

8 Equilibrium

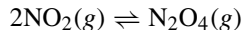
In Chapter 2 we saw that whether or not a process will ‘go’ is controlled by the Second Law of Thermodynamics. What this law says is that a process will only be spontaneous – that is, take place on its own without continuous intervention from us – if it is associated with an *increase* in the entropy of the Universe (Section 2.2 on p. 7). We also saw that another and entirely equivalent way of applying the Second Law is to express it in terms of the Gibbs energy (Section 2.7 on p. 16); using this, a spontaneous process is one in which the Gibbs energy *decreases*.

Using either of these criteria we were able to explain why it is that water will freeze at $-5\text{ }^{\circ}\text{C}$ but not at $+5\text{ }^{\circ}\text{C}$, since it is only at the lower temperature that water \rightarrow ice is accompanied by an increase in the entropy of the Universe or, equivalently, a decrease in the Gibbs energy.

Applying the same ideas to chemical reactions is rather more subtle, as we need to explain what determines the *position of equilibrium*, an idea introduced on p. 5 and illustrated in Fig. 2.1. Some reactions go almost entirely to products so the position of equilibrium lies very much towards the products; others hardly go at all and so the position of equilibrium lies towards the reactants. Other reactions come to equilibrium with significant amounts of reactants and products present. Our task in this chapter will be to work out what determines this position of equilibrium.

8.1 The approach to equilibrium

On p. 6 we discussed the equilibrium between NO_2 and N_2O_4 :



and pointed out that the reaction could come to the equilibrium position (at which significant amounts of both reactants and products are present) either starting from pure reactants (NO_2) or from pure products (N_2O_4). What this implies is that in going from either *pure products* or *pure reactants* to the equilibrium position the Gibbs energy must *decrease*. In other words, the equilibrium mixture of reactants and products has lower Gibbs energy than *either* pure products *or* pure reactants.

Shown in Fig. 8.1 is a plot of the Gibbs energy of the mixture of reactants and products (here NO_2 and N_2O_4) as a function of the composition. Pure reactants correspond to no reaction having taken place and so appear on the left; pure products correspond to complete reaction and so appear on the right. From the graph we see that the Gibbs energy goes to a minimum at some point intermediate between pure reactants and pure products; this minimum corresponds to the equilibrium position.

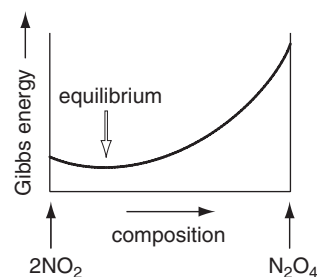


Fig. 8.1 Plot of the Gibbs energy of the reaction mixture as a function of its composition for the dimerization of NO_2 . The left-hand side of the graph corresponds to pure reactants and the right to pure products. The minimum in the Gibbs energy corresponds to the position of equilibrium which can be approached either from pure reactants or pure products.

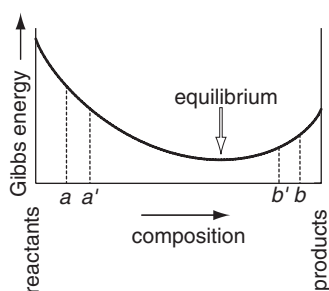


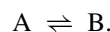
Fig. 8.2 Starting from point *a* the Gibbs energy will fall as we move to point *a'*; such a change will be spontaneous and will take us toward the position of equilibrium by increasing the amount of products. In contrast, from point *b* the direction which involves a reduction in Gibbs energy is towards point *b'*; for this spontaneous change the amount of products is reduced. Starting from either *a* or *b* the direction of spontaneous change is towards the equilibrium position, at which the Gibbs energy is a minimum.

No matter whether we start with pure products, or pure reactants, or some mixture of the two, the Gibbs energy falls as we approach equilibrium. For example, in Fig. 8.2 if we start at composition *a*, moving to *a'* is accompanied by a decrease in the Gibbs energy. The change from *a* to *a'* is therefore a spontaneous process which moves us towards the position of equilibrium by increasing the amount of products. Starting at *b* and moving to *b'* is also accompanied by a decrease in the Gibbs energy and so will be spontaneous; as for the change from *a* to *a'*, the change from *b* to *b'* also moves us towards the equilibrium position but this time by *decreasing* the amount of products.

The shape of the graph therefore funnels the composition towards the value with the minimum Gibbs energy, which is the equilibrium position. From this point any change would involve an *increase* in the Gibbs energy, which is not permitted. So, once at its equilibrium value the composition cannot change. Our task is to try to understand why the plot of Gibbs energy as a function of composition has the form shown in Fig. 8.2 and also to identify the factors which influence the position of the minimum.

8.2 The equilibrium between two species

The simplest kind of equilibrium we can consider is when there is just one reactant (A) and one product (B):



The equilibrium between isomers (illustrated in Fig. 8.3) is an example of this kind of reaction.

Let us imagine that A and B are both gases and that we start out with one mole of pure A sealed in a container such that the pressure is 1 bar (1 bar is 10^5 N m^{-2} , very close to 1 atmosphere pressure). The reaction will come to equilibrium by some of the A converting to B, so we can specify the extent to which this has happened simply by quoting the percentage of B in the mixture. As the reaction involves no change in the number of moles, the pressure does not change as A and B interconvert.

Figure 8.4 shows how the Gibbs energy varies with percentage of B. On the left we have pure A, and so, as there is one mole of A present, the Gibbs energy is the *molar* Gibbs energy of *pure* A, $G_m(\text{A})$. On the right we have pure B, and so the Gibbs energy is just the *molar* Gibbs energy of *pure* B, $G_m(\text{B})$. To draw the graph we have arbitrarily chosen $G_m(\text{B})$ to be less than $G_m(\text{A})$. The task now is to try to explain why the curve has this shape, and in particular why it shows a minimum.

Suppose we start with pure A and then allow a very small amount of A to convert to B; as a consequence there will be a small change in the enthalpy and in the entropy. We will concentrate on the entropy change which we can think of as being due to two contributions.

The first contribution comes from the fact that we have converted some A to B. Given that the two substances are likely to have different molar entropies, changing some A into B is surely going to result in a change in entropy.

The second contribution comes from the *mixing* of this small amount of B into the bulk of A. So far we have not discussed this entropy of mixing, but you

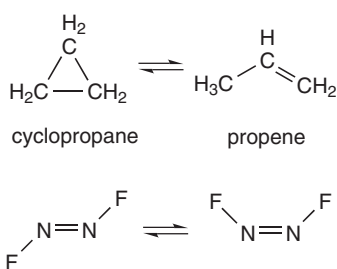


Fig. 8.3 Examples of equilibria involving just two chemical species which are isomers of one another.

