7 Chemical equilibrium

This chapter develops the concept of chemical potential and shows how it is 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 the conditions. The principles of thermodynamics established in the preceding chapters can be applied to 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 and other thermodynamic properties of chemical reactions.

Chemical reactions tend to 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 that of the 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. 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.

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 chemical reactions.

7.1 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

Consider the 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 (xi) 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, then 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:

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} \qquad [7.1]$$

Although Δ normally signifies a *difference* in values, here 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,

$$\Delta_r G = \mu_B - \mu_A \qquad (7.2)$$

We see that $\Delta_r G$ can also be interpreted as the difference between the chemical potentials (the partial molar Gibbs energies) of the reactants and products *at the composition of the reaction mixture*.

Because chemical potential varies 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 plotted against ξ), we see from eqn 7.2 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

$$\Delta_r G = 0 \qquad (7.3)$$

This condition occurs when $\mu_B = \mu_A$ (Fig. 7.1). 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.

(b) Exergonic and endergonic reactions

We can express the spontaneity of a reaction at constant temperature and pressure in terms of the reaction Gibbs energy:

If $\Delta_r G < 0$, the forward reaction is spontaneous.

If $\Delta_r G > 0$, the reverse reaction is spontaneous.

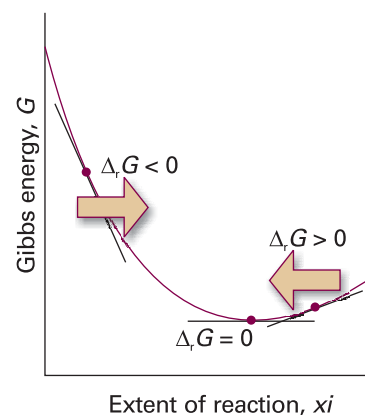If $\Delta_r G = 0$, the reaction is at equilibrium.

Fig. 7.1 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.
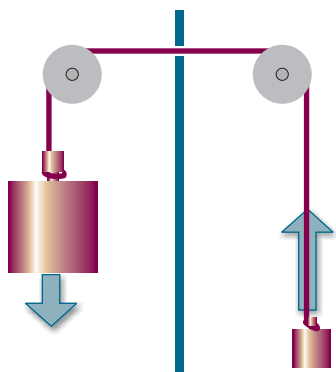
Fig. 7.2 If two weights are coupled as shown here, then the heavier weight will move the lighter weight in its non-spontaneous direction: overall, the process is still spontaneous. The weights are the analogues of two chemical reactions: a reaction with a large negative ΔG can force another reaction with a less ΔG to run in its non-spontaneous direction.

Comment 7.1

Note that in the definition of $\Delta_r G^\ominus$, the Δ_r has its normal meaning as a difference whereas in the definition of $\Delta_r G$ the Δ_r signifies a derivative.

A reaction for which $\Delta_r G < 0$ is called **exergonic** (from the Greek words for work producing). The name signifies that, because the process is spontaneous, it can be used to drive another process, such as another reaction, or used to do non-expansion work. A simple mechanical analogy is a pair of weights joined by a string (Fig. 7.2): the lighter of the pair of weights will be pulled up as the heavier weight falls down. Although the lighter weight has a natural tendency to move downward, its coupling to the heavier weight results in it being raised. In biological cells, the oxidation of carbohydrates act as the heavy weight that drives other reactions forward and results in the formation of proteins from amino acids, muscle contraction, and brain activity. A reaction for which $\Delta_r G > 0$ is called **endergonic** (signifying work consuming). The reaction can be made to occur only by doing work on it, such as electrolysing water to reverse its spontaneous formation reaction. Reactions at equilibrium are spontaneous in neither direction: they are neither exergonic nor endergonic.

7.2 The description of equilibrium

With the background established, we are now ready to see how to apply thermodynamics to the description of chemical equilibrium.

(a) Perfect gas equilibria

When A and B are perfect gases we can use eqn 5.14 ($\mu = \mu^\ominus + RT \ln p$, with p interpreted as $p/p^\ominus$) to write

$$\Delta_r G = \mu_B - \mu_A = (\mu_B^\ominus + RT \ln p_B) - (\mu_A^\ominus + RT \ln p_A)$$

$$= \Delta_r G^\ominus + RT \ln \frac{p_B}{p_A} \qquad (7.4)°$$

If we denote the ratio of partial pressures by Q, we obtain

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q \qquad Q = \frac{p_B}{p_A} \qquad (7.5)°$$

The ratio Q is an example of a **reaction quotient**. It ranges from 0 when $p_B = 0$ (corresponding to pure A) to infinity when $p_A = 0$ (corresponding to 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

$$\Delta_r G^\ominus = G_{B,m}^\ominus - G_{A,m}^\ominus = \mu_B^\ominus - \mu_A^\ominus \qquad (7.6)$$

In Section 3.6 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

$$\Delta_r G^\ominus = \Delta_f G^\ominus(B) - \Delta_f G^\ominus(A) \qquad (7.7)$$

At equilibrium $\Delta_r G = 0$. The ratio of partial pressures at equilibrium is denoted K, and eqn 7.5 becomes

$$0 = \Delta_r G^\ominus + RT \ln K$$

This expression rearranges to

$$RT \ln K = -\Delta_r G^\ominus \qquad K = \left(\frac{p_B}{p_A} \right)_{\text{equilibrium}} \qquad (7.8)°$$

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.

Molecular interpretation 7.1 *The approach to equilibrium*

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 a hypothetical reaction in which A molecules change into B molecules without mingling together. The Gibbs energy of the system changes 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 is a constant and equal to $\Delta_r G^{\ominus}$ at all stages of the reaction (Fig. 7.3). There is no intermediate minimum in the graph. However, in fact, the newly produced B molecules do mix with the surviving A molecules. We have seen that the contribution of a mixing process to the change in Gibbs energy is given by eqn 5.27 ($\Delta_{mix}G = nRT(x_A \ln x_A + x_B \ln x_B)$). This expression makes a U-shaped contribution to the total change in Gibbs energy. As can be seen from Fig. 7.3, there is now an intermediate minimum in the Gibbs energy, and its position corresponds to the equilibrium composition of the reaction mixture.

We see from eqn 7.8 that, when $\Delta_r G^{\ominus} > 0$, the equilibrium constant $K < 1$. Therefore, at equilibrium the partial pressure of A exceeds that of B, which means that the reactant A is favoured in the equilibrium. When $\Delta_r G^{\ominus} < 0$, the equilibrium constant $K > 1$, so at equilibrium the partial pressure of B exceeds that of A. Now the product B is favoured in the equilibrium.

(b) The general case of a reaction

We can easily extend the argument that led to eqn 7.8 to a general reaction. First, we need to generalize the concept of extent of reaction.

Consider the reaction $2\,A + B \rightarrow 3\,C + D$. A more sophisticated way of expressing the chemical equation is to write it in the symbolic form

$$0 = 3\,C + D - 2\,A - B$$

by subtracting the reactants from both sides (and replacing the arrow by an equals sign). This equation has the form

$$0 = \sum_J v_J J \tag{7.9}$$

where J denotes the substances and the v_J are the corresponding **stoichiometric numbers** in the chemical equation. In our example, these numbers have the values $v_A = -2$, $v_B = -1$, $v_C = +3$, and $v_D = +1$. A stoichiometric number is positive for products and negative for reactants. Then we define ξ so that, if it changes by $\Delta\xi$, then the change in the amount of any species J is $v_J \Delta\xi$.

Illustration 7.1 *Identifying stoichiometric numbers*

To express the equation

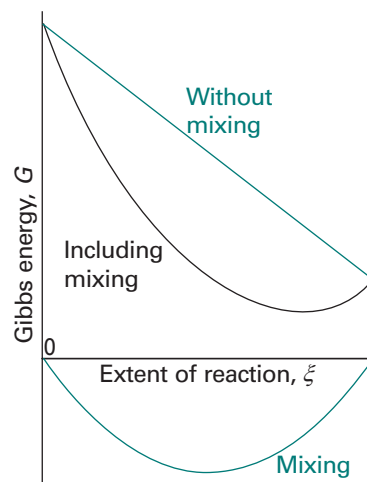$$N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g) \tag{7.10}$$

Fig. 7.3 If the mixing of reactants and products is ignored, then 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.

in the notation of eqn 7.9, we rearrange it to

$$0 = 2\,NH_3(g) - N_2(g) + 3\,H_2(g)$$
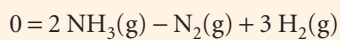
and then identify the stoichiometric numbers as $v_{N_2} = -1$, $v_{H_2} = -3$, and $v_{NH_3} = +2$. Therefore, if initially there is 10 mol N_2 present, then when the extent of reaction changes from $\xi = 0$ to $\xi = 1$ mol, implying that $\Delta\xi = +1$ mol, the amount of N_2 changes from 10 mol 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.

A note on good practice Stoichiometric *numbers* may be positive or negative; stoichiometric *coefficients* are always positive. Few, however, make the distinction between the two types of quantity.

The reaction Gibbs energy, $\Delta_r G$, is defined in the same way as before, eqn 7.1. In the *Justification* below, we show that the Gibbs energy of reaction can always be written

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q \tag{7.11}$$

with the standard reaction Gibbs energy calculated from

$$\Delta_r G^\ominus = \sum_{\text{Products}} v\Delta_f G^\ominus - \sum_{\text{Reactants}} v\Delta_f G^\ominus \tag{7.12a}$$

or, more formally,

$$\Delta_r G^\ominus = \sum_{J} v_J \Delta_f G^\ominus(J) \tag{7.12b}$$

The reaction quotient, Q, has the form

$$Q = \frac{\text{activities of products}}{\text{activities of reactants}} \tag{7.13a}$$

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 Π to denote the product of what follows it (just as Σ denotes the sum), and define Q as

$$Q = \prod_{J} a_J^{v_J} \tag{7.13b}$$

Because reactants have negative stoichiometric numbers, they automatically appear as the denominator when the product is written out explicitly. Recall from Table 5.3 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.

Illustration 7.2 *Writing a reaction quotient*

Consider the reaction $2\,A + 3\,B \rightarrow C + 2\,D$, in which case $v_A = -2$, $v_B = -3$, $v_C = +1$, and $v_D = +2$. The reaction quotient is then

$$Q = a_A^{-2} a_B^{-3} a_C a_D^2 = \frac{a_C a_D^2}{a_A^2 a_B^3}$$

Justification 7.1 *The dependence of the reaction Gibbs energy on the reaction quotient*

Consider the reaction with stoichiometric numbers v_J. When the reaction advances by $d\xi$, the amounts of reactants and products change by $dn_J = v_J d\xi$. The resulting infinitesimal change in the Gibbs energy at constant temperature and pressure is

$$dG = \sum_J \mu_J dn_J = \sum_J \mu_J v_J d\xi = \left(\sum_J v_J \mu_J \right) d\xi \qquad (7.14)$$

It follows that

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{P,T} = \sum_J v_J \mu_J \qquad (7.15)$$

To make further progress, we note that the chemical potential of a species J is related to its activity by eqn 5.25 ($\mu_J = \mu_J^\ominus + RT \ln a_J$). When this expression is substituted into eqn 7.15 we obtain

$$\Delta_r G = \overbrace{\sum_J v_J \mu_J^\ominus}^{\Delta_r G^\ominus} + RT \sum_J v_J \ln a_J$$

$$= \Delta_r G^\ominus + RT \sum_J \ln a_J^{v_J} = \Delta_r G^\ominus + RT \ln \overbrace{\prod_J a_J^{v_J}}^{Q}$$

$$= \Delta_r G^\ominus + RT \ln Q$$

with Q given by eqn 7.13b.

Comment 7.2
Recall that $a \ln x = \ln x^a$ and $\ln x + \ln y + \cdots = \ln xy \cdots$, so $\sum_i \ln x_i = \ln \left(\prod_i x_i \right)$.

Now we conclude the argument based on eqn 7.11. At equilibrium, the slope of G is zero: $\Delta_r G = 0$. The activities then have their equilibrium values and we can write

$$K = \left(\prod_J a_J^{v_J} \right)_{equilibrium} \qquad [7.16]$$

This expression has the same form as Q, eqn 7.13, but is 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 7.16 are often replaced by the numerical values of molalities (that is, by replacing a_J by $b_J/b^\ominus$, where $b^\ominus = 1 \text{ mol kg}^{-1}$), molar concentrations (that is, as $[J]/c^\ominus$, where $c^\ominus = 1 \text{ mol dm}^{-3}$), or the numerical values of partial pressures (that is, by $p_J/p^\ominus$, where $p^\ominus = 1 \text{ bar}$). In such cases, 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 (Section 5.9).

Illustration 7.3 *Writing an equilibrium constant.*

The equilibrium constant for the heterogeneous equilibrium $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ is

$$K = a_{CaCO_3(s)}^{-1} a_{CaO(s)} a_{CO_2(g)} = \frac{\overbrace{a_{CaO(s)} a_{CO_2(g)}}^{1}}{\underbrace{a_{CaCO_3(s)}}_{1}} = a_{CO_2}$$

(Table 5.3). Provided the carbon dioxide can be treated as a perfect gas, we can go on to write

$$K \approx p_{CO_2}/p^{\ominus}$$

and conclude that in this case the equilibrium constant is the numerical value of the decomposition vapour pressure of calcium carbonate.

Comment 7.3

In Chapter 17 we shall see that the right-hand side of eqn 7.17 may be expressed in terms of spectroscopic data for gas-phase species; so this expression also provides a link between spectroscopy and equilibrium composition.

At this point we set $\Delta_r G = 0$ in eqn 7.11 and replace Q by K. We immediately obtain

$$RT \ln K = -\Delta_r G^{\ominus} \qquad (7.17)$$

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.

Example 7.1 *Calculating an equilibrium constant*

Calculate the equilibrium constant for the ammonia synthesis reaction, eqn 7.10, 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 7.12 and convert it to the value of the equilibrium constant by using eqn 7.17. The expression for the equilibrium constant is obtained from eqn 7.16, and because the gases are taken to be perfect, we replace each activity by the ratio $p/p^{\ominus}$, where p is a partial pressure.

