UNIVERSITY OF CAMBRIDGE

Department of Chemistry

Part IA Chemistry
Lent Term 2005

ENERGETICS AND EQUILIBRIA

Nicolas Carnot (1796–1832)

[Classical thermodynamics] is the only physical theory of universal content, which I am convinced, that within the framework of applicability of its basic concepts will never be overthrown.
Albert Einstein

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

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

Dr James Keeler

Contents

1 Introduction

These lectures are concerned with a very important topic in chemistry (and, more generally, in any molecular science): what makes a reaction 'go' and what determines to position of equilibrium. Put another way, we will be looking into what is the *driving force* for chemical reactions in order to explain why some reactions go entirely to products, whereas some come to a position of equilibrium in which there are significant amounts of reactants still present.

We shall see there there is one very important physical law, the *Second Law of Thermodynamics*, which determines whether a reaction (or physical process) will 'go' and what the position of equilibrium is. The Law itself is simple to state, but working from this statement to practical relationships and ideas which we can apply is a fairly involved task. A substantial part of these lectures will be devoted to showing how the Second Law can be developed in this way; we will then go on to look at some applications.

Historically, the topic we are going to look at is usually called *Thermodynamics* although, as we shall see, there is a lot more to it than simply heat! The theory is quantitative; for example, we will see that we can calculate equilibrium constants and predict, in a quantitative way, how they vary with temperature.

Thermodynamics is expressed in mathematical language, but we must not get bogged down in the equations – we must remember that each equation is simply expressing some physical principle. If we keep sight of the physical principles, then the equations will take care of themselves. If we loose sight of the physical meaning, then we will soon get lost in the equations. The really important equations (which you might like to remember) are surrounded by boxes .

In this course we will develop the following relationships, which are perhaps the most important in the whole of chemical thermodynamics:

$$\boxed{\Delta_\mathrm{r} G^\circ = -RT \ln K} \qquad \boxed{\Delta_\mathrm{r} G^\circ = \Delta_\mathrm{r} H^\circ - T \Delta_\mathrm{r} S^\circ.}$$

In these K is the equilibrium constant and $\Delta_\mathrm{r} G^\circ$ is the *standard Gibbs energy change* for the reaction. This, as the second equation shows, can be computed from $\Delta_\mathrm{r} H^\circ$, the *standard enthalpy change* and $\Delta_\mathrm{r} S^\circ$, the *standard entropy change*.

Simple though these equations are, it will take us quite a while to arrive at them as quite a few new ideas need to be introduced. The effort will be worthwhile, though, as these equations, coupled with an understanding of how $\Delta_\mathrm{r} H^\circ$ and $\Delta_\mathrm{r} S^\circ$ are affected by chemical changes, are the basis of understanding chemical equilibrium.

Some additional material (not examinable) is available in the form of an appendix. This can be downloaded from `www-teach.ch.cam.ac.uk`; click on 'Teaching Materials'.

1.1 Books

You will find that any general physical chemistry text book has a section on Thermodynamics and Equilibrium which are the subject of these lectures. The problem is that most books tend to cover far more than we need at the moment, and also there is a tendency to couch the discussion in very mathematical language, which can sometimes obscure the underlying principles. So, when you consult a book, be prepared to be selective.

Probably the best book for this course is G J Price *Thermodynamics of Chemical Processes* (Oxford Chemistry Primers no. 56, Oxford University Press, 1998). Another useful book is P W Atkins *The Elements of Physical Chemistry* (OUP, any edition). This is a simpler version of *Physical Chemistry* (OUP, any edition) also by P W Atkins, which is an excellent book although it is rather comprehensive.

Why Chemical Reactions Happen by J Keeler and P Wothers (OUP, 2003) includes quite a lot of discussion of the ideas from this course, although mainly framed in non-mathematical language.

Atkins has also written a 'coffee table book' called *The Second Law* (Scientific American Library, 1994) which is a well illustrated and very readable informal account of thermodynamics and its applications.

2 The Second Law

2.1 Spontaneous processes

Once set going, some reactions 'go' completely to products with no further intervention from us

Similarly, some physical processes also go without any intervention from us:

The reverse of all these processes do not happen on their own, but we can often force these processes to take place by intervening.

Strong heating can dissociate ammonium chloride:
$$NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$$

Gases can be separated e.g. by liquefaction and fractional distillation

An object can be cooled using a refrigerator

These observations lead to the recognition that there are some physical and chemical processes with can be described as *spontaneous* or *natural*. Once started, such processes take place without any further intervention from us. The reverse of spontaneous processes do not take place naturally but can be forced to take place by intervention. What we are seeking is a physical principal or law which determines which processes will be spontaneous and which will not.

For chemical reactions the situation is a little more complex as it is not usually the case that a reaction either goes or does not go. Rather, the species involved come to a position of equilibrium which involves a particular ratio of reactants and products.

For example, when HCl dissolves in water, the dissociation is virtually complete

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-,$$
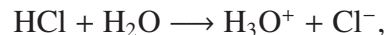
whereas when ethanoic acid dissolves only a small fraction dissociates (about 1% in a 0.1 M solution)

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-.$$
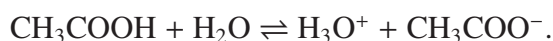
So, for chemical reactions we need to find a physical law or principal which allows us to predict the position of the equilibrium.

2.2   Energy minimization

A tempting idea is that reactions are spontaneous because the products are 'more stable' than the reactants. What do we mean by 'more stable'? Usually we think of this as meaning 'lower in energy'.

If reactions take place because the products are lower in energy than the reactants, then the implication is that spontaneous reactions must give out heat, as they are accompanied by a reduction in energy. In other words, they must be exothermic. Does this work out in practice?