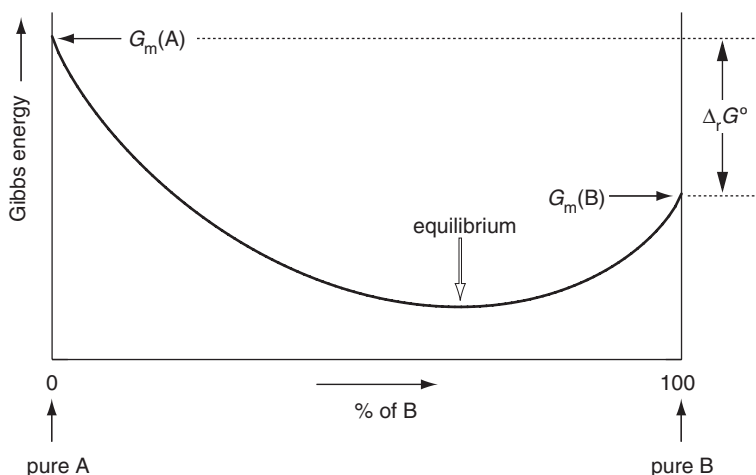


Fig. 8.4 Plot showing an example of how the Gibbs energy for the equilibrium between A and B varies with the composition, which in this case can be specified by the percentage of B. Arbitrarily, we have made the molar Gibbs energy of B lower than that of A.

can see that going from pure A to having a little B mixed in with A certainly gives rise to an increase in the entropy on the grounds that the mixture is more ‘random’ than pure A. We therefore expect this second contribution always to result in an increase in the entropy.

The first contribution might result in an increase or decrease in the entropy, but we argue that the entropy increase due to the second contribution – the one due to mixing – will *always* be dominant as there is a large increase in randomness (that is, in entropy) on going from pure A to a mixture with a small amount of B in it.

Given that ΔG is defined as $(\Delta H - T\Delta S)$ (p. 16), it follows that this increase in entropy will lead to a decrease in the Gibbs energy. Therefore, as we start from the left-hand side of the graph in Fig. 8.4 we expect the Gibbs energy to fall. Similarly, when starting from the right-hand side of the plot we can employ the same reasoning to argue that having a small amount of A mixed in with the bulk of B leads to an increase in the entropy and hence a decrease in the Gibbs energy.

Having now convinced ourselves why the Gibbs energy falls when we start from either side of this plot, we now need to work out what happens in between. A simple argument is to note that as the Gibbs energy falls when we start from the left or right, for the curve to join up there must be a minimum somewhere between these two points.

To determine the exact form of the curve we need some more detailed thermodynamics, which we do not have time to go into here – so for now you will simply have to take the form of these graphs on trust.

Locating the position of equilibrium

The remarkable thing about the plot in Fig. 8.4 is that it turns out that the location of the minimum – that is the percentage of B present at equilibrium – depends only on the *difference* between the molar Gibbs energies of A and B.

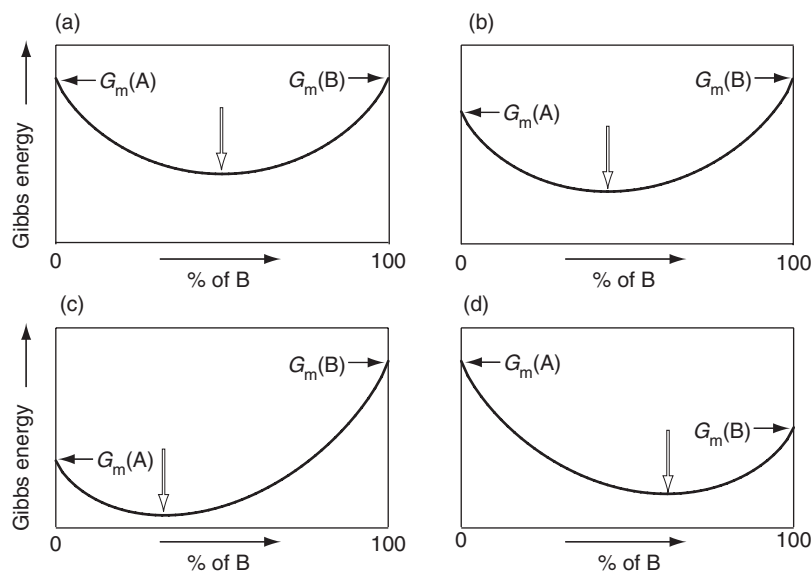


Fig. 8.5 Illustration of how the position of equilibrium (indicated by the open arrow) is affected by changing the relative molar Gibbs energies of A and B. In (a) $G_m(A)$ and $G_m(B)$ are equal, making the curve symmetrical and so the position of equilibrium lies at 50% B. In (b) $G_m(A)$ is less than $G_m(B)$ and so the position of equilibrium lies towards A; in (c) $G_m(A)$ has been reduced further and the equilibrium therefore lies even further towards A. Finally, in (d), $G_m(B)$ is less than $G_m(A)$ and so the position of equilibrium lies towards B.

To prove that this is so needs a deeper study of the principles of thermodynamics than we have time to go into here, so we will simply have to take this result on trust.

Figure 8.5 illustrates how the position of the minimum shifts for different values of $G_m(A)$ and $G_m(B)$. In (a) the molar Gibbs energies of A and B are equal; the minimum in the Gibbs energy of the mixture is at 50% B. In (b) the molar Gibbs energy of A is lower than that of B, and so the position of equilibrium moves to the left, corresponding to the presence of more A than B; in (c) the molar Gibbs energy of A is lower still, and this shifts the position of equilibrium even further towards A. Finally, in (d) the molar Gibbs energy of B is lower than that of A so now the equilibrium lies towards B. We see that the position of equilibrium lies towards the species with the lowest molar Gibbs energy.

If you take a piece of string or chain and hold one end in your left hand and the other in your right, the string falls in a curve rather similar to those in Fig. 8.5. The height of your left hand represents the molar Gibbs energy of A, and the height of your right hand represents the molar Gibbs energy of B. If you hold your two hands level, your will see that the string hangs so as to make a minimum at a position midway between your hands: this is like plot (a). If you lower your left hand, the minimum moves towards the left, just as in plots (b) and (c). Conversely, if you lower your right hand, the minimum moves towards the right, as in plot (d).

As you know, when a reaction has come to equilibrium, the concentrations of products and reactants are related by the value of the *equilibrium constant*.

In the case of the equilibrium between A and B, the equilibrium constant, K , is given by

$$K = \frac{[\text{B}]_{\text{eq}}}{[\text{A}]_{\text{eq}}}$$

where $[\text{A}]_{\text{eq}}$ and $[\text{B}]_{\text{eq}}$ are the *equilibrium* concentrations of A and B respectively. If at equilibrium more B is present than A, K is greater than 1 and the equilibrium lies towards the products. Conversely, if the equilibrium lies towards the reactants there will be more A present than B and the equilibrium constant will be less than 1.

The percentage of B at which the minimum Gibbs energy occurs determines the value of the equilibrium constant. We have already described how the location of the minimum is determined solely by the difference in the molar Gibbs energies of A and B. It therefore follows that the value of the equilibrium constant must be related to this difference, and some more detailed thermodynamics shows us that:

$$G_{\text{m}}(\text{B}) - G_{\text{m}}(\text{A}) = -RT \ln K \quad (8.1)$$

where R is the gas constant ($8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$) and T is the absolute temperature (in K).