Answer The standard Gibbs energy of the reaction is

$$\Delta_r G^{\ominus} = 2\Delta_f G^{\ominus}(NH_3, g) - \{\Delta_f G^{\ominus}(N_2, g) + 3\Delta_f G^{\ominus}(H_2, g)\}$$
$$= 2\Delta_f G^{\ominus}(NH_3, g) = 2 \times (-16.5 \text{ kJ mol}^{-1})$$

Then,

$$\ln K = -\frac{2 \times (-16.5 \times 10^3 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} = \frac{2 \times 16.5 \times 10^3}{8.3145 \times 298}$$

Hence, $K = 6.1 \times 10^5$. This result is thermodynamically exact. The thermodynamic equilibrium constant for the reaction is

$$K = \frac{a_{NH_3}^2}{a_{N_2} a_{H_2}^3}$$

and this ratio has exactly the value we have just calculated. At low overall pressures, the activities can be replaced by the ratios $p/p^{\ominus}$, where p is a partial pressure, and an approximate form of the equilibrium constant is

$$K = \frac{(p_{NH_3}/p^{\ominus})^2}{(p_{N_2}/p^{\ominus})(p_{H_2}/p^{\ominus})^3} = \frac{p_{NH_3}^2 p^{\ominus 2}}{p_{N_2} p_{H_2}^3}$$

Self-test 7.1 Evaluate the equilibrium constant for $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ at 298 K.

$$[K = 0.15]$$

Example 7.2 *Estimating the degree of dissociation at equilibrium*

The degree of dissociation, α, is defined as the fraction of reactant that has decomposed; if the initial amount of reactant is n and the amount at equilibrium is n_{eq}, then $\alpha = (n - n_{eq})/n$. The standard Gibbs energy of reaction for the decomposition $H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$ is $+118.08$ 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 7.17, 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 7.17 in the form

$$\ln K = -\frac{\Delta_r G^{\ominus}}{RT} = -\frac{(+118.08 \times 10^3 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (2300 \text{ K})}$$

$$= -\frac{118.08 \times 10^3}{8.3145 \times 2300}$$

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	$\frac{1}{2}\alpha n$	Total: $(1+\frac{1}{2}\alpha)n$
Mole fraction, x_J	$\dfrac{1-\alpha}{1+\frac{1}{2}\alpha}$	$\dfrac{\alpha}{1+\frac{1}{2}\alpha}$	$\dfrac{\frac{1}{2}\alpha}{1+\frac{1}{2}\alpha}$	
Partial pressure, p_J	$\dfrac{(1-\alpha)p}{1+\frac{1}{2}\alpha}$	$\dfrac{\alpha p}{1+\frac{1}{2}\alpha}$	$\dfrac{\frac{1}{2}\alpha p}{1+\frac{1}{2}\alpha}$	

where, for the entries in the last row, we have used $p_J = x_J p$ (eqn 1.13). 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

$$K \approx \frac{\alpha^{3/2}p^{1/2}}{2^{1/2}}$$

Under the stated condition, $p = 1.00$ bar (that is, $p/p^{\ominus} = 1.00$), so $\alpha \approx (2^{1/2}K)^{2/3} = 0.0205$. That is, about 2 per cent of the water has decomposed.

A note on good practice 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 7.2 Given that the standard Gibbs energy of reaction at 2000 K is $+135.2$ 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]

Comment 7.4

The textbook's web site contains links to online tools for the estimation of equilibrium constants of gas-phase reactions.

(c) 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

$$K = \frac{a_C a_D}{a_A a_B} = \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \times \frac{b_C b_D}{b_A b_B} = K_\gamma K_b \tag{7.18}$$

The activity coefficients must be evaluated at the equilibrium composition of the mixture (for instance, by using one of the Debye–Hückel expressions, Section 5.9), which may involve a complicated calculation, because the activity coefficients are 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 unity 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.
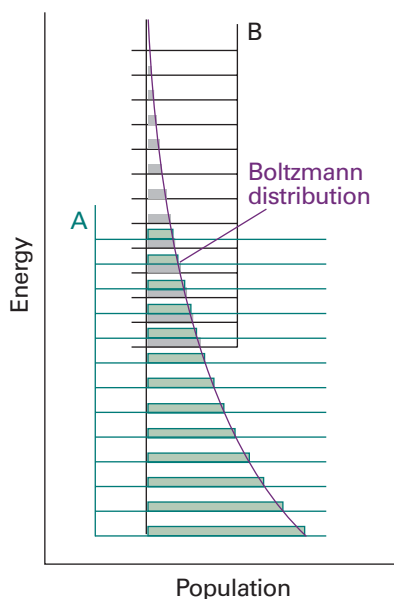

Fig. 7.4 The Boltzmann distribution of populations over the energy levels of two species A and B with similar densities of energy levels; the reaction A → B is endothermic in this example. The bulk of the population is associated with the species A, so that species is dominant at equilibrium.

Molecular interpretation 7.2 *The molecular origin of the equilibrium constant*

We can obtain a deeper insight into the origin and significance of the equilibrium constant by considering the Boltzmann distribution of molecules over the available states of a system composed of reactants and products (recall *Molecular interpretation 3.1*). 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. 7.4). 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. 7.5. 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 (see *Molecular interpretation 3.1*), so in this case we see that entropy effects dominate adverse energy effects. This competition is mirrored in eqn 7.17, 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

$$K = e^{-\Delta_r H^{\ominus}/RT} e^{\Delta_r S^{\ominus}/R} \tag{7.19}$$

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.
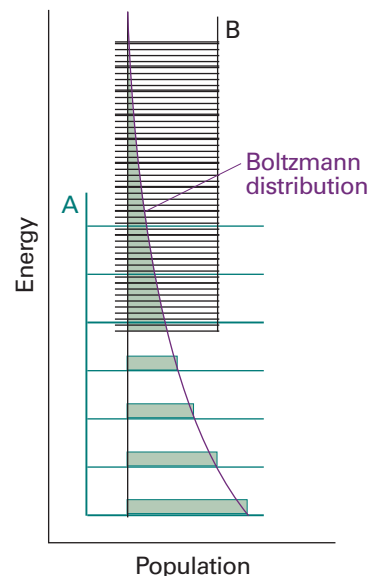
(d) Equilibria in biological systems

We saw in Section 5.7 that for biological systems it is appropriate to adopt the biological standard state, in which $a_{H^+} = 10^{-7}$ and $pH = -\log a_{H^+} = 7$. It follows from eqn 5.56 that the relation between the thermodynamic and biological standard Gibbs energies of reaction for a reaction of the form
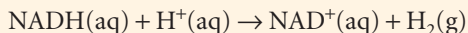
$$A + \nu H^+(aq) \rightarrow P \tag{7.20a}$$

is

$$\Delta_r G^{\oplus} = \Delta_r G^{\ominus} + 7\nu RT \ln 10 \tag{7.20b}$$

Note that there is no difference between the two standard values if hydrogen ions are not involved in the reaction ($\nu = 0$).

Fig. 7.5 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.

Illustration 7.4 *Using the biological standard state*

Consider the reaction

$$NADH(aq) + H^+(aq) \rightarrow NAD^+(aq) + H_2(g)$$

at 37°C, for which $\Delta_r G^{\ominus} = -21.8$ 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 $7 \ln 10 = 16.1$,

$$\Delta_r G^{\oplus} = -21.8 \text{ kJ mol}^{-1} + 16.1 \times (8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (310 \text{ K})$$
$$= +19.7 \text{ kJ mol}^{-1}$$

Note that the biological standard value is opposite in sign (in this example) to the thermodynamic standard value: the much lower concentration of hydronium ions (by seven orders of magnitude) at pH = 7 in place of pH = 0, has resulted in the reverse reaction becoming spontaneous.

Self-test 7.3 For a particular reaction of the form A → B + 2 H$^+$ in aqueous solution, it was found that $\Delta_r G^{\ominus} = +20$ kJ mol^{-1} at 28°C. Estimate the value of $\Delta_r G^{\oplus}$.

[−61 kJ mol^{-1}]

The response of equilibria to the conditions

Equilibria respond to changes in pressure, temperature, and concentrations of reactants and products. The equilibrium constant for a reaction is not affected by the presence of a catalyst or an enzyme (a biological catalyst). As we shall see in detail in Sections 22.* and 24.*, 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.

7.3 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

$$\left(\frac{\partial K}{\partial p} \right)_T = 0 \tag{7.21}$$

The conclusion that K is independent of pressure does not necessarily mean that the equilibrium composition is independent of the pressure, and its effect depends on how the pressure is applied. The pressure within a reaction vessel can be increased by injecting an inert gas into it. However, so long as the gases are perfect, this addition of gas leaves all the partial pressures of the reacting gases unchanged: the partial pressures 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. 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 individual partial pressures are changed but their ratio (as it appears in the equilibrium constant) remains the same. Consider, for instance, the perfect gas equilibrium $A \rightleftharpoons 2\,B$, for which the equilibrium constant is

$$K = \frac{p_B^2}{p_A p^{\ominus}}$$

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. 7.6).

The increase in the number of A molecules and the corresponding decrease in the number of B molecules in the equilibrium $A \rightleftharpoons 2\,B$ is a special case of a principle proposed by the French chemist Henri Le Chatelier.[1] **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 particles in the gas phase, which implies a shift $A \leftarrow 2\,B$.
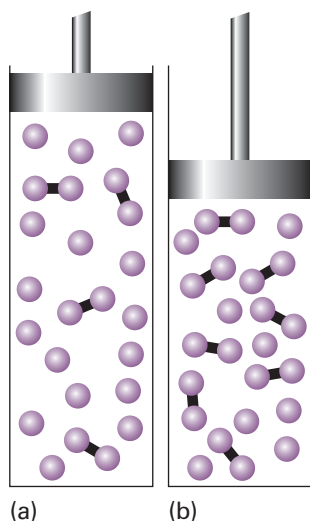

Fig. 7.6 When a reaction at equilibrium is compressed (from *a* to *b*), the reaction responds by reducing the number of molecules in the gas phase (in this case by producing the dimers represented by the linked spheres).

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[1] Le Chatelier also invented oxyacetylene welding.

To treat the effect of compression quantitatively, we 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 $2\alpha n$, where α is the extent of dissociation of A into 2B. 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 is

$$K = \frac{p_B^2}{p_A p^{\ominus}} = \frac{x_B^2 p^2}{x_A p p^{\ominus}} = \frac{4\alpha^2 (p/p^{\ominus})}{1-\alpha^2}$$

which rearranges to

$$\alpha = \left(\frac{1}{1 + 4p/Kp^{\ominus}}\right)^{1/2} \tag{7.22}$$

This formula shows that, even though K is independent of pressure, the amounts of A and B do depend on pressure (Fig. 7.7). It also shows that as p is increased, α decreases, in accord with Le Chatelier's principle.
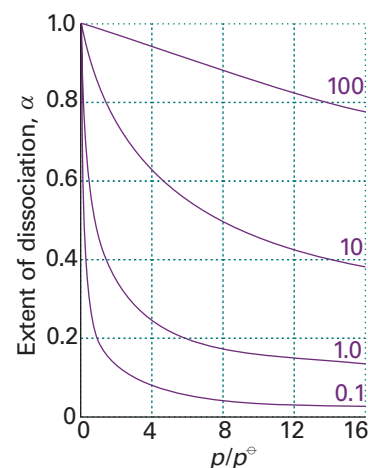

Fig. 7.7 The pressure dependence of the degree of dissociation, α, at equilibrium for an A(g) $\rightleftharpoons$ 2 B(g) reaction for different values of the equilibrium constant K. The value $\alpha = 0$ corresponds to pure A; $\alpha = 1$ corresponds to pure B.

Exploration Plot x_A and x_B against the pressure p for several values of the equilibrium constant K.

Illustration 7.5 *Predicting the effect of compression*

To predict the effect of an increase in pressure on the composition of the ammonia synthesis at equilibrium, eqn 7.10, 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

$$K = \frac{p_{NH_3}^2 p^{\ominus 2}}{p_{N_2} p_{H_2}^3} = \frac{x_{NH_3}^2 p^2 p^{\ominus 2}}{x_{N_2} x_{H_2}^3 p^4} = \frac{K_x p^{\ominus 2}}{p^2}$$

where K_x is the part of the equilibrium constant expression that contains the equilibrium mole fractions of reactants and products (note that, unlike K itself, K_x is not an equilibrium constant). Therefore, doubling the pressure must increase K_x by a factor of 4 to preserve the value of K.

Self-test 7.4 Predict the effect of a tenfold pressure increase on the equilibrium composition of the reaction $3\,N_2(g) + H_2(g) \rightarrow 2\,N_3H(g)$.

[100-fold increase in K_x]

7.4 **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 and the rise in temperature is opposed. Conversely, an equilibrium can be expected to shift in the exothermic direction if the temperature is lowered, for then energy is released and 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:

$$\text{(a)} \quad \frac{d \ln K}{dT} = \frac{\Delta_r H^{\ominus}}{RT^2} \qquad \text{(b)} \quad \frac{d \ln K}{d(1/T)} = -\frac{\Delta_r H^{\ominus}}{R} \qquad\qquad (7.23)$$

....

Justification 7.2 *The van 't Hoff equation*

From eqn 7.17, we know that

$$\ln K = -\frac{\Delta_r G^{\ominus}}{RT}$$

Differentiation of $\ln K$ with respect to temperature then gives

$$\frac{d \ln K}{dT} = -\frac{1}{R} \frac{d(\Delta_r G^{\ominus}/T)}{dT}$$

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 3.53) in the form

$$\frac{d(\Delta_r G^{\ominus}/T)}{dT} = -\frac{\Delta_r H^{\ominus}}{T^2}$$

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 7.23a. The second form of the equation is obtained by noting that

$$\frac{d(1/T)}{dT} = -\frac{1}{T^2}, \qquad \text{so} \quad dT = -T^2 d(1/T)$$

It follows that eqn 7.23a can be rewritten as

$$-\frac{d \ln K}{T^2 d(1/T)} = \frac{\Delta_r H^{\ominus}}{RT^2}$$

which simplifies into eqn 7.23b.

....

Equation 7.23a shows that $d \ln K/dT < 0$ (and therefore that $dK/dT < 0$) 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 comes from the expression $\Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$ written in the form $-\Delta_r G^{\ominus}/T = -\Delta_r H^{\ominus}/T + \Delta_r S^{\ominus}$. When the reaction is exothermic, $-\Delta_r H^{\ominus}/T$ corresponds to a positive change of entropy of the surroundings and favours the formation of products. When the temperature is raised, $-\Delta_r H^{\ominus}/T$ decreases, and the increasing entropy of the surroundings has a less important 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 $\Delta_r H^{\ominus}/T$ is smaller), and the reaction is able to shift towards products.
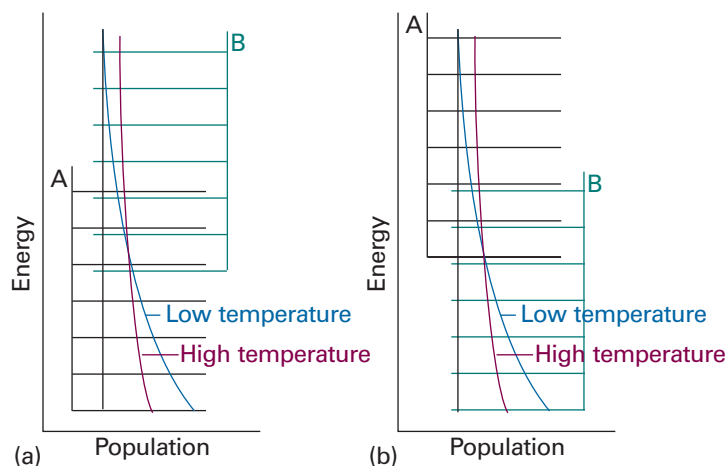
(a)   Population   (b)   Population

Fig. 7.8 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.

