaction responds by reducing the number of molecules in the gas phase (in this case by producing the dimers represented by the ellipses).

The increase in the number of A molecules and the corresponding decrease in the number of B molecules brought about by compression is a special case of a principle proposed by the French chemist (and inventor of oxyacetylene welding) Henri Le Chatelier. Le Chatelier's principle states that:

> **A system at equilibrium, when subjected to a disturbance, responds in a way that tends to minimize the effect of the disturbance.**

The principle implies that, if a system at equilibrium is compressed, then the reaction will adjust so as to minimize the increase in pressure. This it can do by reducing the number of



9.6 The pressure dependence of the degree of dissociation, α, at equilibrium for an $A(g) \rightleftharpoons 2B(g)$ reaction for different values of the equilibrium constant K. The value $\alpha = 0$ corresponds to pure A; $\alpha = 1$ corresponds to pure B.

particles in the gas phase, which implies a shift $A \leftarrow 2B$. The quantitative treatment of the effect of compression set out in the *Justification* below leads to the conclusion that the extent of dissociation, α, of A into 2B is

$$\alpha = \frac{1}{(1 + 4p/K)^{1/2}} \tag{23}$$

where p is to be understood as $p/p^{\ominus}$. This formula shows that, even though K is independent of pressure, the amounts of A and B do depend on pressure (Fig. 9.6). It also shows that, as p is increased, α decreases, in accord with Le Chatelier's principle.

Justification 9.2

Suppose that there is an amount n of A present initially (and no B). At equilibrium the amount of A is $(1 - \alpha)n$ and the amount of B is $2\alpha n$. It follows that the mole fractions present at equilibrium are

$$x_A = \frac{(1-\alpha)n}{(1-\alpha)n + 2\alpha n} = \frac{1-\alpha}{1+\alpha} \qquad x_B = \frac{2\alpha}{1+\alpha}$$

The equilibrium constant for the reaction (with p understood as $p/p^{\ominus}$) is

$$K = \frac{p_B^2}{p_A} = \frac{x_B^2 p^2}{x_A p} = \frac{4\alpha^2 p}{1 - \alpha^2}$$

This expression rearranges into eqn 23.

Illustration

To predict the effect of an increase in pressure on the composition of the ammonia synthesis at equilibrium, eqn 9, we note that the number of gas molecules decreases (from 4 to 2). So, Le Chatelier's principle predicts that an increase in pressure will favour the product. The equilibrium constant is

$$K = \frac{p_{NH_3}^2}{p_{N_2} p_{H_2}^3} = \frac{x_{NH_3}^2 p^2}{x_{N_2} x_{H_2}^3 p^4} = \frac{K_x}{p^2}$$

Therefore, doubling the pressure must increase K_x by a factor of 4 to preserve the value of K.

Self-test 9.3 Predict the effect of a 10-fold pressure increase on the equilibrium composition of the reaction $3N_2(g) + H_2(g) \rightarrow 2N_3H(g)$.

[100-fold increase in K_x]

9.3 The response of equilibria to temperature

Le Chatelier's principle predicts that a system at equilibrium will tend to shift in the endothermic direction if the temperature is raised, for then energy is absorbed as heat. Conversely, an equilibrium can be expected to shift in the exothermic direction if the temperature is lowered, for then the reduction in temperature is opposed. These conclusions can be summarized as follows:

Exothermic reactions: increased temperature favours the reactants.
Endothermic reactions: increased temperature favours the products.

We shall now justify these remarks and see how to express the changes quantitatively.

(a) The van't Hoff equation

The van't Hoff equation, which is derived in the *Justification* below, is an expression for the slope of a plot of the equilibrium constant (specifically, ln K) as a function of temperature. It may be expressed in either of two ways:

$$\text{(a)}\quad \frac{\mathrm{d}\ln K}{\mathrm{d}T}=\frac{\Delta_r H^\ominus}{RT^2}\qquad \text{(b)}\quad \frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)}=-\frac{\Delta_r H^\ominus}{R}\tag{24}$$

Justification 9.3

From eqn 18, we know that

$$\ln K=-\frac{\Delta_r G^\ominus}{RT}$$

Differentiation of ln K with respect to temperature then gives

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T}=-\frac{1}{R}\frac{\mathrm{d}(\Delta_r G^\ominus/T)}{\mathrm{d}T}$$

The differentials are complete because K and $\Delta_r G^\ominus$ depend only on temperature, not on pressure. To develop this equation we use the Gibbs–Helmholtz equation (eqn 5.13) in the form

$$\frac{\mathrm{d}(\Delta_r G^\ominus/T)}{\mathrm{d}T}=-\frac{\Delta_r H^\ominus}{T^2}$$

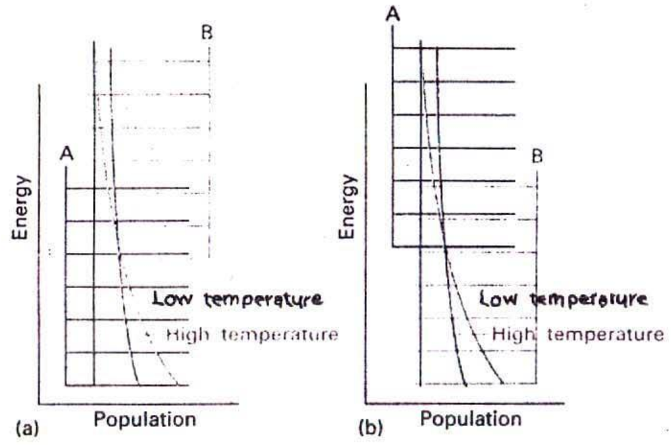
where $\Delta_r H^\ominus$ is the standard reaction enthalpy at the temperature T. Combining the two equations gives the van't Hoff equation, eqn 24*a*. The second form of the equation is obtained by noting that

$$\frac{\mathrm{d}(1/T)}{\mathrm{d}T}=-\frac{1}{T^2},\ \text{so } \mathrm{d}T=-T^2\mathrm{d}(1/T)$$

Equation 24*a* shows that $\mathrm{d}\ln K/\mathrm{d}T<0$ (and therefore that $\mathrm{d}K/\mathrm{d}T<0$) for a reaction that is exothermic under standard conditions ($\Delta_r H^\ominus<0$). A negative slope means that ln K, and therefore K itself, decreases as the temperature rises. Therefore, as asserted above, in the case of an exothermic reaction the equilibrium shifts away from products. The opposite occurs in the case of endothermic reactions.

Some insight into the thermodynamic basis of this behaviour can be found in the expression $\Delta_r G=\Delta_r H-T\Delta_r S$ written in the form $-\Delta_r G/T=-\Delta_r H/T+\Delta_r S$. When the reaction is exothermic, $-\Delta_r H/T$ corresponds to a positive change of entropy of the surroundings, and favours the formation of products. When the temperature is raised, $-\Delta_r H/T$ decreases, and the increasing entropy of the surroundings has a less potent role. As a result, the equilibrium lies less to the right. When the reaction is endothermic, the principal factor is the increasing entropy of the reaction system. The importance of the unfavourable change of entropy of the surroundings is reduced if the temperature is raised (because then $\Delta_r H/T$ is smaller), and the reaction is able to shift towards products.

Molecular interpretation 9.3 The typical arrangement of energy levels for an endothermic reaction is shown in Fig. 9.7a. When the temperature is increased, the Boltzmann distribution adjusts and the populations change as shown. The change corresponds to an increased population of the higher energy states at the expense of the population of the lower energy states. We see that the states that arise from the B molecules become more populated at the expense of the A molecules. Therefore, the total



9.7 The effect of temperature on a chemical equilibrium can be interpreted in terms of the change in the Boltzmann distribution with temperature and the effect of that change in the population of the species. (a) In an endothermic reaction, the population of B increases at the expense of A as the temperature is raised. (b) In an exothermic reaction, the opposite happens.

population of B states increases, and B becomes more abundant in the equilibrium mixture. Conversely, if the reaction is exothermic (Fig. 9.7b), then an increase in temperature increases the population of the A states (which start at higher energy) at the expense of the B states, so the reactants become more abundant.

Example 9.3 Measuring a reaction enthalpy

The data below show the temperature variation of the equilibrium constant of the reaction

$$Ag_2CO_3(s) \rightleftharpoons Ag_2O(s) + CO_2(g)$$

Calculate the standard reaction enthalpy of the decomposition.

T/K	350	400	450	500
K	3.98×10^{-4}	1.41×10^{-2}	1.86×10^{-1}	1.48

Method It follows from eqn 24*b* that, provided the reaction enthalpy can be assumed to be independent of temperature, a plot of $-\ln K$ against $1/T$ should be a straight line of slope $\Delta_r H^\ominus/R$.

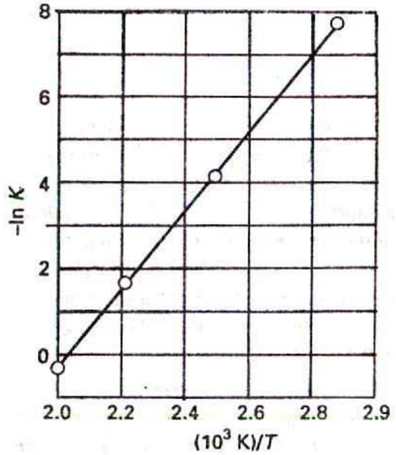
Answer We draw up the following table:

T/K	350	400	450	500
$(10^3\ K)/T$	2.86	2.50	2.22	2.00
$-\ln K$	7.83	4.26	1.68	−0.39

These points are plotted in Fig. 9.8. The slope of the graph is $+9.5 \times 10^3$, so

$$\Delta_r H^\ominus = (+9.5 \times 10^3\ K) \times R = +79\ kJ\ mol^{-1}$$

Comment This is a non-calorimetric method of determining $\Delta_r H^\ominus$. A drawback is that the reaction enthalpy is actually temperature dependent, so the plot is not expected to be perfectly linear. However, the temperature dependence is weak in many cases, so the plot is reasonably straight. In practice, the method is not very accurate, but it is often the only method available.



9.8 When $-\ln K$ is plotted against $1/T$, a straight line is expected with slope equal to $\Delta_r H^\ominus/R$. This is a non-calorimetric method for the measurement of reaction enthalpies.

Self-test 9.4 The equilibrium constant of the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is 4.0×10^{24} at 300 K, 2.5×10^{10} at 500 K, and 3.0×10^{4} at 700 K. Estimate the reaction enthalpy at 500 K.

[-200 kJ mol^{-1}]

(b) The value of K at different temperatures

To find the value of the equilibrium constant at a temperature T_2 in terms of its value K_1 at another temperature T_1, we integrate eqn 24*b* between these two temperatures:

$$\ln K_2 - \ln K_1 = -\frac{1}{R}\int_{1/T_1}^{1/T_2} \Delta_r H^\ominus \, d(1/T) \qquad (25)$$

If we suppose that $\Delta_r H^\ominus$ varies only slightly with temperature over the temperature range of interest, then we may take it outside the integral. It follows that

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (26)$$

Illustration

To estimate the equilibrium constant for the synthesis of ammonia at 500 K from its value at 298 K (6.0×10^5 for the reaction as written in eqn 9) we use the standard reaction enthalpy, which can be obtained from Table 2.6 in the *Data section* because $\Delta_r H^\ominus = 2\Delta_f H^\ominus(NH_3, g)$, and assume that its value is constant over the range of temperatures. Then, with $\Delta_r H^\ominus = -92.2$ kJ mol^{-1}, from eqn 26 we find

$$\ln K_2 = \ln(6.0 \times 10^5) - \frac{(-92.2 \text{ kJ mol}^{-1})}{8.3145 \text{ J K}^{-1} \text{mol}^{-1}}\left(\frac{1}{500 \text{ K}} - \frac{1}{298 \text{ K}}\right)$$
$$= -1.73$$

It follows that $K_2 = 0.18$.

Self-test 9.5 The equilibrium constant for $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ was calculated in Self-test 9.1. Estimate its value at 100°C.

[16]

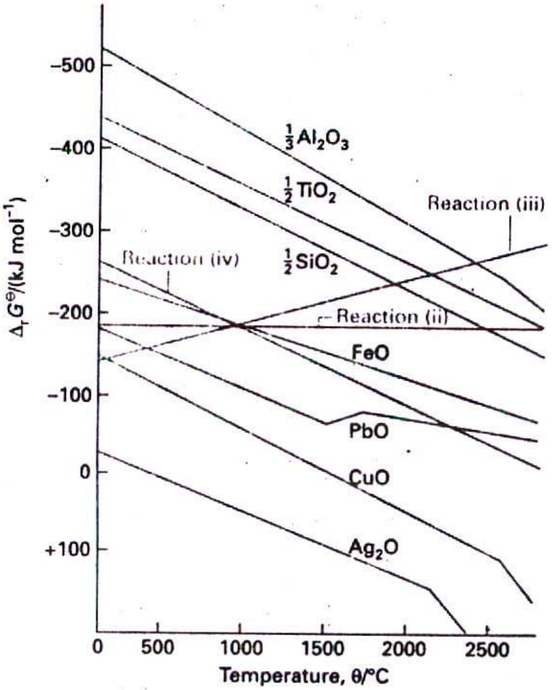
Applications to selected systems

In this section we look at some of the conclusions that can be drawn from the existence of equilibrium constants and from the equation $\Delta_r G^\ominus = -RT \ln K$. Note that $K > 1$ when $\Delta_r G^\ominus < 0$, and products then dominate reactants.

9.4 The extraction of metals from their oxides

Metals can be obtained from their oxides by reduction with carbon or carbon monoxide if any of the equilibria

$$MO(s) + C(s) \rightleftharpoons M(s) + CO(g)$$
$$MO(s) + \tfrac{1}{2}C(s) \rightleftharpoons M(s) + \tfrac{1}{2}CO_2(g)$$
$$MO(s) + CO \rightleftharpoons M(s) + CO_2(g)$$



9.9 An Ellingham diagram for the discussion of metal ore reduction. Note that $\Delta_r G^\ominus$ is most negative at the top of the diagram.

lie to the right (that is, have $K > 1$). As we shall see, these equilibria can be discussed in terms of the thermodynamic functions for the reactions

(i) $M(s) + \frac{1}{2}O_2(g) \longrightarrow MO(s)$
(ii) $\frac{1}{2}C(s) + \frac{1}{2}O_2(g) \longrightarrow \frac{1}{2}CO_2(g)$
(iii) $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$
(iv) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$

The temperature dependences of the standard Gibbs energies of reactions (i)–(iv) depend on the reaction entropy through $d\Delta_r G^\ominus/dT = -\Delta_r S^\ominus$. Because in reaction (iii) there is a net *increase* in the amount of gas, the standard reaction entropy is large and positive; therefore, its $\Delta_r G^\ominus$ decreases sharply with increasing temperature. In reaction (iv), there is a similar net *decrease* in the amount of gas, so $\Delta_r G^\ominus$ increases sharply with increasing temperature. In reaction (ii), the amount of gas is constant, so the entropy change is small and $\Delta_r G^\ominus$ changes only slightly with temperature. These remarks are summarized in Fig. 9.9, which is called an **Ellingham diagram**. Note that $\Delta_r G^\ominus$ decreases upwards!

At room temperature, $\Delta_r G^\ominus$ is dominated by the contribution of the reaction enthalpy ($T\Delta_r S^\ominus$ being relatively small), so the order of increasing $\Delta_r G^\ominus$ is the same as the order of increasing $\Delta_r H^\ominus$ (Al_2O_3 is most exothermic, Ag_2O is least). The standard reaction entropy is similar for all metals because in each case gaseous oxygen is eliminated and a compact, solid oxide is formed. As a result, the temperature dependence of the standard Gibbs energy of oxidation should be similar for all metals, as is shown by the similar slopes of the lines in the diagram. The kinks at high temperatures correspond to the evaporation of the metals; less pronounced kinks occur at the melting temperatures of the metals and the oxides.

Successful reduction of the oxide depends on the outcome of the competition of the carbon for the oxygen bound to the metal. The standard Gibbs energies for the reductions can be expressed in terms of the standard Gibbs energies for the reactions above:

$$\begin{array}{llll} \mathrm{MO(s)} + \mathrm{C(s)} & \longrightarrow \mathrm{M(s)} + \mathrm{CO(g)} & \Delta_r G^\ominus = \Delta_r G^\ominus(\mathrm{iii}) - \Delta_r G^\ominus(\mathrm{i}) \\ \mathrm{MO(s)} + \tfrac{1}{2}\mathrm{C(s)} & \longrightarrow \mathrm{M(s)} + \tfrac{1}{2}\mathrm{CO_2(g)} & \Delta_r G^\ominus = \Delta_r G^\ominus(\mathrm{ii}) - \Delta_r G^\ominus(\mathrm{i}) \\ \mathrm{MO(s)} + \mathrm{CO(g)} & \longrightarrow \mathrm{M(s)} + \mathrm{CO_2(g)} & \Delta_r G^\ominus = \Delta_r G^\ominus(\mathrm{iv}) - \Delta_r G^\ominus(\mathrm{i}) \end{array}$$

The equilibrium lies to the right if $\Delta_r G^\ominus < 0$. This is the case when the line for reaction (i) lies below (is more positive than) the line for one of the reactions (ii) to (iv).

The spontaneity of a reduction at any temperature can be predicted simply by looking at the diagram: a metal oxide is reduced by any carbon reaction lying above it, because the overall reaction then has $\Delta_r G^\ominus < 0$. For example, CuO can be reduced to Cu at any temperature above room temperature. Even in the absence of carbon, Ag_2O decomposes when heated above 200°C because then the standard Gibbs energy for reaction (i) becomes positive (and the reverse reaction is then spontaneous). On the other hand, Al_2O_3 is not reduced by carbon until the temperature has been raised to above 2300°C.

9.5 Acids and bases

One of the most important examples of chemical equilibrium is the one that exists when acids and bases are present in solution. According to the **Brønsted–Lowry classification**:

An acid is a proton donor; a base is a proton acceptor.

These definitions make no mention of the solvent (and apply even if no solvent is present); however, by far the most important medium is aqueous solution, and we confine our attention to that. One of the properties of central interest in aqueous solutions of acids and bases is the **pH**, which is defined as

$$\mathrm{pH} = -\log a_{\mathrm{H_3O^+}} \qquad [27]$$

where H_3O^+ is the hydronium ion, a representation of the state of the proton in aqueous solution. At low concentrations, the activity of hydronium ions is approximately equal to their molality and molar concentration, so a determination of pH is an indication of hydronium ion concentration. However, many thermodynamic observables depend on pH itself, and there is no need to make this approximation and interpretation.

(a) Acid–base equilibria in water

An acid HA takes part in the following proton transfer equilibrium in water:

$$\mathrm{HA(aq)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{H_3O^+(aq)} + \mathrm{A^-(aq)} \qquad K = \frac{a_{\mathrm{H_3O^+}} a_{\mathrm{A^-}}}{a_{\mathrm{HA}} a_{\mathrm{H_2O}}} \qquad (28)$$

In this expression, A^- is the conjugate base of the acid. If we confine attention to dilute solutions, the activity of water is close to 1 (the value for pure water), and the equilibrium can be expressed in terms of the **acidity constant**, K_a:

$$K_a = \frac{a_{\mathrm{H_3O^+}} a_{\mathrm{A^-}}}{a_{\mathrm{HA}}} \qquad [29]$$

When it simplifies the discussion, we shall make the approximations of replacing the activities in acidity constants by the numerical values of the molar concentrations and writing

$$K_a \approx \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \qquad \{30\}$$

where (as indicated by the equation label $\{\cdots\}$) [J] should be understood as [J]/(mol L^{-1}). The approximation $a_J \approx [J]$ is legitimate only if *all* the ions are present at low concentration, not merely the ions of interest, because (as we shall see quantitatively in Section 10.2) all ions contribute to the departures from ideality. Concentrations must be very low for this approximation to be permissible; even for a 10^{-3} M solution of a 1:1 electrolyte in water at 25 °C, activity coefficients are about 0.96, and their neglect introduces an error approaching 10 per cent into the interpretation of equilibrium constants. When concentrations are not low enough for concentrations to be used, activity coefficients can be found from tables (or estimated from the equations derived in Section 10.2).

It is common to report values of K_a in terms of its negative logarithm, pK_a:

$$pK_a = -\log K_a \qquad [31]$$

A high value of pK_a signifies a very small value of K_a (because $K_a = 10^{-pK_a}$) and hence a very weak acid. We shall see that the use of pK_a in place of K_a simplifies the appearance of a number of equations. This simplification stems from the fact that the K_a of the proton transfer equilibrium is related to the standard Gibbs energy of the reaction by

$$\Delta_r G^\ominus = -RT \ln K_a = (RT \ln 10) \times pK_a \qquad (32)$$

Hence, manipulations of pK_a are in fact manipulations of $\Delta_r G^\ominus$ in disguise.

For a base B in water, the characteristic proton transfer equilibrium is

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq) \qquad K = \frac{a_{HB^+}a_{OH^-}}{a_B a_{H_2O}}$$

In this expression, HB^+ is the **conjugate acid** of the base B. In dilute solutions, the activity of water is 1, and we can express this equilibrium in terms of the **basicity constant**, K_b:

$$K_b = \frac{a_{HB^+}a_{OH^-}}{a_B} \qquad [33]$$

Although the basicity constant can be used to assess the strength of a base, it is common to express proton transfer equilibria involving a base in terms of its conjugate acid:

$$HB^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + B(aq) \qquad K_a = \frac{a_{H_3O^+}a_B}{a_{HB^+}}$$

As may be verified by multiplying the expressions for K_a and K_b together, the acidity constant of the conjugate acid HB^+ is related to the basicity constant of the base B by

$$K_a K_b = K_w \qquad (34)$$

where K_w is the **autoprotolysis constant** of water:

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad K_w = a_{H_3O^+}a_{OH^-} \qquad [35]$$

At 25 °C, $K_w = 1.008 \times 10^{-14}$ ($pK_w = 14.00$), showing that only a few of the water molecules are ionized. If we introduce $pOH = -\log a_{OH^-}$ by analogy with pH, then it follows that

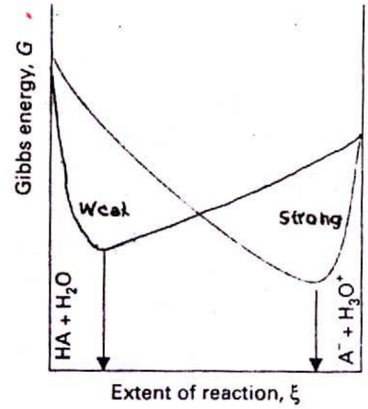
$$pK_w = pH + pOH \qquad (36)$$

Because the molar concentrations of H_3O^+ and OH^- are equal in pure water, it further follows that, for pure water at 25 °C,

$$pH = \tfrac{1}{2}pK_w \approx 7.00 \qquad (37)$$

(b) pH calculations

The calculations of the pH of solutions of acids and bases are fully treated in introductory chemistry courses, and this section is a review of that material. For a strong acid (one that is



9.10 **The Gibbs energy for a solution of a weak acid has a minimum that lies close to HA, and little deprotonation occurs at equilibrium. For a strong acid, the minimum lies close to products and deprotonation is almost complete.**

fully ionized in solution), the molar concentration of hydronium ions is the same as the nominal molar concentration[3] of the acid, as each HA molecule generates one H_3O^+ ion. Similarly, for a Group 1 hydroxide of formula MOH in solution, the molar concentration of hydroxide ions is the same as the nominal molar concentration of the base, as each B molecule generates one OH^- ion. For Group 2 hydroxides, of formula $M(OH)_2$, the OH^- concentration is twice the nominal molar concentration of the base. It follows that we can estimate pOH from the nominal molar concentration of the base, and convert the value to pH by using eqn 36.

For a weak acid or base, we need to take the partial ionization into account by considering the proton transfer equilibrium. The distinction between weak and strong acids and bases is an illustration of the different types of behaviour shown in Fig. 9.10: strong acids and bases are those for which the minimum Gibbs energy of the solution lies close to the (ionized) products; weak acids and bases are those for which the minimum lies close to the (non-ionized) reactants. However, because the extent of ionization is so small (for typical solutions), an approximation is that the molar concentration of HA or B is unchanged from its nominal value. Moreover, because the molar concentrations of the species produced by the proton transfer are equal (to a good approximation), the expression for K_a in eqn 30 simplifies to

$$K_a \approx \frac{[H_3O^+]^2}{[HA]} \qquad \text{or } [H_3O^+] \approx (K_a[HA])^{1/2} \tag*{\{38\}}$$

It then follows, by taking the negative logarithms of both sides, that

$$pH \approx \tfrac{1}{2}pK_a - \tfrac{1}{2}\log[HA] \tag*{\{39\}}$$

Illustration

The pK_a of hydrocyanic acid, HCN(aq), is given in Table 9.1 as 9.31. Therefore, the pH of 0.20 M HCN(aq) is

$$\begin{aligned} pH &\approx \tfrac{1}{2}pK_a - \tfrac{1}{2}\log[HCN] \\ &\approx \tfrac{1}{2}\times 9.31 - \tfrac{1}{2}\log 0.20 = 5.0 \end{aligned}$$

Self-test 9.6 Calculate the pH of 0.10 M NH_3(aq).

[11.1]

Table 9.1* Acidity constants in water at 298 K

	pK_{a1}	pK_{a2}	pK_{a3}
Acetic acid, CH_3COOH	4.75		
Ammonium ion, NH_4^+	9.25		
Carbonic acid, H_2CO_3	6.37	10.25	
Hydrocyanic acid	9.31		
Phosphoric acid, H_3PO_4	2.12	7.21	12.67

* More values are given in the *Data section* at the end of this volume.

(c) Acid–base titrations

At the stoichiometric point[4] of a titration of a weak acid (such as CH_3COOH) and strong base (NaOH) the analyte (the solution being titrated) has become an aqueous solution of the weak acid–strong base salt (sodium acetate). At this point, the solution contains $CH_3CO_2^-$ and Na^+ ions together with any ions stemming from autoprotolysis. The presence of the Brønsted base $CH_3CO_2^-$ means that we can expect a pH of greater than 7. At the stoichiometric point of a titration of a weak base (such as NH_3) and a strong acid (HCl), the analyte is a solution of a strong acid–weak base salt (ammonium chloride) and contains NH_4^+ and Cl^- ions. Because Cl^- is a negligibly weak Brønsted base and NH_4^+ is a weak Brønsted acid, the solution is acidic and its pH will be less than 7.

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[3] By nominal molar concentration is meant the molar concentration of the solute as prepared, ignoring any proton transfer.