This equation has the correct form, as if $G_{\text{m}}(\text{B})$ is less than $G_{\text{m}}(\text{A})$, the left-hand side will be negative and so $\ln K$ will be positive. This means that K is greater than 1 so that at equilibrium the product B is favoured, as depicted in Fig. 8.5 (d).

In contrast, if $G_{\text{m}}(\text{A})$ is less than $G_{\text{m}}(\text{B})$, the left-hand side of Eq. 8.1 will be positive and so $\ln K$ will be negative. This means that K will be a fraction between 0 and 1, favouring the reactant A at equilibrium, as depicted in Fig. 8.5 (b) and (c).

The surprising thing about Eq. 8.1 is that it tells us that the equilibrium constant depends only on the difference between the molar Gibbs energies of *pure* A and *pure* B. This really is quite a remarkable result and worth discussing a little more before we move on.

Interpretation

Suppose that $G_{\text{m}}(\text{B})$ is less than $G_{\text{m}}(\text{A})$. This means that if we start with pure A and convert *all* of it to B the process would be accompanied by a decrease in Gibbs energy and therefore be spontaneous. This change in Gibbs energy is shown as ΔG_1 in Fig. 8.6.

However, what we have seen is that there are some ratios of A to B for which the mixture has lower Gibbs energy than *either* pure A *or* pure B; one of these mixtures has the minimum Gibbs energy and this is the one which corresponds to equilibrium. As is shown in Fig. 8.6, going from pure A to the equilibrium mixture involves a larger decrease in the Gibbs energy, ΔG_2 , than going to pure B.

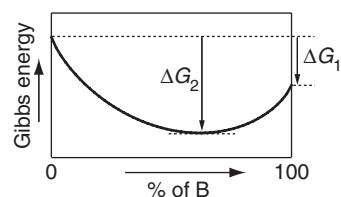


Fig. 8.6 The molar Gibbs energy of the product B is lower than that of the reactant A, so going from pure A to pure B involves a decrease in the Gibbs energy (ΔG_1). However, for certain ratios of A to B the Gibbs energy of the mixture is *lower* than that of pure B; the lowest value of the Gibbs energy corresponds to the equilibrium point and moving to this point from pure A involves the largest decrease in the Gibbs energy (ΔG_2).

8.3 General chemical equilibrium

These ideas about the simple $A \rightleftharpoons B$ equilibrium are just a special case of a more general result which is that for any reaction the equilibrium constant, K , is given by

$$\Delta_r G^\circ = -RT \ln K. \quad (8.2)$$

$\Delta_r G^\circ$ is the *standard Gibbs energy change* which can be computed from

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ \quad (8.3)$$

where $\Delta_r H^\circ$ is the *standard enthalpy change* and $\Delta_r S^\circ$ is the *standard entropy change* for the reaction. The first thing we need to do is describe what we mean by a ‘standard change’.

Standard states and standard changes

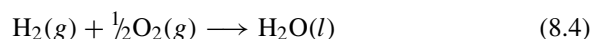
We first need to introduce the concept of a *standard state*; this is a particular state of the substance in question, defined according to the following agreed convention:

substance	standard state
gases	the pure gas at a pressure of 1 bar (10^5 N m^{-2})
solids	the pure solid
liquids	the pure liquid
solutions	the solution at unit concentration

The standard state given in the table for a solution only applies to an *ideal solution* in which there are no solute–solvent interactions; for real solutions in which there are such interactions the definition is more complex and we shall not go into this here.

The standard state is denoted by a superscript $^\circ$ or sometimes a Plimsoll line \ominus . It is sometimes thought, erroneously, that the standard state implies a certain temperature: this is *not* the case. In fact, when quoting values for standard enthalpy, entropy or Gibbs energy changes we must *always* state the temperature at which this value applies as these quantities are temperature dependent.

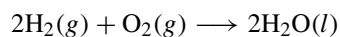
Having introduced the standard state we can now define *standard changes* for reactions. Such changes refer to a particular *balanced chemical equation*. For example, $\Delta_r G^\circ$ for the reaction



is the *change* in Gibbs energy when one mole of $\text{H}_2(\text{g})$ reacts with half a mole of $\text{O}_2(\text{g})$ to give one mole of $\text{H}_2\text{O}(\text{l})$, *all of the species being present at standard conditions and at the stated temperature*.

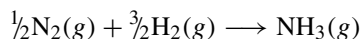
It is very important to understand that the value of $\Delta_r G^\circ$ refers to complete reaction, i.e. the hydrogen and oxygen must be converted completely to water. Note too how the values of the stoichiometric coefficients come into the definition of $\Delta_r G^\circ$.

So, if we doubled the stoichiometric coefficients in Eq. 8.4 and wrote it as



$\Delta_r G^\circ$ would be the change in Gibbs energy when two moles of $\text{H}_2(g)$ react with one mole of $\text{O}_2(g)$ to give two moles of $\text{H}_2\text{O}(l)$. The numerical value of $\Delta_r G^\circ$ for this reaction would be twice the value of that for Eq. 8.4.

A second example is the formation of ammonia:



for which $\Delta_r G^\circ$ is the *change* in Gibbs energy when half a mole of $\text{N}_2(g)$ reacts with $\frac{3}{2}$ moles of $\text{H}_2(g)$ to give one mole of $\text{NH}_3(g)$, all under standard conditions and at the stated temperature.

In many ways $\Delta_r G^\circ$ is a hypothetical quantity as it refers to the change in Gibbs energy when the reactants, in their standard states, are converted *completely* to products, also in their standard states. If we actually mixed the reactants together in their standard states there is no guarantee that the reaction would go completely to products in their standard states. All that we can be sure will actually happen is that the reaction will go to its equilibrium position, which often will not involve complete conversion to products.

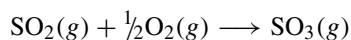
For example, under standard conditions and at room temperature not much ammonia will be formed by mixing N_2 and H_2 . However, this does not stop us from imagining what the change in Gibbs energy would be *if* the reaction went completely from N_2 and H_2 to NH_3 .

The standard enthalpy change is defined in the same way as $\Delta_r G^\circ$: for the stated reaction it is the change in enthalpy when the reaction proceeds completely from reactants to products, all species being in their standard states. Similarly, the standard entropy change is the change in entropy for this process.

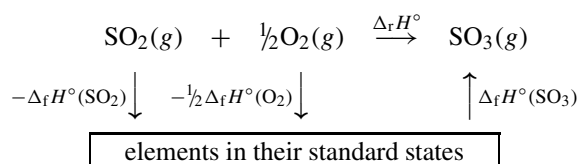
Returning to the simple equilibrium between A and B which was discussed in Section 8.2 on p. 114, we can see that because we took the pressure to be 1 bar, the difference in the molar Gibbs energies of A and B is in fact the same thing as $\Delta_r G^\circ$ for the reaction; this is shown in Fig. 8.4 on p. 115. So, Eq. 8.1 is just a special case of Eq. 8.2.