Molecular interpretation 7.3 *The temperature dependence of the equilibrium constant*

The typical arrangement of energy levels for an endothermic reaction is shown in Fig. 7.8a. 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 population of B states increases, and B becomes more abundant in the equilibrium mixture. Conversely, if the reaction is exothermic (Fig. 7.8b), 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 7.3 *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 7.23b 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
$(10^3 \text{ K})/T$	2.86	2.50	2.22	2.00
$-\ln K$	7.83	4.26	1.68	-0.39

These points are plotted in Fig. 7.9. The slope of the graph is $+9.6 \times 10^3$, so

$$\Delta_r H^{\ominus} = (+9.6 \times 10^3 \text{ K}) \times R = +80 \text{ kJ mol}^{-1}$$
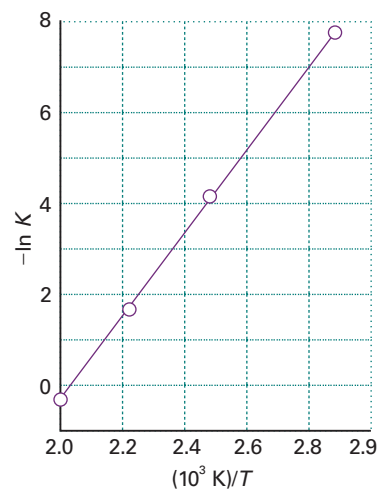

Fig. 7.9 When $-\ln K$ is plotted against $1/T$, a straight line is expected with slope equal to $\Delta_r H^{\ominus}/R$ if the standard reaction enthalpy does not vary appreciably with temperature. This is a non-calorimetric method for the measurement of reaction enthalpies.

Exploration The equilibrium constant of a reaction is found to fit the expression $\ln K = a + b/(T/K) + c/(T/K)^3$ over a range of temperatures. (a) Write expressions for $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$. (b) Plot $\ln K$ against $1/T$ between 400 K and 600 K for $a = -2.0$, $b = -1.0 \times 10^3$, and $c = 2.0 \times 10^7$.

Self-test 7.5 The equilibrium constant of the reaction $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$ 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}]

The temperature dependence of the equilibrium constant provides 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.

(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 7.23b between these two temperatures:

$$\ln K_2 - \ln K_1 = -\frac{1}{R} \int_{1/T_1}^{1/T_2} \Delta_r H^{\ominus} \mathrm{d}(1/T) \tag{7.24}$$

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

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{7.25}$$

Illustration 7.6 *Estimating an equilibrium constant at a different temperature*

To estimate the equilibrium constant for the synthesis of ammonia at 500 K from its value at 298 K (6.1×10^5 for the reaction as written in eqn 7.10) we use the standard reaction enthalpy, which can be obtained from Table 2.7 in the *Data section* by using $\Delta_r H^{\ominus} = 2\Delta_f H^{\ominus}(NH_3, g)$, 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 7.25 we find

$$\ln K_2 = \ln(6.1 \times 10^5) - \frac{(-92.2 \times 10^3\,\mathrm{J\,mol^{-1}})}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\left(\frac{1}{500\,\mathrm{K}} - \frac{1}{298\,\mathrm{K}}\right)$$

$$= -1.71$$

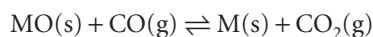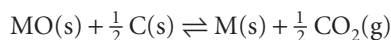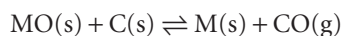It follows that $K_2 = 0.18$, a lower value than at 298 K, as expected for this exothermic reaction.

Self-test 7.6 The equilibrium constant for $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ was calculated in Self-test 7.1. Estimate its value at 100°C.   [15]

Knowledge of the temperature dependence of the equilibrium constant for a reaction can be useful in the design of laboratory and industrial processes. For example, synthetic chemists can improve the yield of a reaction by changing the temperature of the reaction mixture. Also, reduction of a metal oxide with carbon or carbon monoxide results in the extraction of the metal when the process is carried out at a temperature for which the equilibrium constant for the reaction is much greater than one.
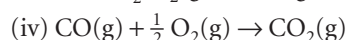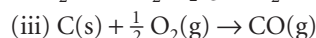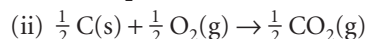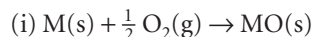
IMPACT ON ENGINEERING

I7.1 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

$$MO(s) + C(s) \rightleftharpoons M(s) + CO(g)$$
$$MO(s) + \tfrac{1}{2} C(s) \rightleftharpoons M(s) + \tfrac{1}{2} CO_2(g)$$
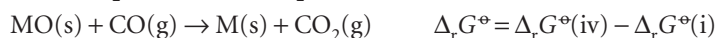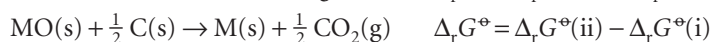$$MO(s) + CO(g) \rightleftharpoons M(s) + CO_2(g)$$

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) $M(s) + \tfrac{1}{2} O_2(g) \rightarrow MO(s)$
(ii) $\tfrac{1}{2} C(s) + \tfrac{1}{2} O_2(g) \rightarrow \tfrac{1}{2} CO_2(g)$
(iii) $C(s) + \tfrac{1}{2} O_2(g) \rightarrow CO(g)$
(iv) $CO(g) + \tfrac{1}{2} O_2(g) \rightarrow CO_2(g)$

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. 7.10, 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:

$$MO(s) + C(s) \rightarrow M(s) + CO(g) \qquad \Delta_r G^{\ominus} = \Delta_r G^{\ominus}(iii) - \Delta_r G^{\ominus}(i)$$
$$MO(s) + \tfrac{1}{2} C(s) \rightarrow M(s) + \tfrac{1}{2} CO_2(g) \qquad \Delta_r G^{\ominus} = \Delta_r G^{\ominus}(ii) - \Delta_r G^{\ominus}(i)$$
$$MO(s) + CO(g) \rightarrow M(s) + CO_2(g) \qquad \Delta_r G^{\ominus} = \Delta_r G^{\ominus}(iv) - \Delta_r G^{\ominus}(i)$$

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 2000°C.
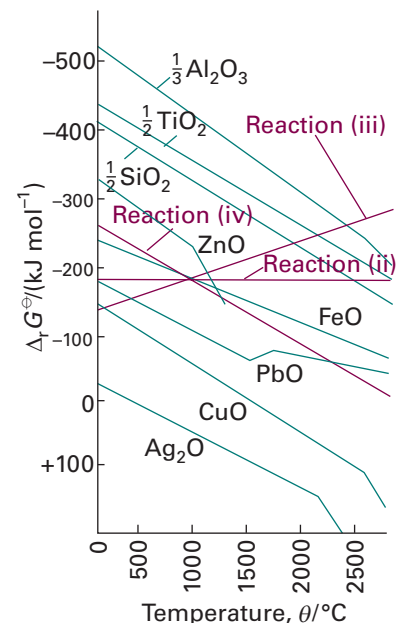

Fig. 7.10 An Ellingham diagram for the discussion of the reduction of metal ores.

Equilibrium electrochemistry

We shall now see how the foregoing ideas, with certain changes of technical detail, can be used to describe the equilibrium properties of reactions taking place in electrochemical cells. The ability to make very precise measurements of currents and potential differences ('voltages') means that electrochemical methods can be used to determine thermodynamic properties of reactions that may be inaccessible by other methods.

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 7.1. Any 'inert metal' shown as part of the specification 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 tube containing a concentrated electrolyte solution (almost always potassium chloride 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.

7.5 Half-reactions and electrodes

It will be familiar from introductory chemistry courses that **oxidation** is the removal of electrons from a species, a **reduction** is the addition of electrons to a species, and 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. It should also be familiar that any redox reaction may be expressed as the difference of two reduction **half-reactions**, which are conceptual reactions showing the gain of electrons. Even reactions that are not redox reactions may often be expressed as the difference of two reduction half-reactions. The reduced and oxidized species in a half-reaction form a **redox couple**. In general we write a couple as Ox/Red and the corresponding reduction half-reaction as

$$\text{Ox} + \nu\,\text{e}^- \rightarrow \text{Red} \tag{7.26}$$

Table 7.1 Varieties of electrode

| Electrode type	Designation	Redox couple	Half-reaction
Metal/metal ion	$M(s)\,|\,M^+(aq)$	M^+/M	$M^+(aq) + e^- \rightarrow M(s)$
Gas	$Pt(s)\,|\,X_2(g)\,|\,X^+(aq)$	X^+/X_2	$X^+(aq) + e^- \rightarrow \frac{1}{2}X_2(g)$
	$Pt(s)\,|\,X_2(g)\,|\,X^-(aq)$	X_2/X^-	$\frac{1}{2}X_2(g) + e^- \rightarrow X^-(aq)$
Metal/insoluble salt	$M(s)\,|\,MX(s)\,|\,X^-(aq)$	$MX/M,X^-$	$MX(s) + e^- \rightarrow M(s) + X^-(aq)$
Redox	$Pt(s)\,|\,M^+(aq),M^{2+}(aq)$	M^{2+}/M^+	$M^{2+}(aq) + e^- \rightarrow M^+(aq)$

Illustration 7.7 *Expressing a reaction in terms of half-reactions*

The dissolution of silver chloride in water $AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$, which is not a redox reaction, can be expressed as the difference of the following two reduction half-reactions:

$$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$$
$$Ag^+(aq) + e^- \rightarrow Ag(s)$$
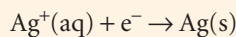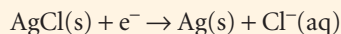
The redox couples are $AgCl/Ag,Cl^-$ and Ag^+/Ag, respectively.

Self-test 7.7 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.
$$[4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2(g),\ O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)]$$
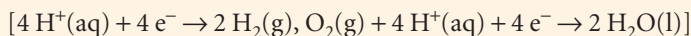
We shall often find it useful to express the composition of an electrode compartment in terms of the reaction quotient, Q, for the half-reaction. This quotient is defined like the reaction quotient for the overall reaction, but the electrons are ignored.

Illustration 7.8 *Writing the reaction quotient of a half-reaction*

The reaction quotient for the reduction of O_2 to H_2O in acid solution, $O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)$, is

$$Q = \frac{a_{H_2O}^2}{a_{H^+}^4 a_{O_2}} \approx \frac{p^\ominus}{a_{H^+}^4 p_{O_2}}$$

The approximations used in the second step are that the activity of water is 1 (because the solution is dilute) and the oxygen behaves as a perfect gas, so $a_{O_2} \approx p_{O_2}/p^\ominus$.

Self-test 7.8 Write the half-reaction and the reaction quotient for a chlorine gas electrode.
$$[Cl_2(g) + 2\,e^- \rightarrow 2\,Cl^-(aq),\ Q = a_{Cl^-}^2 p^\ominus/p_{Cl_2}]$$

The reduction and oxidation processes responsible for the overall reaction in a cell are separated in space: oxidation takes place at one electrode and reduction takes place at the other. As the reaction proceeds, the electrons released in the oxidation $Red_1 \rightarrow Ox_1 + \nu\,e^-$ at one electrode travel through the external circuit and re-enter the cell through the other electrode. There they bring about reduction $Ox_2 + \nu\,e^- \rightarrow Red_2$. 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. 7.11), 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).

7.6 **Varieties of cells**

The simplest type of cell has a single electrolyte common to both electrodes (as in Fig. 7.11). In some cases it is necessary to immerse the electrodes in different electrolytes,
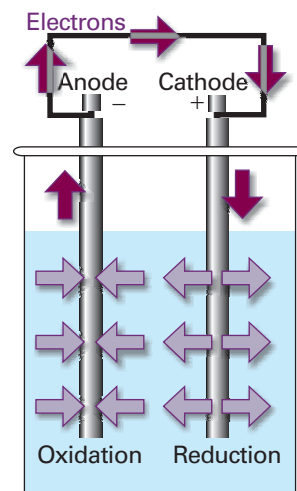
Fig. 7.11 When a spontaneous reaction takes place in a galvanic cell, electrons are deposited in one electrode (the site of oxidation, the anode) and collected from another (the site of reduction, the cathode), and so there is a net flow of current which can be used to do work. Note that the + sign of 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.
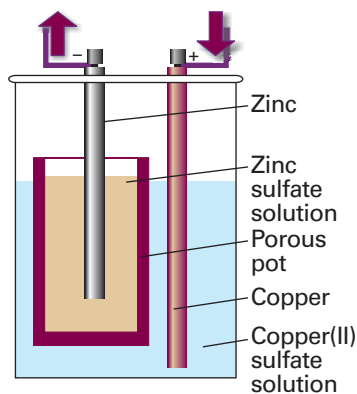
Fig. 7.12 One version of the Daniell cell. The copper electrode is the cathode and the zinc electrode is the anode. Electrons leave the cell from the zinc electrode and enter it again through the copper electrode.

as in the 'Daniell cell' in which the redox couple at one electrode is Cu^{2+}/Cu and at the other is Zn^{2+}/Zn (Fig. 7.12). In an **electrolyte concentration cell**, the electrode compartments are 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.
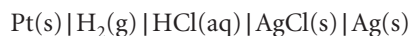
(a) Liquid junction potentials

In a cell with two different electrolyte solutions in contact, as in the Daniell cell, there is an additional source of potential difference across the interface of the two electrolytes. This potential is called the **liquid junction potential**, E_{lj}. 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. 7.13). 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. 7.11 is denoted

$$Pt(s)\,|\,H_2(g)\,|\,HCl(aq)\,|\,AgCl(s)\,|\,Ag(s)$$

A liquid junction is denoted by ⋮, so the cell in Fig. 7.12, is denoted

$$Zn(s)\,|\,ZnSO_4(aq)\,⋮\,CuSO_4(aq)\,|\,Cu(s)$$
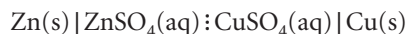
A double vertical line, ∥, denotes an interface for which it is assumed that the junction potential has been eliminated. Thus the cell in Fig. 7.13 is denoted

$$Zn(s)\,|\,ZnSO_4(aq)\,\|\,CuSO_4(aq)\,|\,Cu(s)$$

An example of an electrolyte concentration cell in which the liquid junction potential is assumed to be eliminated is

$$Pt(s)\,|\,H_2(g)\,|\,HCl(aq, b_1)\,\|\,HCl(aq, b_2)\,|\,H_2(g)\,|\,Pt(s).$$

7.7 The electromotive force

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 corresponding 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
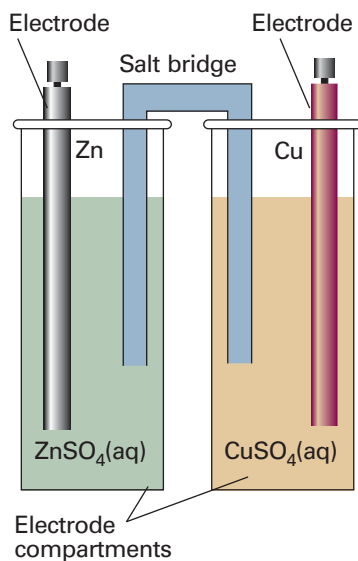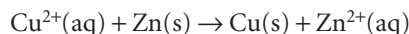

Fig. 7.13 The salt bridge, essentially an inverted U-tube full of concentrated salt solution in a jelly, has two opposing liquid junction potentials that almost cancel.