[4] The stoichiometric point of a titration is still widely called the equivalence point.

The corresponding expression for the pH at the stoichiometric point of a titration of a strong acid with a weak base is

$$\mathrm{pH} = \tfrac{1}{2}\mathrm{p}K_a - \tfrac{1}{2}\log S \qquad \{48\}$$

Illustration

The stoichiometric point of a titration of 25.00 mL of 0.100 M $HClO(aq)$ with 0.100 M $NaOH(aq)$ occurs when the molar concentration of $NaClO$ is 0.050 mol L^{-1} (because the volume of the solution has increased from 25.00 mL to 50.00 mL). Therefore, the pH is

$$\mathrm{pH} = \tfrac{1}{2}\times 7.43 + \tfrac{1}{2}\times 14.00 + \tfrac{1}{2}\log 0.050 = 10.1$$

Self-test 9.8 Estimate the pH at the stoichiometric point of a titration of 25.00 mL of 0.200 M $NH_3(aq)$ with 0.300 M $HCl(aq)$.

[5.1]

When so much strong base has been added that the titration has been carried well past the stoichiometric point, the pH is determined by the excess base present. Then, $[H_3O^+] \approx K_w/[OH^-]$ so, if we write the molar concentration of excess base as B', this expression can be written

$$\mathrm{pH} = \mathrm{p}K_w + \log B' \qquad \{49\}$$

In this expression, as in all the preceding ones, the molar concentrations must take into account the change of volume that occurs as the titrant is added to the analyte.

The general form of the pH curve throughout a titration is illustrated in Fig. 9.11. The pH rises slowly from the value given by the 'weak acid alone' formula (eqn 40) following the values given by the Henderson–Hasselbalch equation (eqn 44) until the stoichiometric point is approached. It then changes rapidly to and through the value given by the 'salt alone' formula (eqn 47 or 48). It then climbs less rapidly towards the value given by the 'base in excess' formula (eqn 49). The stoichiometric point can be detected easily by observing where the pH changes rapidly through the value given by the 'salt alone formula' (eqn 47 or 48).

(d) Buffers and indicators

The slow variation of the pH in the vicinity of $S = A'$, when the molar concentrations of the salt and acid are equal, is the basis of **buffer action**, the ability of a solution to oppose changes in pH when small amounts of strong acids and bases are added to the solution. The mathematical basis of buffer action is the logarithmic dependence given by the Henderson–Hasselbalch equation (eqn 44), which is quite flat near $\mathrm{pH} = \mathrm{p}K_a$. The physical basis of buffer action is that the existence of an abundant supply of A^- ions (because a salt is present) can remove most of the H_3O^+ ions brought by additional strong acid; moreover, the numerous HA molecules can supply H_3O^+ ions to react with any strong base that is added.

Example 9.4 Estimating the pH of a buffer solution

Estimate the pH of an aqueous buffer solution that contains 0.200 mol L^{-1} KH_2PO_4 and 0.100 mol L^{-1} K_2HPO_4.

Method The pH of a solution of a weak acid and its salt can be estimated from the Henderson–Hasselbalch equation. To do so, we must identify the acid HA and its conjugate base A^-

Answer In this example, the acid is the anion $H_2PO_4^-$ and its conjugate base is the anion HPO_4^{2-}:

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$$

The acidity constant we require is therefore pK_{a2} for H_3PO_4, which from Table 9.1 is 7.21. Then, with $A' = 0.200\ \text{mol L}^{-1}$ and $S = 0.100\ \text{mol L}^{-1}$, eqn 44 gives the pH of the solution as

$$\text{pH} = 7.21 - \log\left(\frac{0.200}{0.100}\right) = 6.91$$

Hence, the solution should buffer close to pH = 7.

Self-test 9.9 Calculate the pH of an aqueous buffer solution which contains $0.100\ \text{mol L}^{-1}$ NH_3 and $0.200\ \text{mol L}^{-1}$ NH_4Cl.

[8.95; more realistically: 9]

(e) Acid–base indicators

The rapid change of pH near the stoichiometric point in a titration is the basis of indicator detection. An **acid–base indicator** is normally some large, water-soluble, weakly acidic organic molecule which can exist as acid (HIn) or conjugate base (In^-) forms that differ in colour. The two forms are in equilibrium in solution:

$$HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq)$$

and, if we make the usual assumption that the solution is so dilute that the activity of water is 1, then the equilibrium is described by the constant

$$K_{In} = \frac{a_{H_3O^+}a_{In^-}}{a_{HIn}} \qquad [50]$$

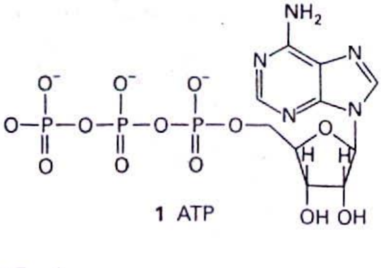
The ratio of acid and base forms at a given pH is found by rearranging this expression to

$$\log\frac{[HIn]}{[In^-]} \approx pK_{In} - \text{pH} \qquad (51)$$

Therefore, when the pH is less than pK_{In}, the indicator is predominantly in its acidic form and has the corresponding colour; when the pH is greater than pK_{In}, the indicator is mainly in its basic form. The **end point** is the pH of the solution when both forms are present in equal abundance, which occurs when pH = pK_{In}.

At the stoichiometric point of an acid–base titration, the pH changes sharply through several units and, if the pH passes through pK_{In}, there is a pronounced colour change. With a well-chosen indicator, the end point coincides with the stoichiometric point of the titration.

Care must be taken to use an indicator that changes colour at the pH appropriate to the type of titration. Thus, in a weak acid–strong base titration, the stoichiometric point lies at the pH given by eqn 47, so an indicator that changes at that pH must be selected. Broadly speaking, an indicator with $pK_{In} > 7$ is required because the stoichiometric point lies at pH > 7. Similarly, in a strong acid–weak base titration, an indicator changing near the pH given by eqn 48 should be used. The stoichiometric points of such titrations lie at pH < 7, so an indicator with $pK_{In} < 7$ is required.



1 ATP

9.6 Biological activity: the thermodynamics of ATP

An important biochemical is adenosine triphosphate, ATP (1). Its function is to store the energy made available when food is metabolized and then to supply it on demand to a wide variety of biological processes. The essence of ATP's action is its ability to lose its terminal phosphate group by hydrolysis and to form adenosine diphosphate (ADP):

$$\mathrm{ATP(aq)} + \mathrm{H_2O(l)} \longrightarrow \mathrm{ADP(aq)} + \mathrm{P_i^-(aq)} + \mathrm{H_3O^+(aq)}$$

(P_i^- denotes an inorganic phosphate group, such as $H_2PO_4^-$.) This reaction is exergonic and can drive an endergonic reaction if suitable enzymes are available.

(a) Biological standard states

The conventional standard state of hydrogen ions (unit activity, $\mathrm{pH} = 0$) is not appropriate to normal biological conditions. Therefore, in biochemistry it is common to adopt the **biological standard state**, in which $\mathrm{pH} = 7$ (an activity of 10^{-7}, neutral solution). We shall adopt this convention in this section, and label the corresponding standard thermodynamic functions as $G^{\oplus}$, $H^{\oplus}$, and $S^{\oplus}$ (some texts use $X^{\ominus\prime}$). The relation between the thermodynamic and biological standard Gibbs energies of reaction for a reaction of the form

$$\mathrm{A} + \nu\,\mathrm{H^+(aq)} \longrightarrow \mathrm{P} \tag{52}$$

is

$$\Delta_r G^{\oplus} = \Delta_r G^{\ominus} + 7\nu RT \ln 10 \tag{53}$$

Note that there is no difference between the two standard values if hydrogen ions are not involved in the reaction ($\nu = 0$).

Justification 9.4

The reaction Gibbs energy is

$$\Delta_r G = \mu_{\mathrm{P}} - \mu_{\mathrm{A}} - \nu\mu_{\mathrm{H^+}}$$

If all the species other than H^+ are in their standard states, this expression becomes

$$\Delta_r G = \mu_{\mathrm{P}}^{\ominus} - \mu_{\mathrm{A}}^{\ominus} - \nu\mu_{\mathrm{H^+}}$$

Then, because

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

(because $\ln x = \ln 10 \log x$, with $\ln 10 = 2.303$), this equation becomes

$$\Delta_r G = \mu_{\mathrm{P}}^{\ominus} - \mu_{\mathrm{A}}^{\ominus} - \nu\mu_{\mathrm{H^+}}^{\ominus} + (RT\nu \ln 10) \times \mathrm{pH}$$

Equation 53 then follows when we set $\mathrm{pH} = 7$.

Illustration

Consider the reaction

$$\mathrm{NADH(aq)} + \mathrm{H^+(aq)} \longrightarrow \mathrm{NAD(aq)} + \mathrm{H_2(g)}$$

at 37°C, for which $\Delta_r G^{\ominus} = -21.8\ \mathrm{kJ\,mol^{-1}}$. NADH is the reduced form of nicotinamide adenine dinucleotide and NAD^+ is its oxidized form; the molecules play an important role in the later stages of the respiratory process. It follows that because $\nu = 1$ and $7 \ln 10 = 16.1$,

$$\begin{aligned}\Delta_r G^{\oplus} &= -21.8\ \mathrm{kJ\,mol^{-1}} + 16.1 \times (8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (310\ \mathrm{K}) \\ &= +19.7\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

Note that the biological standard value is opposite in sign (in this example) to the thermodynamic standard value.

Self-test 9.10 For a particular reaction of the form $A \rightarrow B + 2H^+$ in aqueous solution, it was found that $\Delta_r G^{\ominus} = +20\ \text{kJ mol}^{-1}$ at 28 °C. Estimate the value of $\Delta_r G^{\oplus}$.

[$-61\ \text{kJ mol}^{-1}$]

The standard values for ATP hydrolysis at 37 °C (310 K, blood temperature) are $\Delta_r G^{\oplus} = -30\ \text{kJ mol}^{-1}$, $\Delta_r H^{\oplus} = -20\ \text{kJ mol}^{-1}$, and $\Delta_r S^{\oplus} = +34\ \text{J K}^{-1}\ \text{mol}^{-1}$. The hydrolysis is therefore exergonic ($\Delta_r G^{\oplus} < 0$) under these conditions, and 30 kJ mol^{-1} is available for driving other reactions. Moreover, because the reaction entropy is large, the reaction Gibbs energy is sensitive to temperature. In view of its exergonicity the ADP-phosphate bond has been called a 'high-energy phosphate bond'. The name is intended to signify a high tendency to undergo reaction, and should not be confused with 'strong' bond. In fact, even in the biological sense it is not of very 'high energy'. The action of ATP depends on it being intermediate in activity. Thus it acts as a phosphate donor to a number of acceptors (for example, glucose), but is recharged by more powerful phosphate donors in the respiration cycle.

(b) Anaerobic and aerobic metabolism

The efficiency of some biological processes can be gauged in terms of the value of $\Delta_r G^{\oplus}$ given above, as we shall consider by considering aerobic and anaerobic metabolism. Aerobic metabolism is a series of reactions in which inhaled oxygen plays a role; anaerobic metabolism is a form of metabolism in which inhaled oxygen plays no role. The energy source of anaerobic cells is glycolysis, the partial oxidation of glucose to lactic acid, and at blood temperature $\Delta_r G^{\oplus} = -218\ \text{kJ mol}^{-1}$. The standard reaction enthalpy is $-120\ \text{kJ mol}^{-1}$, the exergonicity exceeding the exothermicity on account of the large increase of entropy accompanying the fracture of the glucose molecule. The glycolysis is coupled to a reaction in which two ADP molecules are converted into two ATP molecules:

$$\text{Glucose} + 2\text{P}_i^- + 2\text{ADP} \longrightarrow 2\text{Lactate}^- + 2\text{ATP} + 2\text{H}_2\text{O}$$

The standard reaction Gibbs energy is $(-218) - 2(-30)\ \text{kJ mol}^{-1} = -158\ \text{kJ mol}^{-1}$. The reaction is exergonic, and therefore spontaneous: the metabolism of the food has been used to 'recharge' the ATP.

Metabolism by aerobic respiration is much more efficient. The standard Gibbs energy of combustion of glucose is $-2880\ \text{kJ mol}^{-1}$, and so terminating its oxidation at lactic acid is a poor use of resources. In aerobic respiration the oxidation is carried out to completion, and an extremely complex set of reactions preserves as much of the energy released as possible. In the overall reaction, 38 ATP molecules are generated for each glucose molecule consumed. Each mole of ATP extracts 30 kJ from the 2880 kJ supplied by 1 mol $C_6H_{12}O_6$ (180 g of glucose), and so 1140 kJ has been stored for later use.

Each ATP molecule can be used to drive an endergonic reaction for which $\Delta_r G^{\oplus}$ does not exceed $+30\ \text{kJ mol}^{-1}$. For example, the biosynthesis of sucrose from glucose and fructose can be driven (if a suitable enzyme system is available) because the reaction is endergonic to the extent $\Delta_r G^{\oplus} = +23\ \text{kJ mol}^{-1}$. The biosynthesis of proteins is strongly endergonic, not only on account of the enthalpy change but also on account of the large decrease in entropy that occurs when many amino acids are assembled into a precisely determined sequence. For instance, the formation of a peptide link is endergonic, with $\Delta_r G^{\oplus} = +17\ \text{kJ mol}^{-1}$, but the biosynthesis occurs indirectly and is equivalent to the consumption of three ATP molecules for each link. In a moderately small protein like myoglobin, with about 150 peptide links, the construction alone requires 450 ATP molecules, and therefore about 12 mol of glucose molecules for 1 mol of protein molecules.

Checklist of key ideas

Spontaneous chemical reactions

9.1 The Gibbs energy minimum

- ☐ extent of reaction (ξ)
- ☐ reaction Gibbs energy (Δ_rG, 1)
- ☐ relation of Δ_rG to the chemical potentials of the species (2)
- ☐ the condition of equilibrium (3)
- ☐ exergonic reaction
- ☐ endergonic reaction
- ☐ reaction quotient (Q)
- ☐ standard reaction Gibbs energy ($\Delta_rG^\ominus$, 6)
- ☐ the equilibrium constant (K) in terms of $\Delta_rG^\ominus$ (8)
- ☐ the general expression for Δ_rG at an arbitrary stage of the reaction (10)
- ☐ $\Delta_rG^\ominus$ in terms of Gibbs energies of formation (11,12)
- ☐ the reaction quotient (13,14)
- ☐ thermodynamic equilibrium constant (18)
- ☐ the relation between equilibrium constants (19)

The response of equilibria to the conditions

9.2 How equilibria respond to pressure

- ☐ the response of K to catalysts and to changes in pressure (21)
- ☐ the effect of pressure on composition
- ☐ Le Chatelier's principle for the effect of pressure

9.3 The response of equilibria to temperature

- ☐ Le Chatelier's principle for the effect of temperature
- ☐ the van't Hoff equation for the effect of temperature on K (24)
- ☐ the equilibrium constant at one temperature in terms of its value at another temperature (26)

Applications to selected systems

9.4 The extraction of metals from their oxides

- ☐ the construction and interpretation of an Ellingham diagram

9.5 Acids and bases

- ☐ the Brønsted–Lowry classification of acids and bases
- ☐ the pH of a solution (27)
- ☐ conjugate base
- ☐ acidity constant (29)
- ☐ the significance of pK_a (31)
- ☐ conjugate acid
- ☐ basicity constant (33)
- ☐ the relation between K_a and K_b (34)
- ☐ autoprotolysis constant (35)
- ☐ the relation between pH and pOH (36)
- ☐ the pH of a solution of a weak acid (39)
- ☐ the changes in pH in the course of a titration
- ☐ the pH of a solution of a weak base (41)
- ☐ the Henderson–Hasselbalch equation for the pH of a mixed solution (43)
- ☐ the pH at the stoichiometric point (47,48)
- ☐ the pH after the stoichiometric point (49)
- ☐ buffer action
- ☐ the selection of buffers
- ☐ acid–base indicator
- ☐ indicator constant (50)
- ☐ the variation of composition with pH (51)
- ☐ selection of indicators

9.6 Biological activity: the thermodynamics of ATP

- ☐ the hydrolysis of ATP
- ☐ biological standard state
- ☐ the relation between thermodynamic and biological standard states (53)
- ☐ the efficiency of metabolism

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Exercises

9.1 (a) The equilibrium constant for the isomerization of *cis*-2-butene to *trans*-2-butene is $K = 2.07$ at 400 K. Calculate the standard reaction Gibbs energy.

9.1 (b) The equilibrium constant for the dissociation of Br_2 at 1600 K is $K = 0.255$. Calculate the standard reaction Gibbs energy.

9.2 (a) The standard reaction Gibbs energy of the isomerization of *cis*-2-pentene to *trans*-2-pentene at 400 K is $-3.67\ \text{kJ mol}^{-1}$. Calculate the equilibrium constant of the isomerization.

9.2 (b) The standard reaction Gibbs energy of the decomposition of $CaCO_3$ to CaO and CO_2 at 1173 K is $+0.178\ \text{kJ mol}^{-1}$. Calculate the equilibrium constant of the decomposition.

9.3 (a) At 2257 K and 1.00 atm total pressure, water is 1.77 per cent dissociated at equilibrium by way of the reaction $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$. Calculate (a) K, (b) $\Delta_r G^\ominus$, and (c) $\Delta_r G$ at this temperature.

9.3 (b) For the equilibrium, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the degree of dissociation, α_e, at 298 K is 0.201 at 1.00 bar total pressure. Calculate (a) $\Delta_r G$, (b) K, and (c) $\Delta_r G^\ominus$ at 298 K.

9.4 (a) Dinitrogen tetroxide is 18.46 per cent dissociated at 25 °C and 1.00 bar in the equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. Calculate (a) K, (b) $\Delta_r G^\ominus$, (c) K at 100 °C given that $\Delta_r H^\ominus = +57.2\ \text{kJ mol}^{-1}$ over the temperature range.

9.4 (b) Molecular bromine is 24 per cent dissociated at 1600 K and 1.00 bar in the equilibrium $Br_2(g) \rightleftharpoons 2Br(g)$. Calculate (a) K, (b) $\Delta_r G^\ominus$, (c) K at 2000 °C given that $\Delta_r H^\ominus = +112\ \text{kJ mol}^{-1}$ over the temperature range.

9.5 (a) From information in the *Data section*, calculate the standard Gibbs energy and the equilibrium constant at (a) 298 K and (b) 400 K for the reaction $PbO(s) + CO(g) \rightleftharpoons Pb(s) + CO_2(g)$. Assume that the reaction enthalpy is independent of temperature.

9.5 (b) From information in the *Data section*, calculate the standard Gibbs energy and the equilibrium constant at (a) 25 °C and (b) 50 °C for the reaction $CH_4(g) + 3Cl_2(g) \rightleftharpoons CHCl_3(l) + 3HCl(g)$. Assume that the reaction enthalpy is independent of temperature.

9.6 (a) In the gas-phase reaction $2A + B \rightleftharpoons 3C + 2D$, it was found that, when 1.00 mol A, 2.00 mol B, and 1.00 mol D were mixed and allowed to come to equilibrium at 25 °C, the resulting mixture contained 0.90 mol C at a total pressure of 1.00 bar. Calculate (a) the mole fractions of each species at equilibrium, (b) K_x, (c) K, and (d) $\Delta_r G^\ominus$.

9.6 (b) In the gas-phase reaction $A + B \rightleftharpoons C + 2D$, it was found that, when 2.00 mol A, 1.00 mol B, and 3.00 mol D were mixed and allowed to come to equilibrium at 25 °C, the resulting mixture contained 0.79 mol C at a total pressure of 1.00 bar. Calculate (a) the mole fractions of each species at equilibrium, (b) K_x, (c) K, and (d) $\Delta_r G^\ominus$.

9.7 (a) The standard reaction enthalpy of $Zn(s) + H_2O(g) \rightarrow ZnO(s) + H_2(g)$ is approximately constant at $+224\ \text{kJ mol}^{-1}$ from 920 K up to 1280 K. The standard reaction Gibbs energy is $+33\ \text{kJ mol}^{-1}$ at 1280 K. Estimate the temperature at which the equilibrium constant becomes greater than 1.

9.7 (b) The standard enthalpy of a certain reaction is approximately constant at $+125\ \text{kJ mol}^{-1}$ from 800 K up to 1500 K. The standard reaction Gibbs energy is $+22\ \text{kJ mol}^{-1}$ at 1120 K. Estimate the temperature at which the equilibrium constant becomes greater than 1.

9.8 (a) The equilibrium constant of the reaction $2C_3H_6(g) \rightleftharpoons C_2H_4(g) + C_4H_8(g)$ is found to fit the expression

$$\ln K = -1.04 - \frac{1088}{(T/\text{K})} + \frac{1.51 \times 10^5}{(T/\text{K})^2}$$

between 300 K and 600 K. Calculate the standard reaction enthalpy and standard reaction entropy at 400 K.

9.8 (b) The equilibrium constant of a reaction is found to fit the expression

$$\ln K = -2.04 - \frac{1176}{(T/\mathrm{K})} + \frac{2.1 \times 10^7}{(T/\mathrm{K})^3}$$

between 400 K and 500 K. Calculate the standard reaction enthalpy and standard reaction entropy at 450 K.

9.9 (a) The standard reaction Gibbs energy of the isomerization of borneol ($C_{10}H_{17}OH$) to isoborneol in the gas phase at 503 K is +9.4 kJ mol^{-1}. Calculate the reaction Gibbs energy in a mixture consisting of 0.15 mol of borneol and 0.30 mol of isoborneol when the total pressure is 600 Torr.

9.9 (b) The equilibrium pressure of H_2 over solid uranium and uranium hydride, UH_3, at 500 K is 1.04 Torr. Calculate the standard Gibbs energy of formation of $UH_3(s)$ at 500 K.

9.10 (a) Calculate the percentage change in the equilibrium constant K_x of the reaction $H_2CO(g) \rightleftharpoons CO(g) + H_2(g)$ when the total pressure is increased from 1.0 bar to 2.0 bar at constant temperature.

9.10 (b) Calculate the percentage change in the equilibrium constant K_x of the reaction $CH_3OH(g) + NOCl(g) \rightleftharpoons HCl(g) + CH_3NO_2(g)$ when the total pressure is increased from 1.0 bar to 2.0 bar at constant temperature.

9.11 (a) The equilibrium constant for the gas-phase isomerization of borneol ($C_{10}H_{17}OH$) to isoborneol at 503 K is 0.106. A mixture consisting of 7.50 g of borneol and 14.0 g of isoborneol in a container of volume 5.0 L is heated to 503 K and allowed to come to equilibrium. Calculate the mole fractions of the two substances at equilibrium.

9.11 (b) The equilibrium constant for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is 1.69×10^{-3} at 2300 K. A mixture consisting of 5.0 g of nitrogen and 2.0 g of oxygen in a container of volume 1.0 L is heated to 2300 K and allowed to come to equilibrium. Calculate the mole fraction of NO at equilibrium.

9.12 (a) Use the data in Table 2.6 of the *Data section* to decide which of the following reactions have $K > 1$ at 298 K.

(a) $HCl(g) + NH_3(g) \rightleftharpoons NH_4Cl(s)$

(b) $2Al_2O_3(s) + 3Si(s) \rightleftharpoons 3SiO_2(s) + 4Al(s)$

(c) $Fe(s) + H_2S(g) \rightleftharpoons FeS(s) + H_2(g)$

9.12 (b) Use the data in Table 2.6 of the *Data section* to decide which of the following reactions have $K > 1$ at 298 K.

(a) $FeS_2(s) + 2H_2(g) \rightleftharpoons Fe(s) + 2H_2S(g)$

(b) $2H_2O_2(l) + H_2S(g) \rightleftharpoons H_2SO_4(l) + 2H_2(g)$

9.13 (a) Which of the equilibria in Exercise 9.12a are favoured (in the sense of K increasing) by a rise in temperature at constant pressure?

9.13 (b) Which of the equilibria in Exercise 9.12b are favoured (in the sense of K increasing) by a reduction in temperature at constant pressure?

9.14 (a) What is the standard enthalpy of a reaction for which the equilibrium constant is (a) doubled, (b) halved when the temperature is increased by 10 K at 298 K?

9.14 (b) What is the standard enthalpy of a reaction for which the equilibrium constant is (a) doubled, (b) halved when the temperature is increased by 15 K at 310 K?

9.15 (a) The standard Gibbs energy of formation of $NH_3(g)$ is -16.5 kJ mol^{-1} at 298 K. What is the reaction Gibbs energy when the partial pressures of the N_2, H_2, and NH_3 (treated as perfect gases) are 3.0 bar, 1.0 bar, and 4.0 bar, respectively? What is the spontaneous direction of the reaction in this case?

9.15 (b) The dissociation vapour pressure of NH_4Cl at 427°C is 608 kPa but at 459°C it has risen to 1115 kPa. Calculate (a) the equilibrium constant, (b) the standard reaction Gibbs energy, (c) the standard enthalpy, (d) the standard entropy of dissociation, all at 427°C. Assume that the vapour behaves as a perfect gas and that $\Delta H^\ominus$ and $\Delta S^\ominus$ are independent of temperature in the range given.

9.16 (a) Estimate the temperature at which $CaCO_3$(calcite) decomposes.

9.16 (b) Estimate the temperature at which $CuSO_4 \cdot 5H_2O$ undergoes dehydration.

9.17 (a) At the half-way point in the titration of a weak acid with a strong base the pH was measured as 5.40. (a) What is the acidity constant and the pK_a of the acid? (b) What is the pH of the solution that is 0.015 M in the acid?

9.17 (b) At the half-way point in the titration of a weak acid with a strong base the pH was measured as 4.82. (a) What is the acidity constant and the pK_a of the acid? (b) What is the pH of the solution that is 0.025 M in the acid?

9.18 (a) Calculate the pH of (a) 0.10 M $NH_4Cl(aq)$, (b) 0.10 M $NaCH_3CO_2$, (c) 0.100 M $CH_3COOH(aq)$.

9.18 (b) Calculate the pH of (a) 0.10 M $NaHCO_2(aq)$, (b) 0.20 M $NaC_6H_5CO_2$, (c) 0.150 M $HCN(aq)$.

9.19 (a) Calculate the pH at the stoichiometric point of the titration of 25.00 mL of 0.100 M lactic acid with 0.175 M $NaOH(aq)$.

9.19 (b) Calculate the pH at the stoichiometric point of the titration of 25.00 mL of 0.100 M chlorous acid with 0.175 M $NaOH(aq)$. The pK_a of chlorous acid is 1.96.