$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s) \qquad \Delta_r H° = -176 \text{ kJ mol}^{-1}$$

$$CH_4(g) + 2O_2(g) \longrightarrow 2H_2O(g) + CO_2(g) \quad \Delta_r H° = -890 \text{ kJ mol}^{-1}$$

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s) \qquad \Delta_r H° = -1204 \text{ kJ mol}^{-1}$$

$$NaOH(s) \text{ dissolving in water} \qquad \Delta_r H° = -45 \text{ kJ mol}^{-1}$$
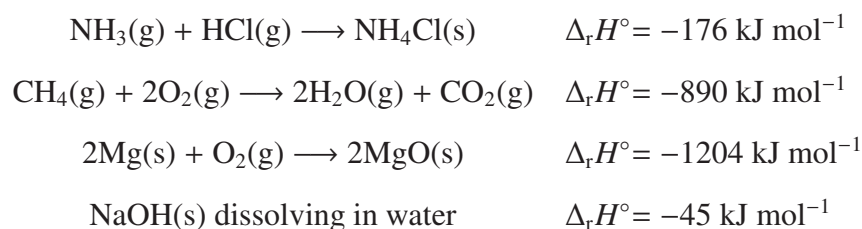
These are all spontaneous exothermic processes, but we can think of examples of processes which are spontaneous but are *not* exothermic:

$$NH_4NO_3(s) \text{ dissolving in water} \quad \Delta_r H° = 45 \text{ kJ mol}^{-1}$$

$$\text{mixing of inert gases} \qquad \text{no energy change}$$
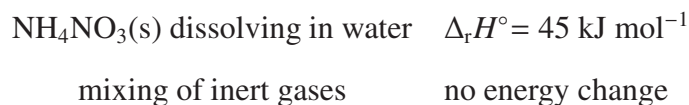
It is clear that the idea that spontaneous processes *have* to be exothermic is not correct.

Chemical equilibrium also illustrates the point well: for example, the dimerization of NO_2 to give N_2O_4:

$$2NO_2(g) \rightleftharpoons N_2O_4(g);$$
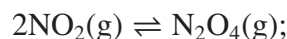
at 25 °C the equilibrium mixture consists of about 70% N_2O_4. The reaction going from left to right involves making a bond (between the two nitrogen atoms) and so it is not surprising that this reaction is exothermic. The reverse, in which the bond is broken, therefore has to be *endothermic*, that is it heat is absorbed.

Suppose we start with pure NO_2 and then allow the system to come to equilibrium. We can actually do this experiment by first lowering the pressure, as this favours dissociation (dissociation involves increasing the number of moles of gas); at sufficiently low pressures it is found that very little of N_2O_4 is present. If we then increase the pressure up to, say, one atmosphere, the position of equilibrium changes and some N_2O_4 is formed; this is illustrated in the picture below. The reaction involved is the exothermic process:

$$2NO_2(g) \longrightarrow N_2O_4(g).$$
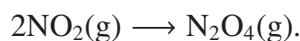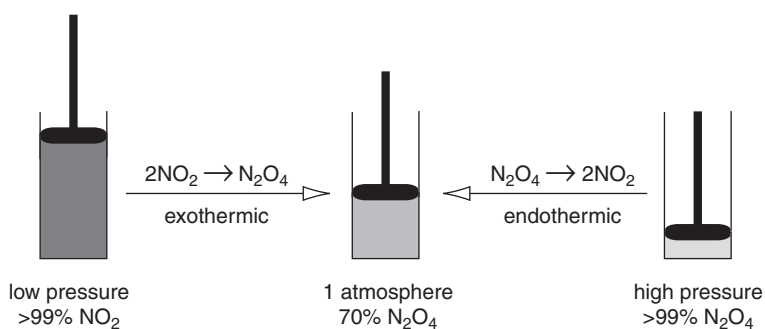
Illustration of how the equilibrium between N_2O_4 and NO_2 can be altered by altering the pressure. Since NO_2 is dark brown and N_2O_4 is colourless the shift in the position of equilibrium can easily be detected by observing the brown colour.

On the other hand, we can approach equilibrium by starting with the pure product, N_2O_4. Experimentally, this can be achieved by increasing the pressure on the system; this favours the dimer and at high enough pressures dimerization is essentially complete. If we then decrease the pressure back to one atmosphere some of the dimer dissociates to NO_2 as the equilibrium position is approached. The reaction involved is the endothermic process:

$$N_2O_4(g) \longrightarrow 2NO_2(g).$$
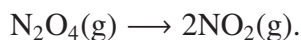
We see that the equilibrium position can be approached *either* starting from solely reactants or solely products. Approaching equilibrium from one side involves an *exothermic* process and approaching from the other side involves an *endothermic* process; both processes are spontaneous.

In summary, it is clear from our experience that spontaneous processes do *not* need to be exothermic. Energy minimization is *not* the criterion for a spontaneous process.

2.3   The Second Law

It is the Second Law of Thermodynamics which governs whether or not a process is spontaneous; we will simply state the law and then go on to explore what it means and what its consequences are.

In a spontaneous process the entropy of the Universe increases

Entropy is a property of matter, just like density and heat capacity. It is given the symbol S and has units $J\ K^{-1}$ or, for a molar quantity, $J\ K^{-1}\ mol^{-1}$.

But what is *entropy*? We will explore this is two ways: the first starts by thinking about how the molecules are distributed amongst the energy levels; the second defines entropy in terms of heat changes.

2.4   Molecular basis of entropy

Entropy is often described as being associated with 'randomness'. So, for example, a gas has higher entropy than a liquid, which in turn has higher entropy than a solid. But what do we mean by 'randomness'? We will see in the next section that by thinking about the energy levels which molecules occupy we can define precisely what we mean by 'randomness' and come to a clear understanding of the molecular basis of entropy.
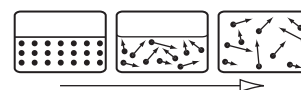
The entropy of a gas is greater than that of a liquid which in turn is greater than that of a gas. This increase in entropy can be associated with the increasing freedom with which the molecules move as we go from a solid to a gas.