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

Right-hand electrode: $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$

Left-hand electrode: $Zn^{2+}(aq) + 2\ e^- \rightarrow Zn(s)$
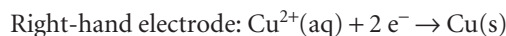
Hence, the overall cell reaction is the difference:

$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$

(a) The Nernst equation

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 ($1\ V = 1\ J\ C^{-1}\ s$). 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 3.5e, we know that the maximum non-expansion work, which in the current context is electrical work, that a system (the cell) can do is given by eqn 3.38 ($w_{e,max} = \Delta G$), with ΔG identified (as we shall show) with the Gibbs energy of the cell reaction, $\Delta_r G$. It follows that, to draw thermodynamic conclusions from measurements of the work a cell can do, we must ensure that the cell is operating reversibly, for only then is it producing maximum work. Moreover, we saw in Section 7.1a that the reaction Gibbs energy is actually a property relating to a specified composition of the reaction mixture. Therefore, to make use of $\Delta_r G$ 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, the composition is constant, and no current flows: in effect, the cell reaction is poised for change, but not actually changing. The resulting potential difference is called the **electromotive force** (emf), E, of the cell.

As we show in the *Justification* below, the relation between the reaction Gibbs energy and the emf of the cell is

$$-\nu FE = \Delta_r G \tag{7.27}$$

where F is Faraday's constant, $F = eN_A$, and ν is the stoichiometric coefficient of the electrons in the half-reactions into which the cell reaction can be divided. This equation 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.

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Justification 7.3 *The relation between the electromotive force and the reaction Gibbs energy*

We consider the change in G when the cell reaction advances by an infinitesimal amount $d\xi$ at some composition. From eqn 7.15 we can write (at constant temperature and pressure)

$$dG = \Delta_r G d\xi$$

The maximum non-expansion (electrical) work that the reaction can do as it advances by $d\xi$ at constant temperature and pressure is therefore
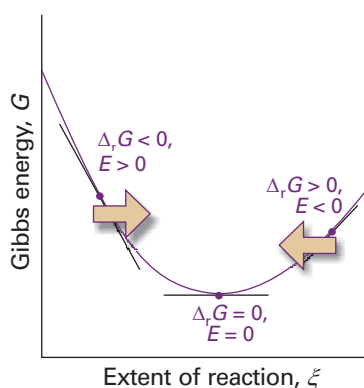
$$dw_e = \Delta_r G d\xi$$

Fig. 7.14 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 emf, 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.

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 $-\nu e N_A d\xi$ (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 *Appendix 3*):

$$dw_e = -\nu F E d\xi$$

When we equate this relation to the one above ($dw_e = \Delta_r G d\xi$), the advancement $d\xi$ cancels, and we obtain eqn 7.27.

It follows from eqn 7.27 that, by knowing the reaction Gibbs energy at a specified composition, we can state the cell emf at that composition. Note that a negative reaction Gibbs energy, corresponding to a spontaneous cell reaction, corresponds to a positive cell emf. Another way of looking at the content of eqn 7.27 is that it shows that the driving power of a cell (that is, its emf) 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. 7.14). When the slope is close to zero (when the cell reaction is close to equilibrium), the emf is small.

Illustration 7.9 *Converting between the cell emf and the reaction Gibbs energy*

Equation 7.27 provides an electrical method for measuring a reaction Gibbs energy at any composition of the reaction mixture: we simply measure the cell's emf and convert it to $\Delta_r G$. Conversely, if we know the value of $\Delta_r G$ at a particular composition, then we can predict the emf. For example, if $\Delta_r G = -1 \times 10^2$ kJ mol^{-1} and $\nu = 1$, then

$$E = -\frac{\Delta_r G}{\nu F} = -\frac{(-1 \times 10^5 \text{ J mol}^{-1})}{1 \times (9.6485 \times 10^4 \text{ C mol}^{-1})} = 1 \text{ V}$$

where we have used 1 J = 1 C V.

We can go on to relate the emf to the activities of the participants in the cell reaction. We know that the reaction Gibbs energy is related to the composition of the reaction mixture by eqn 7.11 ($\Delta_r G = \Delta_r G^\ominus + RT \ln Q$); 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

$$E^\ominus = -\frac{\Delta_r G^\ominus}{\nu F} \qquad\qquad [7.28]$$

and called the **standard emf** of the cell. That is, the standard emf is the standard reaction Gibbs energy expressed as a potential (in volts). It follows that

$$E = E^{\ominus} - \frac{RT}{\nu F} \ln Q \qquad (7.29)$$

This equation for the emf in terms of the composition is called the **Nernst equation**; the dependence of cell potential on composition that it predicts is summarized in Fig. 7.15. One important application of the Nernst equation is to the determination of the pH of a solution and, with a suitable choice of electrodes, of the concentration of other ions (Section 7.9c).

We see from eqn 7.29 that the standard emf (which will shortly move to centre stage of the exposition) can be interpreted as the emf when all the reactants and products in the cell reaction are in their standard states, for then all activities are 1, so $Q = 1$ and $\ln Q = 0$. However, the fact that the standard emf is merely a disguised form of the standard reaction Gibbs energy (eqn 7.28) should always be kept in mind and underlies all its applications.
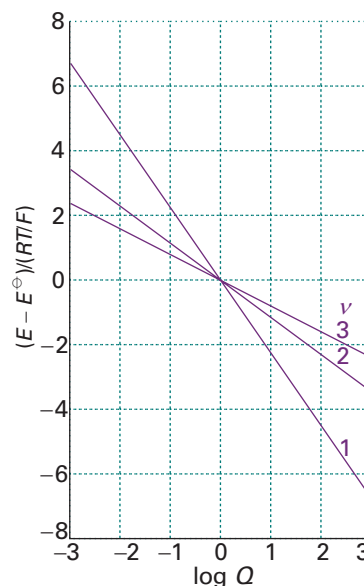

Fig. 7.15 The variation of cell emf with the value of the reaction quotient for the cell reaction for different values of ν (the number of electrons transferred). At 298 K, $RT/F = 25.69$ mV, so the vertical scale refers to multiples of this value.

Exploration Plot the variation of cell emf with the value of the reaction quotient for the cell reaction for different values of the temperature. Does the cell emf become more or less sensitive to composition as the temperature increases?

Illustration 7.10 *Using the Nernst equation*

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 emf decreases by 59.2 mV.

(b) Cells at equilibrium

A special case of the Nernst equation has great importance in electrochemistry and provides a link to the earlier part of the chapter. 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

$$\ln K = \frac{\nu F E^{\ominus}}{RT} \qquad (7.30)$$

This very important equation (which could also have been obtained more directly by substituting eqn 7.29 into eqn 7.17) lets us predict equilibrium constants from measured standard cell potentials. However, before we use it extensively, we need to establish a further result.

Illustration 7.11 *Calculating an equilibrium constant from a standard cell potential*

Because the standard emf of the Daniell cell is +1.10 V, the equilibrium constant for the cell reaction $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$, for which $\nu = 2$, is $K = 1.5 \times 10^{37}$ at 298 K. We conclude that the displacement of copper by zinc goes virtually to completion. Note that an emf of about 1 V is easily measurable but corresponds to an equilibrium constant that would be impossible to measure by direct chemical analysis.

7.8 **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 zero and then assign values to others on that basis. The specially selected electrode is the **standard hydrogen electrode** (SHE):

$$\text{Pt(s)}|\text{H}_2\text{(g)}|\text{H}^+\text{(aq)} \qquad E^{\ominus} = 0 \qquad\qquad\qquad [7.31]$$

at all temperatures. To achieve the standard conditions, the activity of the hydrogen ions must be 1 (that is, pH = 0) and the pressure (more precisely, the fugacity) of the hydrogen gas must be 1 bar. 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.

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':

$$\text{Pt(s)}|\text{H}_2\text{(g)}|\text{HCl(aq)}|\text{AgCl(s)}|\text{Ag(s)} \qquad \tfrac{1}{2}\text{H}_2\text{(g)} + \text{AgCl(s)} \to \text{HCl(aq)} + \text{Ag(s)}$$

for which the Nernst equation is

$$E = E^{\ominus}(\text{AgCl/Ag, Cl}^-) - \frac{RT}{F}\ln\frac{a_{\text{H}^+}a_{\text{Cl}^-}}{a_{\text{H}_2}^{1/2}}$$

We shall set $a_{\text{H}_2} = 1$ from now on, and for simplicity write the standard potential as $E^{\ominus}$; then

$$E = E^{\ominus} - \frac{RT}{F}\ln a_{\text{H}^+}a_{\text{Cl}^-}$$

The activities can be expressed in terms of the molality b of HCl(aq) through $a_{\text{H}^+} = \gamma_{\pm}b/b^{\ominus}$ and $a_{\text{Cl}^-} = \gamma_{\pm}b/b^{\ominus}$ as we saw in Section 5.9), so

$$E = E^{\ominus} - \frac{RT}{F}\ln b^2 - \frac{RT}{F}\ln\gamma_{\pm}^2$$

where for simplicity we have replaced $b/b^{\ominus}$ by b. This expression rearranges to

$$E + \frac{2RT}{F}\ln b = E^{\ominus} - \frac{2RT}{F}\ln\gamma_{\pm} \qquad\qquad\qquad \{7.32\}$$

From the Debye–Hückel limiting law for a 1,1-electrolyte (Section 5.9; a 1,1-electrolyte is a solution of singly charged M$^+$ and X$^-$ ions), we know that $\ln\gamma_{\pm} \propto -b^{1/2}$. The natural logarithm used here is proportional to the common logarithm that appears in eqn 5.69 (because $\ln x = \ln 10 \log x = 2.303 \log x$). Therefore, with the constant of proportionality in this relation written as $(F/2RT)C$, eqn 7.32 becomes

$$E + \frac{2RT}{F}\ln b = E^{\ominus} + Cb^{1/2} \qquad\qquad\qquad \{7.33\}$$

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 $E^{\ominus}$ for the silver/silver-chloride electrode. 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.

Illustration 7.12 *Determining the standard emf of a cell*

The emf of the cell $Pt(s)\,|\,H_2(g, p^{\ominus})\,|\,HCl(aq, b)\,|\,AgCl(s)\,|\,Ag(s)$ at 25°C has the following values:

$b/(10^{-3} b^{\ominus})$	3.215	5.619	9.138	25.63
E/V	0.52053	0.49257	0.46860	0.41824

To determine the standard emf of the cell we draw up the following table, using $2RT/F = 0.051\,39$ V:

$b/(10^{-3} b^{\ominus})$	3.215	5.619	9.138	25.63
$\{b/(10^{-3} b^{\ominus})\}^{1/2}$	1.793	2.370	3.023	5.063
E/V	0.52053	0.49257	0.46860	0.41824
$E/V + 0.051\,39 \ln b$	0.2256	0.2263	0.2273	0.2299

The data are plotted in Fig. 7.16; as can be seen, they extrapolate to $E^{\ominus} = 0.2232$ V.

Self-test 7.9 The data below are for the cell $Pt(s)\,|\,H_2(g, p^{\ominus})\,|\,HBr(aq, b)\,|$ $AgBr(s)\,|\,Ag(s)$ at 25°C. Determine the standard emf of the cell.

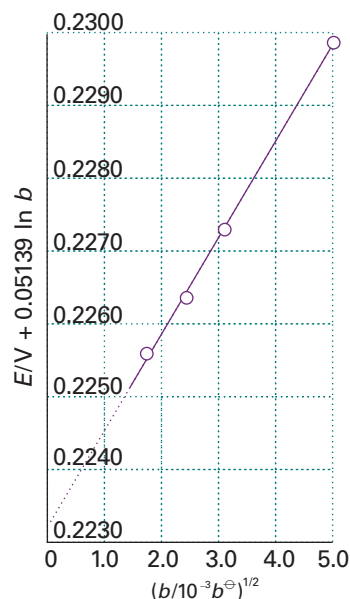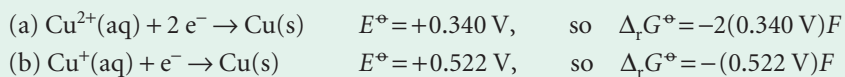| $b/(10^{-4} b^{\ominus})$	4.042	8.444	37.19	
E/V	0.47381	0.43636	0.36173	[0.071 V]

Fig. 7.16 The plot and the extrapolation used for the experimental measurement of a standard cell emf. The intercept at $b^{1/2} = 0$ is $E^{\ominus}$.

Exploration Suppose that the procedure in *Illustration 7.12* results in a plot that deviates from linearity. What might be the cause of this behaviour? How might you modify the procedure to obtain a reliable value of the standard potential?

Table 7.2 lists standard potentials at 298 K. An important feature of standard emf of cells and standard potentials of electrodes 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. However, it also increases the number of electrons transferred by the same factor, and by eqn 7.27 the value of $E^{\ominus}$ remains unchanged. A practical consequence is that a cell emf is independent of the physical size of the cell. In other words, cell emf is an intensive property.

The standard potentials in Table 7.2 may be combined to give values for couples that are not listed there. However, to do so, we must take into account the fact that different couples may correspond to the transfer of different numbers of electrons. The procedure is illustrated in the following *Example*.

Example 7.4 *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 a Hess's law analysis of reaction enthalpies). Therefore, we should convert the $E^{\ominus}$ values to $\Delta G^{\ominus}$ values by using eqn 7.27, add them appropriately, and then convert the overall $\Delta G^{\ominus}$ to the required $E^{\ominus}$ by using eqn 7.27 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:

(a) $Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$ $E^{\ominus} = +0.340$ V,   so $\Delta_r G^{\ominus} = -2(0.340\text{ V})F$

(b) $Cu^{+}(aq) + e^- \rightarrow Cu(s)$ $E^{\ominus} = +0.522$ V,   so $\Delta_r G^{\ominus} = -(0.522\text{ V})F$

Synoptic Table 7.2* Standard potentials at 298 K

Couple	$E^{\ominus}/V$
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.61
$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$	+0.34
$H^+(aq) + e^- \rightarrow \tfrac{1}{2}H_2(g)$	0
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22
$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$	−0.76
$Na^+(aq) + e^- \rightarrow Na(s)$	−2.71

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

The required reaction is

   (c) $Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$ $E^{\ominus} = -\Delta_r G^{\ominus}/F$
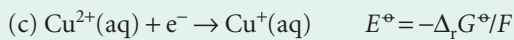
Because (c) = (a) − (b), the standard Gibbs energy of reaction (c) is

   $\Delta_r G^{\ominus} = \Delta_r G^{\ominus}(a) - \Delta_r G^{\ominus}(b) = -(-0.158\ \text{V}) \times F$

Therefore, $E^{\ominus} = +0.158$ V. Note that the generalization of the calculation we just performed is

   $v_c E^{\ominus}(c) = v_a E^{\ominus}(a) + v_b E^{\ominus}(b)$ (7.34)

A note on good practice Whenever combining standard potentials to obtain the standard potential of a third couple, always work via the Gibbs energies because they are additive, whereas, in general, standard potentials are not.

Self-test 7.10 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]

7.9 Applications of standard potentials

Cell emfs are a convenient source of data on equilibrium constants and the Gibbs energies, enthalpies, and entropies of reactions. In practice the standard values of these quantities are the ones normally determined.

(a) The electrochemical series

We have seen that for two redox couples, Ox_1/Red_1 and Ox_2/Red_2, and the cell

   $Red_1, Ox_1 \| Red_2, Ox_2$ $E^{\ominus} = E_2^{\ominus} - E_1^{\ominus}$ (7.35a)

that the cell reaction

   $Red_1 + Ox_2 \rightarrow Ox_1 + Red_2$ (7.35b)

is spontaneous as written if $E^{\ominus} > 0$, and therefore if $E_2^{\ominus} > E_1^{\ominus}$. Because in the cell reaction Red_1 reduces Ox_2, we can conclude that

   Red_1 has a thermodynamic tendency to reduce Ox_2 if $E_1^{\ominus} < E_2^{\ominus}$

More briefly: low reduces high.