9.20 (a) Sketch the pH curve of a solution containing 0.10 M $NaCH_3CO_2(aq)$ and a variable amount of acetic acid.

9.20 (b) Sketch the pH curve of a solution containing 0.15 M $NaC_6H_5CO_2(aq)$ and a variable amount of benzoic acid.

9.21 (a) From the information in Table 9.1, select suitable buffers for (a) pH = 2.2 and (b) pH = 7.0.

9.21 (b) From the information in Table 9.1, select suitable buffers for (a) pH = 4.6 and (b) pH = 10.8.

Problems

Numerical problems

9.1 The equilibrium constant for the reaction, $I_2(s) + Br_2(g) \rightleftharpoons 2IBr(g)$ is 0.164 at 25°C. (a) Calculate $\Delta_r G^\ominus$ for this reaction. (b) Bromine gas is introduced into a container with excess solid iodine. The pressure and temperature are held at 0.164 atm and 25°C. Find the partial pressure of IBr(g) at equilibrium. Assume that all the bromine is in the liquid form and that the vapour pressure of iodine is negligible. (c) In fact, solid iodine has a measurable vapour pressure at 25°C. In this case, how would the calculation have to be modified?

9.2 Consider the dissociation of methane, $CH_4(g)$, into the elements $H_2(g)$ and C(s, graphite). (a) Given that $\Delta_f H^\ominus(CH_4, g) = -74.85\ \mathrm{kJ\,mol^{-1}}$ and that $\Delta_f S^\ominus(CH_4, g) = -80.67\ \mathrm{J\,K^{-1}\,mol^{-1}}$ at 298 K, calculate the value of the equilibrium constant at 298 K. (b) Assuming that $\Delta_f H^\ominus$ is independent of temperature, calculate K at 50°C. (c) Calculate the degree of dissociation, α_e, of methane at 25°C and a total pressure of 0.010 bar. (d) Without doing any numerical calculations, explain how the degree of dissociation for this reaction will change as the pressure and temperature are varied.

9.3 The equilibrium pressure of H_2 over U(s) and $UH_3(s)$ between 450 K and 715 K fits the expression

$$\ln(p/\mathrm{Pa}) = 69.32 - \frac{1.464 \times 10^4}{T/\mathrm{K}} - 5.65 \ln(T/\mathrm{K})$$

Find an expression for the standard enthalpy of formation of $UH_3(s)$ and from it calculate $\Delta_r C_p^\ominus$.

9.4 The degree of dissociation, α_e, of $CO_2(g)$ into CO(g) and $O_2(g)$ at high temperatures was found to vary with temperature as follows:

T/K	1395	1443	1498
$\alpha_e/10^{-4}$	1.44	2.50	4.71

Assuming $\Delta_r H^\ominus$ to be constant over this temperature range, calculate K, $\Delta_r G^\ominus$, $\Delta_r H^\ominus$, and $\Delta_r S^\ominus$. Make any justifiable approximations.

9.5 The standard reaction enthalpy of the decomposition of $CaCl_2 \cdot NH_3(s)$ into $CaCl_2(s)$ and $NH_3(g)$ is nearly constant at $+78\ \mathrm{kJ\,mol^{-1}}$ between 350 K and 470 K. The equilibrium pressure of NH_3 in the presence of $CaCl_2 \cdot NH_3$ is 12.8 Torr at 400 K. Find an expression for the temperature dependence of $\Delta_r G^\ominus$ in the same range.

9.6 Calculate the equilibrium constant of the reaction $CO(g) + H_2(g) \rightleftharpoons H_2CO(g)$ given that, for the production of liquid formaldehyde, $\Delta_r G^\ominus = +28.95\ \mathrm{kJ\,mol^{-1}}$ at 298 K and that the vapour pressure of formaldehyde is 1500 Torr at that temperature.

9.7 Acetic acid was evaporated in a container of volume 21.45 $\mathrm{cm^3}$ at 437 K and at an external pressure of 764.3 Torr, and the container was then sealed. The mass of acid present in the sealed container was 0.0519 g. The experiment was repeated with the same container but at 471 K, and it was found that 0.0380 g of acetic acid was present. Calculate the equilibrium constant for the dimerization of the acid in the vapour and the enthalpy of vaporization.

9.8 Hydrogen and carbon monoxide have been investigated for use in fuel cells, so their solubilities in molten salts are of interest. Their solubilities in a molten $NaNO_3/KNO_3$ mixture were examined (E. Desimoni and P.G. Zambonin, *J. Chem. Soc. Faraday Trans. I*, 2014 (1973)) with the following results:

$$\log s(H_2) = -5.39 - \frac{768}{T/\mathrm{K}} \qquad \log s(CO) = -5.98 - \frac{980}{T/\mathrm{K}}$$

where s is the solubility in $\mathrm{mol\,cm^{-3}\,bar^{-1}}$. Calculate the standard molar enthalpies of solution of the two gases at 570 K.

9.9 The dissociation of I_2 can be monitored by measuring the total pressure, and three sets of results are as follows:

T/K	973	1073	1173
$100p/\mathrm{atm}$	6.244	7.500	9.181
$10^4 n_I$	2.4709	2.4555	2.4366

where n_I is the amount of I atoms per mole of I_2 molecules in the mixture, which occupied 342.68 $\mathrm{cm^3}$. Calculate the equilibrium constants of the dissociation and the standard enthalpy of dissociation at the mean temperature.

Theoretical problems

9.10 Show that if K_p increases with pressure, then K_ϕ must decrease, where $K = K_p K_\phi$, ϕ denoting the fugacity coefficient.

9.11 Express the equilibrium constant of a gas-phase reaction $A + 3B \rightleftharpoons 2C$ in terms of the equilibrium value of the extent of reaction, ξ, given that initially A and B were present in stoichiometric proportions. Find an expression for ξ as a function of the total pressure, p, of the reaction mixture and sketch a graph of the expression obtained.

9.12 When light passes through a cell of length l containing an absorbing gas at a pressure p, the absorption is proportional to pl. Consider the equilibrium $2NO_2 \rightleftharpoons N_2O_4$, with NO_2 the absorbing species. Show that when two cells of lengths l_1 and l_2 are used, and the pressures needed to obtain equal absorptions are p_1 and p_2, respectively, then the equilibrium constant is given by

$$K = \frac{(p_1\rho^2 - p_2)^2}{\rho(\rho - 1)(p_2 - p_1\rho)p^\ominus}$$

with $\rho = l_1/l_2$. The following data were obtained (R.J. Nordstrum and W.H. Chan, *J. Phys. Chem.* **80**, 847 (1976)):

Absorbance	p_1/Torr	p_2/Torr
0.05	1.00	5.47
0.10	2.10	12.00
0.15	3.15	18.65

with $l_1 = 395$ mm and $l_2 = 75$ mm. Determine the equilibrium constant of the reaction.

9.13 Find an expression for the standard reaction Gibbs energy at a temperature T' in terms of its value at another temperature T and the coefficients a, b, and c in the expresson for the molar heat capacity listed in Table 2.2. Evaluate the standard Gibbs energy of formation of $H_2O(l)$ at 372 K from its value at 298 K.

Additional problems supplied by Carmen Giunta and Charles Trapp

9.14 Thorn *et al.* recently carried out a study of $Cl_2O(g)$ by photoelectron ionization (R.P. Thorn, L.J. Stief, S.-C. Kuo, and R.B. Klemm, *J. Phys. Chem.* **100**, 14178 (1996)). From their measurements, they report $\Delta_f H^\ominus(Cl_2O) = +77.2\ \mathrm{kJ\,mol^{-1}}$. They combined this measurement with literature data on the reaction $Cl_2O(g) + H_2O(g) \rightarrow 2HOCl(g)$, for which $K = 8.2 \times 10^{-2}$ and $\Delta_r S^\ominus = +16.38\ \mathrm{J\,K^{-1}\,mol^{-1}}$, and with readily available thermodynamic data on water vapour to report a value for $\Delta_f H^\ominus(HOCl)$. Calculate that value. All quantities refer to 298 K.

9.15 The dimerization of ClO in the Antarctic winter stratosphere is believed to play an important part in that region's severe seasonal depletion of ozone. The following equilibrium constants are based on measurements by Cox and Hayman (R.A. Cox and G.D. Hayman, *Nature* **332**, 796 (1988)) on the reaction $2ClO(g) \rightarrow (ClO)_2(g)$.

T/K	233	248	258	268	273	280	288	295	303
K	4.13×10^8	5.00×10^7	1.45×10^7	5.37×10^6	3.20×10^6	9.62×10^5	4.28×10^5	1.67×10^5	7.02×10^4

(a) Derive the values of $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ for this reaction. (b) Compute the standard enthalpy of formation and the standard molar entropy of $(ClO)_2$ given $\Delta_f H^\ominus(ClO) = +101.8\ \mathrm{kJ\,mol^{-1}}$ and $S_m^\ominus(ClO) = 226.6\ \mathrm{J\,K^{-1}\,mol^{-1}}$ (*CRC Handbook* (1995)).

9.16 Acid rain is an environmental concern in many parts of Western Europe and eastern North America. In assessing the acidity of rainfall, it is important to have an idea of the acidity of natural rainwater. Assuming that natural rainwater (that is, rainwater uncontaminated with nitric or sulfuric acids) is in equilibrium with 3.6×10^{-4} atm CO_2 (the Henry's law constant is 1.25×10^6 Torr), what is the pH of natural rainwater? What would the pH of natural rainwater have been in pre-industrial times, when the partial pressure of CO_2 was about 2.8×10^{-4} atm? State your approximations explicitly.

9.17 The 1980s saw reports of $\Delta_f H^\ominus(SiH_2)$ ranging from 243 to 289 $\mathrm{kJ\,mol^{-1}}$. For example, the lower value was cited in the review article by Walsh (R. Walsh, *Acc. Chem. Res.* **14**, 246 (1981)); Walsh now leans toward the upper end of the range (H.M. Frey, R. Walsh, and I.M. Watts, *J. Chem. Soc., Chem. Commun.* 1189 (1986)). The higher value was reported by S.-K. Shin and J.L. Beauchamp (*J. Phys. Chem.* **90**, 1507 (1986)). If the standard enthalpy of formation is uncertain by this amount, by what factor is the equilibrium constant for the formation of SiH_2 from its elements uncertain at (a) 298 K, (b) 700 K?

9.18 Nitric acid hydrates have received much attention as possible catalysts for heterogeneous reactions which bring about the Antarctic ozone hole. Worsnop *et al.* investigated the thermodynamic stability of these hydrates under conditions typical of the polar winter stratosphere (D.R. Worsnop, L.E. Fox, M.S. Zahniser, and S.C. Wofsy, *Science* **259**, 71 (1993)). Standard reaction Gibbs energies can be computed for the following reactions at 190 K from their data.

(1) $H_2O(g) \longrightarrow H_2O(s) \qquad \Delta_r G^\ominus = -23.6\ \mathrm{kJ\,mol^{-1}}$

(2) $H_2O(g) + HNO_3(g) \longrightarrow HNO_3 \cdot H_2O(s)$
$\Delta_r G^\ominus = -57.2\ \mathrm{kJ\,mol^{-1}}$

(3) $2H_2O(g) + HNO_3(g) \longrightarrow HNO_3 \cdot 2H_2O(s)$
$\Delta_r G^\ominus = -85.6\ \mathrm{kJ\,mol^{-1}}$

(4) $3H_2O(g) + HNO_3(g) \longrightarrow HNO_3 \cdot 3H_2O(s)$
$\Delta_r G^\ominus = -112.8\ \mathrm{kJ\,mol^{-1}}$

Which solid is thermodynamically most stable at 190 K if $p_{H_2O} = 1.3 \times 10^{-7}$ bar and $p_{HNO_3} = 4.1 \times 10^{-10}$ bar? (*Hint*: Try computing $\Delta_r G^\ominus$ for each reaction under the prevailing conditions; if more than one solid forms spontaneously, check on $\Delta_r G^\ominus$ for conversion of one solid to another.)

9.19 Alberty *et al.* report thermochemical properties of polycyclic aromatic hydrocarbons, many estimated by group additivity methods (R.A. Alberty, M.B. Chung, and A.K. Reif, *J. Phys. Chem. Ref. Data* **18**, 77 (1989)). Some of their data are shown below for three isomeric pyrenes of formula $C_{20}H_{12}$ at 1000 K.

Species	$\Delta_f H^\ominus/(\mathrm{kJ\,mol^{-1}})$	$S_m^\ominus/(\mathrm{J\,K^{-1}\,mol^{-1}})$
Perylene	+253.2	987.9
Benzo(e)pyrene	+253.2	993.7
Benzo(a)pyrene	+262.4	999.4

What are the equilibrium mole fractions of these three isomers at 1000 K?

10

Equilibrium electrochemistry

The principles of thermodynamics established in the preceding chapters can be applied to solutions of electrolytes. One important extension of the previous material, however, is the need to take into account activity coefficients, for they can differ significantly from 1 on account of the strong ionic interactions in electrolyte solutions. These coefficients are best treated as empirical quantities, but it is possible to estimate them in very dilute solutions.

The bulk of the chapter is concerned with the description of the thermodynamic properties of reactions that take place in electrochemical cells, in which, as the reaction proceeds, it drives electrons through an external circuit. Thermodynamic arguments can be used to derive an expression for the electric potential of such cells and the potential can be related to their composition. There are two major topics developed in this connection. One is the definition and tabulation of standard potentials; the second is the use of these standard potentials to predict the equilibrium constants of chemical reactions.

Although the thermodynamic properties of electrolyte solutions can be discussed in terms of chemical potentials and activities in much the same way as solutions of non-electrolytes, they have a number of distinctive features. One is the presence of strong interactions between ions in solution, which means that deviations from ideality are marked even in quite dilute systems. Therefore, we must equip ourselves with means of dealing with activity coefficients that differ significantly from 1. A second feature is that, because many reactions of ions involve the transfer of electrons, they can be studied (and utilized) by allowing them to take place in an electrochemical cell. Measurements like those described in this chapter provide data that are very useful for discussing the characteristics of electrolyte solutions and of ionic equilibria in solution.

The thermodynamic properties of ions in solution

Many of the concepts described in previous chapters carry over without change into the discussion of electrolyte solutions. In this section we focus on departures from ideality.

10.1 Thermodynamic functions of formation

The standard enthalpy and Gibbs energy of a reaction involving ions in solution are expressed in terms of standard enthalpies and Gibbs energies of formation listed in Table 2.6 in the *Data section*. These properties are used in exactly the same way as those for neutral compounds. The values of $\Delta_f H^{\ominus}$ and $\Delta_f G^{\ominus}$ refer to the formation of solutions of ions from the reference states of the parent elements. However, solutions of cations cannot be prepared without their accompanying anions. Therefore, although the standard enthalpy of an overall reaction such as

$$\mathrm{Ag(s)} + \tfrac{1}{2}\mathrm{Cl_2(g)} \longrightarrow \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)}$$

for which

$$\Delta_r H^{\ominus} = \Delta_f H^{\ominus}(\mathrm{Ag^+,aq}) + \Delta_f H^{\ominus}(\mathrm{Cl^-,aq})$$

is meaningful and measurable (and found to be $-61.58\ \mathrm{kJ\,mol^{-1}}$), the enthalpies of the individual formation reactions are not measurable.

(a) Standard functions of formation of ions

The problem is solved by defining one ion, conventionally the hydrogen ion, to have zero standard enthalpy and Gibbs energy of formation:

$$\Delta_f H^{\ominus}(\mathrm{H^+,aq}) = 0 \qquad \Delta_f G^{\ominus}(\mathrm{H^+,aq}) = 0 \tag{1}$$

at all temperatures. In essence, this definition adjusts the actual values of the enthalpies and Gibbs energies of formation of ions by a fixed amount, which is chosen so that the standard value for one of them, $\mathrm{H^+(aq)}$, has the value zero. Then in the reaction

$$\tfrac{1}{2}\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{Cl_2(g)} \longrightarrow \mathrm{H^+(aq)} + \mathrm{Cl^-(aq)} \qquad \Delta_r G^{\ominus} = -131.23\ \mathrm{kJ\,mol^{-1}}$$

we can write

$$\Delta_r G^{\ominus} = \Delta_f G^{\ominus}(\mathrm{H^+,aq}) + \Delta_f G^{\ominus}(\mathrm{Cl^-,aq}) = \Delta_f G^{\ominus}(\mathrm{Cl^-,aq})$$

and hence identify $\Delta_f G^{\ominus}(\mathrm{Cl^-,aq})$ as $-131.23\ \mathrm{kJ\,mol^{-1}}$. All the Gibbs energies and enthalpies of formation of ions in Tables 10.1 and 2.6 were calculated in the same way.

Illustration

With the value of $\Delta_f G^{\ominus}(\mathrm{Cl^-,aq})$ established, we can find the value of $\Delta_f G^{\ominus}(\mathrm{Ag^+,aq})$ from

$$\mathrm{Ag(s)} + \tfrac{1}{2}\mathrm{Cl_2(g)} \longrightarrow \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)} \qquad \Delta_r G^{\ominus} = -54.12\ \mathrm{kJ\,mol^{-1}}$$

which leads to $\Delta_f G^{\ominus}(\mathrm{Ag^+,aq}) = +77.11\ \mathrm{kJ\,mol^{-1}}$.

Self-test 10.1 The standard enthalpy of formation of $\mathrm{AgNO_3(aq)}$ is $-99.4\ \mathrm{kJ\,mol^{-1}}$ at 298 K. Calculate the standard enthalpy of formation of the nitrate ion in water by using the standard enthalpy of formation of $\mathrm{Ag^+(aq)}$ in Table 2.6.

[$-205.0\ \mathrm{kJ\,mol^{-1}}$]

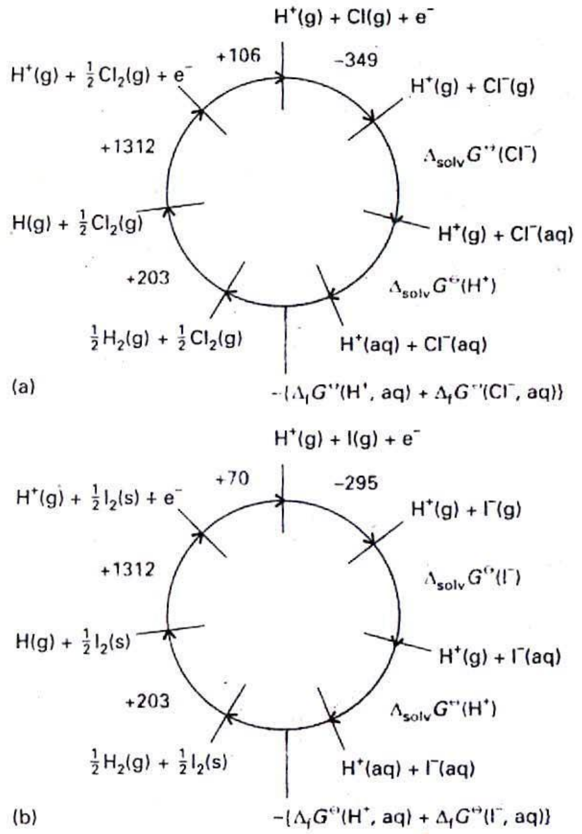
Table 10.1* Standard thermodynamic functions of formation of ions in aqueous solution at 298 K

Ion	$\Delta_f H^{\ominus}/(\mathrm{kJ\,mol^{-1}})$	$\Delta_f G^{\ominus}/(\mathrm{kJ\,mol^{-1}})$
$\mathrm{Cl^-}$	−167.2	−131.2
$\mathrm{Cu^{2+}}$	+64.8	+65.5
$\mathrm{H^+}$	0	0
$\mathrm{K^+}$	−252.4	−283.3
$\mathrm{Na^+}$	−240.1	−261.9
$\mathrm{PO_4^{3-}}$	−1277.0	−1019.0

* More values are given in the *Data section* at the end of this volume; see Table 2.6.

(b) Contributions to the Gibbs energy of formation

The factors responsible for the magnitude of the Gibbs energy of formation of an ion in solution can be identified by analysing it in terms of a thermodynamic cycle. As an illustration, we consider the reasons for the difference between the standard Gibbs energies



10.1 The thermodynamic cycles for the discussion of the Gibbs energies of solvation (hydration) and formation of (a) chloride ions, (b) iodide ions in aqueous solution. The changes in Gibbs energies around the cycle sum to zero because G is a state function.

of formation of Cl^- and I^- in water, which are $-131\ \mathrm{kJ\,mol^{-1}}$ and $-52\ \mathrm{kJ\,mol^{-1}}$, respectively. We do so by treating their formation in the reaction

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}X_2(g) \longrightarrow H^+(aq) + X^-(aq)$$

as the outcome of the sequence of steps shown in Fig. 10.1 (with values taken from the *Data section*, particularly Tables 2.6, 13.4, and 13.5).[1] In each case we use the fact that the sum of the Gibbs energies for all the steps around a closed cycle is zero. It follows that

$$\Delta_f G^\ominus(\mathrm{Cl^-, aq}) = 1272\ \mathrm{kJ\,mol^{-1}} + \Delta_{solv}G^\ominus(\mathrm{H^+}) + \Delta_{solv}G^\ominus(\mathrm{Cl^-})$$
$$\Delta_f G^\ominus(\mathrm{I^-, aq}) = 1290\ \mathrm{kJ\,mol^{-1}} + \Delta_{solv}G^\ominus(\mathrm{H^+}) + \Delta_{solv}G^\ominus(\mathrm{I^-})$$

---

[1] The standard Gibbs energies of formation of the gas-phase ions are unknown. We have therefore used ionization energies and electron affinities (Section 13.4f), and have assumed that any differences from the Gibbs energies arising from conversion to enthalpy and the inclusion of entropies to obtain Gibbs energies in the formation of H^+ are cancelled by the corresponding terms in the electron gain of X. The conclusions from the cycles are therefore only approximate.

Table 10.2* Relative permittivities (dielectric constants) at 298 K

	ε_r
Ammonia	16.9
	22.4 (at −33°C)
Benzene	2.274
Ethanol	24.30
Water	78.54

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

An important point to note is that the value of $\Delta_f G^\ominus$ of an ion is not determined by the properties of the ion alone but includes contributions from the dissociation, ionization, and hydration of hydrogen. The difference between the two values is

$$\begin{aligned}&\Delta_f G^\ominus(\mathrm{Cl^-, aq}) - \Delta_f G^\ominus(\mathrm{I^-, aq}) \\ &\quad= \Delta_{\mathrm{solv}} G^\ominus(\mathrm{Cl^-}) - \Delta_{\mathrm{solv}} G^\ominus(\mathrm{I^-}) - 18\ \mathrm{kJ\ mol^{-1}}\end{aligned} \tag{2}$$

The two unknown quantities are the standard Gibbs energies of solvation $\Delta_{\mathrm{solv}} G^\ominus$, the standard reaction Gibbs energy for the processes

$$\mathrm{M^+(g) \longrightarrow M^+(solution)} \qquad \mathrm{X^-(g) \longrightarrow A^-(solution)} \tag{3}$$

Experimentally, we know that

$$\Delta_f G^\ominus(\mathrm{Cl^-, aq}) - \Delta_f G^\ominus(\mathrm{I^-, aq}) = -79\ \mathrm{kJ\ mol^{-1}}$$

so we can conclude that

$$\Delta_{\mathrm{solv}} G^\ominus(\mathrm{Cl^-}) - \Delta_{\mathrm{solv}} G^\ominus(\mathrm{I^-}) = -61\ \mathrm{kJ\ mol^{-1}}$$

Gibbs energies of solvation of individual ions may be estimated from an equation derived by Max Born, who identified $\Delta_{\mathrm{solv}} G^\ominus$ with the electrical work of transferring an ion from a vacuum into the solvent treated as a continuous dielectric of relative permittivity ε_r (Table 10.2). The resulting **Born equation**, which is derived in the *Justification* below, is

$$\Delta_{\mathrm{solv}} G^\ominus = -\frac{z_i^2 e^2 N_A}{8\pi\varepsilon_0 r_i}\left(1 - \frac{1}{\varepsilon_r}\right) \tag{4}$$

where z_i is the charge number of the ion and r_i its radius[2] (N_A is the Avogadro constant). Note that $\Delta_{\mathrm{solv}} G^\ominus < 0$, and that it is strongly negative for small, highly charged ions in media of high relative permittivity. For water at 25°C,

$$\Delta_{\mathrm{solv}} G^\ominus = -\frac{z_i^2}{(r_i/\mathrm{pm})} \times (6.86 \times 10^4\ \mathrm{kJ\ mol^{-1}}) \tag{5}$$

Justification 10.1

The electrical concepts required in this derivation are reviewed in *Further information 5*. The strategy of the calculation is to identify the Gibbs energy of solvation with the work of transferring an ion from a vacuum into the solvent. That work is calculated by taking the difference of the work of charging an ion when it is in the solution and the work of charging the same ion when it is in a vacuum. We model an ion as a sphere of radius r_i immersed in a medium of permittivity ε. When the charge of the sphere is q, the electric potential, ϕ, at its surface is

$$\phi = \frac{q}{4\pi\varepsilon r_i}$$

The work of bringing up a charge $\mathrm{d}q$ to the sphere is $\phi\,\mathrm{d}q$. Therefore, the total work of charging the sphere from 0 to $z_i e$ is

$$w = \int_0^{z_i e} \phi\,\mathrm{d}q = \frac{1}{4\pi\varepsilon r_i}\int_0^{z_i e} q\,\mathrm{d}q = \frac{z_i^2 e^2}{8\pi\varepsilon r_i}$$

This electrical work of charging, when multiplied by the Avogadro constant, is the molar Gibbs energy for charging the ions.

The work of charging an ion in a vacuum is obtained by setting $\varepsilon = \varepsilon_0$, the vacuum permittivity. The corresponding value for charging the ion in a medium is obtained by

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[2] Ionic radii are given in Table 21.3

setting $\varepsilon = \varepsilon_r\varepsilon_0$, where ε_r is the relative permittivity of the medium. It follows that the change in molar Gibbs energy that accompanies the transfer of ions from a vacuum to a solvent is the difference of these two quantities:

$$\Delta_{\text{solv}}G^{\ominus} = \frac{z_i^2 e^2 N_A}{8\pi\varepsilon_0\varepsilon_r r_i} - \frac{z_i^2 e^2 N_A}{8\pi\varepsilon_0 r_i}$$

which can easily be rearranged into eqn 4.