2.4.1 Energy levels

In the *Shapes and Structures of Molecules* course you came across the idea that molecules have quantized energy levels. Each molecule has available to it a set of energy levels associated with translation, rotation, vibration and electronic structure. At any one moment, a given molecule is in a particular energy level corresponding to a certain amount of translation, rotation etc.

In a macroscopic sample there are a very large number of molecules (10^{20}, say) and each of these has available to it very many energy levels. The question is, how do the molecules distribute themselves amongst the available energy levels?

To answer this question in detail is clearly an impossibly difficult task simply because the numbers of molecules and levels is so high. However, it turns out that such a large assembly of molecules behaves in a way which can be described using statistics and the thermodynamic properties are related to this statistical analysis; we do not need to know the details of what each individual molecule is doing.

2.4.2 Ways of arranging things

We start by imagining a system which has a certain number of molecules, occupying a fixed volume and with a certain amount of energy. Neither molecules nor energy is allowed to flow into or out of the system.

To make the numbers tractable, we will suppose that there are just 16 molecules in our system, and that there are five energy levels with energy 0, 1, 2, 3, 4 units. We will also suppose that the system has 15 units of energy. These numbers are very very much smaller than we would find in a real system, but they are large enough to show the essential details.

One possible distribution of molecules amongst the energy levels is:

energy	0	1	2	3	4
population, n_i					

We can quickly confirm that all 16 molecules are accounted for

$$8 + 4 + 2 + 1 + 1 = 16$$

and that the total energy, found by multiplying the population of level *i* by its energy and summing over all levels, is 15 units

$$8 \times 0 + 4 \times 1 + 2 \times 2 + 1 \times 3 + 1 \times 4 = 15.$$

There are clearly lots of different ways of slotting the molecules into the energy levels to give this overall distribution. For example, any one of the sixteen molecules can be in the level with energy = 3. In fact, the total number of ways, *W*, that a particular distribution can be achieved is given by

$$W = \frac{N!}{n_0! \, n_1! \, n_2! \, n_3! \, n_4!}$$

where n_i is the *population* of level *i* i.e. the number of molecules in that level and *N* is the total number of molecules. *n*! is called '*n* factorial' and is computed from

$$n! = n \times (n-1) \times (n-2) \ldots 1$$

The five energy levels available in our hypothetical system.

so, for example, $3! = 3 \times 2 \times 1 = 6$. For reasons we cannot go into here $0! = 1$.

In fact this expression for W is computed assuming that the molecules are distinguishable from one another. Clearly this is not actually the case, but assuming it is makes the mathematics simpler and does not affect the final outcome; we will therefore continue with this expression.

For the distribution shown above we can easily work out that $W = 1.1 \times 10^7$.

Another distribution for the 16 molecules with a total of 15 units of energy is

energy	0	1	2	3	4
population, n_i					

This has $W = 7280$. Another distribution is

energy	0	1	2	3	4
population, n_i					

This has $W = 1.3 \times 10^5$. Clearly there are many other possible distributions we could think of.

2.4.3 The most probable distribution

At this point we introduce the hypothesis that the system has no preference for one arrangement of molecules over any other. We can imagine that, as the molecules jostle and collide with one another, the molecules are being constantly moved from one level to another, thus continuously changing their arrangement amongst the energy levels.

Each arrangement of molecules belongs to one of the possible distributions. The number of arrangements which correspond to the same distribution are the number of ways, W, in which that distribution can be achieved.

The greater the number of ways (arrangements) that a particular distribution can be achieved, the more likely it is that distribution will be observed. In other words, as the molecules constantly rearrange themselves, a distribution which can be achieved in a greater number of ways will occur more often.

It turns out that one distribution has a larger value of W than all of the others; in this case it is the first distribution given. This distribution is called the *most probable distribution*.

As the number of particles becomes larger, this most probable distribution becomes overwhelmingly more probable (i.e. has the largest value of W) than any of the others and we can safely assume, to all intents and purposes, that the particles are distributed in this way.

2.4.4 The Boltzmann distribution

To find the most probable distribution we need to maximise W for a given total number of particles and total energy; the details of how this is actually done are well beyond the present course. We will simply content ourselves to use the outcome of this calculation, which is that the most probable distribution is that known as the *Boltzmann distribution*. In this, the number of molecules

in level i, n_i, which has energy ε_i is given by

$$n_i = n_0 \exp\left(-\varepsilon_i/kT\right)$$

where it is assumed that the lowest energy level, with $i = 0$, has energy 0; n_0 is the population of this level.

k is *Boltzmann's constant*, which in SI has the value 1.38×10^{-23} J K^{-1}; k is related to the gas constant, R: $R = N_A k$, where N_A is Avogadro's number. It follows that kT has the dimensions of energy, making the argument of the exponential dimensionless, as required.

In words, the Boltzmann distribution says that as the energy of a level increases its population decreases. Levels whose energies are much greater than kT have vanishingly small populations, whereas those whose energy is less than or comparable to kT have significant populations. The ground state, level 0, is always the most highly populated.

Thus, as the temperature is raised, molecules move to higher energy levels. At very low temperatures, the molecules all cluster in the lowest levels. From a knowledge of the energy levels of individual molecules and the way in which molecules are distributed amongst them we can calculate the bulk properties of matter. The theory thus connects the microscopic world of quantum mechanics with the macroscopic world of thermodynamics.