Illustration 7.13 *Using the electrochemical series*

Because $E^{\ominus}(Zn^{2+},Zn) = -0.76$ V $< E^{\ominus}(Cu^{2+},Cu) = +0.34$ V, zinc has a thermodynamic tendency to reduce Cu^{2+} ions in aqueous solution.

Table 7.3 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 potentials 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

Table 7.3 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 7.2.

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.

The reactions of the electron transport chains of respiration are good applications of this principle.

IMPACT ON BIOCHEMISTRY
I7.2 Energy conversion in biological cells

The whole of life's activities depends on the coupling of exergonic and endergonic reactions, for the oxidation of food drives other reactions forward. In biological cells, the energy released by the oxidation of foods is stored in adenosine triphosphate (ATP, **1**). The essence of the action of ATP is its ability to lose its terminal phosphate group by hydrolysis and to form adenosine diphosphate (ADP):

$$ATP(aq) + H_2O(l) \rightarrow ADP(aq) + P_i^-(aq) + H_3O^+(aq)$$

where P_i^- denotes an inorganic phosphate group, such as $H_2PO_4^-$. The biological standard values for ATP hydrolysis at 37°C (310 K, blood temperature) are $\Delta_r G^\oplus = -31$ kJ mol^{-1}, $\Delta_r H^\oplus = -20$ kJ mol^{-1}, and $\Delta_r S^\oplus = +34$ J K^{-1} mol^{-1}. The hydrolysis is therefore exergonic ($\Delta_r G^\oplus < 0$) under these conditions and 31 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 ATP acts as a phosphate donor to a number of acceptors (for example, glucose), but is recharged by more powerful phosphate donors in a number of biochemical processes.

We now use the oxidation of glucose to CO_2 and H_2O by O_2 as an example of how the breakdown of foods is coupled to the formation of ATP in the cell. The process begins with *glycolysis*, a partial oxidation of glucose by nicotinamide adenine dinucleotide (NAD$^+$, **2**) to pyruvate ion, $CH_3COCO_2^-$, continues with the *citric acid cycle*, which oxidizes pyruvate to CO_2, and ends with *oxidative phosphorylation*, which reduces O_2 to H_2O. Glycolysis is the main source of energy during *anaerobic metabolism*, a form of metabolism in which inhaled O_2 does not play a role. The citric acid cycle and oxidative phosphorylation are the main mechanisms for the extraction of energy from carbohydrates during *aerobic metabolism*, a form of metabolism in which inhaled O_2 does play a role.
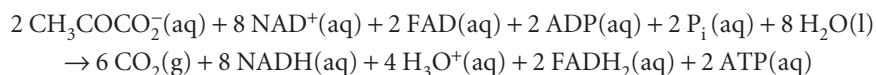

1 ATP

2 NAD+
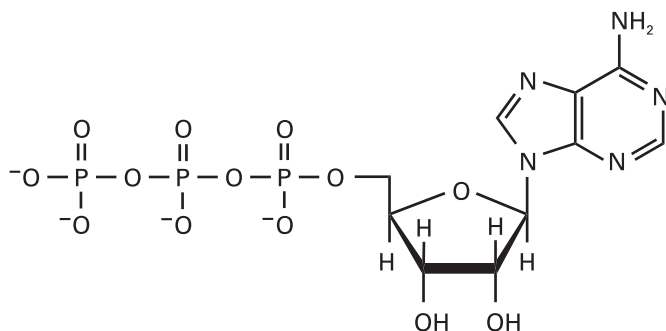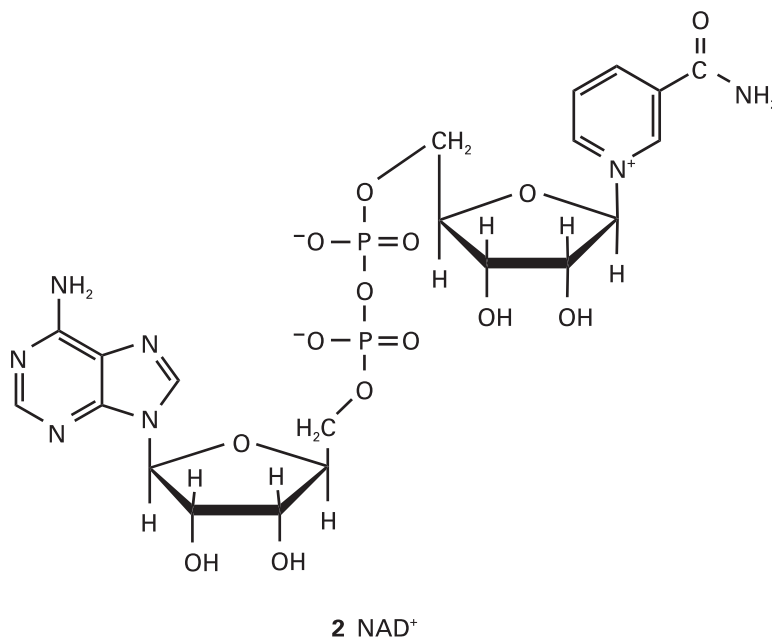
Glycolysis

Glycolysis occurs in the *cytosol*, the aqueous material encapsulated by the cell membrane, and consists of ten enzyme-catalysed reactions. At blood temperature, $\Delta_r G^{\ominus} = -147$ kJ mol^{-1} for the oxidation of glucose by NAD+ to pyruvate ions. The oxidation of one glucose molecule is coupled to the conversion of two ADP molecules to two ATP molecules, so the net reaction of glycolysis is:

$$C_6H_{12}O_6(aq) + 2\ NAD^+(aq) + 2\ ADP(aq) + 2\ P_i^-(aq) + 2\ H_2O(l)$$
$$\rightarrow 2\ CH_3COCO_2^-(aq) + 2\ NADH(aq) + 2\ ATP(aq) + 2\ H_3O^+(aq)$$

The standard reaction Gibbs energy is $(-147) - 2(-31)$ kJ mol^{-1} = -85 kJ mol^{-1}. The reaction is exergonic, and therefore spontaneous: the oxidation of glucose is used to 'recharge' the ATP. In cells that are deprived of O_2, pyruvate ion is reduced to lactate ion, $CH_3C(OH)CO_2^-$, by NADH.[2] Very strenuous exercise, such as bicycle racing, can decrease sharply the concentration of O_2 in muscle cells and the condition known as muscle fatigue results from increased concentrations of lactate ion.

The citric acid cycle

The standard Gibbs energy of combustion of glucose is -2880 kJ mol^{-1}, so terminating its oxidation at pyruvate is a poor use of resources. In the presence of O_2, pyruvate is oxidized further during the citric acid cycle and oxidative phosphorylation, which occur in a special compartment of the cell called the *mitochondrion*. The citric acid cycle requires eight enzymes that couple the synthesis of ATP to the oxidation of pyruvate by NAD+ and flavin adenine dinucleotide (FAD, **3**):

$$2\ CH_3COCO_2^-(aq) + 8\ NAD^+(aq) + 2\ FAD(aq) + 2\ ADP(aq) + 2\ P_i(aq) + 8\ H_2O(l)$$
$$\rightarrow 6\ CO_2(g) + 8\ NADH(aq) + 4\ H_3O^+(aq) + 2\ FADH_2(aq) + 2\ ATP(aq)$$

The NADH and FADH$_2$ go on to reduce O_2 during oxidative phosphorylation, which also produces ATP. The citric acid cycle and oxidative phosphorylation generate as many as 38 ATP molecules for each glucose molecule consumed. Each mole of ATP molecules extracts 31 kJ from the 2880 kJ supplied by 1 mol $C_6H_{12}O_6$ (180 g of

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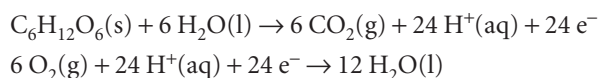[2] In yeast, the terminal products are ethanol and CO_2.
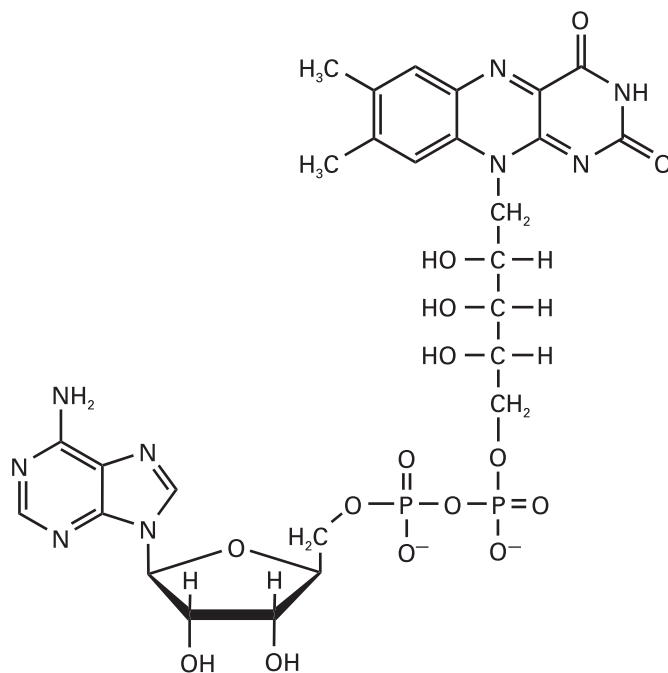
3 FAD

glucose), so 1178 kJ is stored for later use. Therefore, aerobic oxidation of glucose is much more efficient than glycolysis.
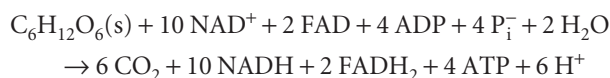
In the cell, each ATP molecule can be used to drive an endergonic reaction for which $\Delta_r G^\ominus$ does not exceed $+31$ kJ mol^{-1}. For example, the biosynthesis of sucrose from glucose and fructose can be driven by plant enzymes because the reaction is endergonic to the extent $\Delta_r G^\ominus = +23$ 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 $\Delta_r G^\ominus = +17$ 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.
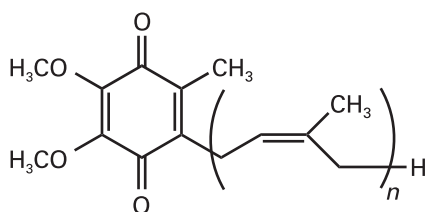
The respiratory chain

In the exergonic oxidation of glucose 24 electrons are transferred from each $C_6H_{12}O_6$ molecule to six O_2 molecules. The half-reactions for the oxidation of glucose and the reduction of O_2 are

$$C_6H_{12}O_6(s) + 6\ H_2O(l) \rightarrow 6\ CO_2(g) + 24\ H^+(aq) + 24\ e^-$$
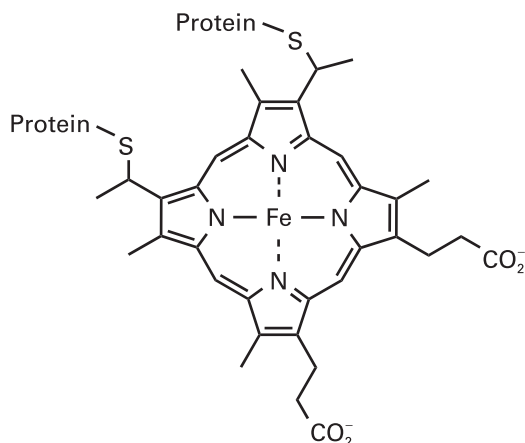$$6\ O_2(g) + 24\ H^+(aq) + 24\ e^- \rightarrow 12\ H_2O(l)$$

The electrons do not flow directly from glucose to O_2. We have already seen that, in biological cells, glucose is oxidized to CO_2 by NAD^+ and FAD during glycolysis and the citric acid cycle:

$$C_6H_{12}O_6(s) + 10\ NAD^+ + 2\ FAD + 4\ ADP + 4\ P_i^- + 2\ H_2O$$
$$\rightarrow 6\ CO_2 + 10\ NADH + 2\ FADH_2 + 4\ ATP + 6\ H^+$$

4 Coenzyme Q, Q

5 Heme *c*

In the *respiratory chain*, electrons from the powerful reducing agents NADH and FADH$_2$ pass through four membrane-bound protein complexes and two mobile electron carriers before reducing O$_2$ to H$_2$O. We shall see that the electron transfer reactions drive the synthesis of ATP at three of the membrane protein complexes.
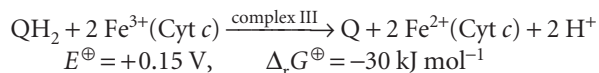
The respiratory chain begins in complex I (NADH-Q oxidoreductase), where NADH is oxidized by coenzyme Q (Q, **4**) in a two-electron reaction:

$$H^+ + NADH + Q \xrightarrow{\text{complex I}} NAD^+ + QH_2 \qquad E^\oplus = +0.42 \text{ V}, \quad \Delta_r G^\oplus = -81 \text{ kJ mol}^{-1}$$

Additional Q molecules are reduced by FADH$_2$ in complex II (succinate-Q reductase):

$$FADH_2 + Q \xrightarrow{\text{complex II}} FAD + QH_2 \qquad E^\oplus = +0.015 \text{ V}, \qquad \Delta_r G^\oplus = -2.9 \text{ kJ mol}^{-1}$$

Reduced Q migrates to complex III (Q-cytochrome *c* oxidoreductase), which catalyses the reduction of the protein cytochrome *c* (Cyt *c*). Cytochrome *c* contains the haem *c* group (**5**), the central iron ion of which can exist in oxidation states +3 and +2. The net reaction catalysed by complex III is

$$QH_2 + 2 \text{ Fe}^{3+}(\text{Cyt } c) \xrightarrow{\text{complex III}} Q + 2 \text{ Fe}^{2+}(\text{Cyt } c) + 2 \text{ H}^+$$
$$E^\oplus = +0.15 \text{ V}, \qquad \Delta_r G^\oplus = -30 \text{ kJ mol}^{-1}$$

Reduced cytochrome *c* carries electrons from complex III to complex IV (cytochrome *c* oxidase), where O$_2$ is reduced to H$_2$O:
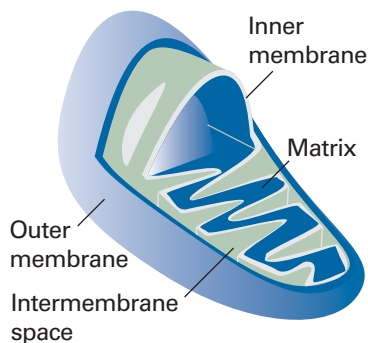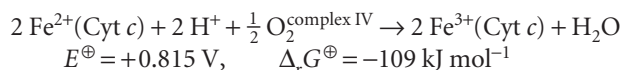
$$2 \text{ Fe}^{2+}(\text{Cyt } c) + 2 \text{ H}^+ + \tfrac{1}{2} O_2 \xrightarrow{\text{complex IV}} 2 \text{ Fe}^{3+}(\text{Cyt } c) + H_2O$$
$$E^\oplus = +0.815 \text{ V}, \qquad \Delta_r G^\oplus = -109 \text{ kJ mol}^{-1}$$

Oxidative phosphorylation

The reactions that occur in complexes I, III, and IV are sufficiently exergonic to drive the synthesis of ATP in the process called *oxidative phosphorylation*:

$$ADP + P_i^- + H^+ \rightarrow ATP \qquad \Delta_r G^\oplus = +31 \text{ kJ mol}^{-1}$$

We saw above that the phosphorylation of ADP to ATP can be coupled to the exergonic dephosphorylation of other molecules. Indeed, this is the mechanism by which ATP is synthesized during glycolysis and the citric acid cycle. However, oxidative phosphorylation operates by a different mechanism.