Illustration

To see how closely the Born equation reproduces the experimental data, we calculate that the difference in the values of $\Delta_f G^{\ominus}$ for Cl^- and I^- in water, for which $\varepsilon_r = 78.54$ at 25 °C, given their radii as 181 pm and 220 pm (Table 21.3), respectively, is

$$\begin{aligned}\Delta_{\text{solv}}G^{\ominus}(\text{Cl}^-) - \Delta_{\text{solv}}G^{\ominus}(\text{I}^-) &= -\left(\frac{1}{181} - \frac{1}{220}\right) \times (6.86 \times 10^4\ \text{kJ mol}^{-1}) \\ &= -67\ \text{kJ mol}^{-1}\end{aligned}$$

This estimated difference is in good agreement with the experimental difference.

Self-test 10.2 Estimate the value of $\Delta_{\text{solv}}G^{\ominus}(\text{Cl}^-,\text{aq}) - \Delta_{\text{solv}}G^{\ominus}(\text{Br}^-,\text{aq})$ from experimental data and from the Born equatioin.

[$-26\ \text{kJ mol}^{-1}$ experimental; $-29\ \text{kJ mol}^{-1}$ calculated]

(c) Standard entropies of ions in solution

Although the partial molar entropy of the solute in an electrolyte solution can be measured, there is no experimental way of ascribing a part of that entropy to the cations and a part to the anions. Therefore, yet again we are forced to define the partial molar entropy of one species and set up a table of values for other ions on that basis. The entropies of ions in solution are reported on a scale in which the standard entropy of the H^+ ions in water is taken as zero at all temperatures:

$$S^{\ominus}(\text{H}^+,\text{aq}) = 0 \qquad [6]$$

The values based on this choice are listed in Table 10.3 and more fully in Table 2.6 in the *Data section*.

Because the entropies of ions in water are values relative to the hydrogen ion in water, they may be either positive or negative. A positive éntropy means that an ion has a higher partial molar entropy than H^+ in water and a negative entropy means that the ion has a lower partial molar entropy than H^+ in water. For instance, the entropy of Cl^-(aq) is $+57\ \text{J K}^{-1}\ \text{mol}^{-1}$ and that of Mg^{2+}(aq) is $-128\ \text{J K}^{-1}\ \text{mol}^{-1}$. Partial molar ion entropies vary as expected on the basis that they are related to the degree to which the ions order the water molecules around them in the solution. Small, highly charged ions induce local structure in the surrounding water, and the disorder of the solution is decreased more than in the case of large, singly charged ions. The absolute, Third-Law standard partial molar entropy of the proton in water can be estimated by proposing a model of the structure it induces, and there is some agreement on the value $-21\ \text{J K}^{-1}\ \text{mol}^{-1}$. The negative value indicates that the proton induces order in the solvent.

Table 10.3* Standard entropies of ions in aqueous solution at 298 K

	$S_m^{\ominus}/(\text{J K}^{-1}\ \text{mol}^{-1})$	
Cl^-	+56.5	
Cu^{2+}	−99.6	
H^+	0	by definition
K^+	−102.5	
Na^+	−59.0	
PO_4^{3-}	−221.8	

* More values are given in the *Data section*; see Table 2.6.

10.2 Ion activities

Interactions between ions are so strong that the approximation of replacing activities by molalities is valid only in very dilute solutions (less than 10^{-3} mol kg^{-1} in total ion concentration) and in precise work activities themselves must be used.

(a) The definition of activity

We saw in Section 7.7c that the chemical potential of a solute in a real solution is related to its activity a by

$$\mu = \mu^{\ominus} + RT \ln a \tag{7}$$

where the standard state is a hypothetical solution with molality $b^{\ominus} = 1$ mol kg^{-1} in which the ions are behaving ideally. The activity is related to the molality,[3] b, by

$$a = \gamma b/b^{\ominus} \tag{8}$$

where the activity coefficient, γ, depends on the composition, molality, and temperature of the solution. As the solution approaches ideality (in the sense of obeying Henry's law) at low molalities, the activity coefficient tends towards 1:

$$\gamma \rightarrow 1 \quad \text{and } a \rightarrow b/b^{\ominus} \text{ as } b \rightarrow 0 \tag{9}$$

Because all deviations from ideality are carried in the activity coefficient, the chemical potential can be written[4]

$$\mu = \mu^{\ominus} + RT \ln b + RT \ln \gamma = \mu^{\text{ideal}} + RT \ln \gamma \qquad \{10\}$$

where μ^{ideal} is the chemical potential of the ideal-dilute solution of the same molality.

(b) Mean activity coefficients

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

$$G_{\text{m}}^{\text{ideal}} = \mu_+^{\text{ideal}} + \mu_-^{\text{ideal}} \qquad (11)^{\circ}$$

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

$$\begin{aligned} G_{\text{m}} &= \mu_+ + \mu_- = \mu_+^{\text{ideal}} + \mu_-^{\text{ideal}} + RT \ln \gamma_+ + RT \ln \gamma_- \\ &= G_{\text{m}}^{\text{ideal}} + RT \ln \gamma_+\gamma_- \end{aligned} \tag{12}$$

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

There is no experimental way of separating the product $\gamma_+\gamma_-$ into contributions from the cations and the anions. The best we can do experimentally is to assign responsibility for the nonideality equally to both kinds of ion. Therefore, for a 1,1-electrolyte, we introduce the **mean activity coefficient** as the geometric mean[5] of the individual coefficients:

$$\gamma_{\pm} = (\gamma_+\gamma_-)^{1/2} \qquad [13]$$

and express the individual chemical potentials of the ions as

$$\mu_+ = \mu_+^{\text{ideal}} + RT \ln \gamma_{\pm} \qquad \mu_- = \mu_-^{\text{ideal}} + RT \ln \gamma_{\pm} \tag{14}$$

---

[3] The IUPAC recommendation for the symbol is either m or b; whereas the former is more commonly used, b has the advantage that it is less likely to be confused with mass, m.

[4] In accord with the convention adopted in earlier chapters, the notation has been simplified by interpreting b as $b/b^{\ominus}$ and labelling the equation $\{\cdots\}$.

[5] The geometric mean of x and y is $(xy)^{1/2}$.

10.2 The picture underlying the Debye–Hückel theory is of a tendency for anions to be found around cations, and of cations to be found around anions (one such local clustering region is shown by the sphere). The ions are in ceaseless motion, and the diagram represents the time average of their motion.

The sum of these two chemical potentials is the same as before, eqn 12, but now the nonideality is shared equally.

This approach can be generalized to the case of a compound M_pX_q that dissolves to give a solution of p cations and q anions from each formula unit. The molar Gibbs energy of the ions is the sum of their partial molar Gibbs energies:

$$G_m = p\mu_+ + q\mu_- = G_m^{\text{ideal}} + pRT\ \ln\gamma_+ + qRT\ \ln\gamma_- \qquad (15)$$

If we introduce the mean activity coefficient

$$\gamma_\pm = (\gamma_+^p\gamma_-^q)^{1/s} \qquad s = p + q \qquad [16]$$

and write the chemical potential of each ion as

$$\mu_i = \mu_i^{\text{ideal}} + RT\ \ln\gamma_\pm \qquad (17)$$

we get the same expression as in eqn 15 for G_m when we write

$$G = p\mu_+ + q\mu_- \qquad (18)$$

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

(c) The Debye–Hückel limiting law

The long range and strength of the Coulombic interaction between ions means that it is likely to be primarily responsible for the departures from ideality in ionic solutions and to dominate all the other contributions to nonideality. This domination is the basis of the Debye–Hückel theory of ionic solutions, which was devised by Peter Debye and Erich Hückel in 1923. We give here a qualitative account of the theory and its principal conclusions. The calculation itself, which is a profound example of how a seemingly intractable problem can be formulated and then resolved by drawing on physical insight, is outlined in the *Justification* on p. 250.

Oppositely charged ions attract one another. As a result, anions are more likely to be found near cations in solution, and vice versa (Fig. 10.2). Overall the solution is electrically neutral, but near any given ion there is an excess of counter-ions (ions of opposite charge). Averaged over time, counter-ions are more likely to be found near any given ion. This time-averaged, spherical haze, in which counter-ions outnumber ions of the same charge as the central ion, has a net charge equal in magnitude but opposite in sign to that on the central ion, and is called its **ionic atmosphere**. The energy, and therefore the chemical potential, of any given central ion is lowered as a result of its electrostatic interaction with its ionic atmosphere. This lowering of energy appears as the difference between the molar Gibbs energy G_m and the ideal value G_m^{ideal} of the solute, and hence can be identified with $sRT\ \ln\gamma_\pm$. The stabilization of ions by their interaction with their ionic atmospheres is part of the explanation why chemists commonly use dilute solutions, in which the stabilization is less important, to achieve precipitation of ions from electrolyte solutions.

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

$$\log\gamma_\pm = -|z_+z_-|AI^{1/2} \qquad (19)$$

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

$$I = \tfrac{1}{2}\sum_i z_i^2(b_i/b^\ominus) \qquad [20]$$

In this expression z_i is the charge number of an ion i (positive for cations and negative for anions) and b_i is its molality. The ionic strength occurs widely wherever ionic solutions are

Table 10.4 Ionic strength and molality, $I = k \times b/b^{\ominus}$

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

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

discussed, as we shall see. The sum extends over all the ions present in the solution. For solutions consisting of two types of ion at molalities b_+ and b_-,

$$I = \tfrac{1}{2}(b_+ z_+^2 + b_- z_-^2)/b^{\ominus} \qquad (21)$$

The ionic strength emphasizes the charges of the ions because the charge numbers occur as their squares. Table 10.4 summarizes the relation of ionic strength and molality in an easily usable form.

Justification 10.2

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

$$\ln \gamma_\pm = \frac{w_e}{sRT} \qquad s = p + q \qquad (22)$$

It follows that we must first find the final distribution of the ions and then the work of charging them in that distribution.

The Coulomb potential at a distance *r* from an isolated ion of charge z_ie in a medium of permittivity ε is

$$\phi_i = \frac{Z_i}{r} \qquad Z_i = \frac{z_ie}{4\pi\varepsilon} \qquad (23)$$

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

$$\phi_i = \frac{Z_i}{r}\mathrm{e}^{-r/r_\mathrm{D}} \qquad (24)$$

where r_D is called the **Debye length**. When r_D is large, the shielded potential is virtually the same as the unshielded potential. When it is small, the shielded potential is much smaller than the unshielded potential, even for short distances (Fig. 10.3).

To calculate r_D, we need to know how the charge density, ρ_i, of the ionic atmosphere, the charge in a small region divided by the volume of the region, varies with distance from the ion. This step draws on another standard result of electrostatics, in which charge density and potential are related by **Poisson's equation**. Because we are considering only a spherical ionic atmosphere, we can use a simplified form of this equation in which the charge density varies only with distance from the central ion:

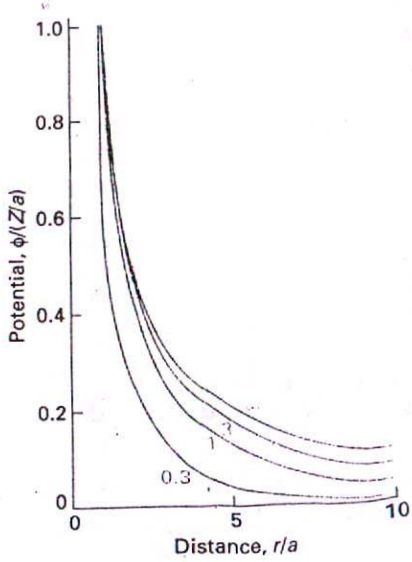
$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\phi_i}{\mathrm{d}r}\right) = -\frac{\rho_i}{\varepsilon} \qquad (25)$$

Substitution of the expression for the shielded potential, eqn 24, results in

$$r_\mathrm{D}^2 = -\frac{\varepsilon\phi_i}{\rho_i} \qquad (26)$$

To solve this equation we need to relate ρ_i and ϕ_i.

For the next step we draw on the fact that the energy of an ion depends on its closeness to the central ion, and then use the Boltzmann distribution to work out the probability that an ion will be found at each distance. The energy of an ion of charge z_je at a distance



10.3 The variation of the shielded Coulomb potential with distance for different values of the Debye length, *r*/*a*. The smaller the Debye length, the more sharply the potential decays to zero. In each case, *a* is an arbitrary unit of length.

where it experiences the potential ϕ_i of the central ion i relative to its energy when it is far away in the bulk solution is its charge times the potential:

$$E = z_j e\phi_i \tag{27}$$

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

$$\frac{c_j}{c_j^\circ} = \mathrm{e}^{-E/kT} \tag{28}$$

The charge density, ρ_i, at a distance r from the ion i is the molar concentration of each type of ion multiplied by the charge per mole of ions, $z_j eN_A$. The quantity eN_A, the magnitude of the charge per mole of electrons, occurs widely throughout electrochemistry, and is called the **Faraday constant**, F:

$$F = eN_A = 96.485 \text{ kC mol}^{-1} \tag*{[29]}$$

It follows that

$$\rho_i = c_+z_+F + c_-z_-F = c_+^\circ z_+F\mathrm{e}^{-z_+e\phi_i/kT} + c_-^\circ z_-F\mathrm{e}^{-z_-e\phi_i/kT} \tag{30}$$

At this stage we need to simplify the expression to avoid the awkward exponential terms. Because the average electrostatic interaction energy is small compared with kT, we may write eqn 30 as

$$\rho_i = (c_+^\circ z_+ + c_-^\circ z_-)F - (c_+^\circ z_+^2 + c_-^\circ z_-^2)\left(\frac{F^2\phi_i}{RT}\right) + \cdots \tag{31}$$

(To obtain this expression, we have replaced an e by F/N_A and recognized that $N_Ak = R$.) The first term in the expansion is zero because it is the charge density in the bulk, uniform solution, and the solution is electrically neutral. The unwritten terms are assumed to be too small to be significant. The one remaining term can be expressed in terms of the ionic strength, eqn 20, by noting that in the dilute aqueous solutions we are considering there is little difference between molality and molar concentration, and $c \approx b\rho$, where ρ is the mass density of the solvent

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

With these approximations, eqn 31 becomes

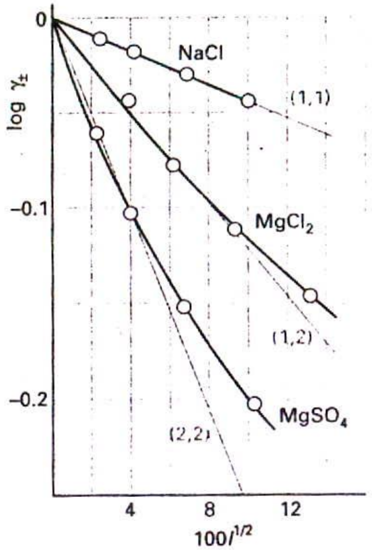
$$\rho_i = -\frac{2\rho F^2 Ib^\ominus\phi_i}{RT} \tag{32}$$

We can now solve eqn 26 for r_D:

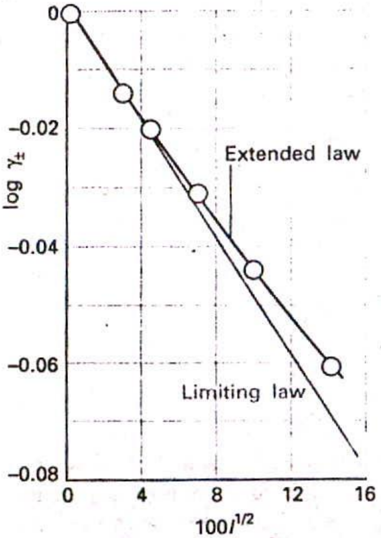
$$r_D = \left(\frac{\varepsilon RT}{2\rho F^2 Ib^\ominus}\right)^{1/2} \tag{33}$$

To calculate the activity coefficient we need to find the electrical work of charging the central ion when it is surrounded by its atmosphere. To do so, we need to know the potential at the ion due to its atmosphere, ϕ_{atmos}. This potential is the difference between the total potential, given by eqn 24, and the potential due to the central ion itself:

$$\phi_{\text{atmos}} = \phi - \phi_{\text{central ion}} = Z_i\left(\frac{\mathrm{e}^{-r/r_D}}{r} - \frac{1}{r}\right) \tag{34}$$



10.4 An experimental test of the Debye–Hückel limiting law. Although there are marked deviations for moderate ionic strengths, the limiting slopes as $I \rightarrow 0$ are in good agreement with the theory, so the law can be used for extrapolating data to very low molalities.



10.5 The extended Debye–Hückel law gives agreement with experiment over a wider range of molalities (as shown here for a 1,1-electrolyte), but it fails at higher molalities.

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

$$\phi_{\text{atmos}}(0) = -\frac{Z_i}{r_{\text{D}}} \tag{35}$$

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

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

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

$$\mathrm{d}w_{\text{e}} = \phi_{\text{atmos}}(0)\,\mathrm{d}q$$

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

$$\begin{aligned} w_{\text{e}} &= N_{\text{A}}\int_0^{z_i e}\phi_{\text{atmos}}(0)\,\mathrm{d}q = -\frac{N_{\text{A}}}{4\pi\varepsilon r_{\text{D}}}\int_0^{z_i e} q\,\mathrm{d}q \\ &= -\frac{N_{\text{A}} z_i^2 e^2}{8\pi\varepsilon r_{\text{D}}} = -\frac{z_i^2 F^2}{8\pi\varepsilon N_{\text{A}} r_{\text{D}}} \end{aligned} \tag{36}$$

It follows from eqn 22 that the mean activity coefficient of the ions is

$$\ln\gamma_{\pm} = \frac{pw_{\text{e},+} + qw_{\text{e},-}}{sRT} = -\frac{(pz_+^2 + qz_-^2)F^2}{8\pi\varepsilon s N_{\text{A}} RT r_{\text{D}}}$$

However, for neutrality $pz_+ + qz_- = 0$, so[6]

$$\ln\gamma_{\pm} = -\frac{|z_+ z_-|F^2}{8\pi\varepsilon N_{\text{A}} RT r_{\text{D}}} \tag{37}$$

When we replace r_{D} by using eqn 33, and convert to common logarithms, this expression turns into eqn 19 with

$$A = \frac{F^3}{4\pi N_{\text{A}}\ \ln 10}\left(\frac{\rho b^{\ominus}}{2\varepsilon^3 R^3 T^3}\right)^{1/2} \tag{38}$$

Illustration

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

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

where b is the molality of the solution (and $b_+ = b_- = b$). Then, from eqn 19,

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

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

---

[6] For this step, multiply $pz_+ + qz_- = 0$ by p and also, separately, by q; add the two expressions and rearrange the result by using $p + q = s$ and $z_+ z_- = -|z_+ z_-|$.

Table 10.5* Mean activity coefficients in water at 298 K

$b/(\text{mol kg}^{-1})$	KCl	$CaCl_2$
0.001	0.966	0.888
0.01	0.902	0.732
0.1	0.770	0.524
1.0	0.607	0.725

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

Self-test 10.3 Calculate the ionic strength and the mean activity coefficient of 1.00×10^{-3} mol kg^{-1} $CaCl_2$(aq) at 25 °C.

[3.00×10^{-3} mol kg^{-1}, 0.880]

The name 'limiting law' is applied to eqn 19 because ionic solutions of moderate molalities may have activity coefficients that differ from the values given by this expression, yet all solutions are expected to conform in the limit of arbitrarily low molalities. Some experimental values of activity coefficients for salts of various valence types are listed in Table 10.5. Figure 10.4 shows some of these values plotted against $I^{1/2}$, and compares them with the theoretical straight lines calculated from eqn 19. The agreement at very low molalities (less than about 1 mmol kg^{-1}, depending on charge type) is impressive and convincing evidence in support of the model. Nevertheless, the departures from the theoretical curves above these molalities are large and show that the approximations are valid only at very low concentrations.

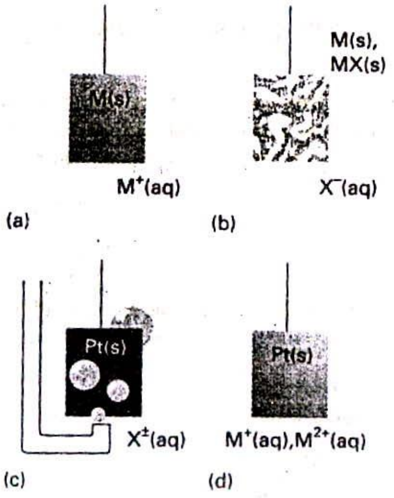
(d) The extended Debye–Hückel law

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

$$\log \gamma_{\pm} = -\frac{A|z_+z_-|I^{1/2}}{1 + BI^{1/2}} \qquad (39)$$

where B is another dimensionless constant. Although B can be interpreted as a measure of the closest approach of the ions, it is best regarded as an adjustable empirical parameter. A curve drawn in this way is shown in Fig. 10.5. It is clear that eqn 39 accounts for some activity coefficients over a moderate range of dilute solutions (up to about 0.1 mol kg^{-1}); nevertheless it remains very poor near 1 mol kg^{-1}.

Current theories of activity coefficients for ionic solutes take an indirect route. They set up a theory for the dependence of the activity coefficient of the *solvent* on the concentration of the solute, and then use the Gibbs–Duhem equation (eqn 7.12) to estimate the activity coefficient of the solute. The results are reasonably reliable for solutions with molalities greater than about 0.1 mol kg^{-1} and are valuable for the discussion of mixed salt solutions, such as sea water.



10.6 Typical electrode types: (a) metal/metal ion; (b) metal/insoluble salt; (c) gas; (d) redox electrodes.

Electrochemical cells

An **electrochemical cell** consists of two **electrodes**, or metallic conductors, in contact with an **electrolyte**, an ionic conductor (which may be a solution, a liquid, or a solid). An electrode and its electrolyte comprise an **electrode compartment**. The two electrodes may share the same compartment. The various kinds of electrode are summarized in Table 10.6 and illustrated in Fig. 10.6. When an 'inert metal' is part of the specification, it is present to act as a source or sink of electrons, but takes no other part in the reaction other than acting as a catalyst for it. If the electrolytes are different, the two compartments may be joined by a **salt bridge**, which is a concentrated electrolyte solution in agar jelly that completes the electrical circuit and enables the cell to function.

A **galvanic cell** is an electrochemical cell that produces electricity as a result of the spontaneous reaction occurring inside it. An **electrolytic cell** is an electrochemical cell in which a non-spontaneous reaction is driven by an external source of current.

Table 10.6 Varieties of electrode

Electrode type	**Designation**	**Redox couple**	**Half-reaction**
Metal/metal-ion	$M(s)\vert M^+(aq)$	M^+/M	$M^+(aq) + e^- \rightarrow M(s)$
Gas electrode	$Pt(s)\vert X_2(g)\vert X^+(aq)$	X^+/X_2	$X^+(aq) + e^- \rightarrow \frac{1}{2}X_2(g)$
	$Pt(s)\vert X_2(g)\vert X^-(aq)$	X_2/X^-	$\frac{1}{2}X_2(g) + e^- \rightarrow X^-(aq)$
Metal/insoluble-salt	$M(s)\vert MX(s)\vert X^-(aq)$	$MX/M,X^-$	$MX(s) + e^- \rightarrow M(s) + X^-(aq)$
Redox	$Pt(s)\vert M^+(aq),M^{2+}(aq)$	M^{2+}/M^+	$M^{2+}(aq) + e^- \rightarrow M^+(aq)$

10.3 Half-reactions and electrodes

It will be familiar from introductory chemistry courses that **oxidation** is the removal of electrons from a species and **reduction** is the addition of electrons to a species. A **redox reaction** is a reaction in which there is a transfer of electrons from one species to another. The electron transfer may be accompanied by other events, such as atom or ion transfer, but the net effect is electron transfer and hence a change in oxidation number of an element. The **reducing agent** (or 'reductant') is the electron donor; the **oxidizing agent** (or 'oxidant') is the electron acceptor.

(a) Half-reactions

Any redox reaction may be expressed as the difference of two reduction **half-reactions**, which are conceptual reactions showing the gain of electrons. For example, the reduction of Cu^{2+} ions by zinc can be expressed as the difference of the following two half-reactions:

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \qquad Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$$

The difference of the two (copper − zinc) is

$$Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq) \tag{40}$$

Even reactions that are not redox reactions may be expressed as the difference of two reduction half-reactions.

Example 10.1 Expressing a reaction in terms of half-reactions

Express the dissolution of silver chloride in water as the difference of two reduction half-reactions.

Method First, write the overall chemical equation. Then select one of the reactants, and write a half-reaction in which it is reduced to one of the products. Next, subtract that half-reaction from the overall reaction to identify the second half-reaction. Finally, write the second half-reaction as a reduction.

Answer The chemical equation of the overall reaction is

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

We select as one half-reaction the reduction of AgCl (more precisely, the reduction of the Ag(I) in AgCl to Ag(0)):

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

Subtraction of this equation from the overall reaction leaves

$$-e^- \longrightarrow Ag^+(aq) - Ag(s)$$

which rearranges to

$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$

Comment There is no net change of oxidation number in dissolution of AgCl, so it is not a redox reaction.

Self-test 10.4 Express the formation of H_2O from H_2 and O_2 in acidic solution (a redox reaction) as the difference of two reduction half-reactions.

[$4H^+(aq) + 4e^- \rightarrow 2H_2(g)$, $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$]

The oxidized and reduced substances in a half-reaction form a **redox couple**, denoted Ox/Red. Thus, the redox couples mentioned so far are Cu^{2+}/Cu and Zn^{2+}/Zn. In general we write a couple as Ox/Red and the corresponding reduction half-reaction as

$$\mathrm{Ox} + \nu e^- \longrightarrow \mathrm{Red} \tag{41}$$

We shall often find it useful to express the composition of an electrode compartment in terms of the reaction quotient, Q, for the half-reaction. This quotient is defined like the reaction quotient for the overall reaction, but the electrons are ignored. Thus, for the copper half-reaction $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$, we write

$$Q = \frac{1}{a_{Cu^{2+}}}$$

We have used the fact that the pure metal (the standard state of the element) has unit activity (recall Table 7.3).

Example 10.2 Writing the half-reaction and reaction quotient for an electrode

Write the half-reaction and the reaction quotient for the reduction of oxygen to water in dilute acidic solution.

Method The first step is a simple balancing exercise: use H^+ ions to balance the H atoms and electrons to balance the charge. For the reaction quotient, include activities of products in the numerator and reactants (other than electrons) in the denominator.