2.4.5 Entropy and distributions

Boltzmann postulated that the entropy was related to the number of ways that a distribution could be achieved:

$$S = k \ln W \tag{2.1}$$

Despite its simplicity, this is undoubtedly one of the most profound results in physical science. This relationship puts into quantitative form the idea that an increase in 'randomness' represents an increase in entropy. Randomness is measured as the number of ways, W, that a particular distribution can be achieved; in practice, this distribution will be the most probable distribution. We can see how Eq. 2.1 works in practice by considering some particular cases.

Heating the system

The heat supplied to the system is stored as internal energy of the molecules. Increasing the internal energy of the molecules means that they must move up to higher energy levels. As the molecules spread themselves out more amongst the energy levels, there are more ways of achieving the resulting distribution, so from Eq. 2.1 the entropy goes up.

Expanding the system

Quantum mechanics tells us that as the system is expanded the spacing of the energy levels decreases. Thus there are more energy levels available to the molecules (that is, levels within kT of the ground state), so the molecules are distributed over more levels and W is increased. Thus increasing the volume increases the entropy.

A physical transformation, such as solid going to liquid or gas, is also associated with a large increase in the number of energy levels available to
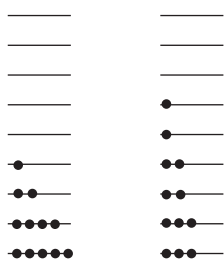
Visualization of how the population of energy levels depends on kT. The size of kT is indicated in relation to the energy levels by the arrow: $T_2 > T_1$. Note how the molecules move to higher levels as the temperature increases, but the population always tails off in the higher energy levels.
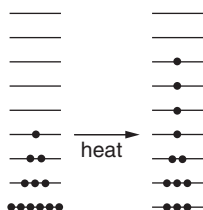
Heating a system causes its internal energy to rise and hence the molecules to move to higher levels. The arrangement on the right can be achieved in a larger number of ways that that on the left, and is thus of higher entropy.
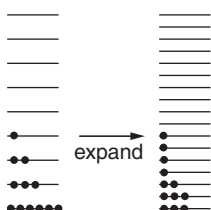
Expanding a system causes its energy levels to move closer together and hence the molecules can spread themselves over more levels. The arrangement on the right can be achieved in a larger number of ways that that on the left, and is thus of higher entropy. Note that energy is conserved in this expansion.

the system. In a solid the molecules (or atoms) are only able to vibrate about fixed positions in the lattice and so only vibrational energy levels are available to them. In a liquid or gas the molecules are free to translate, and this gives them access to the large number of translational energy levels; thus W is larger and the entropy of the liquid or gas is much greater than that of the solid.

The effect of temperature

We have seen that supplying energy to the system increases its entropy. However, the size of the entropy change depends on the temperature of the system. This is illustrated in the diagram below.
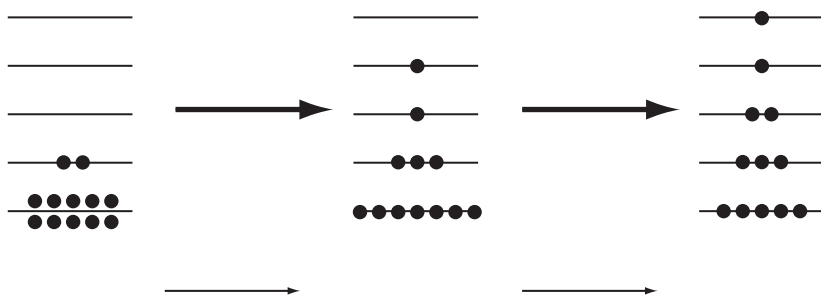
On the left is shown a 'cold' system which has little energy: the particles are clustered in the lower levels. When six units of energy are added the particles move up the ladder of levels and we obtain the distribution in the middle. As expected, W increases.

Now if we add a further six units of energy, the particles can move up further, and we obtain the distribution shown in the right. Again, W increases. However, the crucial thing to notice is that the increase in W is much less when going from the 'warmer' to the 'hottest' system than it was when going from the 'coldest' to the 'warmer' system.

We therefore conclude that the increase in entropy resulting from a certain amount of heat being supplied is *greater* the lower the temperature of the system.

2.4.6   Entropy as a microscopic property: summary

To summarize what we have found so far:

- Molecules have available to them a large number of energy levels. For a given total energy and number of molecules, any arrangement of the molecules amongst the energy levels is possible; however, in practice one such arrangement is overwhelmingly more probable than the others. This arrangement corresponds to the Boltzmann distribution.

- The entropy is related to the number of ways, W, a particular arrangement can be achieved: $S = k \ln W$.

- Supplying energy to the molecules (in the form of heat) increases W and hence the entropy.

- Increasing the number of energy levels available, for example by increasing the volume of a gas, increases W and hence the entropy.

- The entropy increase resulting from supplying a certain amount of energy is greater the lower the temperature of the system.

At this point we will have to abandon further discussion of this microscopic approach. It can be developed much further to provide a complete description of chemical equilibrium in terms of molecular energy levels – the theory is called *Statistical Thermodynamics* and is covered in our second year course. However, a rather simpler approach is to use the 'classical' version of thermodynamics in which entropy is defined in a different way.

This is not to say that a statistical view of entropy is not useful – far from it. We will appeal frequently to these ideas when we want to rationalize or understand trends in entropies.

2.5   Classical view of entropy

In 'classical' thermodynamics we define entropy in the following way:

$$\boxed{dS = \frac{\delta q_{\text{rev}}}{T}.} \tag{2.2}$$

This gives the small change in entropy, dS, when a small amount of heat, δq_{rev}, is absorbed by an object at temperature T under reversible conditions. We have used the language of calculus to write the small change in S as dS.

We will discuss what 'reversible conditions' means later on in section 4.4.1 on p. 21.