Determining standard changes

The usual way of finding $\Delta_r H^\circ$ is to use tabulated values of *standard enthalpies of formation*, $\Delta_f H^\circ$. These are defined in such a way that for any balanced chemical equation we can find $\Delta_r H^\circ$ by adding together the $\Delta_f H^\circ$ values of the products and subtracting those of the reactants, taking into account the stoichiometric coefficients. For example, to find $\Delta_r H^\circ$ for the reaction



we can imagine a Hess' Law cycle in which the reactants are broken down into their elements (in their standard states) and then these are re-formed to products:



$\Delta_r H^\circ$ is thus given by

$$\Delta_r H^\circ = \Delta_f H^\circ(\text{SO}_3(g)) - \Delta_f H^\circ(\text{SO}_2(g)) - \frac{1}{2}\Delta_f H^\circ(\text{O}_2(g)).$$

As you will recall, the standard enthalpy of formation of an element is zero, so in the above equation $\Delta_f H^\circ(\text{O}_2(g)) = 0$.

Similarly, $\Delta_r S^\circ$ values are found by adding together the standard (absolute) entropies (S°) of the products and subtracting those of the reactants, taking into account the stoichiometric coefficients. So, for the above reaction:

$$\Delta_r S^\circ = S^\circ(\text{SO}_3(g)) - S^\circ(\text{SO}_2(g)) - \frac{1}{2}S^\circ(\text{O}_2(g)).$$

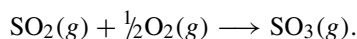
As with enthalpies of formation, extensive tabulations of standard entropies are available. Note that the standard absolute entropies of the elements are *not* zero.

Having found $\Delta_r H^\circ$ and $\Delta_r S^\circ$ we then find $\Delta_r G^\circ$ using Eq. 8.3

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ.$$

An example

Let us use this approach to find $\Delta_r G^\circ$ for



From tables we find (all at 298 K and for the gaseous state) $\Delta_f H^\circ(\text{SO}_3) = -396 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ(\text{SO}_2) = -297 \text{ kJ mol}^{-1}$; so, remembering that $\Delta_f H^\circ$ for O_2 is zero,

$$\begin{aligned}
 \Delta_r H^\circ &= \Delta_f H^\circ(\text{SO}_3(g)) - \Delta_f H^\circ(\text{SO}_2(g)) - \frac{1}{2}\Delta_f H^\circ(\text{O}_2(g)) \\
 &= -396 - (-297) - \frac{1}{2} \times 0 \\
 &= -99 \text{ kJ mol}^{-1}.
 \end{aligned}$$

The same tables give us the following standard entropies: $S^\circ(\text{SO}_3) = 257 \text{ J K}^{-1} \text{ mol}^{-1}$, $S^\circ(\text{SO}_2) = 248 \text{ J K}^{-1} \text{ mol}^{-1}$ and $S^\circ(\text{O}_2) = 205 \text{ J K}^{-1} \text{ mol}^{-1}$; so

$$\begin{aligned}
 \Delta_r S^\circ &= S^\circ(\text{SO}_3(g)) - S^\circ(\text{SO}_2(g)) - \frac{1}{2}S^\circ(\text{O}_2(g)) \\
 &= 257 - 248 - \frac{1}{2} \times 205 \\
 &= -93.5 \text{ J K}^{-1} \text{ mol}^{-1}.
 \end{aligned}$$

These values allow us to find $\Delta_r G^\circ$ at 298 K:

$$\begin{aligned}
 \Delta_r G^\circ &= \Delta_r H^\circ - T \Delta_r S^\circ \\
 &= -99 \times 10^3 - 298 \times (-93.5) \\
 &= -71 \times 10^3 \text{ J mol}^{-1}.
 \end{aligned}$$

Next we will see what this implies for the value of the equilibrium constant.

Equilibrium constants

The equilibrium constant and the standard Gibbs energy change for a reaction are related according to Eq. 8.2

$$\Delta_r G^\circ = -RT \ln K$$

which can be rewritten to give K as

$$K = \exp\left(\frac{-\Delta_r G^\circ}{RT}\right).$$

This relationship tells us that if $\Delta_r G^\circ$ is negative, the exponent (the expression in the brackets) will be positive and so the equilibrium constant will be greater than 1, i.e. the products are favoured. On the other hand, if $\Delta_r G^\circ$ is positive, the exponent will be negative, giving an equilibrium constant of less than 1, which means that the reactants are favoured. These points are illustrated in Fig. 8.7.

In the case of the formation of SO_3 from SO_2 and O_2 we found that at 298 K, $\Delta_r G^\circ = -71 \times 10^3 \text{ J mol}^{-1}$ and so

$$\begin{aligned} K &= \exp\left(\frac{-\Delta_r G^\circ}{RT}\right) \\ &= \exp\left(\frac{-(-71 \times 10^3)}{8.3145 \times 298}\right) \\ &= 2.29 \times 10^{12}. \end{aligned}$$

The equilibrium constant is very large, implying that the equilibrium will be totally in favour of the products in this reaction.

Before we move on there is one point of possible confusion we need to clear up. In Chapter 2 we showed that a spontaneous process must be accompanied by a decrease in the Gibbs energy, and we have used this criterion to discuss chemical equilibrium. Consider the situation shown in Fig. 8.8, in which $\Delta_r G^\circ$ is positive, i.e. the pure product, B, is higher in Gibbs energy than the pure reactant, A. It therefore follows that the conversion of pure A to pure B (under standard conditions) will *not* take place as this would be accompanied by an increase in the Gibbs energy.

However, this does not mean that the conversion of *some* A to B is forbidden – far from it. We see this clearly in Fig. 8.8 where the conversion of pure A to the equilibrium mixture is accompanied by a decrease in the Gibbs energy, even though $\Delta_r G^\circ$ is positive.

So, if a reaction has a positive $\Delta_r G^\circ$ this does *not* mean that the reaction will not take place; rather, it means that the reaction will come to an equilibrium position which favours the reactants. Similarly, a reaction which has a negative $\Delta_r G^\circ$ will not go entirely to products, but it will go to an equilibrium position which favours the products.

In fact, because of the exponential relationship between $\Delta_r G^\circ$ and the equilibrium constant, once $\Delta_r G^\circ$ becomes more positive than a certain value the equilibrium constant becomes so small that the equilibrium lies entirely to the

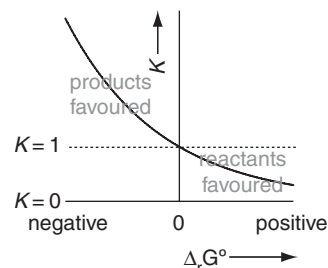


Fig. 8.7 Graph showing how the sign of $\Delta_r G^\circ$ affects the position of equilibrium. If $\Delta_r G^\circ$ is positive the equilibrium constant is less than 1 (but still positive) which means that the reactants are favoured. If $\Delta_r G^\circ$ is negative the equilibrium constant is greater than 1 and the products are favoured.