Answer The reduction of O_2 in acidic solution produces H_2O according to the half-reaction

$$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$$

The reaction quotient for the half-reaction is therefore

$$Q = \frac{a_{H_2O}^2}{a_{H^+}^4 (f_{O_2}/p^{\ominus})} \approx \frac{p^{\ominus}}{a_{H^+}^4 p_{O_2}}$$

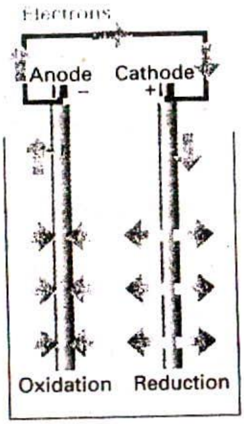
The approximations used in the second step are that the activity of water is 1 (because the solution is dilute and the water almost pure) and the oxygen behaves like a perfect gas.

Self-test 10.5 Write the half-reaction and the reaction quotient for a chlorine gas electrode.

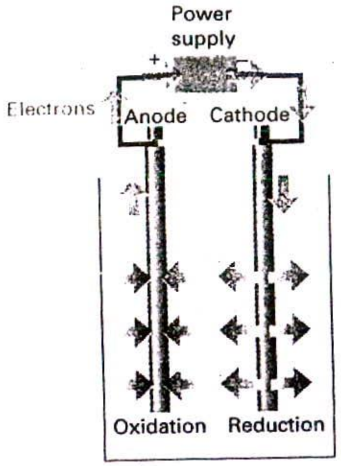
[$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$, $Q = a_{Cl^-}^2 p^{\ominus}/p_{Cl_2}$]

(b) Reactions at electrodes

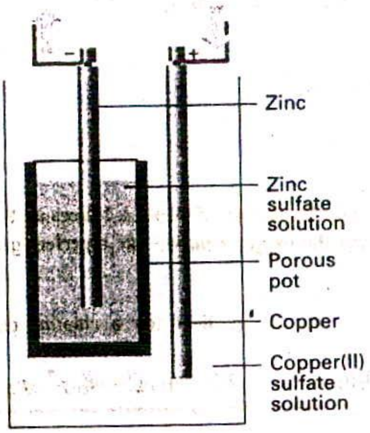
In an electrochemical cell, the reduction and oxidation processes responsible for the overall reaction are separated in space: oxidation takes place in one electrode compartment and



10.7 When a spontaneous reaction takes place in a galvanic cell, electrons are deposited in one electrode (the site of oxidation, the anode) and collected from another (the site of reduction, the cathode), and so there is a net flow of current which can be used to do work. Note that the + sign of the cathode can be interpreted as indicating the electrode at which electrons enter the cell, and the − sign of the anode is where the electrons leave the cell.



10.8 In an electrolytic cell, electrons are forced through the circuit by an external source. Although the cathode is still the site of reduction, it is now the negative electrode whereas the anode, the site of oxidation, is positive.



10.9 One version of the Daniell cell. The copper electrode is the cathode and the zinc electrode is the anode. Electrons leave the cell from the zinc and enter it again through the copper electrode.

reduction takes place in the other compartment. As the reaction proceeds, the electrons released in the oxidation

$$\mathrm{Red}_1 \longrightarrow \mathrm{Ox}_1 + \nu e^-$$

at one electrode travel through the external circuit and re-enter the cell through the other electrode. There they bring about reduction:

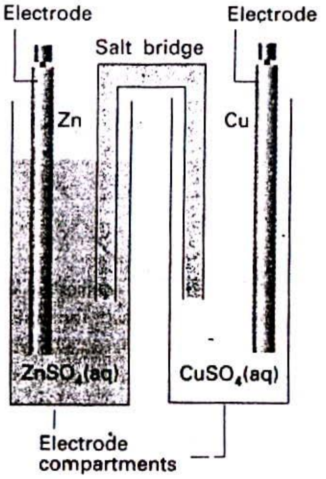
$$\mathrm{Ox}_2 + \nu e^- \longrightarrow \mathrm{Red}_2$$

The electrode at which oxidation occurs is called the **anode**; the electrode at which reduction occurs is called the **cathode.**

In a *galvanic cell*, the cathode has a higher potential than the anode: the species undergoing reduction, Ox_2, withdraws electrons from its electrode (the cathode, Fig. 10.7), so leaving a relative positive charge on it (corresponding to a high potential). At the anode, oxidation results in the transfer of electrons to the electrode, so giving it a relative negative charge (corresponding to a low potential). In an *electrolytic cell*, the anode is still the location of oxidation (by definition), but now electrons must be withdrawn from the species in that compartment because oxidation does not occur spontaneously, and at the cathode there must be a supply of electrons to drive the reduction. Therefore, in an electrolytic cell the anode must be made relatively positive to the cathode (Fig. 10.8).

10.4 Varieties of cells

The simplest type of cell has a single electrolyte common to both electrodes (as in Fig. 10.7). In some cases it is necessary to immerse the electrodes in different electrolytes, as in the 'Daniell cell' in which the redox couple at one electrode is $\mathrm{Cu}^{2+}/\mathrm{Cu}$ and at the other is $\mathrm{Zn}^{2+}/\mathrm{Zn}$ (Fig. 10.9). In an **electrolyte concentration cell**, the electrode compartments are



10.10 The salt bridge, essentially an inverted U-tube full of concentrated salt solution in a jelly, has two opposing liquid junction potentials which almost cancel.

identical except for the concentrations of the electrolytes. In an **electrode concentration** cell the electrodes themselves have different concentrations, either because they are gas electrodes operating at different pressures or because they are amalgams (solutions in mercury) with different concentrations.

(a) Liquid junction potentials

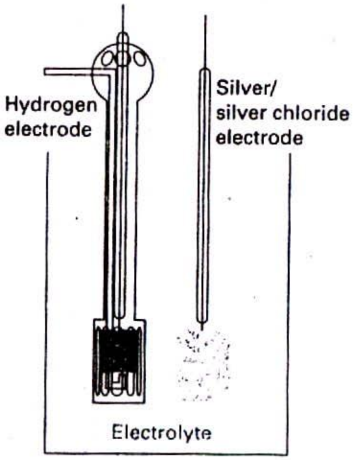
In a cell with two different electrolyte solutions in contact, as in the Daniell cell, there is an additional source of potential difference, the **liquid junction potential,** E_{lj}, across the interface of the two electrolytes. Another example of a junction potential is that between different concentrations of hydrochloric acid. At the junction, the mobile H^+ ions diffuse into the more dilute solution. The bulkier Cl^- ions follow, but initially do so more slowly, which results in a potential difference at the junction. The potential then settles down to a value such that, after that brief initial period, the ions diffuse at the same rates. Electrolyte concentration cells always have a liquid junction; electrode concentration cells do not.

The contribution of the liquid junction to the potential can be reduced (to about 1 to 2 mV) by joining the electrolyte compartments through a salt bridge (Fig. 10.10). The reason for the success of the salt bridge is that the liquid junction potentials at either end are largely independent of the concentrations of the two dilute solutions, and so nearly cancel.

(b) Notation

In the notation for cells, phase boundaries are denoted by a vertical bar. For example, the cell in Fig. 10.11 is denoted

$$Pt|H_2(g)|HCl(aq)|AgCl(s)|Ag(s)$$



10.11 A typical cell for measuring a standard potential consists of a hydrogen electrode (on the left) and the electrode for the couple of interest (on the right).

A liquid junction is denoted by ⁝, so the cell in Fig. 10.9 is denoted

$$Zn(s)|ZnSO_4(aq)\vdots CuSO_4(aq)|Cu(s)$$

A double vertical line, ||, denotes an interface for which it is assumed that the junction potential has been eliminated. Thus the cell in Fig. 10.10 is denoted

$$Zn(s)|ZnSO_4(aq)||CuSO_4(aq)|Cu(s)$$

An electrolyte concentration cell in which the liquid junction potential is assumed to be eliminated is denoted

$$Pt|H_2(g)|HCl(aq, b_1)||HCl(aq, b_2)|H_2(g)|Pt$$

(c) The cell reaction

The current produced by a galvanic cell arises from the spontaneous chemical reaction taking place inside it. The cell reaction is the reaction in the cell written on the assumption that the right-hand electrode is the cathode, and hence that the spontaneous reaction is one in which reduction is taking place in the right-hand compartment. Later we see how to predict if the right-hand electrode is in fact the cathode; if it is, then the cell reaction is spontaneous as written. If the left-hand electrode turns out to be the cathode, then the reverse of the cell reaction is spontaneous.

To write the cell reaction corresponding to a cell diagram, we first write the right-hand half-reaction as a reduction (because we have assumed that to be spontaneous). Then we subtract from it the left-hand reduction half-reaction (for, by implication, that electrode is the site of oxidation). Thus, in the cell

$$Zn(s)|ZnSO_4(aq)||CuSO_4(aq)|Cu(s)$$

the two electrodes and their reduction half-reactions are

$$\text{Right}: \quad \mathrm{Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)}$$
$$\text{Left}: \quad \mathrm{Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)}$$

Hence, the overall cell reaction is the difference:

$$\mathrm{Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq)}$$

(d) The cell potential

A cell in which the overall cell reaction has not reached chemical equilibrium can do electrical work as the reaction drives electrons through an external circuit. The work that a given transfer of electrons can accomplish depends on the potential difference between the two electrodes. This potential difference is called the **cell potential** and is measured in volts, V. When the cell potential is large, a given number of electrons travelling between the electrodes can do a large amount of electrical work. When the cell potential is small, the same number of electrons can do only a small amount of work. A cell in which the overall reaction is at equilibrium can do no work, and then the cell potential is zero.

According to the discussion in Section 4.6d, we know that the maximum electrical work that a system (the cell) can do is given by the value of ΔG, and in particular that, for a spontaneous process (in which both ΔG and w are negative) at constant temperature and pressure,

$$w_{\mathrm{e,max}} = \Delta G \tag{42}$$

Therefore, to make thermodynamic measurements on the cell by measuring the work it can do, we must ensure that it is operating reversibly. Only then is it producing maximum work and only then can eqn 42 be used to relate that work to ΔG. Moreover, we saw in Section 9.1a that the reaction Gibbs energy, $\Delta_r G$, is actually a derivative evaluated at a specified composition of the reaction mixture. Therefore, to measure $\Delta_r G$ we must ensure that the cell is operating reversibly at a specific, constant composition. Both these conditions are achieved by measuring the cell potential when it is balanced by an exactly opposing source of potential so that the cell reaction occurs reversibly and the composition is constant: in effect, the cell reaction is poised for change, but not actually changing. The resulting potential difference is called the **zero-current cell potential**, E (formerly, and still commonly, the 'electromotive force', or emf, of the cell).

(e) The relation between E and $\Delta_r G$

The relation between the reaction Gibbs energy and the zero-current cell potential is

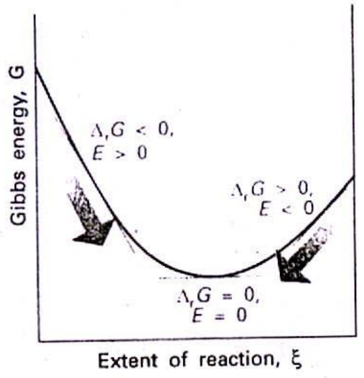
$$-\nu FE = \Delta_r G \tag{43}$$

where F is the Faraday constant. This equation, which is derived in the *Justification* below, is the key connection between electrical measurements on the one hand and thermodynamic properties on the other. It will be the basis of all that follows.

Justification 10.3

We consider the change in G when the cell reaction advances by an infinitesimal amount $\mathrm{d}\xi$ at some composition. We saw in *Justification 9.1* that, at constant temperature and pressure, G changes by

$$\mathrm{d}G = \sum_J \mu_J \,\mathrm{d}n_J = \sum_J \nu_J \mu_J \,\mathrm{d}\xi$$



10.12 As explained in Chapter 9, a spontaneous reaction occurs in the direction of decreasing Gibbs energy. When expressed in terms of a cell potential, the spontaneous direction of change can be expressed in terms of the cell potential E. The reaction is spontaneous as written (from left to right on the illustration) when $E>0$. The reverse reaction is spontaneous when $E<0$. When the cell reaction is at equilibrium, the cell potential is zero.

The reaction Gibbs energy, Δ_rG, at the specified composition is

$$\Delta_rG = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \sum_J \nu_J\mu_J$$

So we can write

$$dG = \Delta_rG\, d\xi$$

The maximum non-expansion work that the reaction can do as it advances by $d\xi$ at constant temperature and pressure is therefore

$$dw_e = \Delta_rG\, d\xi$$

This work is infinitesimal, and the composition of the system is virtually constant when it occurs.

Suppose that the reaction advances by $d\xi$, then $\nu\, d\xi$ electrons must travel from the anode to the cathode. The total charge transported between the electrodes when this change occurs is $-\nu eN_A\, d\xi$ (because $\nu\, d\xi$ is the amount of electrons and the charge per mole of electrons is $-eN_A$). Hence, the total charge transported is $-\nu F\, d\xi$ because $eN_A = F$.

The work done when an infinitesimal charge $-\nu F\, d\xi$ travels from the anode to the cathode is equal to the product of the charge and the potential difference E (see Table 2.1 and *Further information 5*):

$$dw_e = -\nu FE\, d\xi$$

When this relation is equated to the one above, the advancement $d\xi$ cancels, and eqn 43 is obtained.

It follows from eqn 43 that, by knowing the reaction Gibbs energy at a specified composition, we can state the zero-current cell potential at that composition. Note that a negative reaction Gibbs energy, corresponding to a spontaneous cell reaction, corresponds to a positive zero-current cell potential. Another way of looking at the content of eqn 43 is that it shows that the driving power of a cell (that is, the cell potential), is proportional to the slope of the Gibbs energy with respect to the extent of reaction. It is plausible that a reaction that is far from equilibrium (when the slope is steep) has a strong tendency to drive electrons through an external circuit (Fig. 10.12). When the slope is close to zero (when the cell reaction is close to equilibrium), the cell potential is small.

Illustration

To estimate the potential that can be expected for a typical cell we set $\Delta_rG \approx -100\ \text{kJ mol}^{-1}$ and $\nu = 1$; we find

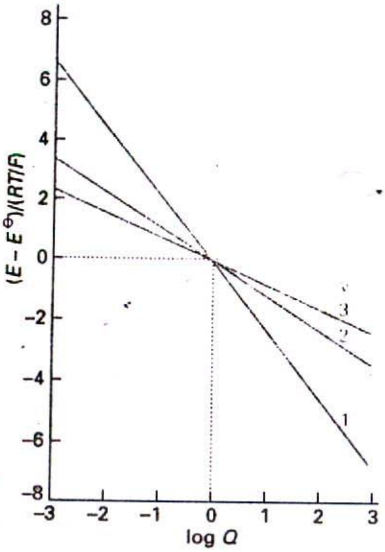
$$E \approx -\frac{(-100\times 10^3\ \text{J mol}^{-1})}{1\times(96\times 10^3\ \text{C mol}^{-1})} \approx 1\ \text{V}$$

We have used 1 J = 1 C V.

(f) The Nernst equation

We can go on to relate the zero-current cell potential to the activities of the participants in the cell reaction. We know from eqn 9.10 that the reaction Gibbs energy is related to the composition of the reaction mixture by

$$\Delta_rG = \Delta_rG^\ominus + RT\ \ln Q$$



10.13 The variation of cell potential with the value of the reaction quotient for the cell reaction for different values of ν (the number of electrons transferred). At 298 K, $RT/F = 25.69$ mV, so the vertical scale refers to multiples of this value.

with Q the reaction quotient. It follows, on division of both sides by $-\nu F$, that

$$E = -\frac{\Delta_r G^{\ominus}}{\nu F} - \frac{RT}{\nu F} \ln Q$$

The first term on the right is written

$$E^{\ominus} = -\frac{\Delta_r G^{\ominus}}{\nu F} \qquad [44]$$

and called the **standard cell potential**. That is, the standard cell potential, $E^{\ominus}$, is the standard reaction Gibbs energy expressed as a potential (in volts). It follows that

$$E = E^{\ominus} - \frac{RT}{\nu F} \ln Q \qquad (45)$$

This equation for the cell potential in terms of the composition is called the **Nernst equation**; the dependence of cell potential on composition that it predicts is summarized in Fig. 10.13.

We see from eqn 45 that the standard cell potential (which will shortly move to centre stage of the exposition) can be interpreted as the zero-current cell potential when all the reactants and products are in their standard states, for then all activities are 1, so $Q = 1$ and $\ln Q = 0$. However, the fact that it is merely a disguised form of the standard reaction Gibbs energy should always be kept in mind and underlies all its applications.

Illustration

Because $RT/F = 25.7$ mV at 25 °C, a practical form of the Nernst equation is

$$E = E^{\ominus} - \frac{25.7\ \text{mV}}{\nu} \ln Q$$

It then follows that, for a reaction in which $\nu = 1$, if Q is increased by a factor of 10, then the cell potential decreases by 59.2 mV.

(g) Concentration cells

The Nernst equation can be used to derive an expression for the potential of an electrolyte concentration cell. Consider the cell

$$\mathrm{M|M^+(aq,L)||M^+(aq,R)|M}$$

where the solutions L and R have different molalities. The cell reaction is

$$\mathrm{M^+(aq,R)} \longrightarrow \mathrm{M^+(aq,L)} \qquad Q = \frac{a_L}{a_R} \qquad \nu = 1$$

The standard cell potential is zero, because a cell cannot drive a current through a circuit when the two electrode compartments are identical (and, specifically, $\Delta_r G^{\ominus} = 0$ for the cell reaction). Therefore, the cell potential when the compartments have different concentrations is

$$E = -\frac{RT}{F} \ln \frac{a_L}{a_R} \approx -\frac{RT}{F} \ln \frac{b_L}{b_R} \qquad (46)$$

If R is the more concentrated solution, $E > 0$. Physically, the positive potential arises because positive ions tend to be reduced, so withdrawing electrons from the electrode. This process is dominant in the more concentrated right-hand electrode compartment.

One important example of a system that resembles this description is the biological cell wall, which is more permeable to K^+ ions than to either Na^+ or Cl^- ions. The concentration of K^+ inside the cell is about 20 to 30 times that on the outside, and is maintained at that level by a specific pumping operation fuelled by ATP and governed by enzymes. It follows from eqn 46 that the potential difference between the two sides is predicted to be about 77 mV. This estimate accords quite well with the measured value.

The transmembrane potential difference plays a particularly interesting role in the transmission of nerve impulses. Potassium and sodium ion pumps occur throughout the nervous system, and when the nerve is inactive there is a high K^+ concentration inside the cells and a high Na^+ concentration outside. The potential difference across the cell wall is about 70 mV. When the cell wall is subjected to a pulse of about 20 mV, the structure of the membrane adjusts and it becomes permeable to Na^+. This adjustment causes a decrease in membrane potential as the Na^+ flood into the interior of the cell. The change in potential difference triggers the adjacent part of the cell wall, and the pulse of collapsing potential passes along the nerve. Behind the pulse, the sodium and potassium pumps restore the concentration difference ready for the next pulse.

(h) Cells at equilibrium

A special case of the Nernst equation has great importance in electrochemistry. Suppose the reaction has reached equilibrium; then $Q = K$, where K is the equilibrium constant of the cell reaction. However, a chemical reaction at equilibrium cannot do work, and hence it generates zero potential difference between the electrodes of a galvanic cell. Therefore, setting $E = 0$ and $Q = K$ in the Nernst equation gives

$$\ln K = \frac{\nu F E^\ominus}{RT} \qquad (47)$$

This very important equation lets us predict equilibrium constants from measured standard cell potentials.

Illustration

Because the standard potential of the Daniell cell is +1.10 V, the equilibrium constant for the cell reaction (eqn 40, for which $\nu = 2$) is $K = 1.5 \times 10^{37}$. We conclude that the displacement of copper by zinc goes virtually to completion.

10.5 Standard potentials

A galvanic cell is a combination of two electrodes, and each one can be considered as making a characteristic contribution to the overall cell potential. Although it is not possible to measure the contribution of a single electrode, we can define the potential of one of the electrodes as having a zero potential and then assign values to others on that basis. The specially selected electrode is the **standard hydrogen electrode (SHE)**:

$$\mathrm{Pt}|\mathrm{H_2(g)}|\mathrm{H^+(aq)} \qquad E^\ominus = 0 \qquad [48]$$

at all temperatures. The **standard potential**, $E^\ominus$, of another couple is then assigned by constructing a cell in which it is the right-hand electrode and the standard hydrogen electrode is the left-hand electrode. For example, the standard potential of the Ag^+/Ag couple is the standard potential of the following cell:

$$\mathrm{Pt}|\mathrm{H_2(g)}|\mathrm{H^+(aq)}||\mathrm{Ag^+(aq)}|\mathrm{Ag(s)} \qquad E^\ominus(\mathrm{Ag^+/Ag}) = E^\ominus = +0.80\ \mathrm{V}$$

Likewise, the standard potential of the AgCl/Ag, Cl^- couple is the standard potential of the following cell:

$$\mathrm{Pt}|\mathrm{H_2(g)}|\mathrm{H^+(aq)Cl^-(aq)}|\mathrm{AgCl(s)}|\mathrm{Ag(s)}$$

$$E^\ominus(\mathrm{AgCl/Ag, Cl^-}) = E^\ominus = +0.22\ \mathrm{V}$$

Table 10.7* Standard potentials at 298 K

Couple	$E^\ominus$/V
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.61
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.76
$Na^+(aq) + e^- \rightarrow Na(s)$	−2.71

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

(Here and from now on, all values refer to 298 K.) Although a standard potential is written as though it refers to a half-reaction such as

$$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq) \qquad E^\ominus(AgCl/Ag, Cl^-) = +0.22\ V$$

it should be understood that these equations are only shorthand for writing

$$AgCl(s) + \tfrac{1}{2}H_2(g) \longrightarrow Ag(s) + H^+(aq) + Cl^-(aq) \qquad E^\ominus = +0.22\ V$$

and that the standard potential is determined by properties of the hydrogen electrode as well as the couple to which the potential refers. Table 10.7 lists standard potentials at 298 K.

An important feature of standard cell potentials and standard potentials is that they are unchanged if the chemical equation for the cell reaction or a half-reaction is multiplied by a numerical factor. A numerical factor increases the value of the standard Gibbs energy for the reaction, but it also increases the number of electrons transferred by the same factor, and by eqn 44 the value of $E^\ominus$ remains unchanged.

(a) The standard potential of a cell in terms of individual standard potentials

The standard potential of a cell formed from any two electrodes can be calculated by taking the difference of their standard potentials. This rule follows from the fact that a cell such as

$$Ag(s)|Ag^+(aq)||Cl^-(aq)|AgCl(s)|Ag(s)$$

is equivalent to two cells joined back-to-back:

$$Ag(s)|Ag^+(aq)||H^+(aq)|H_2(g)|Pt\text{—}Pt|H_2(g)|H^+(aq)||Cl^-(aq)|AgCl(s)|Ag(s)$$

The overall potential of this composite cell, and therefore of the cell of interest, is

$$E^\ominus = E^\ominus(AgCl/Ag, Cl^-) - E^\ominus(Ag^+/Ag) = -0.58\ V$$

The standard potentials in Table 10.7 can all be used in the same way, and the standard cell potential is the difference right – left of the corresponding standard potentials. Because $\Delta G^\ominus = -\nu FE^\ominus$, it then follows that, if the result gives $E^\ominus > 0$, then the corresponding cell reaction has $K > 1$.

Example 10.3 Identifying the spontaneous direction of a reaction

One of the reactions important in corrosion in an acidic environment is

$$Fe(s) + 2H^+(aq) + \tfrac{1}{2}O_2(g) \longrightarrow Fe^{2+}(aq) + H_2O(l)$$

Does the equilibrium constant favour the formation of $Fe^{2+}(aq)$?

Method We need to decide whether the standard potential for the reaction as written is positive, for a positive value would imply that $\Delta G^\ominus < 0$ and hence that $K > 1$. The sign of the cell potential is found by identifying the half-reactions that make up the overall reaction, and then taking their standard potentials from Table 10.7 in the *Data section* at the end of the book.

Answer The two reduction half-reactions are

$$(a)\ Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s) \qquad E^\ominus = -0.44\ V$$

$$(b)\ 2H^+(aq) + \tfrac{1}{2}O_2(g) + 2e^- \longrightarrow H_2O(l) \qquad E^\ominus = +1.23\ V$$

The difference (b) – (a) is

$$Fe(s) + 2H^+(aq) + \tfrac{1}{2}O_2(g) \longrightarrow Fe^{2+}(aq) + H_2O(l) \qquad E^\ominus = +1.67\ V$$

Therefore, because $E^{\ominus} > 0$, the reaction has $K > 1$, favouring products.

Comment Recall the point made earlier that the chemical equation for a half-reaction can be multiplied by any common factor without affecting its standard potential. Therefore, if either half-reaction needs to be multiplied by a factor before forming the difference (to ensure that the electrons in the equations cancel), the standard potentials are not affected.

Self-test 10.6 Does the displacement of copper by iron (that is, the reduction of Cu^{2+} by iron metal) have $K > 1$?

[Yes]

Example 10.4 Calculating an equilibrium constant

Calculate the equilibrium constant for the disproportionation $2Cu^+(aq) \rightarrow Cu(s) + Cu^{2+}(aq)$ at 298 K.

Method The strategy is to calculate the standard potential for the cell in which the reaction of interest is the cell reaction, and then to use eqn 47. To proceed, express the overall reaction as the difference of two reduction half-reactions and then find the corresponding standard potentials by referring to Table 10.7 in the *Data section*. Use $RT/F = 0.025693$ V at 298.15 K.

Answer The half-reactions and standard potentials we require are

$$\text{R: } Cu(s)|Cu^+(aq) \qquad Cu^+(aq) + e^- \longrightarrow Cu(s) \qquad E^{\ominus} = +0.52\text{ V}$$

$$\text{L: } Pt|Cu^{2+}(aq), Cu^+(aq) \qquad Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq) \qquad E^{\ominus} = +0.16\text{ V}$$

The standard cell potential is therefore

$$E^{\ominus} = +0.52\text{ V} - 0.16\text{ V} = +0.36\text{ V}$$

Then, because $\nu = 1$,

$$\ln K = \frac{0.36\text{ V}}{0.025693\text{ V}} = 14$$

Hence, $K = 1.2 \times 10^6$.

Comment The equilibrium lies strongly towards the right of the reaction as written, and so Cu^+ disproportionates almost totally in solution.

Self-test 10.7 Calculate the equilibrium constant for the reaction $Sn^{2+}(aq) + Pb(s) \rightarrow Sn(s) + Pb^{2+}(aq)$ at 298 K.