We cannot 'prove' that this definition of entropy is correct; all we can do is accept it and show that its predictions are in accord with the Second Law and our experience.

Let's start this by thinking about what happens when heat is supplied to an object. In section 2.4.5 on p. 8 we saw that this results in an increase in the entropy. This is precisely what Eq. 2.2 predicts: if the system absorbs heat, δq will be positive (endothermic) and so dS will also be positive implying that the entropy *increases*, just as expected. Our definition of entropy thus fits in with this expectation.

In Eq. 2.2 the entropy change depends inversely on the temperature. This means that the entropy increase is *greater* the cooler the object to which the heat is supplied. We came to the same conclusion when discussing the microscopic basis of entropy.

Try as we might, Eq. 2.2 still seems rather abstract and to have little connection with the real world of chemical reactions and equilibria. In the next section, we will put this definition to use and show that is has real predictive power.

2.6   The Second Law in action: how to make ice

In this section we are going to use the Second Law:

In a spontaneous process the entropy of the Universe increases

to explain how to make ice from water.

2.6.1   Separating the Universe into the system and the surroundings

It is important to note that the Second Law says that the entropy of the *Universe* increases. So, we have to think not just about the entropy changes in the thing we are interested in (the chemical or physical process), but of the whole Universe. This seems like a very difficult task, but we will see that because the Universe is so large, it is relatively simple to calculate its entropy change.

The way we proceed is to divide the Universe into two parts:

- the *system*, which is the thing we are interested in i.e. the chemical species which are reacting;

- the *surroundings*, which are the rest of the Universe.

We can the write the entropy change of the universe, ΔS_{univ}, as the sum of the entropy change of the system, ΔS_{sys}, and that of the surroundings ΔS_{surr}:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}.$$

To evaluate whether or not a process will be spontaneous, we need to compute the entropy change of the system and the surroundings; this enables us to find the entropy change of the Universe, which we can then examine in the light of the Second Law.

The Universe is separated into the part we are interested in—the system, and the rest—the surroundings. For example, the system would be our chemical reactants in a beaker and the surroundings would be the bench, the laboratory and everything else in the Universe.

Entropy change of the system

As entropy is a property of matter, ΔS_{sys} can be evaluated from tabulated values of the entropies of substances. We will see later in section 6.1 on p. 31 how such values are determined experimentally.

Entropy change of the surroundings

ΔS_{surr} initially represents more of a challenge. How can we find the entropy change of something as large as the rest of the Universe?

We usually arrange it that the only thing which is exchanged between the system and the surroundings is *heat*; such a system is said to be *isolated*, which means that no exchange of matter is allowed between the system and the surroundings. The entropy change of the surroundings is simply a result of the gain or loss of heat.

We can thus compute the entropy change directly using the definition of entropy, Eq. 2.2 on p. 10:

$$\mathrm{d}S = \frac{\delta q_{\text{rev}}}{T}.$$

For the case of the *surroundings* there are two special circumstances which make it possible to use this equation in a simple way. Both of these arise because the surroundings are very large (the rest of the Universe!).

- The temperature of the surroundings does not change when they absorb heat from, or lose heat to, the system;

- any heat exchanged with the system can be considered as reversible from the point of view of the surroundings.

These points mean that the very large surroundings are equally 'happy' to give up or receive energy, something which is not true of the much smaller system. We can therefore write, for the surroundings, that

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T_{\text{surr}}}. \tag{2.3}$$

This has been written for a finite change: q_{surr} is the heat absorbed by the surroundings, T_{surr} is their temperature and ΔS_{surr} is the entropy change of the surroundings.

So, what this boils down to is that to determine the entropy change of the surroundings we just need to know how much heat is transferred to (or from) the surroundings.

Heat changes of the surroundings

In an exothermic process the heat given out by the system is absorbed by the surroundings. Conversely, in an endothermic process the surroundings supply heat to the system. We can see that the heat change of the surroundings is *opposite* in sign to that of the system

$$q_{\text{surr}} = -q_{\text{sys}} ,$$

where q_{sys} is the heat change of the system. Using this, and assuming that the surroundings are at the same temperature as the system, we can write the entropy change of the surroundings as

$$\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{T_{\text{sys}}} .$$

So to compute the entropy change of the *surroundings* we simply need to know the heat change of the *system*.

The entropy change of the Universe

Using the above result, we can therefore write

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}.$$

as

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \frac{q_{\text{sys}}}{T_{\text{sys}}} .$$

This is a practical relationship that we can use to discuss chemical and physical processes.

2.6.2   Water freezing

If water freezes to ice, there is clearly a reduction in entropy (liquid $\longrightarrow$ solid), so ΔS_{sys} is negative. For the process to be spontaneous (i.e. for ΔS_{univ} to be positive), therefore, we have to make ΔS_{surr} sufficiently positive to overcome the negative ΔS_{sys}.

How do we make a positive ΔS_{surr}? As $\Delta S_{\text{surr}} = -q_{\text{sys}}/T$ we need to have a negative q_{sys}, i.e. the process must be exothermic. We know that ice melting

exothermic   endothermic
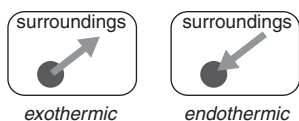
Illustration of the heat flow between the system (the black circle) and the surroundings. An exothermic process results in the flow of heat into the surroundings; an endothermic process results in the flow of heat out of the surroundings.

to water is an endothermic process, so the reverse, water freezing to ice, is therefore exothermic.

$$\text{ice} \xrightarrow{\text{endothermic}} \text{water}$$

$$\text{water} \xrightarrow{\text{exothermic}} \text{ice}$$
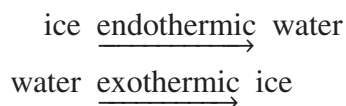
From $\Delta S_{\text{surr}} = -q_{\text{sys}}/T$ it follows that ΔS_{surr} will be positive for water freezing to ice. For ΔS_{surr} to be sufficiently positive to overcome the negative ΔS_{sys}, the temperature has to be *below* a certain value; the overall idea is illustrated below.
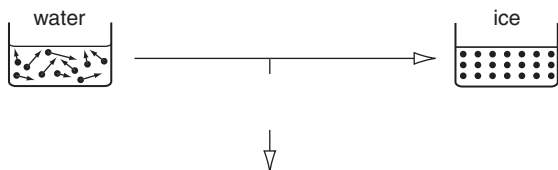
This is why water freezes only when the surroundings are below a certain temperature. This point can be illustrated with some numbers.