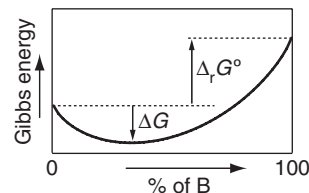


Fig. 8.8 Illustration of how a reaction which has a positive $\Delta_r G^\circ$ still takes place to a certain extent, i.e. comes to a position of equilibrium in which some product is present. Going from pure A to pure B would involve an increase in the Gibbs energy and so is not allowed. Nevertheless, going from pure A to the equilibrium mixture involves a decrease in the Gibbs energy and so is allowed. A reaction with a positive $\Delta_r G^\circ$ is not 'forbidden' but simply comes to a position of equilibrium which favours the reactants.

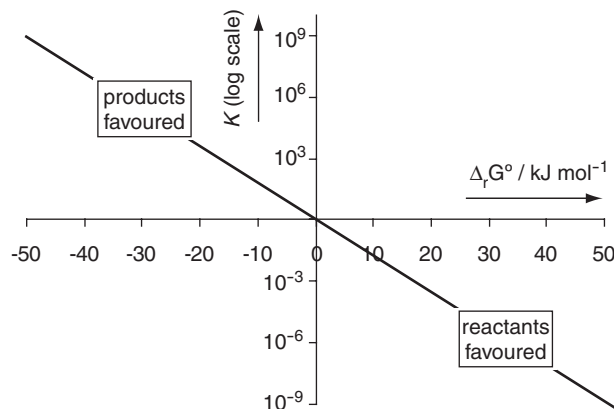


Fig. 8.9 Plot showing how the equilibrium constant, K , varies with the standard Gibbs energy change of the reaction ($\Delta_r G^\circ$) at a temperature of 298 K; note that the vertical scale is logarithmic. If $\Delta_r G^\circ$ is more negative than about -40 kJ mol^{-1} the equilibrium constant is so large that essentially the conversion to products is complete. Similarly, if $\Delta_r G^\circ$ is more positive than about $+40 \text{ kJ mol}^{-1}$ the equilibrium constant is so small that essentially no products are formed.

reactants, i.e. the reaction does not proceed to a significant extent. Similarly, once $\Delta_r G^\circ$ is more negative than a certain value, the equilibrium constant becomes so large that to all intents and purposes the equilibrium lies entirely in favour of the products.

Figure 8.9 shows how K varies with $\Delta_r G^\circ$; note that the vertical scale is logarithmic. We see from this plot that once $\Delta_r G^\circ$ exceeds around $+40 \text{ kJ mol}^{-1}$ the equilibrium constant is so small that essentially none of the reactants have become products. On the other end of the scale, if $\Delta_r G^\circ$ is more negative than about -40 kJ mol^{-1} the equilibrium constant is so large that to all practical intents and purposes the reaction has gone entirely to products. Finally, note that if $\Delta_r G^\circ = 0$ the equilibrium constant is one, implying an equal balance between products and reactants.

8.4 Influencing the position of equilibrium

For a given reaction the value of the equilibrium constant is fixed once we specify the temperature and the states of the reactants (solid, liquid, gas, etc.). This section describes a number of ways in which the actual amount of products can be increased – in other words, how to increase the yield of the reaction, something we often want to do for practical reasons.

Temperature

Both the equation relating $\Delta_r G^\circ$ to the equilibrium constant

$$\Delta_r G^\circ = -RT \ln K \quad (8.2)$$

and the definition of $\Delta_r G^\circ$

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ \quad (8.3)$$

involve temperature explicitly, so we can expect the temperature to have an influence on the value of the equilibrium constant. It turns out that the values of $\Delta_r S^\circ$ and $\Delta_r H^\circ$ also depend on temperature, although not very strongly. Over a modest temperature range it is reasonable to assume that they are constant, which is what we will do from now on.

As both Eq. 8.2 and Eq. 8.3 are expressions for $\Delta_r G^\circ$ we can equate their right-hand sides to give

$$-RT \ln K = \Delta_r H^\circ - T \Delta_r S^\circ.$$

Dividing both sides by $-RT$ gives

$$\ln K = -\frac{\Delta_r H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta_r S^\circ}{R}. \quad (8.5)$$

This equation tells us that the way in which the equilibrium constant varies with temperature depends on $\Delta_r H^\circ$.

If the reaction is *endothermic* ($\Delta_r H^\circ$ is positive) the term $(-\Delta_r H^\circ/RT)$ is negative and so increasing the temperature makes it *less negative*. This means that as T increases both $\ln K$ and K increase, as is illustrated in Fig. 8.10. In other words, for an endothermic reaction increasing the temperature shifts the equilibrium towards the products.

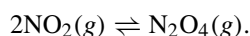
If the reaction is *exothermic* ($\Delta_r H^\circ$ is negative) the term $(-\Delta_r H^\circ/RT)$ is positive and so increasing the temperature makes it *less positive*. As a result increasing the temperature makes both $\ln K$ and K smaller (see Fig. 8.10). In words, for an exothermic reaction, increasing the temperature shifts the equilibrium towards the reactants.

You are probably familiar with these conclusions as they are often described as being a consequence of *Le Chatelier's Principle*, one statement of which is that 'the equilibrium shifts in order to oppose the change'. So, for an endothermic reaction, an increase in the temperature is opposed by absorbing heat which means that the reaction must move further to products, i.e. the equilibrium constant must increase. Equation 8.5 puts this application of Le Chatelier's Principle on a quantitative footing.

We will look at two examples of the effect of temperature on the position of equilibrium.

Dimerization of NO_2

For our first example, let us look again at the dimerization of $\text{NO}_2(g)$:



From tables, we find for this reaction that at 298 K, $\Delta_r H^\circ = -57 \text{ kJ mol}^{-1}$ and $\Delta_r S^\circ = -176 \text{ J K}^{-1} \text{ mol}^{-1}$. These values make sense as a bond is being made, so we expect the release of energy, and the reduction in entropy is associated with two moles of gas going to one.

At 298 K we can compute $\Delta_r G^\circ$ and then K :

$$\begin{aligned} \Delta_r G^\circ &= \Delta_r H^\circ - T \Delta_r S^\circ \\ &= -57 \times 10^3 - 298 \times (-176) \\ &= -4.6 \times 10^3 \text{ J mol}^{-1}. \end{aligned}$$

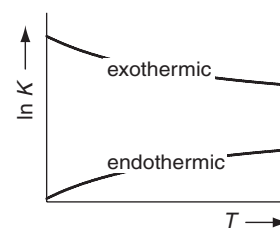


Fig. 8.10 Graph showing the different ways in which $\ln K$ varies with temperature (as predicted by Eq. 8.5) for an exothermic and an endothermic reaction. For an endothermic reaction the equilibrium constant increases with temperature; for an exothermic reaction, the opposite is the case. Thus, Eq. 8.5 is an expression of Le Chatelier's Principle.

$$\begin{aligned}
 K &= \exp\left(\frac{-\Delta_r G^\circ}{RT}\right) \\
 &= \exp\left(\frac{-(-4.6 \times 10^3)}{8.3145 \times 298}\right) \\
 &= 6.3
 \end{aligned}$$

We see that $\Delta_r G^\circ$ is negative and so the equilibrium constant is greater than 1, showing that at equilibrium the products are preferred. However, $\Delta_r G^\circ$ is not that negative and so the equilibrium constant is modest (6.3) which tells us that although the equilibrium lies on the side of the products, there are still plenty of reactants present.