[0.5]

(b) The measurement of standard potentials

The procedure for measuring a standard potential can be illustrated by considering a specific case, the silver chloride electrode. The measurement is made on the 'Harned cell':

$$Pt|H_2(g)|HCl(aq)|AgCl(s)|Ag(s) \qquad \tfrac{1}{2}H_2(g) + AgCl(s) \longrightarrow HCl(aq) + Ag(s)$$

for which

$$E = E^{\ominus}(AgCl/Ag, Cl^-) - \frac{RT}{F}\ln\left(\frac{a_{H^+}a_{Cl^-}}{f_{H_2}/p^{\ominus}}\right)$$

We shall set $f = p^{\ominus}$ from now on. The activities can be expressed in terms of the molality, b, and the mean activity coefficient, $\gamma_{\pm}$, through eqn 13:

$$E = E^{\ominus}(\mathrm{AgCl/Ag, Cl^-}) - \frac{RT}{F}\ln b^2 - \frac{RT}{F}\ln \gamma_{\pm}^2 \tag{49}$$

This expression rearranges to

$$E + \frac{2RT}{F}\ln b = E^{\ominus}(\mathrm{AgCl/Ag, Cl^-}) - \frac{2RT}{F}\ln \gamma_{\pm} \tag{50}$$

From the Debye–Hückel limiting law for a 1,1-electrolyte,

$$\ln \gamma_{\pm} \propto -b^{1/2}$$

(the natural logarithm used here is proportional to the common logarithm that appears in eqn 19). Therefore, with the constant of proportionality in this relation written A':

$$E + \frac{2RT}{F}\ln b = E^{\ominus}(\mathrm{AgCl/Ag, Cl^-}) + \frac{2RTA'}{F}b^{1/2} \tag{51}$$

(in precise work, the $b^{1/2}$ term is brought to the left, and a higher order correction term from the extended Debye–Hückel law is used on the right.) The expression on the left is evaluated at a range of molalities, plotted against $b^{1/2}$, and extrapolated to $b = 0$. The intercept at $b^{1/2} = 0$ is the value of $E^{\ominus}(\mathrm{Ag/AgCl, Cl^-})$.

Example 10.5 Determining the standard potential of a cell

The potential of the cell $\mathrm{Zn|ZnCl_2(aq,}b\mathrm{)|AgCl(s)|Ag}$ at 25 °C has the following values:

$b/(10^{-3}b^{\ominus})$	0.772	1.253	1.453	3.112	6.022
E/V	1.2475	1.2289	1.2235	1.1953	1.1742

Determine the standard potential of the cell.

Method Proceed as described above, but adjusted to the cell reaction. Start by writing the Nernst equation for the cell, and then express the activities that occur in Q in terms of the mean activity coefficient. The latter can be written as proportional to $b^{1/2}$ by using the Debye–Hückel limiting law. However, there is no need to write all the constants because the standard cell potential is obtained by extrapolation, as explained in the text.

Answer The ionic equation for the cell reaction is

$$\mathrm{Zn(s) + 2AgCl(s) \longrightarrow 2Ag(s) + Zn^{2+}(aq) + 2Cl^-(aq)}$$

$$Q = a_{\mathrm{Zn^{2+}}}a_{\mathrm{Cl^-}}^2 \qquad \nu = 2$$

because all the solids are at unit activity. The Nernst equation is therefore

$$E = E^{\ominus} - \frac{RT}{2F}\ln a_{\mathrm{Zn^{2+}}}a_{\mathrm{Cl}}^2$$

The activities are related to the molality, b, of $\mathrm{ZnCl_2}$ by

$$a_{\mathrm{Zn^{2+}}}a_{\mathrm{Cl^-}}^2 = \gamma_{\pm}^3 b_{\mathrm{Zn^{2+}}}b_{\mathrm{Cl^-}}^2 = 4\gamma_{\pm}^3 b^3$$

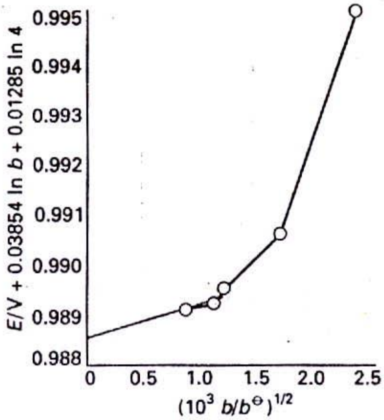
because $b_{\mathrm{Zn^{2+}}} = b$ and $b_{\mathrm{Cl^-}} = 2b$ for a fully dissociated salt. Only a little work is then needed to convert the Nernst equation into

$$E + \frac{3RT}{2F}\ln b + \frac{RT}{2F}\ln 4 = E^{\ominus} + Cb^{1/2}$$

where C is a collection of constants that come from the limiting law. We now draw up the following table, using $RT/2F = 0.01285$ V:

$b/(10^{-3}\,b^{\ominus})$	0.772	1.253	1.453	3.112	6.022
$(b/(10^{-3}\,b^{\ominus}))^{1/2}$	0.879	1.119	1.205	1.764	2.454
$E/\mathrm{V} + 0.03854 \ln b$ $+ 0.01285 \ln 4$	0.9891	0.9892	0.9895	0.9906	0.9950

The data are plotted in Fig. 10.14; as can be seen, they extrapolate to $E^{\ominus} = +0.9886$ V



10.14 The plot, and the extrapolation used for the experimental measurement of a standard cell potential. The intercept at $b^{1/2} = 0$ is $E^{\ominus}$.

Self-test 10.8 The data below are for the cell $\mathrm{Pt|H_2(g,}\,p^{\ominus})|\mathrm{HBr(aq,}\,b)|\mathrm{AgBr(s)|Ag}$ at 25°C. Determine the standard cell potential.

$b/(10^{-4}\,b^{\ominus})$	4.042	8.444	37.19
E/V	0.47381	0.43636	0.36173

[0.071 V]

(c) The measurement of activity coefficients

Once the standard potential of an electrode in a cell is known, the activities of the ions with respect to which it is reversible can be determined simply by measuring the cell potential with the ions at the concentration of interest. For example, the mean activity coefficient of the ions in hydrochloric acid of molality b is obtained from eqn 50 in the form

$$\ln \gamma_{\pm} = \frac{E^{\ominus}(\mathrm{AgCl/Ag, Cl^-}) - E}{2RT/F} - \ln b \qquad \{52\}$$

once E has been measured.

Applications of standard potentials

Zero-current cell potentials are a convenient source of data on the Gibbs energies, enthalpies, and entropies of reactions. In practice the standard values of these quantities are the ones normally determined.

10.6 The electrochemical series

We have seen that for two redox couples, $\mathrm{Ox_1/Red_1}$ and $\mathrm{Ox_2/Red_2}$, and the cell

$$\mathrm{Red_1, Ox_1 \| Red_2, Ox_2} \qquad E^{\ominus} = E_2^{\ominus} - E_1^{\ominus} \qquad (53a)$$

that the cell reaction

$$\mathrm{Red_1 + Ox_2 \longrightarrow Ox_1 + Red_2} \qquad (53b)$$

is spontaneous as written if $E^{\ominus} > 0$, and therefore if $E_2^{\ominus} > E_1^{\ominus}$. Because in the cell reaction $\mathrm{Red_1}$ reduces $\mathrm{Ox_2}$, we can conclude that $\mathrm{Red_1}$ has a thermodynamic tendency to reduce $\mathrm{Ox_2}$ if $E_1^{\ominus}$ is lower than $E_2^{\ominus}$. More briefly: low reduces high.

Illustration

Because $E^{\ominus}(\mathrm{Zn^{2+}, Zn}) = -0.76\ \mathrm{V} < E^{\ominus}(\mathrm{Cu^{2+}, Cu}) = +0.34$ V, zinc has a thermodynamic tendency to reduce $\mathrm{Cu^{2+}}$ ions in aqueous solution.

Table 10.8* The electrochemical series of the metals

Least strongly reducing
Gold
Platinum
Silver
Mercury
Copper
(Hydrogen)
Lead
Tin
Nickel
Iron
Zinc
Chromium
Aluminium
Magnesium
Sodium
Calcium
Potassium
Most strongly reducing

* The complete series can be inferred from Table 10.7

Table 10.8 shows a part of the electrochemical series, the metallic elements (and hydrogen) arranged in the order of their reducing power as measured by their standard potential in aqueous solution. A metal low in the series (with a lower standard potential) can reduce the ions of metals with higher standard potentials. This conclusion is qualitative. The quantitative value of K is obtained by doing the calculations we have described previously. For example, to determine whether zinc can displace magnesium from aqueous solutions at 298 K, we note that zinc lies above magnesium in the electrochemical series, so zinc cannot reduce magnesium ions in aqueous solution. Zinc can reduce hydrogen ions, because hydrogen lies higher in the series. However, even for reactions that are thermodynamically favourable, there may be kinetic factors that result in very slow rates of reaction.

10.7 Solubility constants

We can discuss the solubility S (the molality of the saturated solution) of a sparingly soluble salt MX in terms of the equilibrium

$$\mathrm{MX(s)} \rightleftharpoons \mathrm{M^{+}(aq)} + \mathrm{X^{-}(aq)} \qquad K_s = a_{\mathrm{M^+}}a_{\mathrm{X^-}} \qquad [54]$$

where the activities are those at equilibrium (that is, in the saturated solution) and we have used $a = 1$ for a pure solid. The equilibrium constant K_s is called the **solubility constant** (formerly, and still commonly, the *solubility product*) of the salt. When the solubility is so low that $\gamma_\pm \approx 1$ even in the saturated solution, we can write $a = b/b^\ominus$; moreover, because both molalities are equal to S in the saturated solution, we can conclude that

$$K_s \approx S^2$$

and hence that

$$S \approx K_s^{1/2} \qquad \{55\}$$

It follows that we can estimate S from the standard potential of a cell with a reaction corresponding to the solubility equilibrium.

Example 10.6 Evaluating a solubility from electrochemical data

Evaluate the solubility of AgCl(s) from cell potential data at 298 K.

Method We need to find an electrode combination that reproduces the solubility equilibrium, and then identify the solubility constant with the equilibrium constant of the cell reaction. The solubility itself is obtained from an equation like eqn 55 in conjunction with eqn 47 ($\ln K = \nu FE^\ominus/RT$).

Answer The solubility equilibrium is

$$\mathrm{AgCl(s)} \rightleftharpoons \mathrm{Ag^{+}(aq)} + \mathrm{Cl^{-}(aq)} \qquad K_s = a_{\mathrm{Ag^+}}a_{\mathrm{Cl^-}}$$

and we saw in Example 10.1 that this equation can be expressed as the difference of the following half-reactions:

$$\mathrm{AgCl(s)} + \mathrm{e^-} \longrightarrow \mathrm{Ag(s)} + \mathrm{Cl^-(aq)} \qquad E^\ominus = +0.22\ \mathrm{V}$$
$$\mathrm{Ag^+(aq)} + \mathrm{e^-} \longrightarrow \mathrm{Ag(s)} \qquad E^\ominus = +0.80\ \mathrm{V}$$

The cell potential is therefore -0.58 V. Then, because $\nu = 1$,

$$\ln K_s = \frac{\nu E^\ominus}{RT/F} = \frac{1 \times (-0.58\ \mathrm{V})}{2.5693 \times 10^{-2}\ \mathrm{V}} = -23$$

Therefore, $K_s = 1.0 \times 10^{-10}$ and $S = 1.0 \times 10^{-5}\ \mathrm{mol\,kg^{-1}}$.

Self-test 10.9 Calculate the solubility constant and the solubility of mercury(I) chloride at 298 K. (*Hint*: The mercury(I) ion is the diatomic species Hg_2^{2+}.)

[2.6×10^{-18}, 8.7×10^{-7} mol kg^{-1}]

10.8 The measurement of pH and pK

The potential of a hydrogen electrode in which the half-reaction is

$$H^+(aq) + e^- \longrightarrow \tfrac{1}{2}H_2(g) \qquad Q = \frac{(f_{H_2}/p^\ominus)^{1/2}}{a_{H^+}} \qquad \nu = 1$$

with $f_{H_2} = p^\ominus$ is

$$E(H^+/H_2) = \frac{RT}{F} \ln a_{H^+} = -\frac{RT \ln 10}{F} \mathrm{pH} \tag{56}$$

(because $E^\ominus(H^+/H_2) = 0$). This expression makes sense physically. Increasing the pH above 0 (lowering the hydrogen ion activity below 1) decreases the tendency of the positive ions to discharge at the electrode, so we should expect its potential to become negative. At 25 °C, when $RT/F = 25.69$ mV, this relation becomes

$$E(H^+/H_2) = -59.16 \text{ mV} \times \mathrm{pH} \tag{57}$$

Each unit increase in pH decreases the electrode potential by 59 mV.

(a) The determination of pH

The measurement of the pH of a solution is simple in principle, for it is based on the measurement of the potential of a hydrogen electrode immersed in the solution. The left-hand electrode of the cell is typically a saturated calomel ($Hg_2Cl_2(s)$) reference electrode with potential E(cal); the right-hand electrode is the hydrogen electrode with potential given by eqn 56. The pH of the cell is therefore

$$\mathrm{pH} = \frac{E + E(\mathrm{cal})}{(-59.16 \text{ mV})} \tag{58}$$

The practical definition of the pH of a solution X is

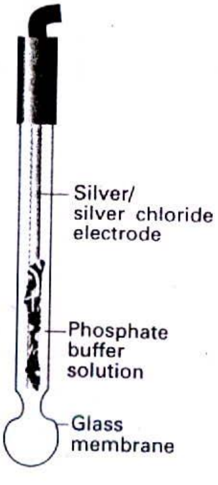
$$\mathrm{pH} = \mathrm{pH(S)} - \frac{FE}{RT \ln 10} \qquad [59]$$

where E is the potential of the cell

$$\mathrm{Pt}|H_2(g)|S(aq)||3.5 \text{ M KCl(aq)}||X(aq)|H_2(g)|\mathrm{Pt}$$

and S is a solution of standard pH. The currently recommended primary standards include a saturated aqueous solution of potassium hydrogen tartrate, which has pH = 3.557 at 25 °C and 0.0100 mol kg^{-1} disodium tetraborate, which has pH = 9.180 at that temperature.

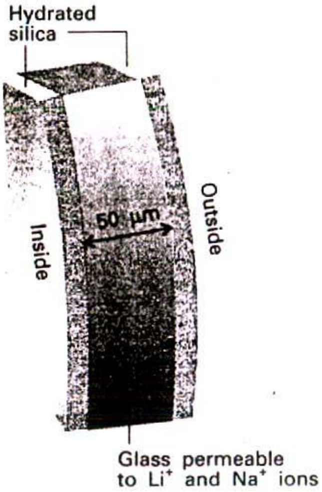
In practice, indirect methods are much more convenient, and the hydrogen electrode is replaced by the glass electrode (Fig. 10.15). This electrode is sensitive to hydrogen ion activity, and has a potential proportional to pH. It is filled with a phosphate buffer containing Cl^- ions, and conveniently has $E = 0$ when the external medium is at pH = 7. The glass electrode is much more convenient to handle than the gas electrode itself, and can be calibrated using solutions of known pH.



10.15 The glass electrode. It is usually used in conjunction with a calomel electrode that makes contact with the test solution through a salt bridge.

The responsiveness of a glass electrode to the hydronium ion activity is a result of complex processes at the interface between the glass membrane and the solutions on either side of it. The membrane itself is permeable to Na^+ and Li^+ ions but not to H^+ ions. Therefore, the potential difference across the glass membrane must arise by a mechanism that is different from that responsible for biological transmembrane potentials. A clue to the mechanism comes from a detailed inspection of the glass membrane, for each face is coated with a thin layer of hydrated silica (Fig. 10.16). The hydrogen ions in the test solution modify this layer to an extent that depends on their activity in the solution, and the charge modification of the outside layer is transmitted to the inner layer by the Na^+ and Li^+ ions in the glass. The hydronium ion activity gives rise to a membrane potential by this indirect mechanism.

The electrochemical determination of pH opens up a route to the electrochemical determination of pK_a, for we saw in Section 9.5c that the pK_a of an acid is equal to the pH of a solution containing equal amounts of the acid and its conjugate base.



10.16 A section through the wall of a glass electrode.

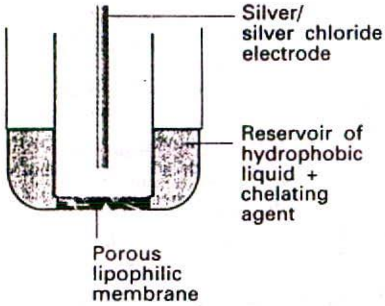
(b) Species-selective electrodes

A suitably adapted glass electrode can be used to detect the presence of certain gases. A simple form of a gas-sensing electrode consists of a glass electrode contained in an outer sleeve filled with an aqueous solution and separated from the test solution by a membrane that is permeable to gas. When a gas such as sulfur dioxide or ammonia diffuses into the aqueous solution, it modifies its pH, which in turn affects the potential of the glass electrode.

Somewhat more sophisticated devices are used as ion-selective electrodes that give potentials according to the presence of specific ions present in a test solution. In one arrangement, a porous lipophilic (hydrocarbon-attracting) membrane is attached to a small reservoir of a hydrophobic (water-repelling) liquid, such as dioctylphenylphosphonate, that saturates it (Fig. 10.17). The liquid contains a chelating agent, such as $(RO)_2PO_2^-$ with R a C_8 to C_{18} chain, that acts as a kind of solubilizing agent for the ions with which it can form a complex. The chelated ions are able to migrate through the lipophilic membrane, and hence give rise to a transmembrane potential, which is detected by a silver/silver chloride electrode in the interior of the assembly. Electrodes of this construction can be designed to be sensitive to a variety of ionic species, including calcium, zinc, iron, lead, and copper ions.

10.9 Thermodynamic functions from cell potential measurements

The standard cell potential is related to the standard reaction Gibbs energy through eqn 44 ($\Delta_r G^\ominus = -\nu F E^\ominus$). Therefore, by measuring $E^\ominus$ we can obtain this important thermodynamic quantity. Its value can then be used to calculate the Gibbs energy of formation of ions using the convention explained in Section 10.1a.



10.17 The structure of an ion-selective electrode. Chelated ions are able to migrate through the lipophilic membrane.

Illustration

The cell reaction of

$$\mathrm{H_2|H^+(aq)||Ag^+(aq)|Ag} \qquad E^\ominus = +0.7996\ \mathrm{V}$$

is

$$\mathrm{Ag^+(aq) + \tfrac{1}{2}H_2(g) \longrightarrow H^+(aq) + Ag(s)} \qquad \Delta_r G^\ominus = -\Delta_f G^\ominus(\mathrm{Ag^+, aq})$$

Therefore, with $\nu = 1$, we find

$$\Delta_f G^\ominus(\mathrm{Ag^+, aq}) = -(-FE^\ominus) = +77.10\ \mathrm{kJ\,mol^{-1}}$$

as in Table 2.6 in the *Data section.*

Example 10.7 Evaluating a standard potential from two others

Given that the standard potentials of the Cu^{2+}/Cu and Cu^+/Cu couples are +0.340 V and +0.522 V, respectively, evaluate $E^\ominus(Cu^{2+}, Cu^+)$.

Method First, we note that reaction Gibbs energies may be added (as in Hess's law analyses of reaction enthalpies). Therefore, we should convert the $E^\ominus$ values to $\Delta G^\ominus$ values by using eqn 44, add them appropriately, and then convert the overall $\Delta G^\ominus$ to the required $E^\ominus$ by using eqn 44 again. This roundabout procedure is necessary because, as we shall see, although the factor F cancels, the factor ν in general does not.

Answer The electrode reactions are as follows:

$$\text{(a) } Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$

$$E^\ominus = +0.340\text{ V, so } \Delta_r G^\ominus = -2(0.340\text{ V})F$$

$$\text{(b) } Cu^{+}(aq) + e^- \longrightarrow Cu(s)$$

$$E^\ominus = +0.522\text{ V, so } \Delta_r G^\ominus = -(0.522\text{ V})F$$

The required reaction is

$$\text{(c) } Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq) \qquad E^\ominus = -\Delta_r G^\ominus/F$$

Because (c) = (a) − (b), the standard Gibbs energy of reaction (c) is

$$\Delta_r G^\ominus = \Delta_r G^\ominus(a) - \Delta_r G^\ominus(b) = -(0.160\text{ V}) \times F$$

Therefore, $E^\ominus = +0.160$ V.

Comment Note that we cannot combine the $E^\ominus$ values directly and we must always work via $\Delta G^\ominus$. Alternatively, note that the generalization of the calculation illustrated above is

$$\nu_c E^\ominus(c) = \nu_a E^\ominus(a) - \nu_b E^\ominus(b)$$

Self-test 10.10 Calculate the standard potential of the Fe^{3+}/Fe couple from the values for the Fe^{3+}/Fe^{2+} and Fe^{2+}/Fe couples.

[−0.037 V]

The temperature coefficient of the cell potential gives the entropy of the cell reaction. This conclusion follows from the thermodynamic relation $(\partial G/\partial T)_p = -S$ and eqn 44, which combine to give

$$\frac{dE^\ominus}{dT} = \frac{\Delta_r S^\ominus}{\nu F} \tag{60}$$

(The derivative is complete because $E^\ominus$, like $\Delta_r G^\ominus$, is independent of the pressure.) Hence we have an electrochemical technique for obtaining standard reaction entropies and through them the entropies of ions in solution.

Finally, we can combine the results obtained so far and use them to obtain the standard reaction enthalpy:

$$\Delta_r H^\ominus = \Delta_r G^\ominus + T\Delta_r S^\ominus = -\nu F\left(E^\ominus - T\frac{dE^\ominus}{dT}\right) \tag{61}$$

This expression provides a noncalorimetric method for measuring $\Delta_r H^\ominus$ and, through the convention $\Delta_f H^\ominus(H^+, aq) = 0$, the standard enthalpies of formation of ions in solution. Thus, electrical measurements can be used to calculate all the thermodynamic properties with which this chapter began.

Example 10.8 Using the temperature coefficient of the cell potential

The standard cell potential of

$$\mathrm{Pt|H_2(g)|HBr(aq)|AgBr(s)|Ag(s)}$$

was measured over a range of temperatures, and the data were fitted to the following polynomial:

$$E^\ominus/\mathrm{V} = 0.07131 - 4.99\times10^{-4}(T/\mathrm{K}-298) - 3.45\times10^{-6}(T/\mathrm{K}-298)^2$$

Evaluate the standard reaction Gibbs energy, enthalpy, and entropy at 298 K.

Method The standard Gibbs energy of reaction is obtained by using eqn 44 after evaluating $E^\ominus$ at 298 K. The standard entropy of reaction is obtained by using eqn 60, which involves differentiating the polynomial with respect to T and then setting $T = 298$ K. The reaction enthalpy is obtained by combining the values of the standard Gibbs energy and entropy.

Answer At $T = 298$ K, $E^\ominus = +0.07131$ V, so

$$\begin{aligned}\Delta_r G^\ominus &= -\nu F E^\ominus = -(1)\times(96.485\ \mathrm{kC\,mol^{-1}})\times(+0.07131\ \mathrm{V})\\ &= -6.880\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

The temperature coefficient of the cell potential is

$$\frac{dE^\ominus}{dT} = -4.99\times10^{-4}\ \mathrm{V\,K^{-1}} - 2(3.45\times10^{-6})(T/\mathrm{K}-298)\ \mathrm{V\,K^{-1}}$$

At $T = 298$ K this expression evaluates to

$$\frac{dE}{dT} = -4.99\times10^{-4}\ \mathrm{V\,K^{-1}}$$

So, from eqn 60, the reaction entropy is

$$\begin{aligned}\Delta_r S^\ominus &= 1\times(9.6485\times10^4\ \mathrm{C\,mol^{-1}})\times(-4.99\times10^{-4}\ \mathrm{V\,K^{-1}})\\ &= -48.2\ \mathrm{J\,K^{-1}\,mol^{-1}}.\end{aligned}$$

It then follows that

$$\begin{aligned}\Delta_r H^\ominus &= \Delta_r G^\ominus + T\Delta_r S^\ominus\\ &= -6.880\ \mathrm{kJ\,mol^{-1}} + (298\ \mathrm{K})\times(-0.0482\ \mathrm{kJ\,K^{-1}\,mol^{-1}})\\ &= -21.2\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

Comment One difficulty with this procedure lies in the accurate measurement of small temperature coefficients of cell potential. Nevertheless, it is another example of the striking ability of thermodynamics to relate the apparently unrelated, in this case to relate electrical measurements to thermal properties.

Self-test 10.11 Predict the standard potential of the Harned cell at 303 K from tables of thermodynamic data.

[+0.2190 V]

Checklist of key ideas

The thermodynamic properties of ions in solution

10.1 Thermodynamic functions of formation

- ☐ the standard enthalpy of formation of ions in solution
- ☐ the definition of standard enthalpy and Gibbs energy of formation of ions (1)
- ☐ the analysis of contributions to $\Delta_f G^{\ominus}$
- ☐ the use of a thermodynamic cycle
- ☐ the Born equation (4)
- ☐ the standard entropy of a hydrogen ion in water (6)
- ☐ the standard (partial molar) entropies of other ions

10.2 Ion activities

- ☐ the activity of an ion in solution (7)
- ☐ the activity coefficient (8)
- ☐ the chemical potential of an ion (10)
- ☐ mean activity coefficient (13,16)
- ☐ total Gibbs energy of ions in solution (18)
- ☐ Debye–Hückel theory
- ☐ ionic atmosphere
- ☐ Debye–Hückel limiting law (19)
- ☐ ionic strength (20)
- ☐ shielded Coulomb potential (24)
- ☐ Debye length (24,33)
- ☐ Poisson's equation (25)
- ☐ Faraday constant (29)
- ☐ extended Debye–Hückel law (39)

Electrochemical cells

- ☐ electrochemical cell
- ☐ electrode
- ☐ electrolyte
- ☐ electrode compartment
- ☐ salt bridge
- ☐ galvanic cell
- ☐ electrolytic cell

10.3 Half-reactions and electrodes

- ☐ oxidation
- ☐ reduction
- ☐ redox reaction
- ☐ reducing agent
- ☐ oxidizing agent
- ☐ half-reaction
- ☐ redox couple
- ☐ reaction quotient for a half-reaction
- ☐ anode
- ☐ cathode

10.4 Varieties of cells

- ☐ electrolyte concentration cell
- ☐ electrode concentration cell
- ☐ liquid junction potential
- ☐ cell notation
- ☐ the convention for writing the cell reaction
- ☐ cell potential
- ☐ zero-current cell potential (emf)
- ☐ the cell potential in terms of the reaction Gibbs energy (43)
- ☐ standard cell potential (44)
- ☐ Nernst equation for the cell potential (45)
- ☐ the potential of an electrolyte concentration cell (46) and transmembrane potentials
- ☐ the relation between the equilibrium constant for the cell reaction and the standard cell potential (47)

10.5 Standard potentials

- ☐ standard hydrogen electrode (SHE)
- ☐ standard potential ($E^{\ominus}$)
- ☐ the standard cell potential in terms of the standard potentials of the electrodes
- ☐ the graphical determination of standard potential
- ☐ the electrochemical determination of activity coefficients (52)

Applications of standard potentials

10.6 The electrochemical series

- ☐ the interpretation of the relative sizes of standard potentials
- ☐ the electrochemical series

10.7 Solubility constants

- ☐ solubility constant (54)
- ☐ the relation between solubility constant and solubility (55)

10.8 The measurement of pH and pK

- ☐ the variation of cell potential with **pH** (57)
- ☐ practical definition of **pH**
- ☐ glass electrode
- ☐ the determination of $\mathrm{p}K_a$
- ☐ the action of ion-selective electrodes

10.9 Thermodynamic functions from cell potential measurements

- ☐ the temperature coefficient of cell potential (60)
- ☐ the determination of standard reaction entropy and enthalpy (60,61)

Further reading

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Exercises

10.1 (a) Calculate $\Delta_r H^\ominus$ for the reaction $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$ from the information in Table 2.6 in the *Data section*.