The structure of a mitochondrion is shown in Fig. 7.17. The protein complexes associated with the electron transport chain span the inner membrane and phosphorylation takes place in the intermembrane space. The Gibbs energy of the reactions

Inner membrane

Matrix

Outer membrane

Intermembrane space

Fig. 7.17 The general features of a typical mitochondrion.

in complexes I, III, and IV is first used to do the work of moving protons across the mitochondrial membrane. The complexes are oriented asymmetrically in the inner membrane so that the protons abstracted from one side of the membrane can be deposited on the other side. For example, the oxidation of NADH by Q in complex I is coupled to the transfer of four protons across the membrane. The coupling of electron transfer and proton pumping in complexes III and IV contribute further to a gradient of proton concentration across the membrane. Then the enzyme H^+-ATPase uses the energy stored in the proton gradient to phosphorylate ADP to ATP. Experiments show that 11 molecules of ATP are made for every three molecules of NADH and one molecule of $FADH_2$ that are oxidized by the respiratory chain. The ATP is then hydrolysed on demand to perform useful biochemical work throughout the cell.

The *chemiosmotic theory* proposed by Peter Mitchell explains how H^+-ATPases synthesize ATP from ADP. The energy stored in a transmembrane proton gradient come from two contributions. First, the difference in activity of H^+ ion results in a difference in molar Gibbs energy across the mitochrondrial membrane

$$\Delta G_{m,1} = G_{m,in} - G_{m,out} = RT \ln \frac{a_{H^+,in}}{a_{H^+,out}}$$

Second, there is a membrane potential difference $\Delta\phi = \phi_{in} - \phi_{out}$ that arises from differences in Coulombic interactions on each side of the membrane. The charge difference across a membrane per mole of H^+ ions is $N_A e$, or F, where $F = eN_A$. It follows from *Justification 7.3*, that the molar Gibbs energy difference is then $\Delta G_{m,2} = F\Delta\phi$. Adding this contribution to $\Delta G_{m,1}$ gives the total Gibbs energy stored by the combination of an an activity gradient and a membrane potential gradient:

$$\Delta G_m = RT \ln \frac{[H^+]_{in}}{[H^+]_{out}} + F\Delta\phi$$

where we have replaced activities by molar concentrations. This equation also provides an estimate of the Gibbs energy available for phosphorylation of ADP. After using $\ln [H^+] \approx \ln 10 \times \log [H^+]$ and substituting $\Delta pH = pH_{in} - pH_{out} = -\log [H^+]_{in} + \log [H^+]_{out}$, it follows that

$$\Delta G_m = F\Delta\phi - (RT \ln 10)\Delta pH$$

In the mitochondrion, $\Delta pH \approx -1.4$ and $\Delta\phi \approx 0.14$ V, so $\Delta G_m \approx +21.5$ kJ mol^{-1}. Because 31 kJ mol^{-1} is needed for phosphorylation, we conclude that at least 2 mol H^+ (and probably more) must flow through the membrane for the phosphorylation of 1 mol ADP.

(b) The determination of activity coefficients

Once the standard potential of an electrode in a cell is known, we can use it to determine mean activity coefficients by measuring the cell emf 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 7.32 in the form

$$\ln \gamma_\pm = \frac{E^\ominus - E}{2RT/F} - \ln b \qquad \{7.36\}$$

once E has been measured.

(c) The determination of equilibrium constants

The principal use for standard potentials is to calculate the standard emf of a cell formed from any two electrodes. To do so, we subtract the standard potential of the left-hand electrode from the standard potential of the right-hand electrode:
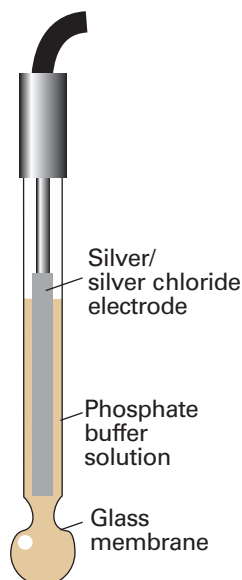
Fig. 7.18 The glass electrode. It is commonly used in conjunction with a calomel electrode that makes contact with the test solution through a salt bridge.
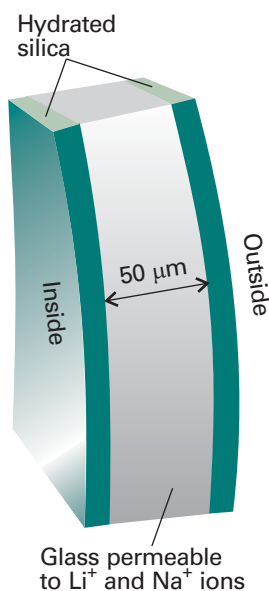
$$E^{\ominus} = E^{\ominus}(\text{right}) - E^{\ominus}(\text{left}) \tag{7.37}$$

Because $\Delta G^{\ominus} = -\nu F E^{\ominus}$, it then follows that, if the result gives $E^{\ominus} > 0$, then the corresponding cell reaction has $K > 1$.
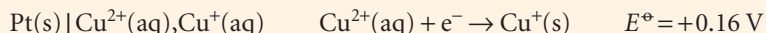

Illustration 7.14 *Calculating an equilibrium constant from standard potentials*

A disproportionation is a reaction in which a species is both oxidized and reduced. To study the disproportionation $2\,Cu^+(aq) \rightarrow Cu(s) + Cu^{2+}(aq)$ we combine the following electrodes:

Right-hand electrode:
$Cu(s)|Cu^+(aq)$ $Cu^+(aq) + e^- \rightarrow Cu(aq)$ $E^{\ominus} = +0.52\,V$

Left-hand electrode:
$Pt(s)|Cu^{2+}(aq),Cu^+(aq)$ $Cu^{2+}(aq) + e^- \rightarrow Cu^+(s)$ $E^{\ominus} = +0.16\,V$
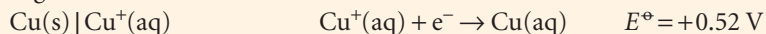
where the standard potentials are measured at 298 K. The standard emf of the cell is therefore

$$E^{\ominus} = +0.52\,V - 0.16\,V = +0.36\,V$$

We can now calculate the equilibrium constant of the cell reaction. Because $\nu = 1$, from eqn 7.30

$$\ln K = \frac{0.36\,V}{0.025693\,V} = \frac{0.36}{0.025693}$$

Hence, $K = 1.2 \times 10^6$.

Self-test 7.11 Calculate the solubility constant (the equilibrium constant for the reaction $Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2\,Cl^-(aq)$) and the solubility of mercury(I) chloride at 298.15 K. *Hint*. The mercury(I) ion is the diatomic species Hg_2^{2+}.

[2.6×10^{-18}, 8.7×10^{-7} mol kg^{-1}]

Fig. 7.19 A section through the wall of a glass electrode.

(d) Species-selective electrodes

An **ion-selective electrode** is an electrode that generates a potential in response to the presence of a solution of specific ions. An example is the **glass electrode** (Fig. 7.18), which 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. It is necessary to calibrate the glass electrode before use with solutions of known pH.

The responsiveness of a glass electrode to the hydrogen 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 different from that responsible for biological transmembrane potentials (*Impact on biochemistry 7.2*). 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. 7.19). 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 hydrogen ion activity gives rise to a membrane potential by this indirect mechanism.

Electrodes sensitive to hydrogen ions, and hence to pH, are typically glasses based on lithium silicate doped with heavy-metal oxides. The glass can also be made responsive to Na^+, K^+, and NH_4^+ ions by being doped with Al_2O_3 and B_2O_3.

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. The presence of an enzyme that converts a compound, such as urea or an amino acid, into ammonia, which then affects the pH, can be used to detect these organic compounds.

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. 7.20). The liquid contains an 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 complex's 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.

In theory, the transmembrane potential should be determined entirely by differences in the activity of the species that the electrode was designed to detect. In practice, a small potential difference, called the **asymmetry potential**, is observed even when the activity of the test species is the same on both sides of the membrane. The asymmetry potential is due to the fact that it is not possible to manufacture a membrane material that has the same structure and the same chemical properties throughout. Furthermore, all species-selective electrodes are sensitive to more than one species. For example, a Na^+ selective electrode also responds, albeit less effectively, to the activity of K^+ ions in the test solution. As a result of these effects, the potential of an electrode sensitive to species X^+ that is also susceptible to interference by species Y^+ is given by a modified form of the Nernst equation:

$$E = E_{ap} + \beta \frac{RT}{F} \ln(a_{X^+} + k_{X,Y} a_{Y^+}) \qquad (7.38)$$

where E_{ap} is the asymmetry potential, β is an experimental parameter that captures deviations from the Nernst equation, and $k_{X,Y}$ is the **selectivity coefficient** of the electrode and is related to the response of the electrode to the interfering species Y^+. A value of $\beta = 1$ indicates that the electrode responds to the activity of ions in solution in a way that is consistent with the Nernst equation and, in practice, most species-selective electrodes of high quality have $\beta \approx 1$. The selectivity coefficient, and hence interference effects, can be minimized when designing and manufacturing a species-selective electrode. For precise work, it is necessary to calibrate the response of the electrode by measuring E_{ap}, β, and $k_{X,Y}$ before performing experiments on solutions of unknown concentration of X^+.

(e) The determination of thermodynamic functions

The standard emf of a cell is related to the standard reaction Gibbs energy through eqn 7.28 ($\Delta_r G^\ominus = -\nu F E^\ominus$). 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 by using the convention explained in Section 3.6.
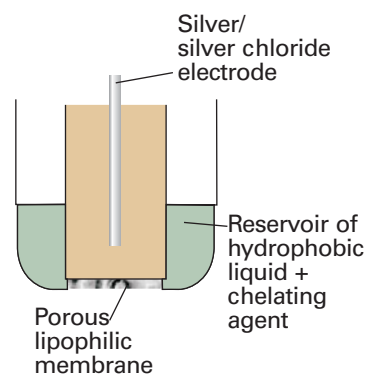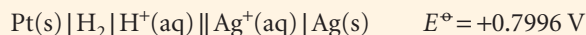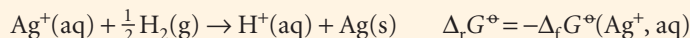

Silver/silver chloride electrode

Reservoir of hydrophobic liquid + chelating agent

Porous lipophilic membrane

Fig. 7.20 The structure of an ion-selective electrode. Chelated ions are able to migrate through the lipophilic membrane.

Illustration 7.15 *Determining the Gibbs energy of formation of an ion electrochemically*

The cell reaction taking place in

$$Pt(s)\,|\,H_2\,|\,H^+(aq)\,\|\,Ag^+(aq)\,|\,Ag(s) \qquad E^{\ominus} = +0.7996\ V$$

is

$$Ag^+(aq) + \tfrac{1}{2}H_2(g) \rightarrow H^+(aq) + Ag(s) \qquad \Delta_r G^{\ominus} = -\Delta_f G^{\ominus}(Ag^+, aq)$$

Therefore, with $\nu = 1$, we find

$$\Delta_f G^{\ominus}(Ag^+, aq) = -(-FE^{\ominus}) = +77.15\ kJ\ mol^{-1}$$

which is in close agreement with the value in Table 2.6 of the *Data section*.

The temperature coefficient of the standard cell emf, $dE^{\ominus}/dT$, gives the standard entropy of the cell reaction. This conclusion follows from the thermodynamic relation $(\partial G/\partial T)_p = -S$ and eqn 7.27, which combine to give

$$\frac{dE^{\ominus}}{dT} = \frac{\Delta_r S^{\ominus}}{\nu F} \tag{7.39}$$

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:

$$\Delta_r H^{\ominus} = \Delta_r G^{\ominus} + T\Delta_r S^{\ominus} = -\nu F\left(E^{\ominus} - T\frac{dE^{\ominus}}{dT}\right) \tag{7.40}$$

This expression provides a non-calorimetric 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 (Section 2.8). Thus, electrical measurements can be used to calculate all the thermodynamic properties with which this chapter began.

Example 7.5 *Using the temperature coefficient of the cell potential*

The standard emf of the cell $Pt(s)\,|\,H_2(g)\,|\,HBr(aq)\,|\,AgBr(s)\,|\,Ag(s)$ was measured over a range of temperatures, and the data were fitted to the following polynomial:

$$E^{\ominus}/V = 0.07131 - 4.99 \times 10^{-4}(T/K - 298) - 3.45 \times 10^{-6}(T/K - 298)^2$$

Evaluate the standard reaction Gibbs energy, enthalpy, and entropy at 298 K.

Method The standard Gibbs energy of reaction is obtained by using eqn 7.28 after evaluating $E^{\ominus}$ at 298 K and by using 1 V C = 1 J. The standard entropy of reaction is obtained by using eqn 7.39, 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

$$\Delta_r G^{\ominus} = -\nu F E^{\ominus} = -(1) \times (9.6485 \times 10^4\ C\ mol^{-1}) \times (+0.07131\ V)$$
$$= -6.880 \times 10^3\ V\ C\ mol^{-1} = -6.880\ kJ\ mol^{-1}$$

The temperature coefficient of the cell potential is

$$\frac{dE^{\oplus}}{dT} = -4.99 \times 10^{-4} \text{ V K}^{-1} - 2(3.45 \times 10^{-6})(T/K - 298) \text{ V K}^{-1}$$

At $T = 298$ K this expression evaluates to

$$\frac{dE}{dT} = -4.99 \times 10^{-4} \text{ V K}^{-1}$$

So, from eqn 7.39, the reaction entropy is

$$\Delta_r S^{\oplus} = 1 \times (9.6485 \times 10^4 \text{ C mol}^{-1}) \times (-4.99 \times 10^{-4} \text{ V K}^{-1})$$
$$= -48.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

It then follows that

$$\Delta_r H^{\oplus} = \Delta_r G^{\oplus} + T\Delta_r S^{\oplus} = -6.880 \text{ kJ mol}^{-1} + (298 \text{ K}) \times (-0.0482 \text{ kJ K}^{-1} \text{ mol}^{-1})$$
$$= -21.2 \text{ kJ mol}^{-1}$$

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 7.12 Predict the standard potential of the Harned cell at 303 K from tables of thermodynamic data.   [+0.2222 V]

Checklist of key ideas

□ 1. The extent of reaction (ξ) is defined such that, when the extent of reaction changes by a finite amount $\Delta\xi$, the amount of A present changes from $n_{A,0}$ to $n_{A,0} - \Delta\xi$.