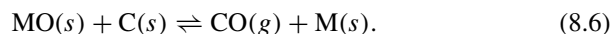
As the reaction is exothermic, lowering the temperature will increase the proportion of products. Let us repeat the same calculation at 273 K:

$$\begin{aligned}
 \Delta_r G^\circ &= -57 \times 10^3 - 273 \times (-176) = -9.0 \times 10^3 \text{ J mol}^{-1} \\
 K &= \exp\left(\frac{-(-9.0 \times 10^3)}{8.3145 \times 273}\right) = 52.
 \end{aligned}$$

The equilibrium constant is now much larger, meaning that at this lower temperature the proportion of dimer (N_2O_4) present is larger than it was at 298 K. Repeating the calculation at 373 K gives $K = 0.062$, showing that at this higher temperature the fraction of dimer present is very small. These calculations illustrate very nicely how we can shift the equilibrium one way or the other simply by altering the temperature.

Extraction of metals

Our second example is rather different, and concerns the commercially very important process of extracting metals from their oxides. Typically, this is done by heating the oxide with carbon which acts as a reducing agent, thus releasing the free metal and forming CO or CO_2 . The chemical processes involved are often fairly complex, but for a simple divalent metal oxide (general formula MO) we can get a flavour of what is going on by just considering the reaction



The following table gives thermochemical data (at 298 K) for C, CO, the metals copper, lead and zinc and their oxides.

	C	CO	Cu	CuO	Pb	PbO	Zn	ZnO
$\Delta_f H^\circ / \text{kJ mol}^{-1}$		-111		-157		-219		-348
$S^\circ / \text{J K}^{-1} \text{ mol}^{-1}$	5.74	198	33.2	42.6	64.8	66.5	25.4	40.3

Using these we can compute $\Delta_r G^\circ$ for the reaction of Eq. 8.6 at any temperature (provided we assume that $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are not temperature dependent). The results for reaction at 1000 °C and 1500 °C are shown in the following table (you can check to see if you agree with the numbers); similar data are also shown in Fig. 8.11.

oxide	$\Delta_r H^\circ / \text{kJ mol}^{-1}$	$\Delta_r S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	at 1000 °C		at 1500 °C	
			$\Delta_r G^\circ / \text{kJ mol}^{-1}$	$\Delta_r G^\circ / \text{kJ mol}^{-1}$	$\Delta_r G^\circ / \text{kJ mol}^{-1}$	$\Delta_r G^\circ / \text{kJ mol}^{-1}$
CuO	46.8	182	-185	-277		
PbO	108	190	-133	-229		
ZnO	274	177	12.3	-76.2		

As expected, for all the metals the reaction has a positive $\Delta_r S^\circ$ resulting from the generation of one mole of gas on the right-hand side of the equation. The reactions are all endothermic which means that, as $\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$, a negative value of $\Delta_r G^\circ$ can only be achieved by a positive $\Delta_r S^\circ$ (which is what we have here) and a sufficiently high temperature that the $-T \Delta_r S^\circ$ term is dominant.

We need to be careful here not to fall into making an error about how temperature influences the *equilibrium constant*. Read casually, the previous paragraph makes it sound as if it is the sign of $\Delta_r S^\circ$ which determines how the equilibrium will change with temperature. This is not what the paragraph says: what it says is that the sign of $\Delta_r S^\circ$ determines whether $\Delta_r G^\circ$ rises or falls with temperature, but $\Delta_r G^\circ$ is *not* the equilibrium constant. To find the equilibrium constant from $\Delta_r G^\circ$ we need to use $\Delta_r G^\circ = -RT \ln K$, a relationship which introduces another temperature dependence; so knowing how $\Delta_r G^\circ$ varies with temperature is not the whole story.

In fact, as we have seen, the effect of temperature on the equilibrium constant is given by Eq. 8.5

$$\ln K = -\frac{\Delta_r H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta_r S^\circ}{R}.$$

This shows that it is the sign of $\Delta_r H^\circ$ which determines how the equilibrium constant depends on temperature as it is $\Delta_r H^\circ$ which is multiplying the $(1/T)$ term. So, although it is true that if $\Delta_r S^\circ$ is positive, increasing the temperature will cause $\Delta_r G^\circ$ to decrease, to understand the effect of temperature on the equilibrium constant we need to look at the sign of $\Delta_r H^\circ$. What the table tells us therefore is that *as the reactions are all endothermic*, increasing the temperature will move the equilibrium to the products.

This subtle point about the temperature dependence does not alter the basic idea that if $\Delta_r G^\circ$ is substantially negative the position of equilibrium will lie almost entirely toward the products. At 1000 °C, $\Delta_r G^\circ$ is substantially negative for copper and lead, showing that metal + carbon monoxide will be formed. However, for zinc $\Delta_r G^\circ$ is positive at this temperature, which tells us that the equilibrium will favour the reactants ($\text{ZnO} + \text{C}$) and so zinc metal will not be extracted.

In order for the reduction to produce zinc we have to raise the temperature higher, and we can see from the table that at 1500 °C, $\Delta_r G^\circ$ is now substantially negative for the ZnO reduction. We therefore conclude that to obtain copper or lead from their oxides, reduction with carbon at a temperature of 1000 °C will be sufficient, but to obtain zinc from its oxide a substantially higher temperature will be needed. Figure 8.11 presents the results in a slightly different way, and from this graph we can see that for Zn the switch over from a positive to a negative $\Delta_r G^\circ$ occurs at around 1100 °C. In practice we need to

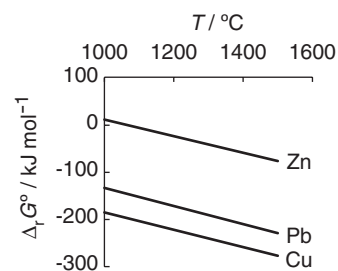


Fig. 8.11 Plot showing how the standard Gibbs energy change for the reaction of Eq. 8.6 varies with temperature for three different metals; the process will only be successful if $\Delta_r G^\circ$ is significantly negative. It is clear, therefore, that the extraction of Zn requires a higher temperature than for Cu or Pb. The values of $\Delta_r G^\circ$ have been computed assuming that $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are independent of temperature, and so the plots are straight lines.

be at a higher temperature than this to ensure that $\Delta_r G^\circ$ is sufficiently negative for the equilibrium to favour products strongly.

Concentration

The value of the equilibrium constant determines the ratio of the concentrations of products and reactants, and this has a fixed value at a particular temperature. However, we can influence the *actual* concentration of a product by altering the concentrations of the other species. How this works is best illustrated by an example, such as the equilibrium shown in Fig. 8.12 which is the reaction used to form an ester (**E**) from an alcohol (**A**) and a carboxylic acid (**C**).