10.1 (b) Calculate $\Delta_r H^\ominus$ for the reaction $NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + NaNO_3(aq)$ from the information in Table 2.6 in the *Data section*.

10.2 (a) Calculate the molar solubility of mercury(II) chloride at 25 °C from standard Gibbs energies of formation.

10.2 (b) Calculate the molar solubility of lead(II) sulfide at 25 °C where the standard Gibbs energy of formation is $-98.7\ \mathrm{kJ\,mol^{-1}}$.

10.3 (a) Estimate the standard Gibbs energy of formation of $F^-(aq)$ from the value for $Cl^-(aq)$, taking the radius of F^- as 131 pm.

10.3 (b) Estimate the standard Gibbs energy of formation of $NO_3^-(aq)$ from the value for $Cl^-(aq)$, taking the radius of the nitrate ion as 189 pm (its thermochemical radius).

10.4 (a) Relate the ionic strengths of (a) KCl, (b) $FeCl_3$, and (c) $CuSO_4$ solutions to their molalities, *b*.

10.4 (b) Relate the ionic strengths of (a) $MgCl_2$, (b) $Al_2(SO_4)_3$, and (c) $Fe_2(SO_4)_3$ solutions to their molalities, *b*.

10.5 (a) Calculate the ionic strength of a solution that is $0.10\ \mathrm{mol\,kg^{-1}}$ in KCl(aq) and $0.20\ \mathrm{mol\,kg^{-1}}$ in $CuSO_4(aq)$.

10.5 (b) Calculate the ionic strength of a solution that is $0.040\ \mathrm{mol\,kg^{-1}}$ in $K_3[Fe(CN)_6](aq)$, $0.030\ \mathrm{mol\,kg^{-1}}$ in KCl(aq), and $0.050\ \mathrm{mol\,kg^{-1}}$ in NaBr(aq).

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

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

10.7 (a) What molality of $CuSO_4$ has the same ionic strength as $1.00\ \mathrm{mol\,kg^{-1}}$ KCl(aq)?

10.7 (b) What molality of $Al_2(SO_4)_3$ has the same ionic strength as $0.500\ \mathrm{mol\,kg^{-1}}\ Ca(NO_3)_2(aq)$?

10.8 (a) Express the mean activity coefficient of the ions in a solution of $CaCl_2$ in terms of the activity coefficients of the individual ions.

10.8 (b) Express the mean activity coefficient of the ions in a solution of $Al_2(SO_4)_3$ in terms of the activity coefficients of the individual ions.

10.9 (a) Estimate the mean ionic activity coefficient for $CaCl_2$ in a solution that is $0.010\ \mathrm{mol\,kg^{-1}}\ CaCl_2(aq)$ and $0.030\ \mathrm{mol\,kg^{-1}}$ NaF(aq).

10.9 (b) Estimate the mean ionic activity coefficient for NaCl in a solution that is $0.020\ \mathrm{mol\,kg^{-1}}$ NaCl(aq) and $0.035\ \mathrm{mol\,kg^{-1}}\ Ca(NO_3)_2(aq)$.

10.10 (a) The mean activity coefficient in a $0.500\ \mathrm{mol\,kg^{-1}}\ LaCl_3(aq)$ solution is 0.303 at 25 °C. What is the percentage error in the value predicted by the Debye–Hückel limiting law?

10.10 (b) The mean activity coefficient in a $0.100\ \mathrm{mol\,kg^{-1}}\ CaCl_2(aq)$ solution is 0.524 at 25 °C. What is the percentage error in the value predicted by the Debye–Hückel limiting law?

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

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

10.12 (a) For CaF_2, $K_s = 3.9 \times 10^{-11}$ at 25 °C and the standard Gibbs energy of formation of $CaF_2(s)$ is $-1167\ \mathrm{kJ\,mol^{-1}}$. Calculate the standard Gibbs energy of formation of $CaF_2(aq)$.

10.12 (b) For PbI_2, $K_s = 1.4 \times 10^{-8}$ at 25 °C and the standard Gibbs energy of formation of $PbI_2(s)$ is -173.64 kJ mol^{-1}. Calculate the standard Gibbs energy of formation of $PbI_2(aq)$.

10.13 (a) Consider a hydrogen electrode in aqueous HBr solution at 25 °C operating at 1.15 atm. Calculate the change in the electrode potential when the molality of the acid is changed from 5.0 mmol kg^{-1} to 20.0 mol kg^{-1}. Activity coefficients are given in Exercise 10.11a.

10.13 (b) Consider a hydrogen electrode in aqueous HCl solution at 25 °C operating at 105 kPa. Calculate the change in the electrode potential when the molality of the acid is changed from 5.0 mmol kg^{-1} to 50 mol kg^{-1}. Activity coefficients are given in Table 10.5.

10.14 (a) Devise a cell in which the cell reaction is $Mn(s) + Cl_2(g) \rightarrow MnCl_2(aq)$. Give the half-reactions for the electrodes and from the standard cell potential of 2.54 V deduce the standard potential of the Mn^{2+}/Mn couple.

10.14 (b) Devise a cell in which the cell reaction is $Cd(s) + Ni(OH)_3(s) \rightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$. Give the half-reactions for the electrodes.

10.15 (a) Write the cell reactions and electrode half-reactions for the following cells:

(a) $Zn|ZnSO_4(aq)||AgNO_3(aq)|Ag$

(b) $Cd|CdCl_2(aq)||HNO_3(aq)|H_2(g)|Pt$

(c) $Pt|K_3[(CN)_6](aq), K_4[(CN)_6](aq)||CrCl_3(aq)|Cr$

10.15 (b) Write the cell reactions and electrode half-reactions for the following cells:

(a) $Pt|Cl_2(g)|HCl(aq)||K_2CrO_4(aq)|Ag_2CrO_4(s)|Ag$

(b) $Pt|Fe^{3+}(aq), Fe^{2+}(aq)||Sn^{4+}(aq), Sn^{2+}(aq)|Pt$

(c) $Cu|Cu^{2+}(aq)||Mn^{2+}(aq), H^+(aq)|MnO_2(s)|Pt$

10.16 (a) Devise cells in which the following are the reactions:

(a) $Zn(s) + CuSO_4(aq) \longrightarrow ZnSO_4(aq) + Cu(s)$

(b) $2AgCl(s) + H_2(g) \longrightarrow 2HCl(aq) + 2Ag(s)$

(c) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

10.16 (b) Devise cells in which the following are the reactions:

(a) $2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$

(b) $H_2(g) + I_2(g) \longrightarrow 2HI(aq)$

(c) $H_3O^+(aq) + OH^-(aq) \longrightarrow 2H_2O(l)$

10.17 (a) Use standard potentials to calculate the standard potentials of the cells in Exercise 10.15a.

10.17 (b) Use standard potentials to calculate the standard potentials of the cells in Exercise 10.15b.

10.18 (a) Use standard potentials to calculate the standard potentials of the cells in Exercise 10.16a.

10.18 (b) Use standard potentials to calculate the standard potentials of the cells in Exercise 10.16b.

10.19 (a) Calculate the standard Gibbs energies at 25 °C of the following reactions from the standard potential data in Table 10.7:

(a) $2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$

(b) $2K(s) + 2H_2O(l) \longrightarrow 2KOH(aq) + H_2(g)$

10.19 (b) Calculate the standard Gibbs energies at 25 °C of the following reactions from the standard potential data in Table 10.7:

(a) $K_2S_2O_8(aq) + 2KI(aq) \longrightarrow I_2(s) + 2K_2SO_4(aq)$

(b) $Pb(s) + Zn(NO_3)_2(aq) \longrightarrow Pb(NO_3)_2(aq) + Zn(s)$

10.20 (a) The standard reaction Gibbs energy for

$K_2CrO_4(aq) + 2Ag(s) + 2FeCl_3(aq) \longrightarrow$
$Ag_2CrO_4(s) + 2FeCl_2(aq) + 2KCl(aq)$

is -62.5 kJ mol^{-1} at 298 K. (a) Calculate the standard potential of the corresponding galvanic cell and (b) the standard potential of the $Ag_2CrO_4/Ag, CrO_4^{2-}$ couple.

10.20 (b) Two half-cell reactions may be combined in such a way as to form (a) a new half-cell reaction or (b) a complete cell reaction. Illustrate both (a) and (b) by using the half-cell reactions listed below and calculate $E^\ominus$ for both the new half-cell and complete cell reaction.

(i) $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad E_1^\ominus = -0.828$ V

(ii) $Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad E_2^\ominus = +0.799$ V

10.21 (a) Calculate the standard potential of the couple $Ag_2S, H_2O/Ag, S^{2-}, O_2, H^+$ from the following data:

$Ag_2S(s) + 2e^- \longrightarrow 2Ag(s) + S^{2-}(aq) \qquad E^\ominus = -0.69$ V

$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l) \qquad E^\ominus = +1.23$ V

10.21 (b) Consider the cell $Pt|H_2(g, p^\ominus)|HCl(aq)|AgCl(s)|Ag$, for which the cell reaction is $2AgCl(s) + H_2(g) \rightarrow 2Ag(s) + 2HCl(aq)$. At 25 °C and a molality of HCl of 0.010 mol kg^{-1}, $E = +0.4658$ V. (a) Write the Nernst equation for the cell reaction. (b) Calculate $\Delta_r G$ for the cell reaction. (c) Assuming that the Debye–Hückel limiting law holds at this concentration, calculate $E^\ominus(AgCl, Ag)$.

10.22 (a) Use the Debye–Hückel limiting law and the Nernst equation to estimate the potential of the cell $Ag|AgBr(s)|KBr(aq, 0.050\ mol\ kg^{-1})||Cd(NO_3)_2(aq, 0.010\ mol\ kg^{-1})|Cd$ at 25 °C.

10.22 (b) Use the information in Table 10.7 to calculate the standard potential of the cell $Ag|AgNO_3(aq)||Fe(NO_3)_2(aq)|Fe$ and the standard Gibbs energy and enthalpy of the cell reaction at 25 °C. Estimate the value of $\Delta_r G^\ominus$ at 35 °C.

10.23 (a) Calculate the equilibrium constants of the following reactions at 25 °C from standard potential data:

(a) $Sn(s) + Sn^{4+}(aq) \rightleftharpoons 2Sn^{2+}(aq)$

(b) $Sn(s) + 2AgCl(s) \rightleftharpoons SnCl_2(aq) + 2Ag(s)$

10.23 (b) Calculate the equilibrium constants of the following reactions at 25 °C from standard potential data:

(a) $Sn(s) + CuSO_4(aq) \rightleftharpoons Cu(s) + SnSO_4(aq)$

(b) $Cu^{2+}(aq) + Cu(s) \rightleftharpoons 2Cu^+(aq)$

10.24 (a) Use the standard potentials of the couples Au^+/Au (+1.69 V), Au^{3+}/Au (+1.40 V), and Fe^{3+}/Fe^{2+} (+0.77 V) to calculate $E^\ominus$ and the equilibrium constant for the reaction $2Fe^{2+}(aq) + Au^{3+}(aq) \rightleftharpoons 2Fe^{3+}(aq) + Au^+(aq)$.

10.24 (b) Determine the standard potential of a cell in which the reaction is $Co^{3+}(aq) + 3Cl^-(aq) + 3Ag(s) \rightarrow 3AgCl(s) + Co(s)$ from the standard potentials of the couples $AgCl/Ag, Cl^-$ (+0.22 V), Co^{3+}/Co^{2+} (+1.81 V), and Co^{2+}/Co (−0.28 V).

10.25 (a) The solubilities of AgCl and $BaSO_4$ in water are 1.34×10^{-5} mol kg^{-1} and 9.51×10^{-4} mol kg^{-1} respectively at 25 °C. Calculate their solubility constants. Is there any significant difference when activity coefficients are ignored?

10.25 (b) The solubilities of AgI and Bi_2S_3 in water are 1.2×10^{-8} mol kg^{-1} and 1.6×10^{-20} mol kg^{-1}, respectively, at 25 °C. Calculate their solubility constants. Is there any significant difference when activity coefficients are ignored?

10.26 (a) Derive an expression for the potential of an electrode for which the half-reaction is the reduction of $Cr_2O_7^{2-}$ ions to Cr^{3+} ions in acidic solution.

10.26 (b) Derive an expression for the potential of an electrode for which the half-reaction is the reduction of MnO_4^- ions to Mn^{2+} ions in acidic solution.

10.27 (a) The zero-current potential of the cell $Pt|H_2(g)|HCl(aq)|AgCl(s)|Ag$ was +0.322 V at 25 °C. What is the pH of the electrolyte solution?

10.27 (b) The zero-current potential of the cell $Pt|H_2(g)|HI(aq)|AgI(s)|Ag$ was 1.00 V at 25 °C. What is the pH of the electrolyte solution?

10.28 (a) The solubility of AgBr is 2.6 μmol kg^{-1} at 25 °C. What is the zero-current potential of the cell $Ag|AgBr(aq)|AgBr(s)|Ag$ at that temperature?

10.28 (b) The solubility of AgI is 12 nmol kg^{-1} at 25 °C. What is the zero-current potential of the cell $Ag|AgI(aq)|AgI(s)|Ag$ at that temperature?

10.29 (a) The standard potential of the cell $Ag|AgI(s)|AgI(aq)|Ag$ is +0.9509 V at 25 °C. Calculate (a) the solubility of AgI and (b) its solubility constant.

10.29 (b) The standard potential of the cell $Bi|Bi_2S_3(s)|Bi_2S_3(aq)|Bi$ is +0.96 V at 25 °C. Calculate (a) the solubility of Bi_2S_3 and (b) its solubility constant.

Problems

Numerical problems

10.1 Devise a cell in which the overall reaction is $Pb(s) + Hg_2SO_4(s) \rightarrow PbSO_4(s) + 2Hg(l)$. What is its potential when the electrolyte is saturated with both salts at 25 °C? (The solubility constants of Hg_2SO_4 and $PbSO_4$ are 6.6×10^{-7} and 1.6×10^{-8}, respectively.)

10.2 Given that $\Delta_r G^\ominus = -212.7$ kJ mol^{-1} for the reaction in the Daniell cell at 25 °C, and $b(CuSO_4) = 1.0\times10^{-3}$ mol kg^{-1} and $b(ZnSO_4) = 3.0\times10^{-3}$ mol kg^{-1}, calculate (a) the ionic strengths of the solutions, (b) the mean ionic activity coefficients in the compartments, (c) the reaction quotient, (d) the standard cell potential, and (e) the cell potential. (Take $\gamma_+ = \gamma_- = \gamma_\pm$ in the respective compartments.)

10.3 Although the hydrogen electrode may be conceptually the simplest electrode and is the basis for our reference state of electrical potential in electrochemical systems, it is cumbersome to use. Therefore, several substitutes for it have been devised. One of these alternatives is the quinhydrone electrode (quinhydrone, $Q{\cdot}QH_2$, is a complex of quinone, $C_6H_4O_2 = Q$, and hydroquinone, $C_6H_4O_2H_2 = QH_2$). The electrode half-reaction is $Q(aq) + 2H^+(aq) + 2e^- \rightarrow QH_2(aq)$, $E^\ominus = +0.6994$ V. If the cell $Hg|Hg_2Cl_2(s)|HCl(aq)|Q{\cdot}QH_2|Au$ is prepared, and the measured cell potential is +0.190 V, what is the pH of the HCl solution? Assume that the Debye–Hückel limiting law is applicable.

10.4 A fuel cell develops an electric potential from the chemical reaction between reagents supplied from an outside source. What is the zero-current potential of a cell fuelled by (a) hydrogen and oxygen, (b) the combustion of butane at 1.0 atm and 298 K?

10.5 Consider the cell, $Zn(s)|ZnCl_2(0.0050\ \text{mol kg}^{-1})|Hg_2Cl_2(s)|Hg(l)$, for which the cell reaction is $Hg_2Cl_2(s) + Zn(s) \rightarrow 2Hg(l) + 2Cl^-(aq) + Zn^{2+}(aq)$. Given that $E^\ominus(Zn^{2+},Zn) = -0.7628$ V, $E^\ominus(Hg_2Cl_2,Hg) = +0.2676$ V, and that the measured value of the cell potential is +1.2272 V, (a) write the Nernst equation for the cell. Determine (b) the standard cell potential, (c) $\Delta_r G$, $\Delta_r G^\ominus$, and K for the cell reaction, (d) the mean ionic activity and activity coefficient of $ZnCl_2$ from the measured cell potential, and (e) the mean ionic activity coefficient of $ZnCl_2$ from the Debye–Hückel limiting law. (f) Given that $(\partial E/\partial T)_p = -4.52\times10^{-4}$ V K^{-1}, calculate ΔS and ΔH.

10.6 The zero-current potential of the cell $Pt|H_2(g,p^\ominus)|HCl(aq,b)|Hg_2Cl_2(s)|Hg(l)$ has been measured with high precision (G.J. Hills and D.J.G. Ives, *J. Chem. Soc.*, 311 (1951)) with the following results at 25 °C:

$b/(\text{mmol kg}^{-1})$	1.6077	3.0769	5.0403	7.6938	10.9474
E/V	0.60080	0.56825	0.54366	0.52267	0.50532

Determine the standard potential of the cell and the mean activity coefficient of HCl at these molalities. (Make a least-squares fit of the data to the best straight line.)

10.7 Careful measurements of the potential of the cell $Pt|H_2(g,p^\ominus)|NaOH(aq,0.0100\ \text{mol kg}^{-1}),NaCl(aq,0.01125\ \text{mol kg}^{-1})|AgCl(s)|Ag$ have been reported (C.P. Bezboruah, M.F.G.F.C. Camoes, A.K. Covington, and J.V. Dobson, *J. Chem. Soc. Faraday Trans. I*, **69**, 949 (1973)). Among the data is the following information:

θ/°C	20.0	25.0	30.0
E/V	1.04774	1.04864	1.04942

Calculate pK_w at these temperatures and the standard enthalpy and entropy of the autoprotolysis of water at 25.0 °C.

10.8 Measurements of the potentials of cells of the type $Ag|AgX(s)MX(b_1)|M_xHg|MX(b_2)|AgX(s)|Ag$, where M_xHg denotes an amalgam and the electrolyte is an alkali metal halide dissolved in ethylene glycol, have been reported (U. Sen, *J. Chem. Soc. Faraday Trans. I* **69**, 2006 (1973)) and some values for LiCl are given below.

Estimate the activity coefficient at the concentration marked • and then use this value to calculate activity coefficients from the measured cell potential at the other concentrations. Base your answer on the following version of the extended Debye–Hückel law:

$$\log \gamma_{\pm} = -\frac{AI^{1/2}}{1 - BI^{1/2}} + kI$$

with $A = 1.461$, $B = 1.70$, $k = 0.20$, and $I = b/b^{\ominus}$. For $b_2 = 0.09141\ \text{mol kg}^{-1}$:

$b_1/(\text{mol kg}^{-1})$	0.0555	0.09141•	0.1652	0.2171	1.040	1.350
E/V	−0.0220	0.0000	0.0263	0.0379	0.1156	0.1336

10.9 Suppose the extended Debye–Hückel law for a 1,1-electrolyte is written in the simplified form $\log \gamma_{\pm} = -0.509I^{1/2} + kI$, where k is a constant and $I = b/b^{\ominus}$. Show that a plot of y against I, where

$$y = E + 0.1183 \log I - 0.0602\, I^{1/2}$$

should give a straight line with intercept $E^{\ominus}$ and slope $-0.1183k$. Apply the technique to the following data (at 25°C) on the cell $\text{Pt}|\text{H}_2(\text{g},p^{\ominus})|\text{HCl(aq},b)|\text{AgCl(s)}|\text{Ag}$:

$b/(\text{mmol kg}^{-1})$	123.8	25.63	9.138	5.619	3.215
E/mV	341.99	418.24	468.60	492.57	520.53

(a) Find the standard cell potential and the standard potential of the AgCl/Ag, Cl⁻ couple. (b) The zero-current cell potential was measured as 352.4 mV when $b = 100.0\ \text{mol kg}^{-1}$. What is the pH and the mean ionic activity coefficient?

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

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

10.11 The standard potential of the AgCl/Ag, Cl⁻ couple has been measured very carefully over a range of temperature (R.G. Bates and V.E. Bowers, *J. Res. Nat. Bur. Stand.* 53, 283 (1954)) and the results were found to fit the expression

$$\begin{aligned} E^{\ominus}/\text{V} &= 0.23659 - 4.8564 \times 10^{-4}(\theta/{}^{\circ}\text{C}) \\ &\quad - 3.4205 \times 10^{-6}(\theta/{}^{\circ}\text{C})^2 + 5.869 \times 10^{-9}(\theta/{}^{\circ}\text{C})^3 \end{aligned}$$

Calculate the standard Gibbs energy and enthalpy of formation of Cl^-(aq) and its entropy at 298 K.

10.12 Use the data below to confirm that the Debye–Hückel limiting law correctly predicts the limiting values of the mean activity coefficient of acetic acid by demonstrating that $\text{p}K'_{\text{a}}$, where $K_{\text{a}} = K'_{\text{a}}K_{\gamma}$, plotted against $(\alpha b)^{1/2}$, where b is the molality of the acid and α its degree of ionization, should be a straight line.

$b/(\text{mmol kg}^{-1})$	0.0280	0.1114	0.2184	1.0283	2.414	5.9115
α	0.5393	0.3277	0.2477	0.1238	0.0829	0.0540

10.13 The $\text{Sb}|\text{Sb}_2\text{O}_3\text{(s)}|\text{OH}^-\text{(aq)}$ electrode is reversible with respect to OH⁻ ions. Derive an expression for its potential in terms of (a) the pOH and (b) the pH of the solution. (c) By how much does the potential change when the molality of NaOH(aq) in the electrode compartment is increased from $0.010\ \text{mol kg}^{-1}$ to $0.050\ \text{mol kg}^{-1}$ at 25°C? Use the Debye–Hückel limiting law to estimate any activity coefficients required.

10.14 Superheavy elements are now of considerable interest. Shortly before it was (falsely) believed that the first had been discovered, an attempt was made to predict the chemical properties of ununpentium (Uup, element 115, O.L. Keller, C.W. Nestor, and B. Fricke, *J. Phys. Chem.* **78**, 1945 (1974)). In one part of the paper the standard enthalpy and entropy of the reaction $\text{Uup}^+\text{(aq)} + \frac{1}{2}\text{H}_2\text{(g)} \rightarrow \text{Uup(s)} + \text{H}^+\text{(aq)}$ were estimated from the following data: $\Delta_{\text{sub}}H^{\ominus}(\text{Uup}) = +1.5\ \text{eV}$, $I(\text{Uup}) = 5.52\ \text{eV}$, $\Delta_{\text{hyd}}H^{\ominus}(\text{Uup}^+,\text{aq}) = -3.22\ \text{eV}$, $S^{\ominus}(\text{Uup}^+,\text{aq}) = +1.34\ \text{meV/K}^{-1}$, $S^{\ominus}(\text{Uup,s}) = 0.69\ \text{meV K}^{-1}$. Estimate the expected standard potential of the Uup⁺/Uup couple.

Theoretical problems

10.15 Show that the solubility, S, of a sparingly soluble 1 : 1 salt is related to its solubility constant by $S = K_{\text{s}}^{1/2}\text{e}^{1.172S^{1/2}}$.

10.16 Suppose that a sparingly soluble salt MX has solubility constant K_{s} and solubility S. Show that, in an ideal solution that is of concentration C of a freely soluble salt NX, the solubility of MX is changed to

$$S' = \tfrac{1}{2}(C^2 + 4K_{\text{s}}^2)^{1/2} - \tfrac{1}{2}C$$

and that $S' \approx K_{\text{s}}/C$ when K_{s} is small (in a sense to be specified).

10.17 Show that, if the ionic strength of a solution of the sparingly soluble salt MX and the freely soluble salt NX is dominated by the concentration C of the latter, and if it is valid to use the Debye–Hückel limiting law, the solubility S' in the mixed solution is given by

$$S' = \frac{K_{\text{s}}\text{e}^{4.606AC^{1/2}}}{C}$$

when K_{s} is small (in a sense to be specified).

10.18 Show that the freezing-point depression of a real solution in which the solvent of molar mass M has activity a_{A} obeys

$$\frac{\text{d} \ln a_{\text{A}}}{\text{d}(\Delta T)} = -\frac{M}{K_{\text{f}}}$$

and use the Gibbs–Duhem equation to show that

$$\frac{\text{d} \ln a_{\text{B}}}{\text{d}(\Delta T)} = -\frac{1}{b_{\text{B}}K_{\text{f}}}$$

where a_{B} is the solute activity and b_{B} is its molality. Use the Debye–Hückel limiting law to show that the osmotic coefficient (ϕ, Problem 7.12) is given by $\phi = 1 - \frac{1}{3}A'I$ with $A' = 2.303A$ and $I = b/b^{\ominus}$.