This is why we have to put water in the freezer to make ice. It is not that the cold freezer 'sucks out the heat'. Rather, it is so that the temperature of the surroundings are low enough that the entropy increase of the surroundings is large enough to compensate for the entropy decreases of the system.

Equilibrium

We have seen that a spontaneous process has $\Delta S_{univ} > 0$ and that a process in which $\Delta S_{univ} < 0$ does not take place. What about the case where $\Delta S_{univ} = 0$, in which there is *no* change in the entropy of the Universe?

In the case of water freezing to ice we can compute the temperature at which $\Delta S_{univ} = 0$.
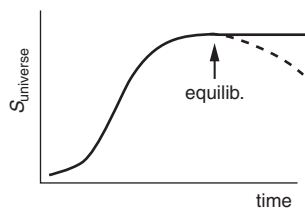
In a spontaneous process the entropy of the Universe increases; once equilibrium has been reached the entropy is at a maximum. Once at equilibrium no further change takes place, as this would inevitably lead to a reduction in the entropy of the Universe, as indicated by the dotted line.

In summary:

- The entropy of the Universe increases in a spontaneous process;

- ΔS_{univ} is zero at equilibrium.

It therefore follows that the entropy of the Universe increases in a spontaneous process and reaches a *maximum* at equilibrium.

The way forward

We have begun to see how the Second Law can be used to predict which processes will and will not take place, but we are quite some way yet from being able to describe chemical equilibrium. To do this we need to introduce some additional ideas, in particular the *Gibbs energy*, but before that we need to back-track somewhat and sharpen-up our understanding of the different forms of energy we will encounter. This is the domain of the *First Law of Thermodynamics*.

3 The First Law of Thermodynamics

The First Law of Thermodynamics is a statement about the conservation of different forms of energy. Like the Second Law, it is based on experience.

In words, the First Law says that *energy cannot be created or destroyed but is just transformed from one form into another*.

The 'forms' of energy are *heat*, *work* and *internal energy*. Heat and (mechanical) work are perhaps familiar concepts, whose precise definitions we will consider in the following sections. Internal energy is something that objects posses – it is a property of matter. The internal energy of a system can be changed by supplying heat to it or by the system doing work.

The First Law can be expressed mathematically in the following way. If we take a system from state A to state B, then there is a definite change in the internal energy, ΔU: $\Delta U = U_B - U_A$ where U_A and U_B are the internal energies of the system in state A and state B. Such a change can be brought about by the system absorbing a certain amount of heat, q, and a certain amount of work, w, being done on the system. The First Law relates these three quantities:

$$\boxed{\Delta U = q + w.} \tag{3.1}$$

q is the heat absorbed by the system: it will be positive if heat flows into the system (an endothermic process) and negative if heat flows out of the system (an exothermic change). w is the work done on the system: it will be negative if the system does work on its surroundings.

3.1 What is heat?

Heat is not really a thing – it is not a fluid or a substance. Rather it is the means by which energy is transferred from a hotter body to a cooler one in order to equalize their temperatures.

It is very hard to talk about heat without using words which imply that it 'flows' between objects. Inevitably we will fall into this error, but we must remember that heat is something that is 'done' to an object, not something which 'flows' into an object.

Heat is a form of energy and so in SI it has units of Joules.

3.2 What is work?

Work is done when a force moves. A force F moving a distance x does work $F \times x$. An example would be the work done pushing an object along a rough surface, where the force is due to friction. Like heat, work is something that is done to objects – for example when they are compressed by the action of an external force.

Like heat, work is a form of energy and in SI it has units of Joules.

3.3 What is internal energy?

Internal energy is quite distinct from heat and work. It is a property that an object possesses; different substances have different internal energies, and the
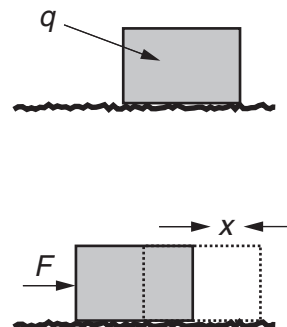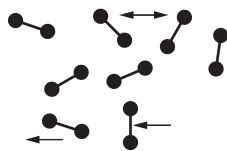
amount of internal energy also depends on temperature, pressure and so on.

Internal energy is the sum of the kinetic energy of the particles, together with their energies of interaction, including bond energies. The internal energy is locked up inside a substance as the kinetic energy of the particles and the interactions between the particles, particularly chemical bonds. Internal energy is closely analogous to potential energy in mechanical systems – it is stored up energy.

Internal energy is also closely related to temperature. For an ideal gas (in which there are no interactions between particles) all of the internal energy is present as the kinetic energy of the particles. If the temperature is raised, the particles move more quickly and the internal energy is therefore raised. Similarly, for solids and liquids an increase in temperature implies an increase in internal energy.

3.4   State functions and path functions

There is another important distinction between U on the one hand and q and w on the other. U is a *state function*, whereas q and w are *path functions*. State functions play a particularly important role in thermodynamics and several such functions will be introduced in this course.