□ 2. The reaction Gibbs energy is the slope of the graph of the Gibbs energy plotted against the extent of reaction: $\Delta_r G = (\partial G/\partial\xi)_{p,T}$; at equilibrium, $\Delta_r G = 0$.

□ 3. An exergonic reaction is a reaction for which $\Delta_r G < 0$; such a reaction can be used to drive another process. An endergonic reaction is a reaction for which $\Delta_r G > 0$.

□ 4. The general expression for $\Delta_r G$ at an arbitrary stage of the reaction is $\Delta_r G = \Delta_r G^{\oplus} + RT \ln Q$.

□ 5. The equilibrium constant (K) may be written in terms of $\Delta_r G^{\oplus}$ as $\Delta_r G^{\oplus} = -RT \ln K$.

□ 6. The standard reaction Gibbs energy may be calculated from standard Gibbs energies of formation, $\Delta_r G^{\oplus} = \sum_{\text{Products}} v\Delta_f G^{\oplus} - \sum_{\text{Reactants}} v\Delta_f G^{\oplus} = \sum_J v_J \Delta_f G^{\oplus}(J)$.

□ 7. Thermodynamic equilibrium constant is an equilibrium constant K expressed in terms of activities (or fugacities):

$$K = \left(\prod_J a_J^{v_J} \right)_{\text{equilibrium}}.$$

□ 8. A catalyst does not affect the equilibrium constant.

□ 9. Changes in pressure do not affect the equilibrium constant: $(\partial K/\partial p)_T = 0$. However, partial pressures and concentrations can change in response to a change in pressure.

□ 10. 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.

□ 11. Increased temperature favours the reactants in exothermic reactions and the products in endothermic reactions.

□ 12. The temperature dependence of the equilibrium constant is given by the van 't Hoff equation: $d \ln K/dT = \Delta_r H^{\oplus}/RT^2$. To calculate K at one temperature in terms of its value at another temperature, and provided $\Delta_r H^{\oplus}$ is independent of temperature, we use $\ln K_2 - \ln K_1 = -(\Delta_r H^{\oplus}/R)(1/T_2 - 1/T_1)$.

□ 13. 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.

□ 14. Oxidation is the removal of electrons from a species; 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.

☐ 15. The anode is the electrode at which oxidation occurs. The cathode is the electrode at which reduction occurs.

☐ 16. The electromotive force (emf) is the cell potential when it is balanced by an exactly opposing source of potential so that the cell reaction occurs reversibly, the composition is constant, and no current flows.

☐ 17. The cell potential and the reaction Gibbs energy are related by $-vFE = \Delta_r G$.

☐ 18. The standard emf is the standard reaction Gibbs energy expressed as a potential: $E^{\ominus} = \Delta_r G^{\ominus}/vF$.

☐ 19. The Nernst equation is the equation for the emf of a cell in terms of the composition: $E = E^{\ominus} - (RT/vF) \ln Q$.

☐ 20. The equilibrium constant for a cell reaction is related to the standard emf by $\ln K = vFE^{\ominus}/RT$.

☐ 21. The standard potential of a couple ($E^{\ominus}$) is the standard emf of a cell in which a couple forms the right-hand electrode and the standard hydrogen electrode is the left-hand electrode.

☐ 22. To calculate the standard emf, form the difference of electrode potentials: $E^{\ominus} = E^{\ominus}(\text{right}) - E^{\ominus}(\text{left})$.

☐ 23. The temperature coefficient of cell potential is given by $dE^{\ominus}/dT = \Delta_r S^{\ominus}/vF$.

☐ 24. The standard reaction entropy and enthalpy are calculated from the temperature dependence of the standard emf by: $\Delta_r S^{\ominus} = vF dE^{\ominus}/dT$, $\Delta_r H^{\ominus} = -v(FE^{\ominus} - T dE^{\ominus}/dT)$.

Further reading

Articles and texts

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Sources of data and information

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Discussion questions

7.1 Explain how the mixing of reactants and products affects the position of chemical equilibrium.

7.2 Suggest how the thermodynamic equilibrium constant may respond differently to changes in pressure and temperature from the equilibrium constant expressed in terms of partial pressures.

7.3 Account for Le Chatelier's principle in terms of thermodynamic quantities.

7.4 Explain the molecular basis of the van 't Hoff equation for the temperature dependence of K.

7.5 (a) How may an Ellingham diagram be used to decide whether one metal may be used to reduce the oxide of another metal? (b) Use the Ellingham

diagram in Fig. 7.10 to identify the lowest temperature at which zinc oxide can be reduced to zinc metal by carbon.

7.6 Distinguish between cell potential and electromotive force and explain why the latter is related to thermodynamic quantities.

7.7 Describe the contributions to the emf of cells formed by combining the electrodes specified in Table 7.1.

7.8 Describe a method for the determination of a standard potential of a redox couple.

7.9 Devise a method for the determination of the pH of an aqueous solution.

Exercises

7.1(a) At 2257 K and 1.00 atm total pressure, water is 1.77 per cent dissociated at equilibrium by way of the reaction $2 H_2O(g) \rightleftharpoons 2 H_2(g) + O_2(g)$. Calculate (a) K, (b) $\Delta_r G^\ominus$, and (c) $\Delta_r G$ at this temperature.

7.1(b) For the equilibrium, $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$, the degree of dissociation, α_e, at 298 K is 0.201 at 1.00 bar total pressure. Calculate (a) $\Delta_r G$, (2) K, and (3) $\Delta_r G^\ominus$ at 298 K.

7.2(a) Dinitrogen tetroxide is 18.46 per cent dissociated at 25°C and 1.00 bar in the equilibrium $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$. Calculate (a) K at 25°C, (b) $\Delta_r G^\ominus$, (c) K at 100°C given that $\Delta_r H^\ominus = +57.2$ kJ mol^{-1} over the temperature range.

7.2(b) Molecular bromine is 24 per cent dissociated at 1600 K and 1.00 bar in the equilibrium $Br_2(g) \rightleftharpoons 2 Br(g)$. Calculate (a) K at 25°C, (b) $\Delta_r G^\ominus$, (c) K at 2000°C given that $\Delta_r H^\ominus = +112$ kJ mol^{-1} over the temperature range.

7.3(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.

7.3(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 $CH_4(g) + 3 Cl_2(g) \rightleftharpoons CHCl_3(l) + 3 HCl(g)$. Assume that the reaction enthalpy is independent of temperature.

7.4(a) In the gas-phase reaction $2 A + B \rightleftharpoons 3 C + 2 D$, 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) $\Delta_r G^\ominus$.

7.4(b) In the gas-phase reaction $A + B \rightleftharpoons C + 2 D$, 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) $\Delta_r G^\ominus$.

7.5(a) The standard reaction enthalpy of $Zn(s) + H_2O(g) \rightarrow ZnO(s) + H_2(g)$ is approximately constant at +224 kJ mol^{-1} from 920 K up to 1280 K. The standard reaction Gibbs energy is +33 kJ mol^{-1} at 1280 K. Estimate the temperature at which the equilibrium constant becomes greater than 1.

7.5(b) The standard enthalpy of a certain reaction is approximately constant at +125 kJ mol^{-1} from 800 K up to 1500 K. The standard reaction Gibbs energy is +22 kJ mol^{-1} at 1120 K. Estimate the temperature at which the equilibrium constant becomes greater than 1.

7.6(a) The equilibrium constant of the reaction $2 C_3H_6(g) \rightleftharpoons C_2H_4(g) + C_4H_8(g)$ is found to fit the expression $\ln K = A + B/T + C/T^2$ between 300 K and 600 K, with $A = -1.04$, $B = -1088$ K, and $C = 1.51 \times 10^5$ K^2. Calculate the standard reaction enthalpy and standard reaction entropy at 400 K.

7.6(b) The equilibrium constant of a reaction is found to fit the expression $\ln K = A + B/T + C/T^3$ between 400 K and 500 K with $A = -2.04$, $B = -1176$ K, and $C = 2.1 \times 10^7$ K^3. Calculate the standard reaction enthalpy and standard reaction entropy at 450 K.

7.7(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.

7.7(b) The equilibrium pressure of H_2 over solid uranium and uranium hydride, UH_3, at 500 K is 139 Pa. Calculate the standard Gibbs energy of formation of $UH_3(s)$ at 500 K.

7.8(a) Calculate the percentage change in K_x for 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.

7.8(b) Calculate the percentage change in K_x for 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.

7.9(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 dm^3 is heated to 503 K and allowed to come to equilibrium. Calculate the mole fractions of the two substances at equilibrium.

7.9(b) The equilibrium constant for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2 NO(g)$ 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 dm^3 is heated to 2300 K and allowed to come to equilibrium. Calculate the mole fraction of NO at equilibrium.

7.10(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?

7.10(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?

7.11(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?

7.11(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.

7.12(a) Estimate the temperature at which $CaCO_3$(calcite) decomposes.

7.12(b) Estimate the temperature at which $CuSO_4 \cdot 5H_2O$ undergoes dehydration.

7.13(a) For $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2 F^-(aq)$, $K = 3.9 \times 10^{-11}$ at 25°C and the standard Gibbs energy of formation of $CaF_2(s)$ is -1167 kJ mol^{-1}. Calculate the standard Gibbs energy of formation of $CaF_2(aq)$.

7.13(b) For $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2 I^-(aq)$, $K = 1.4 \times 10^{-8}$ 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 $PbI_2(aq)$.

7.14(a) Write the cell reaction and electrode half-reactions and calculate the standard emf of each of 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) $Pt|K_3[Fe(CN)_6](aq),K_4[Fe(CN)_6](aq)||CrCl_3(aq)|Cr$

7.14(b) Write the cell reaction and electrode half-reactions and calculate the standard emf of each 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) $Cu|Cu^{2+}(aq)||Mn^{2+}(aq),H^+(aq)|MnO_2(s)|Pt$

7.15(a) Devise cells in which the following are the reactions and calculate the standard emf in each case:

(a) $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$

(b) $2\,AgCl(s) + H_2(g) \rightarrow 2\,HCl(aq) + 2\,Ag(s)$

(c) $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l)$

7.15(b) Devise cells in which the following are the reactions and calculate the standard emf in each case:

(a) $2\,Na(s) + 2\,H_2O(l) \rightarrow 2\,NaOH(aq) + H_2(g)$

(b) $H_2(g) + I_2(g) \rightarrow 2\,HI(aq)$

(c) $H_3O^+(aq) + OH^-(aq) \rightarrow 2\,H_2O(l)$

7.16(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.

7.16(b) Consider the cell $Pt|H_2(g,p^\oplus)|HCl(aq)|AgCl(s)|Ag$, for which the cell reaction is $2\,AgCl(s) + H_2(g) \rightarrow 2\,Ag(s) + 2\,HCl(aq)$. 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 $E^\oplus(AgCl, Ag)$.

7.17(a) Calculate the equilibrium constants of the following reactions at 25°C from standard potential data:

(a) $Sn(s) + Sn^{4+}(aq) \rightleftharpoons 2\,Sn^{2+}(aq)$

(b) $Sn(s) + 2\,AgCl(s) \rightleftharpoons SnCl_2(aq) + 2\,Ag(s)$

7.17(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) $Cu^{2+}(aq) + Cu(s) \rightleftharpoons 2\,Cu^+(aq)$

7.18(a) The emf of the cell $Ag|AgI(s)|AgI(aq)|Ag$ is +0.9509 V at 25°C. Calculate (a) the solubility product of AgI and (b) its solubility.

7.18(b) The emf of the cell $Bi|Bi_2S_3(s)|Bi_2S_3(aq)|Bi$ is −0.96 V at 25°C. Calculate (a) the solubility product of Bi_2S_3 and (b) its solubility.

Problems*

Numerical problems

7.1 The equilibrium constant for the reaction, $I_2(s) + Br_2(g) \rightleftharpoons 2\,IBr(g)$ is 0.164 at 25°C. (a) Calculate $\Delta_r G^\oplus$ 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, respectively. 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?

7.2 Consider the dissociation of methane, $CH_4(g)$, into the elements $H_2(g)$ and C(s, graphite). (a) Given that $\Delta_f H^\oplus(CH_4, g) = -74.85\ kJ\ mol^{-1}$ and that $\Delta_f S^\oplus(CH_4, g) = -80.67\ J\ K^{-1}\ mol^{-1}$ at 298 K, calculate the value of the equilibrium constant at 298 K. (b) Assuming that $\Delta_f H^\oplus$ 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.

7.3 The equilibrium pressure of H_2 over U(s) and $UH_3(s)$ between 450 K and 715 K fits the expression $\ln(p/Pa) = A + B/T + C\ln(T/K)$, with $A = 69.32$, $B = -1.464 \times 10^4$ K, and $C = -5.65$. Find an expression for the standard enthalpy of formation of $UH_3(s)$ and from it calculate $\Delta_r C_p^\oplus$.

7.4 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 $\Delta_r H^\oplus$ to be constant over this temperature range, calculate K, $\Delta_r G^\oplus$, $\Delta_r H^\oplus$, and $\Delta_r S^\oplus$. Make any justifiable approximations.

7.5 The standard reaction enthalpy for the decomposition of $CaCl_2 \cdot NH_3(s)$ into $CaCl_2(s)$ and $NH_3(g)$ is nearly constant at $+78\ kJ\ mol^{-1}$ between 350 K and 470 K. The equilibrium pressure of NH_3 in the presence of $CaCl_2 \cdot NH_3$ is

1.71 kPa at 400 K. Find an expression for the temperature dependence of $\Delta_r G^\oplus$ in the same range.

7.6 Calculate the equilibrium constant of the reaction $CO(g) + H_2(g) \rightleftharpoons H_2CO(g)$ given that, for the production of liquid formaldehyde, $\Delta_r G^\oplus = +28.95\ kJ\ mol^{-1}$ at 298 K and that the vapour pressure of formaldehyde is 1500 Torr at that temperature.

7.7 Acetic acid was evaporated in container of volume 21.45 cm^3 at 437 K and at an external pressure of 101.9 kPa, 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.

7.8 A sealed container was filled with 0.300 mol $H_2(g)$, 0.400 mol $I_2(g)$, and 0.200 mol HI(g) at 870 K and total pressure 1.00 bar. Calculate the amounts of the components in the mixture at equilibrium given that $K = 870$ for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$.

7.9 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/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 cm^3. Calculate the equilibrium constants of the dissociation and the standard enthalpy of dissociation at the mean temperature.

7.10‡ Thorn *et al.* 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 $\Delta_f H^\oplus(Cl_2O) = +77.2\ kJ\ mol^{-1}$. They combined this measurement with literature data on the reaction $Cl_2O(g) + H_2O(g) \rightarrow 2\,HOCl(g)$, for which $K = 8.2 \times 10^{-2}$ and $\Delta_r S^\oplus =$

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

+16.38 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.

7.11‡ The 1980s saw reports of $\Delta_f H^\ominus(SiH_2)$ ranging from 243 to 289 kJ mol^{-1}. For example, the lower value was cited in the review article by R. Walsh (*Acc. Chem. Res.* **14**, 246 (1981)); Walsh later leant towards 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 in 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?

7.12 Fuel cells provide electrical power for spacecraft (as in the NASA space shuttles) and also show promise as power sources for automobiles. 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. 1*, 2014 (1973)) with the following results:

$$\log s_{H_2} = -5.39 - \frac{980}{T/K} \qquad \log s_{CO} = -5.98 - \frac{980}{T/K}$$

where s is the solubility in mol cm^{-3} bar^{-1}. Calculate the standard molar enthalpies of solution of the two gases at 570 K.