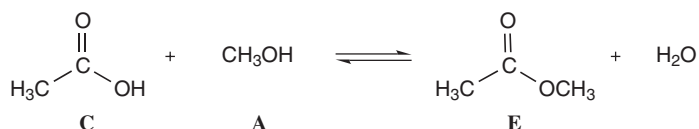


Fig. 8.12 An ester, **E**, is formed from the reaction between a carboxylic acid, **C**, and an alcohol, **A**; water is also produced in the reaction. Here the reaction is between ethanoic (acetic) acid and methanol to give methyl ethanoate (methyl acetate).

The equilibrium constant, K , for this reaction is given by:

$$K = \frac{[\text{E}]_{\text{eq}}[\text{H}_2\text{O}]_{\text{eq}}}{[\text{C}]_{\text{eq}}[\text{A}]_{\text{eq}}} \quad (8.7)$$

where $[\text{E}]_{\text{eq}}$ means the equilibrium concentration of the ester, and so on. Remember that at a particular temperature the value of K is fixed, so the concentrations of the four species must adjust themselves so that the ratio on the right-hand side of Eq. 8.7 is equal to the value of K .

Suppose we let the reaction come to equilibrium, but then by some means we start to remove one of the products (say the ester); what will happen? The moment the concentration of the ester falls the ratio on the right-hand side of Eq. 8.7 will be too small; to restore it to the correct value we have to either *increase* the amounts of ester and water or *decrease* the amounts of carboxylic acid and alcohol. Both of these things are achieved if some of the acid and alcohol react to give more water and ester.

So, by removing the ester we disturb the equilibrium in such a way that the only way it can be restored is for more ester to be produced; we say that the reaction has been ‘forced to the right’ by removing the product. For the particular reaction shown in Fig. 8.12 it turns out that the ester is more volatile than any of the other species, so it can simply be distilled off constantly forcing the reaction to the right and so increasing the yield of the ester.

Another way of forcing the reaction to the right is to add more of one of the reactants. Once again, this reduces the value of the ratio on the right-hand side of Eq. 8.7 and so to restore the correct value some of the alcohol and carboxylic acid have to react to form more ester. If the alcohol is a simple one, such as methanol, we would probably use it as the solvent for the reaction, thus ensuring that its concentration was very high.

A similar example is in the formation of an imine from the reaction of a ketone with an amine, Fig. 8.13. In this reaction water is produced on the right-hand side of this equilibrium and so the yield of the imine can be increased by

removing the water. This can be achieved by adding a solid material known as a *molecular sieve* which is a special kind of zeolite clay which has cavities into which water will bind tightly. This effectively removes the water, so forcing the reaction to produce more of the imine in an attempt to restore the equilibrium.

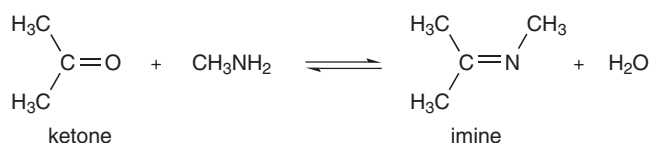


Fig. 8.13 An imine is formed from the reaction of a ketone and an amine.

We can use the same strategy to shift the reaction the other way; suppose, for example, we want to hydrolyse an ester back to the alcohol and the carboxylic acid – this is the reverse reaction shown in Fig. 8.12. To force the reaction to the left, we need to increase the amount of the species on the right and this is easily done by making water the solvent. Now its concentration will be very large, and so the reaction will be shifted to the left, in favour of the hydrolysed products.

The formation of an acetal from the reaction of a ketone with an alcohol, shown in Fig. 8.14, is an equilibrium reaction which we sometimes want to force one way and sometimes the other.

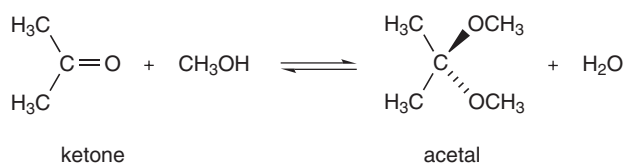
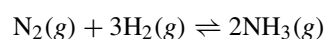


Fig. 8.14 The formation of an acetal from a ketone and an alcohol is a readily reversible reaction which we can 'force' one way or the other by altering the conditions.

If we wish to form the acetal we use the alcohol as the solvent and add a dehydrating agent – both choices force the equilibrium to the right. On the other hand, if we wish to regenerate the ketone from the acetal, we run the reaction in aqueous solution so that the excess of water will force the reaction to the left.

The Haber process

Our final example is the formation of ammonia from hydrogen and nitrogen (the *Haber process*):



which is the way in which millions of tonnes of ammonia are synthesized each year. In order to make the reaction go at a reasonable rate temperatures of around 400 °C are needed together with a solid iron oxide catalyst. Unfortunately, the reaction is exothermic ($\Delta_r H^\circ = -92 \text{ kJ mol}^{-1}$) so raising the temperature shifts the equilibrium towards the reactants (Section 8.4 on p. 122); it is found that at this high temperature the equilibrium constant is about 10^{-2} .

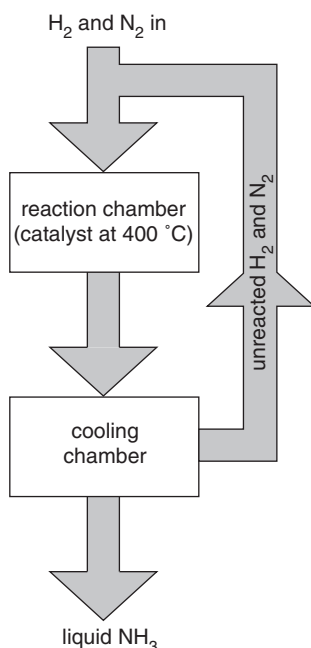


Fig. 8.15 Simplified picture of the arrangement for the Haber process for synthesizing ammonia. After coming to equilibrium over the catalyst, only a small fraction of the hydrogen and nitrogen has been converted to ammonia. The ammonia is separated from the other gases by liquefying it, and the unreacted nitrogen and hydrogen are returned to the reaction chamber.

The strategy for increasing the yield of ammonia is simply to remove the ammonia and then let the nitrogen and hydrogen come back to equilibrium, thus generating more ammonia. In practice this is done by passing the gases over the catalyst so that they come to equilibrium, then separating out the ammonia and finally recycling the unreacted gases back over the catalyst; the process is illustrated in Fig. 8.15.

Removing the ammonia is quite easy as ammonia will liquefy at a temperature (around $-35\text{ }^{\circ}\text{C}$) well above the temperature at which either nitrogen or hydrogen will liquefy. So, simply by cooling the gases the ammonia can be separated as a liquid.