3.4.1   State functions

A state function is one whose value depends only on the state of the substance under consideration; it has the same value for a given state, no matter how that state was arrived at.

By state we mean specified temperature, pressure, chemical composition and so on – in fact all the necessary variables to define the state of the system. For example, the state of an ideal gas is specified completely by the number of moles, the temperature and pressure. For a mixture of ideal gases, we would also need to know the amount of each substance present.

For chemical reactions the idea of a state function is used in Hess's Law. For example, consider the cycle

$$C + O_2 \xrightarrow{\ \ \mathbf{1}\ \ } CO_2$$

$$\Big\downarrow \mathbf{2}$$

$$CO + \tfrac{1}{2}O_2 \qquad \mathbf{3}$$
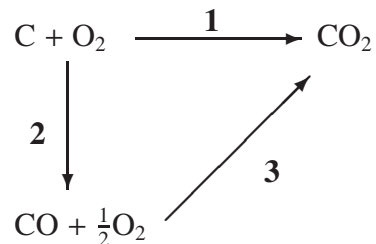
The change in (internal) energy on going from $C + O_2$ to CO_2 is the same whether it is done directly, step **1**, or via step **2** and then step **3**.

We have not proved that U is a state function. We will just appeal to experience and say that all we know about heat, work and internal energy in chemical and physical processes confirms that U is indeed a state function.

3.4.2 Path functions

The value which a path function takes depends on the path which the system takes going from A to B.

For example, consider the reaction between hydrogen and oxygen to give water: $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$. We could just let the hydrogen burn, releasing heat and doing no work. Alternatively, we could react the gases in a fuel cell, thereby creating electrical energy which could be used to drive a motor and hence do mechanical work, such as lifting a weight. The amount of heat and work done depends on how the overall conversion $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$ is carried out, that is on the path taken. Hence the description of heat and work as path functions.

Having now seen what U, q and w are, and the distinction between state and path functions, we can interpret the First Law in the following way

$$A \longrightarrow B \qquad \Delta U = U_B - U_A$$
$$= q + w.$$

State A has a certain amount of internal energy, U_A, and similarly state B has internal energy U_B. In going from A to B there is a change in internal energy $\Delta U = U_B - U_A$, which is the same regardless of the path taken between A and B. This energy can appear as heat or work, and these can be in any proportions provided that their sum, $q + w$, is equal to ΔU. The way in which the change in internal energy is partitioned between heat and work will depend on the path taken.

What the First Law really does is to establish the idea of internal energy, U, as a state function.

A change from A to B is accompanied by an increase in internal energy U. This can appear as heat or work, in any combination, provided that $\Delta U = q + w$. In the diagram, upward pointing arrows represent positive quantities, and downward pointing arrows represent negative quantities.

3.5 Sign conventions

Heat and work are signed quantities, and we need to have a convention about what the signs mean. The convention we use is that positive values correspond to those done to the system. For heat, q is the heat *absorbed by the system*. It is therefore *positive* for a change in which heat is absorbed by the system, that is an *endothermic* process, and *negative* for a change in which heat is given out by the system, an *exothermic* process.

For work, w is the work *done on the system*. This means that when a gas is compressed by an external force the work is positive, whereas when a gas expands by pushing against an external force the work is negative.

Sometimes it is convenient to think about the work done *by the system*. This is given the symbol w' and is simply the reverse of the work done on the system: $w' = -w$.

In going from state A to B there is a definite change in the value of a state function, such as U, as it has a particular value for A and for B; it is thus acceptable to write this change as ΔU, meaning $(U_B - U_A)$. In contrast, for a path function such as heat, was *cannot* talk about its value for state A or state B and hence a change in q 'Δq'. All we can specify is the amount of heat, q, involved in going from A to B. The Δ symbol is therefore only appropriate for state functions.

The way forward

We have seen that there is a strong distinction between, on the one hand, internal energy and, on the other, heat and work. This distinction is brought more sharply into light by considering what happens when a gas expands.

Unpromising though this may seem, we will find that this simple process allows us not only to appreciate the difference between state and path functions, but also to define what we mean be a *reversible* process.

4 Gas expansions

To explore the idea of heat and work as path functions, and to illustrate the important concept of reversibility, we will look at the work done when a gas expands. The results which we will obtain turn out to be practically useful and lead to ideas which are applicable in a much wider context. However, before starting on this we will remind ourselves about *gas laws*.

4.1 Gas laws

For n moles of a gas, the pressure, p, volume, V, and absolute temperature, T, are related by what is called an *equation of state* or *gas law*. An ideal gas is one which has the following equation of state

$$\boxed{pV = nRT} \tag{4.1}$$

where R is the gas constant (8.3145 J K^{-1} mol^{-1}). At a molecular level such a law is expected for a gas which is composed of molecules (or atoms) which do not interact significantly with one another and are negligibly small compared to the space between the molecules.

This gas law embodies *Boyle's Law*, which states that, at constant temperature, the volume and pressure are inversely proportional to one another and *Charles' Law*, which states that for a fixed volume the pressure is proportional to the temperature.

If the molecules start to interact with one another, the gas ceases to be ideal and no longer obeys the ideal gas law. For simplicity, we will assume that all of the gases we are dealing with are ideal – an approximation which is reasonable provided we stick to modest pressures and temperatures.

For non-ideal gases the equation of state is much more complex and different for each gas.

Exercise 1

4.2 How to think about a gas expansion

We start out by thinking of a gas confined inside a cylinder by a piston. The gas, cylinder and piston form our system, and, so that we can just focus on the work done by the gas, we will assume that the piston has no mass and that it moves without friction.

The pressure of the gas inside the cylinder is p_{int}, and the pressure of gas outside is p_{ext}. Both gas pressures exert a force on the piston; the higher the pressure the higher the force.