7.13 Given that $\Delta_r G^\ominus = -212.7$ kJ mol^{-1} for the reaction in the Daniell cell at 25°C, and $b(CuSO_4) = 1.0 \times 10^{-3}$ mol kg^{-1} and $b(ZnSO_4) = 3.0 \times 10^{-3}$ 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.)

7.14 A fuel cell develops an electric potential from the chemical reaction between reagents supplied from an outside source. What is the emf of a cell fuelled by (a) hydrogen and oxygen, (b) the combustion of butane at 1.0 bar and 298 K?

7.15 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·QH$_2$, is a complex of quinone, C$_6$H$_4$O$_2$ = Q, and hydroquinone, C$_6$H$_4$O$_2$H$_2$ = QH$_2$). The electrode half–reaction is Q(aq) + 2 H$^+$(aq) + 2 e$^-$ → QH$_2$(aq), $E^\ominus = +0.6994$ V. If the cell Hg|Hg$_2$Cl$_2$(s)|HCl(aq)|Q·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.

7.16 Consider the cell, Zn(s)|ZnCl$_2$ (0.0050 mol kg^{-1})|Hg$_2$Cl$_2$(s) Hg(l), for which the cell reaction is Hg$_2$Cl$_2$(s) + Zn(s) → 2 Hg(l) + 2 Cl$^-$(aq) + Zn^{2+}(aq). Given that $E^\ominus$ (Zn^{2+},Zn) = −0.7628 V, $E^\ominus$ (Hg$_2$Cl$_2$, Hg) = +0.2676 V, and that the emf is +1.2272 V, (a) write the Nernst equation for the cell. Determine (b) the standard emf, (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 $(\partial E/\partial T)_p = -4.52 \times 10^{-4}$ V K^{-1}. Calculate ΔS and ΔH.

7.17 The emf of the cell Pt|H$_2$(g, $p^\ominus$)|HCl(aq,b)|Hg$_2$Cl$_2$(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/(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 emf 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.)

7.18 Careful measurements of the emf of the cell Pt|H$_2$(g, $p^\ominus$)|NaOH(aq, 0.0100 mol kg^{-1}), NaCl(aq, 0.01125 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.

7.19 Measurements of the emf of cells of the type Ag|AgX(s)MX(b_1)|M$_x$ Hg|MX(b_2)|AgX(s)|Ag, where M$_x$Hg 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:

$$\log \gamma = -\frac{AI^{1/2}}{1 - BI^{1/2}} + kI$$

with $A = 1.461$, $B = 1.70$, $k = 0.20$, and $I = b/b^\ominus$. For $b_2 = 0.09141$ mol kg^{-1}:

b_1/(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

7.20 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

$$E^\ominus/V = 0.23659 - 4.8564 \times 10^{-4}(\theta/°C) - 3.4205 \times 10^{-6}(\theta/°C)^2 + 5.869 \times 10^{-9}(\theta/°C)^3$$

Calculate the standard Gibbs energy and enthalpy of formation of Cl$^-$(aq) and its entropy at 298 K.

7.21‡ (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 TlCl(s) + CNS$^-$(aq) → TlCNS(s) + Cl$^-$(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 emf of the cell Tl(Hg)|TlCNS(s)|KCNS∶KCl|TlCl|Tl(Hg) at pressures 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.

7.22‡ The table below summarizes the emf observed for the cell Pd|H$_2$(g, 1 bar)|BH(aq, b), B(aq, b)|AgCl(s)|Ag. Each measurement is made at equimolar 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 $0 \leq I \leq 0.1$.

$b/(\text{mol kg}^{-1})$	0.01	0.02	0.03	0.04	0.05
$E(25°C)/V$	0.74452	0.72853	0.71928	0.71314	0.70809
$b/(\text{mol kg}^{-1})$	0.06	0.07	0.08	0.09	0.10
$E(25°C)/V$	0.70380	0.70059	0.69790	0.69571	0.69338

Hint. Use mathematical software or a spreadsheet.

7.23 Superheavy elements are now of considerable interest, particularly because signs of stability are starting to emerge with element 114, which has recently been made. Shortly before it was (falsely) believed that the first superheavy element 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 Uup$^+$(aq) + $\frac{1}{2}$H$_2$(g) → Uup(s) + H$^+$(aq) were estimated from the following data: $\Delta_{sub}H^{\ominus}$(Uup) = +1.5 eV, I(Uup) = 5.52 eV, $\Delta_{hyd}H^{\ominus}$(Uup$^+$, aq) = −3.22 eV, $S^{\ominus}$(Uup$^+$, aq) = +1.34 meV K^{-1}, $S^{\ominus}$(Uup, s) = 0.69 meV K^{-1}. Estimate the expected standard potential of the Uup$^+$/Uup couple.

7.24 Sodium fluoride is routinely added to public water supplies because it is known that fluoride ion can prevent tooth decay. In a fluoride-selective electrode used in the analysis of water samples a crystal of LaF$_3$ doped with Eu^{2+}, denoted as Eu^{2+}:LaF$_3$, provides a semipermeable barrier between the test solution and the solution inside the electrode (the filling solution), which contains 0.1 mol kg^{-1} NaF(aq) and 0.1 mol kg^{-1} NaCl(aq). A silver–silver chloride electrode immersed in the filling solution is connected to a potentiometer and the emf of the cell can be measured against an appropriate reference electrode. It follows that the half-cell for a fluoride-selective electrode is represented by

Ag(s)|AgCl(s)|NaCl(aq, b_1), NaF (aq, b_1)|Eu^{2+}:LaF$_3$ (s)|F$^-$(aq, b_2)

where b_1 and b_2 are the molalities of fluoride ion in the filling and test solutions, respectively. (a) Derive an expression for the emf of this half-cell. (b) The fluoride-selective electrode just described is not sensitive to HF(aq). Hydroxide ion is the only interfering species, with $k_{F^-,OH^-} = 0.1$. Use this information and the fact that K_a of HF is 3.5×10^{-4} at 298 K to specify a range of pH values in which the electrode responds accurately to the activity of F$^-$ in the test solution at 298 K.

Theoretical problems

7.25 Express the equilibrium constant of a gas-phase reaction A + 3 B $\rightleftharpoons$ 2 C 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.

7.26 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 expression for the molar heat capacity listed in Table 2.2. Evaluate the standard Gibbs energy of formation of H$_2$O(l) at 372 K from its value at 298 K.

7.27 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

$$S' = \frac{K_s e^{4.606AC^{1/2}}}{C}$$

when K_s is small (in a sense to be specified).

Applications: to biology, environmental science, and chemical engineering

7.28 Here we investigate the molecular basis for the observation that the hydrolysis of ATP is exergonic at pH = 7.0 and 310 K. (a) It is thought that the exergonicity of ATP hydrolysis is due in part to the fact that the standard entropies of hydrolysis of polyphosphates are positive. Why would an increase in entropy accompany the hydrolysis of a triphosphate group into a diphosphate and a phosphate group? (b) Under identical conditions, the Gibbs energies of hydrolysis of H$_4$ATP and MgATP^{2-}, a complex between the Mg^{2+} ion and ATP^{4-}, are less negative than the Gibbs energy of hydrolysis of ATP^{4-}. This observation has been used to support the hypothesis that electrostatic repulsion between adjacent phosphate groups is a factor that controls the exergonicity of ATP hydrolysis. Provide a rationale for the hypothesis and discuss how the experimental evidence supports it. Do these electrostatic effects contribute to the $\Delta_r H$ or $\Delta_r S$ terms that determine the exergonicity of the reaction? *Hint.* In the MgATP^{2-}complex, the Mg^{2+} ion and ATP^{4-} anion form two bonds: one that involves a negatively charged oxygen belonging to the terminal phosphate group of ATP^{4-} and another that involves a negatively charged oxygen belonging to the phosphate group adjacent to the terminal phosphate group of ATP^{4-}.

7.29 To get a sense of the effect of cellular conditions on the ability of ATP to drive biochemical processes, compare the standard Gibbs energy of hydrolysis of ATP to ADP with the reaction Gibbs energy in an environment at 37°C in which pH = 7.0 and the ATP, ADP, and P$_i^-$ concentrations are all 1.0 μmol dm^{-3}.

7.30 Under biochemical standard conditions, aerobic respiration produces approximately 38 molecules of ATP per molecule of glucose that is completely oxidized. (a) What is the percentage efficiency of aerobic respiration under biochemical standard conditions? (b) The following conditions are more likely to be observed in a living cell: $p_{CO_2} = 5.3 \times 10^{-2}$ atm, $p_{O_2} = 0.132$ atm, [glucose] = 5.6×10^{-2} mol dm^{-3}, [ATP] = [ADP] = [P$_i$] = 1.0×10^{-4} mol dm^{-3}, pH = 7.4, $T = 310$ K. Assuming that activities can be replaced by the numerical values of molar concentrations, calculate the efficiency of aerobic respiration under these physiological conditions. (c) A typical diesel engine operates between $T_c = 873$ K and $T_h = 1923$ K with an efficiency that is approximately 75 per cent of the theoretical limit of $(1 - T_c/T_h)$ (see Section 3.2). Compare the efficiency of a typical diesel engine with that of aerobic respiration under typical physiological conditions (see part b). Why is biological energy conversion more or less efficient than energy conversion in a diesel engine?

7.31 In anaerobic bacteria, the source of carbon may be a molecule other than glucose and the final electron acceptor is some molecule other than O$_2$. Could a bacterium evolve to use the ethanol/nitrate pair instead of the glucose/O$_2$ pair as a source of metabolic energy?

7.32 If the mitochondrial electric potential between matrix and the intermembrane space were 70 mV, as is common for other membranes, how much ATP could be synthesized from the transport of 4 mol H$^+$, assuming the pH difference remains the same?

7.33 The standard potentials of proteins are not commonly measured by the methods described in this chapter because proteins often lose their native structure and function when they react on the surfaces of electrodes. In an alternative method, the oxidized protein is allowed to react with an appropriate electron donor in solution. The standard potential of the protein is then determined from the Nernst equation, the equilibrium concentrations of all species in solution, and the known standard potential of the electron donor. We shall illustrate this method with the protein cytochrome *c*. The one-electron reaction between cytochrome *c*, cyt, and 2,6-dichloroindophenol, D, can be followed spectrophotometrically because each of the four species in solution has a distinct colour, or absorption spectrum. We write the reaction as cyt$_{ox}$ + D$_{red}$ $\rightleftharpoons$ cyt$_{red}$ + D$_{ox}$, where the

subscripts 'ox' and 'red' refer to oxidized and reduced states, respectively. (a) Consider $E^\oplus_{cyt}$ and $E^\oplus_D$ to be the standard potentials of cytochrome c and D, respectively. Show that, at equilibrium ('eq'), a plot of $\ln([D_{ox}]_{eq}/[D_{red}]_{eq})$ versus $\ln([cyt_{ox}]_{eq}/[cyt_{red}]_{eq})$ is linear with slope of 1 and y-intercept $F(E^\oplus_{cyt}-E^\oplus_D)/RT$, where equilibrium activities are replaced by the numerical values of equilibrium molar concentrations. (b) The following data were obtained for the reaction between oxidized cytochrome c and reduced D in a pH 6.5 buffer at 298 K. The ratios $[D_{ox}]_{eq}/[D_{red}]_{eq}$ and $[cyt_{ox}]_{eq}/[cyt_{red}]_{eq}$ were adjusted by titrating a solution containing oxidized cytochrome c and reduced D with a solution of sodium ascorbate, which is a strong reductant. From the data and the standard potential of D of 0.237 V, determine the standard potential cytochrome c at pH 6.5 and 298K.
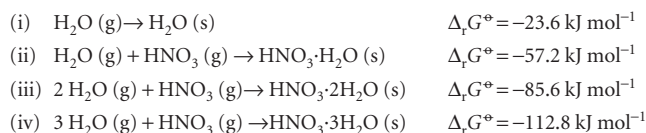
$[D_{ox}]_{eq}/[D_{red}]_{eq}$	0.00279	0.00843	0.0257	0.0497	0.0748	0.238	0.534
$[cyt_{ox}]_{eq}/[cyt_{red}]_{eq}$	0.0106	0.0230	0.0894	0.197	0.335	0.809	1.39

7.34‡ 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 R.A. Cox and C.A. Hayman (*Nature* **332**, 796 (1988)) on the reaction $2ClO\,(g) \rightarrow (ClO)_2\,(g)$.

T/K	233	248	258	268	273	280
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

T/K	288	295	303
K	4.28×10^5	1.67×10^5	7.02×10^4

(a) Derive the values of $\Delta_r H^\oplus$ and $\Delta_r S^\oplus$ for this reaction. (b) Compute the standard enthalpy of formation and the standard molar entropy of $(ClO)_2$ given $\Delta_f H^\oplus(ClO) = +101.8$ kJ mol^{-1} and $S^\oplus_m(ClO) = 226.6$ J K^{-1} mol^{-1} (*CRC Handbook 2004*).

7.35‡ Nitric acid hydrates have received much attention as possible catalysts for heterogeneous reactions that 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:

(i) $H_2O\,(g) \rightarrow H_2O\,(s)$ $\Delta_r G^\oplus = -23.6$ kJ mol^{-1}

(ii) $H_2O\,(g) + HNO_3\,(g) \rightarrow HNO_3 \cdot H_2O\,(s)$ $\Delta_r G^\oplus = -57.2$ kJ mol^{-1}

(iii) $2 H_2O\,(g) + HNO_3\,(g) \rightarrow HNO_3 \cdot 2H_2O\,(s)$ $\Delta_r G^\oplus = -85.6$ kJ mol^{-1}

(iv) $3 H_2O\,(g) + HNO_3\,(g) \rightarrow HNO_3 \cdot 3H_2O\,(s)$ $\Delta_r G^\oplus = -112.8$ 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 $\Delta_r G$ for each reaction under the prevailing conditions; if more than one solid forms spontaneously, examine $\Delta_r G$ for the conversion of one solid to another.

7.36‡ Suppose that an iron catalyst at a particular manufacturing plant produces ammonia in the most cost–effective manner at 450°C when the pressure is such that $\Delta_r G$ for the reaction $\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \rightarrow NH_3(g)$ is equal to -500 J mol^{-1}. (a) What pressure is needed? (b) Now suppose that a new catalyst is developed that is most cost-effective at 400°C when the pressure gives the same value of $\Delta_r G$. What pressure is needed when the new catalyst is used? What are the advantages of the new catalyst? Assume that (i) all gases are perfect gases or that (ii) all gases are van der Waals gases. Isotherms of $\Delta_r G(T, p)$ in the pressure range 100 atm $\leq p \leq$ 400 atm are needed to derive the answer. (c) Do the isotherms you plotted confirm Le Chatelier's principle concerning the response of equilibrium changes in temperature and pressure?

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PART 2 Structure

In Part 1 we examined the properties of bulk matter from the viewpoint of thermodynamics. In Part 2 we examine the structures and properties of individual atoms and molecules from the viewpoint of quantum mechanics. The two viewpoints merge in Chapters 16 and 17.

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