Coupling reactions together

Suppose that the reaction we are interested in has a positive $\Delta_r G^\circ$, which means that the equilibrium constant will be less than 1, and very little of the products will be formed. One way to force the formation of larger amounts of the products is to ‘couple’ the reaction to another reaction which has a negative $\Delta_r G^\circ$ so that, when taken together, the overall $\Delta_r G^\circ$ is negative. What we are doing is driving the reaction with the unfavourable $\Delta_r G^\circ$ using a reaction with a favourable $\Delta_r G^\circ$.

For the two reactions to be coupled in this way they must be able to influence one another; having the reactions take place in separate beakers on the bench or simply mixing all the reagents together will not achieve the required coupling. In Nature this coupling is achieved using enzymes which control and direct the chemistry, and indeed very many of the important chemical processes of life are driven by this kind of coupling. We do not have time here to go into the details of exactly how enzymes achieve this coupling, but will just illustrate the outcome for one very fundamental reaction in living systems – the formation of the peptide bond.

In living systems, proteins are synthesized by the polymerization of amino acids into long chains. The key reaction in forming the chain is for amino acids to condense together by forming *peptide bonds*, as shown in Fig. 8.16 for the formation of a dipeptide.

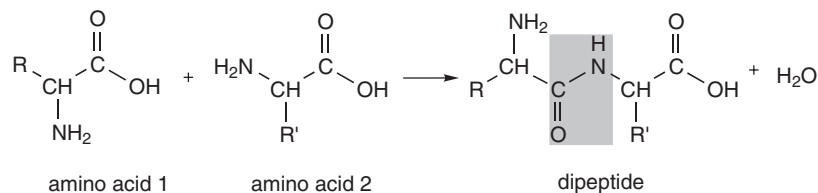
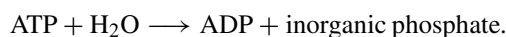


Fig. 8.16 Two amino acids condense together to form a dipeptide, and in doing so form the –CONH– peptide bond, shown in the grey box. Different amino acids have different side groups, R and R’.

This reaction has a rather unfavourable $\Delta_r G^\circ$ of $+17\text{ kJ mol}^{-1}$ and so at equilibrium very little of the dipeptide will be formed. To get round this, Nature couples this reaction with the hydrolysis of adenosine triphosphate (ATP) to adenosine diphosphate (ADP):



This reaction has a very favourable $\Delta_r G^\circ$ of -30 kJ mol^{-1} , sufficiently negative to outweigh the positive $\Delta_r G^\circ$ for the formation of the peptide bond. So, taken together the two reactions have an overall negative $\Delta_r G^\circ$ making the formation of the peptide bond thermodynamically feasible.

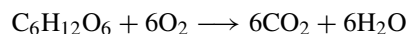
Nature frequently uses the hydrolysis of ATP to ADP to drive reactions which have unfavourable (positive) values of $\Delta_r G^\circ$, and so ATP is often regarded as the source of the energy which drives the chemistry of life. We can now see that by ‘energy’ we really mean Gibbs energy, as this is what drives reactions forward. So, when biochemists describe ATP as a high energy molecule, what they mean is a high *Gibbs* energy molecule.

For all of this to work, the cell has to be able to make ATP, for example from ADP by running the hydrolysis reaction backwards:



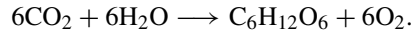
but this reaction has an unfavourable $\Delta_r G^\circ$ of $+30 \text{ kJ mol}^{-1}$ and so will not go on its own. As with peptide bond formation, Nature drives the formation of ATP by coupling it to another reaction, such as the oxidation of glucose.

This oxidation is often described as the fundamental source of ‘energy’ for many living systems, including ourselves. The overall reaction is



and this has a very large negative $\Delta_r G^\circ$ of $-2880 \text{ kJ mol}^{-1}$. In Nature the oxidation of one molecule of glucose is coupled by a very complex series of enzymatically controlled reactions to the formation of around 38 molecules of ATP from ADP, and in this way the high energy ATP molecules needed in many other processes in the cell are generated.

We obtain sugars, such as glucose, from plants which synthesize them from carbon dioxide and water, releasing oxygen in the process. The formation of glucose in this way is simply the reverse of the oxidation given above:

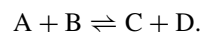


However, this reaction has a very large positive $\Delta_r G^\circ$ so how can it be made to go? The answer is that plants utilize the energy from light, in a process known as *photosynthesis*, to force this reaction. A very complex and subtle series of processes and reactions are used to harvest the energy from light and utilize it to form glucose – Nature has perfected this scheme over the millennia of evolution that have led to the green plants we know today.

The coupling of an unfavourable reaction to a favourable one is absolutely crucial in the chemistry of life. We can only marvel at the subtle and efficient way in which Nature is able to achieve this coupling.

8.5 Equilibrium and rates of reaction

Suppose that we have an equilibrium between reactants A and B and products C and D:



Let us start out with just A and B mixed together; they will react at some rate to generate some of the products C and D. However, the moment these are formed they will start to react together and, via the reverse reaction, regenerate the reactants A and B.

The more of the products C and D that are formed, the faster the reverse rate becomes; in contrast the more of the reactants A and B that are used up the slower the forward rate becomes. We know that eventually we will reach the equilibrium point at which the concentrations are all constant – what must have happened therefore is that the rates of the forward and reverse reactions have become equal. When this is the case, as fast as A and B are removed by the forward reaction they are replenished by the reverse reaction in such a way that their concentrations do not change. Equilibrium is thus a dynamic situation – it is not that the reactions have stopped, it is just that the rate of the forward and back reactions are equal so that it appears that nothing is happening.

This brings us on to the whole topic of the rates of reactions – something which we have been carefully ignoring, or at least sidestepping, up to now. The problem is that even if a reaction is favourable in thermodynamic terms, i.e. has a large negative $\Delta_r G^\circ$, this does not guarantee that the reaction will actually take place at a measurable rate.

For example, the oxidation of glucose is accompanied by a very large negative $\Delta_r G^\circ$ of some $-2880 \text{ kJ mol}^{-1}$, yet we can go out and buy glucose powder safe in the knowledge that it will not burst into flames spontaneously. The reaction is thermodynamically feasible, but kinetically very slow.

Other reactions are both thermodynamically feasible and fast. For example, the neutralization of acids and bases (essentially the aqueous phase reaction $\text{H}_3\text{O}^+ + \text{OH}^- \longrightarrow 2\text{H}_2\text{O}$) is both thermodynamically feasible and very fast. Even reactions in which the position of equilibrium lies close to the reactants can come to equilibrium quickly. For example, the dissociation of ethanoic (acetic) acid has an equilibrium constant of only 10^{-5} but nevertheless the equilibrium is established very quickly once the acid is dissolved in water.

Reactions involving ions – particularly if they are oppositely charged as in the case of the neutralization of acids and alkalis – tend to be quite fast, and similarly reactions involving simple proton transfer (for example from ethanoic acid to water) are often rapid. However, reactions involving the breaking and making of bonds (say to carbon) are likely to proceed much more slowly.

In the next chapter we will look at the factors which control the rates of reactions and then go on to see what a study of reaction rates can tell us about the mechanism of a reaction.