Additional problems supplied by Carmen Giunta and Charles Trapp

10.19 The list of standard potentials compiled by Bratsch shows that europium has the least negative reduction potential for the M^{3+}/M couple in strong acid (pH = 0) of all the lanthanides (S.G. Bratsch, *J. Phys. Chem. Ref. Data* 18, 1 (1989)). $E^\ominus(\text{Eu}^{3+}/\text{Eu}) = -1.991$ V, while the next easiest to reduce is ytterbium, with $E^\ominus(\text{Yb}^{3+}/\text{Yb}) = -2.19$ V. (a) Describe the criteria for a reducing agent that would deposit Eu metal from an acidic solution of M^{3+} lanthanide ions while leaving the other lanthanides in solution under standard conditions (unit activities and fugacities; pH = 0). Is there such a reagent in Table 10.7? (b) Now suppose the conditions are not standard. What is the maximum value of the ratio $a_{\text{Yb}^{3+}}/a_{\text{Eu}^{3+}}$ such that Eu still deposits spontaneously (just barely) but Yb does not?

10.20 Larson studied the thermochemistry of vanadium (V) ions in aqueous solution (J.W. Larson, *J. Chem. Eng. Data* 40, 1276 (1995)). At neutral pH, the dominant species are $H_2VO_4^-$ and $V_4O_{12}^{4-}$. The equilibrium constant for the reaction $4H_2VO_4^-(aq) \rightarrow V_4O_{12}^{4-}(aq) + 4H_2O(l)$ was determined to be 106.4 at 50°C. How is vanadium distributed between these two species at 50°C and unit ionic strength if the total vanadium concentration is 1.0×10^{-2} mol kg^{-1}? Take the ionic strength to be 1.000 and use the following extended Debye–Hückel equation to estimate activity coefficients where $A = 0.5373$ at 50°C.

$$\log \gamma = -\frac{Az^2 I^{1/2}}{1 + I^{1/2}}$$

10.21 (a) Derive a general relation for $(\partial E/\partial p)_{T,n}$ for electrochemical cells employing reactants in any state of matter. (b) E. Cohen and K. Piepenbroek (*Z. physik. Chem.* 167A, 365 (1933)) calculated the change in volume for the reaction $\text{TlCl(s)} + \text{CNS}^-(\text{aq}) \rightarrow \text{TlCNS(s)} + \text{Cl}^-(\text{aq})$ at 30°C from density data and obtained $\Delta_r V = -2.666 \pm 0.080$ cm^3 mol^{-1}. They also measured the potential of the cell Tl(Hg)|TlCNS(s)|KCNS⋮KCl|TlCl(s)|Tl(Hg) at temperatures up to 1500 atm. Their results are given in the following table.

p/atm	1.00	250	500	750	1000	1250	1500
E/mV	8.56	9.27	9.98	10.69	11.39	12.11	12.82

From this information, obtain $(\partial E/\partial p)_{T,n}$ at 30°C and compare to the value obtained from $\Delta_r V$. (c) Fit the data to a polynomial for E against p. How constant is $(\partial E/\partial p)_{T,n}$? (d) From the polynomial, estimate an effective isothermal compressibility for the cell as a whole.

10.22 Because the hydrogen electrode is the fundamental reference electrode, it is important to study the effect of pressure on cells containing it. W.R. Hainsworth, H.J. Rowley, and D.A. MacInnes (*J. Am. Chem. Soc.* 46, 1437 (1924)) investigated the influence of pressure on the hydrogen/calomel cell, $\text{Pt}|\text{H}_2(\text{g}, p)|\text{HCl}(0.1\ \text{M})|\text{Hg}_2\text{Cl}_2(\text{s})|\text{Hg(l)}$, up to pressures of 1000 atm at 25°C with the following results, where $\Delta E = E(p) - E(1\ \text{atm})$.

p/atm	1.00	10	38	51	108	210
ΔE/mV	0	29.5	47	51	61	69
p/atm	380	430	560	720	900	1020
ΔE/mV	79	82	86	91	95	98

(a) Derive an expression for ΔE using the perfect gas law. Compare the expression with the experimental results. (b) Fit the values of ΔE and $(\partial E/\partial p)_T$ to a polynomial expression in p. (c) Obtain a theoretical equation for these quantities using both the virial form of the van der Waals equation and the empirical virial equation $Z = 1 + 0.000537(p/\text{atm}) + 3.5 \times 10^{-8}(p/\text{atm})^2$ used by Hainsworth *et al.* Plot the experimental and theoretical data for this cell on the same graph. How well do they fit? (d) Calculate the fugacity of H_2 from the cell potential data.

MicroProjects Part 1:

Prepared by M. Cady and C. A. Trapp

1.1 Equations of state for gases, liquids, and solids

(a) What is the difference between the equation of state of a perfect gas, that of a van der Waals gas, and the virial equation of state? Why are there so many equations of state for the gas phase and why should one equation be preferred over another?

(b) Derive the relation between the critical constants and the Dieterici equation parameters. Show that $Z_c = 2e^{-2}$ and derive the reduced form of the Dieterici equation of state. Compare the van der Waals and Dieterici predictions of the critical compression factor. Which is closer to typical experimental values?

(c) How would the expansion coefficient and the isothermal compressibility be used to establish an equation of state for a liquid or solid? Write an approximate equation of state for liquid water at ordinary temperatures and pressures. Calculate V_m for both $H_2O(l)$ and $H_2O(g)$ at 5.0 bar and 75°C.

1.2 The second virial coefficient

The second virial coefficient of methane can be approximated by the empirical equation $B'(T) = a + be^{-c/T^2}$, where $a = -0.1993\ \text{bar}^{-1}$, $b = 0.2002\ \text{bar}^{-1}$, and $c = 1131\ \text{K}^2$ with $300\ \text{K} \le T \le 600\ \text{K}$.

(a) What is the value of the Boyle temperature for methane?

(b) Compare the molar volume of methane at 50 bar as predicted by both the virial equation and the perfect gas equation at (i) 25°C, (ii) 100°C.

(c) Derive an equation for the computation of each of the following properties for methane: (i) π_T at 25°C and 100 bar, (ii) ΔS_m, ΔH_m, and ΔG_m when the gas is compressed isothermally from 1 bar to 100 bar at 25°C. Assume that $B(T) = RTB'(T)$.

1.3 Supercritical fluid solvents

The solubility parameter, δ, is defined as $(\Delta U_{\text{cohesive}}/V_m)^{1/2}$, where $\Delta U_{\text{cohesive}}$ is the cohesive energy of the solvent, the energy per mole needed to increase the volume isothermally to an infinite value. Diethyl ether, carbon tetrachloride, and dioxane have solubility parameter ranges of 7–8, 8–9, and 10–11, respectively.

(a) Derive a practical equation for the computation of the isotherms for the reduced internal energy change, $\Delta U_r(T_r, V_r)$ defined as

$$\Delta U_r(T_r, V_r) = \frac{U_r(T_r, V_r) - U_r(T_r, \infty)}{p_c V_c}$$

(b) Draw a graph of ΔU_r against p_r for the isotherms $T_r = 1$, 1.2, and 1.5 in the reduced pressure range for which $0.7 \le V_r \le 2$.

(c) Draw a graph of δ against p_r for the carbon dioxide isotherms $T_r = 1$ and 1.5 in the reduced pressure range for which $1 \le V_r \le 3$. In what pressure range at $T_r = 1$ will carbon dioxide have solvent properties similar to those of liquid carbon tetrachloride?

1.4 Solution calorimetry

When 1.3584 g of sodium acetate trihydrate was mixed into 100.0 mL of 0.2000 M HCl(aq) at 25°C, the temperature of the calorimeter fell by 0.397°C. This cooling occurred on account of the reaction:

$$H_3O^+(aq) + NaCH_3CO_2 \cdot 3H_2O \longrightarrow Na^+(aq) + CH_3COOH(aq) + 4H_2O(l)$$

The heat capacity of the calorimeter is $91.0\ \text{J K}^{-1}$ and the heat capacity density of the acid solution is $4.144\ \text{J K}^{-1}\ \text{mL}^{-1}$. Determine the standard enthalpy of formation of the aqueous sodium cation. The standard enthalpy of formation of sodium acetate trihydrate is $-1604\ \text{kJ mol}^{-1}$.

1.5 Sublimation and atomization enthalpies

The standard enthalpy of combustion of 7,8-benzoquinoline (benz) is $-6556 \pm 4\ \text{kJ mol}^{-1}$ for the pure solid at 25°C. The combustion reaction is:

$$C_{13}H_9N(s) + \tfrac{61}{4}O_2(g) \longrightarrow 13CO_2(g) + \tfrac{9}{2}H_2O(l) + \tfrac{1}{2}N_2(g)$$

A restricted molecular flow apparatus has been used to determine the very small vapour pressures, p, of the solid by measuring solid mass loss, Δm, in measured time periods Δt, at a fixed temperature. Theoretical analysis of the apparatus yields the relation

$$p/\text{Torr} = 17.4\left(\frac{f(\Delta m/\text{g})}{\alpha(A/\text{cm}^2)(\Delta t/\text{s})}\right)\left(\frac{T/\text{K}}{M/(\text{g mol}^{-1})}\right)^{1/2}$$

where A is the surface area of the sample ($A = 3.64\ \text{cm}^2$). The apparatus constants are $f = 8.99$ and $\alpha = 1$. The table below contains the experimental data.

(a) Determine the enthalpy of sublimation and the entropy of sublimation for a vapour pressure of 1.00 Torr.

(b) Use the combustion and sublimation enthalpies, along with any other necessary information, to calculate an experimentally based atomization enthalpy. SCF-CNDO computations yield a value of $11\,533 \pm 8\ \text{kJ mol}^{-1}$. Do the experimental and theoretical values agree?

T/K	293.10	298.20	303.13	308.23	313.17	318.24	323.15
Δt/s	21 600	19 200	18 000	7140	4200	3600	1800
Δm/g	0.0481	0.0797	0.1275	0.0823	0.0801	0.1055	0.0877

Equilibrium

1.6 Low and high temperature heat capacity of $Ce_2Si_2O_7$

It is found that the molar heat capacity of β-$Ce_2Si_2O_7$ at 1 bar in the range of temperatures 0–30 K is described by

$$C_{p,\mathrm{m}}(T) = a(T/\mathrm{K})^3\left(1 - \mathrm{e}^{-b/T^2}\right)$$

where $a = 5.597 \times 10^{-4}\ \mathrm{J\,mol^{-1}\,K^{-4}}$ and $b = 1701.8\ \mathrm{K}^2$ are empirical parameters. In the high-temperature range, 500–900 K, the molar heat capacity is described by

$$\begin{aligned} C_{p,\mathrm{m}}(T)/(\mathrm{J\,mol^{-1}\,K^{-1}}) &= 222.3716 \\ &\quad + 0.076\,790\,42(T/\mathrm{K}) - 3\,631\,886(T/\mathrm{K})^{-2} \end{aligned}$$

No phase transition has been detected below 900 K.

(a) Draw graphs of $S_\mathrm{m}(T)$, $H_\mathrm{m}(T) - H_\mathrm{m}(0)$, and $G_\mathrm{m}(T) - G_\mathrm{m}(0)$ in the range $0 \leq T \leq 30$ K.

(b) According to the law of Dulong and Petit, the high-temperature heat capacity per mole of atoms of a crystalline material is $3R$. How does the classical prediction compare with the experimental?

1.7 The destruction of chlorofluorocarbon stockpiles

Protocols have outlawed the use of certain CFC refrigerants. It has been suggested that sodium oxalate, $Na_2(CO_2)_2$, at elevated temperatures can be used to destroy existing CFC stockpiles. The mineralization of freon-12, for example, is

$$\begin{aligned} &CF_2Cl_2(g) + 2Na_2(CO_2)_2(s) \longrightarrow \\ &\quad 2NaF(s) + 2NaCl(s) + C(s) + 4CO_2(g) \end{aligned}$$

(a) Without performing a calculation, what is your expectation concerning the spontaneity of the reaction? Why is the high temperature required? Why should reaction mixtures not be heated to temperatures much higher than 270°C?

(b) Use library, internet, or PC database resources to find thermodynamic data which will make possible the calculation of $\Delta_\mathrm{r}G^\circ(T)$. Estimate the value of any thermodynamic property that cannot be found. For general information about internet chemistry resources try these URLs: http://www.acs.org/; http://www.indiana.edu/cheminfo/. For specific thermodynamic data try the NIST Chemistry Webbook: http://webbook.nist.gov/.

1.8 Calorimetric determination of hydrogen bond strengths

The excess enthalpy of mixing data for 1-propanol and tripropylamine at 25°C is found to fit the expression

$$H^\mathrm{E}/(\mathrm{J\,mol^{-1}}) = x_1(1 - x_1)\sum_{r=0}^{3} A_r(1 - 2x_1)^r$$

where $A_r/(\mathrm{J\,mol^{-1}}) = -1131, 1355, -855, 1127$ for $r = 0, 1, 2, 3$.

(a) Draw a graph of H^E against x_1 and compare the graph shape to that expected for a solution in which $H^\mathrm{E} = \omega x_1 x_2$. What do the graphs imply about intermolecular interaction energies?

(b) At 25°C and infinite dilution the excess enthalpy of mixing 1-propanol in heptane is $H^\mathrm{E} = +25.3\ \mathrm{kJ\,mol^{-1}}$, whereas for the mixing of tripropylamine in heptane $H^\mathrm{E} = +121\ \mathrm{J\,mol^{-1}}$. Deduce the strength of the alcohol-amine hydrogen bond. Assume that intermolecular structural reorganization enthalpies cancel for the cycle.

1.9 Vapour–liquid equilibrium

The compound *tert*-amyl methyl ether (TAME) has potential use as a gasoline antiknock agent. The Redlich–Kister empirical equation for the excess Gibbs energy of mixing of methanol (1) and TAME (2) is:

$$G^\mathrm{E}/RT = x_1 x_2 \sum_{n=0}^{4} A_n(1 - 2x_1)^n$$

where $A_n = 1.4170, -0.05245, 0.1599, 0.1061, -0.09159$ for $n = 0, 1, \cdots, 4$. The activity coefficients are given by

$$\ln\gamma_1 = x_2^2\sum_{n=0}^{4} A_n f_n(x_1) \qquad \ln\gamma_2 = x_1^2\sum_{n=0}^{4}(-1)^n A_n f_n(x_2)$$

where

$$f_n(x) = \{1 - 2(n+1)x\}(1 - 2x)^{n-1}$$

The vapour pressure and molar volume of pure TAME are 6.09 kPa and $131.78\ \mathrm{cm^3\,mol^{-1}}$ at 288.15 K and those of methanol are 9.86 kPa and $40.254\ \mathrm{cm^3\,mol^{-1}}$.

(a) What is the thermodynamic criterion for solution–vapour equilibrium? What law relates vapour pressure to ideal solution composition? How is this law modified so as to describe the vapour pressure of real solutions?

(b) Draw a graph of $\ln\gamma$ against x_1. Do the graphs reflect correct values at infinite dilutions of either TAME or methanol?

(c) Draw a graph of $G^\mathrm{E}(x_1)$. What does this graph reveal about the spontaneity of mixing? Does the curve have the shape expected for a regular solution?

(d) Draw a graph of total vapour pressure, $p = p_1 + p_2$, and also show the curves for $p(x_1)$ and $p(y_1)$, where y is the mole fraction in the vapour. What is the vapour pressure and composition of the azeotrope? What is the equilibrium pressure when $x_1 = 0.2$?

(e) Draw a graph of total vapour and partial vapour pressures. The curves would be $p(x_1)$, $p_1(x_1)$, and $p_2(x_1)$. What do these curves reveal about deviations from ideality? Calculate the Henry's law constant for both methanol and TAME.

(f) Estimate the vapour pressure of pure TAME at 288.15 K when subjected to an applied pressure of 2.0 bar.

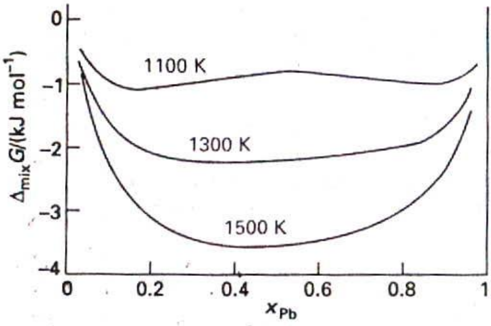
1.10 Solubility and miscibility of Cu/Pb mixtures

The illustration below shows the $\Delta_{\text{mix}}G(x_{\text{Pb}}, T)$ for a mixture of copper and lead.

(a) What does the graph reveal about the miscibility of copper and lead and the spontaneity of solution formation? What is the variance (F) at (i) 1500 K, (ii) 1100 K?

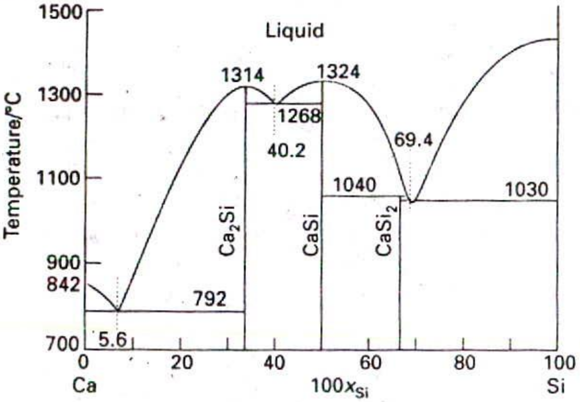
(b) Suppose that at 1500 K a mixture of composition (i) $x_{\text{Pb}} = 0.1$, (ii) $x_{\text{Pb}} = 0.7$, is slowly cooled to 1100 K. What is the equilibrium composition of the final mixture? Include an estimate of the relative amounts of each phase.

(c) What is the solubility of (i) lead in copper, (ii) copper in lead at 1100 K?



1.11 The temperature–composition diagram for the Ca/Si binary system

(a) Identify eutectics, congruent melting compounds, and incongruent melting compounds that are shown in the calcium/silicon phase diagram shown below.



(b) If a 20 per cent by atom composition melt of silicon at 1500°C is cooled to 1000°C, what phases (and phase composition) would be at equilibrium? Estimate the relative amounts of each phase.

(c) If $CaSi_2$ melts completely at 1040°C, what phases (and phase composition and relative amounts) would be at equilibrium?

(d) Describe the equilibrium phases observed when an 80 per cent by atom composition Si melt is cooled to 1030°C. What phases, and relative amounts, would be at equilibrium at a temperature (i) slightly higher than 1030°C, (ii) slightly lower than 1030°C? Draw a graph of the mole percentages of both Si(s) and $CaSi_2$(s) as a function of mole percentage of melt that is freezing at 1030°C.

1.12 Aspects of ammonia production

Suppose that an iron catalyst at a particular plant produces ammonia in the most cost-effective manner at 450°C when the pressure is such that Δ_rG for the reaction $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$ is equal to $-500\ \text{J mol}^{-1}$. What pressure is needed? Now suppose that a new catalyst is developed that is most cost-effective at 400°C when the pressure gives the same value of Δ_rG. What pressure is needed when the new catalyst is used? What are the advantages of the new catalyst? Assume that (a) all gases are perfect gases or that (b) all gases are van der Waals gases. Isotherms of $\Delta_rG(T,p)$ in the pressure range $100\ \text{atm} \le p \le 400\ \text{atm}$ are needed to derive the answer. Do these graphs confirm Le Chatelier's principle concerning the response of equilibrium changes in temperature and pressure?

1.13 Silica reduction with graphite

Large quantities of silicon are made by reducing SiO_2 with carbon in arc furnaces at elevated temperatures. Many chemical species may be present in these high-temperature SiO_2/graphite mixtures, including C(s), SiO_2(s), SiO_2(l), Si(s), Si(l), SiC(s), SiO(g), and CO(g). The table below contains information about the temperature dependence of $G(T) - H_{\text{SER}} = a + bT$ for each of these species, and several others, in the temperature range 1500–2500 K and at 1 bar, where $G(T) - H_{\text{SER}}$ is the Gibbs energy at temperature T relative to the enthalpies of the pure constituent elements in their reference states at the conventional temperature. Use these data alone to answer the following questions. Assume perfect gas behaviour and ideal solutions when necessary.

	$a/(\text{kJ mol}^{-1})$	$b/(\text{kJ K}^{-1}\ \text{mol}^{-1})$
graphite	34.38	−0.04054
Si(s)	44.281	−0.06671
SiO_2(l)	−757.039	−0.18456
Si(g)	484.667	−0.20808
SiO(g)	−41.075	−0.28123
O_2(g)	57.858	−0.26856
SiO_2(s)	−818.448	−0.15281
SiC(s)	2.521	−0.09838
Si(l)	96.980	−0.09743
SiO_2(g)	−209.039	−0.34203
CO(g)	−54.581	−0.26312
CO_2(g)	−302.873	−0.32021

(a) Calculate the normal melting point of silica and silicon. Make graphs of the vapour pressures of each in the temperature range 1500–2500 K and at a pressure of 1 bar.

(b) Draw an Ellingham diagram for the smelting reduction of silica with graphite in the temperature range 1500–2500 K and at a pressure of 1 bar. What does the diagram reveal about the evolution of carbon dioxide during smelting?

(c) Determine the equilibrium purity of silicon made by reducing silica with graphite at 2000 K and 1 bar. Assume that graphite is soluble in the silicon but that SiO_2 and SiC are not. Also determine the equilibrium partial pressures of SiO(g) and CO(g). Equilibria to consider include $SiO_2(l) + C(\text{graphite}, s) \rightleftharpoons SiO(g) + CO(g)$, $SiO_2(l) + 2C(\text{graphite}, s) \rightleftharpoons Si(l) + 2CO(g)$, and $SiO_2(l) + 3C(\text{graphite}, s) \rightleftharpoons SiC(s) + 2CO(g)$.

1.14 pH–concentration curves for carbon dioxide

The ocean's ability to dissolve carbon is an important sink when modelling the carbon cycle. Draw a graph of α_J against pH for carbon dioxide solutions in the pH range 0–14 where the fraction α_J of species J is defined as

$$\alpha_J = \frac{[J]}{[\text{total carbon}]} = \frac{[J]}{[CO_2] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]}$$

Assume that solutions are ideal.

(a) What are the major chemical species at the physiological pH of 7.4 and equilibrium?

(b) What is the maximum mass of ocean carbon dissolved as CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-} if the ocean has an average pH of 8, an average temperature of 298 K, and a volume of 1.37×10^{18} m³? The partial pressure of atmospheric carbon dioxide is 3.3×10^{-4} atm.

1.15 Sulfuric acid solutions and lead electrochemistry

A cell of the lead–acid battery may be represented as

$$Pb(s)|PbSO_4(s)|H_2SO_4(aq)|PbO_2(s)|PbSO_4(s)|Pb(s)$$

where the aqueous solution is about 35 per cent by mass sulfuric acid. The sulfuric acid molality, b, is related to the solution density, d, at 25°C by the empirical equation:

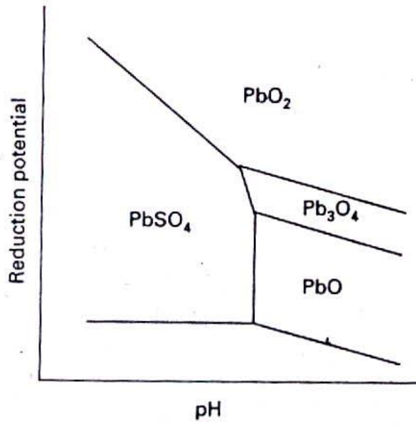
$$b(H_2SO_4)/(\text{mol kg}^{-1}) = a(d - d_{25})/(\text{g cm}^{-3}) + c(d - d_{25})^2/(\text{g cm}^{-3})^2$$

where d_{25} is the density of pure water at 25°C, $a = 14.523$, and $c = 25.031$.

(a) Draw graphs of molality, mass percentage, and molar concentration functions of density for densities in the range 1.0–1.4 g cm^{-3}.

(b) Write balanced equations for the half-reactions and the cell reaction for the lead–acid battery. Determine $E^\ominus$, $\Delta_r G^\ominus$, $\Delta_r S^\ominus$, and $\Delta_r H^\ominus$ for the cell reaction at 25°C. Estimate $E^\ominus$(15°C). Calculate the cell potential at 25°C when $Q = 6.0 \times 10^{-5}$.

(c) The illustration below shows a simplified 'Pourbaix diagram' for the redox chemistry of $PbO_2/PbSO_4/Pb$ systems. The horizontal and slanted lines of the diagram are equilibrium half-cell potentials when all chemical species have unit activity. Vertical lines are non-redox equilibria. Prove that the redox potential lines at 25°C are given by $E = E^\ominus - (0.0592\ \text{V})\nu\text{pH}$, where ν is the number of hydrogen ions used in the half-reaction. Calculate $E(PbO_2/PbSO_4)$ at pH values of 5 and 8. What is $E(PbSO_4/Pb)$ at any pH?



1.16 Weak acidity of 2-aminopyridinium chloride

The table below summarizes the zero current potentials observed for the cell $Pd|H_2(g, 1\ \text{bar})|BH(aq, b), B(aq, b)|AgCl(s)|Ag$. Each measurement is made at equimolal concentrations of 2-aminopyridinium chloride (BH) and 2-aminopyridine (B). The data are for 25°C and it is found that $E^\ominus = 0.22251$ V. Use the data to determine pK_a for the acid at 25°C and the mean activity coefficient ($\gamma_\pm$) of BH as a function of molality (b) and ionic strength (I). Use the extended Debye–Hückel equation for the mean activity coefficient in the form:

$$-\log \gamma_\pm = \frac{AI^{1/2}}{1 + BI^{1/2}} - kb$$

where $A = 0.5091$ and B and k are parameters that depend upon the ions. Draw a graph of the mean activity coefficient with $b = 0.04$ mol kg^{-1} and $0 \le I \le 0.1$.

$b/(\text{mol kg}^{-1})$	0.01	0.02	0.03	0.04	0.05
$E^\ominus(25°C)/V$	0.744 52	0.728 53	0.719 28	0.713 14	0.708 09
$b/(\text{mol kg}^{-1})$	0.06	0.07	0.08	0.09	0.10
$E^\ominus(25°C)/V$	0.703 80	0.700 59	0.697 90	0.695 71	0.693 38

The table below summarizes p$K_a(T)$ for BH; add your value of pK_a(25°C) to those of the table. Determine the coefficients a_0, a_1, and a_2 such that the regression equation p$K_a(T) = a_0 + a_1/(T/K) + a_2 \ln(T/K)$ gives the best least-squares fit of the data. Draw graphs of $\Delta_r G^\ominus(T)$, $\Delta_r H^\ominus(T)$, and $\Delta_r S^\ominus(T)$ for the proton transfer reaction.

θ/°C	5	10	15	20	25	30	35	40
pK_a	7.177	7.060	6.949	6.841	?	6.640	6.543	6.449