Suppose that the pressure outside is lower than the pressure inside. The forces on the piston will be such that it moves out. What is the work done? The key point to understand here is that the force which the system moves against is that due to the *external pressure*. Of course, the fact that the internal pressure is higher is the reason that the piston moves out, but nevertheless the force which is being pushed back is that due to the external pressure.

Suppose that the piston has area A. Then, as pressure is force per unit area, the force on the piston due to the external pressure is $p_{ext} \times A$. If the piston
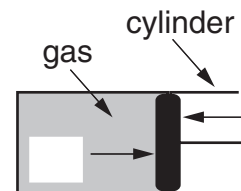
pressure × area
= (force/area) × area
= force

moves out by a small distance dx (we are using the language of calculus) then the small amount of work done by the gas, $\delta w'$, is

$$\begin{aligned}\delta w' &= \text{force} \times \text{distance} \\ &= p_{\text{ext}} A \times dx.\end{aligned}$$

area, A

The quantity $(A\,dx)$ is the volume by which the gas inside the piston has increased (recall that the volume of a cylinder is the area of the base times the height – here the base area is A and the height is dx). Writing this volume as dV, the work done is

$$\boxed{\delta w' = p_{\text{ext}}\,dV.} \tag{4.2}$$

The volume swept out by the piston of area A when it moves through a distance dx is $A \times dx$.

If we want to think in terms of the work done on the gas, w, then as $w' = -w$ (section 3.5 on p. 17), the relationship becomes

$$\delta w = -p_{\text{ext}}\,dV.$$

We can now use this relationship to find the work done in some special cases. Rather trivially, if the external pressure is zero, then clearly no work is done i.e. no work is done expanding against a vacuum.

4.3 Expansion against constant external pressure

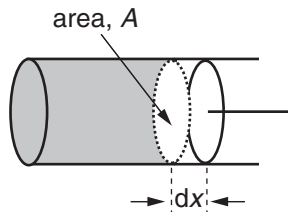If the external pressure is constant, Eq. 4.2 is easy to integrate. If the gas expands from volume V_i to volume V_f, then the work done is found by integrating between these two limits:
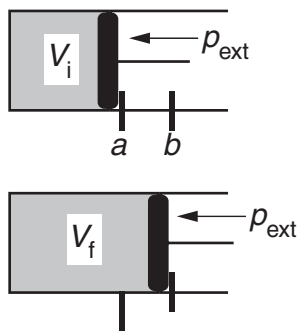
$$\begin{aligned}w' &= \int_{V_i}^{V_f} p_{\text{ext}}\,dV \\ &= p_{\text{ext}} \int_{V_i}^{V_f} dV \\ &= p_{\text{ext}} \big[V\big]_{V_i}^{V_f} \\ &= p_{\text{ext}}\,(V_f - V_i).\end{aligned}$$

On the second line we have assumed that p_{ext} is constant, and so it can be moved outside the integral. The final result is

Visualization of expansion against a constant external pressure. To start with the internal pressure is greater than the external pressure, so the piston wants to move out but is restrained from doing so by the peg a; the volume is V_i. When peg a is removed the piston moves out until it hits peg b; the volume is now V_f.

Example 1

$$\boxed{w' = p_{\text{ext}}\,(V_f - V_i).} \qquad \text{const. external pressure} \tag{4.3}$$

This expression assumes that throughout the expansion the internal pressure is always greater than the external pressure; remember that as the gas expands the internal pressure will fall.

If the external pressure exceeds the internal pressure, the gas will be compressed; the final volume will be less than the initial volume and so w' is negative. This is as expected, as in this situation work is done on the gas.

4.4   Expansion doing maximum work

For a given initial gas pressure in the cylinder, how can we arrange things so that the maximum amount of work is done? As it is the *external pressure* which provides the force against which the gas pushes, it follows that to maximize the work the external pressure needs to be as high as possible. However, this pressure cannot exceed the internal pressure, otherwise the gas would not expand but would instead be compressed.

So, to obtain the maximum work the external pressure needs to be infinitesimally less that the internal pressure.

If we start with this situation, the gas will expand and as a result the internal pressure will fall. Eventually the internal pressure will fall to the value of the external pressure, and the expansion will stop. To continue the expansion the external pressure needs to be lowered, again by an amount that makes it infinitesimally less that the internal pressure. Again, the gas expands until the pressures are equalized, and then once more we have to lower the external pressure.

In summary, the condition for doing the maximum work is that the external pressure should always be kept infinitesimally less than the internal pressure.

4.4.1   Reversible and irreversible processes

An expansion in which the external pressure is always just less than the internal pressure does the maximum work but takes place infinitely slowly. At any point the expansion can be turned into a compression simply by making the external pressure infinitesimally *greater* that the internal pressure. Such a process, whose direction can be changed by an infinitesimal change in some variable (in this case the pressure), is said to be *reversible*.

In contrast, an expansion against a fixed external pressure proceeds at a finite rate until the internal and external pressures are equalized. Such a process cannot be reversed by an infinitesimal change in the external pressure – rather it would need to be increased by a significant amount until it exceeds the internal pressure. Such a process is said to be *irreversible*. Spontaneous processes are inherently irreversible.

From the previous discussion we have seen that a reversible expansion of a gas does the maximum work. Although we only demonstrated it for the case of a gas expansion, it turns out to be generally true that any reversible process does the maximum work:

> **a reversible process is one in which the work is a maximum**
> *or* **the work done in a reversible process is a maximum.**

reversible processes:
• *infinitely slow*
• *at equilibrium*
• *do maximum work*

The converse is that an irreversible process always does less work than the corresponding reversible processes.

Reversible processes are also called *equilibrium processes*. The idea is that in a reversible process, such as a gas expansion, the system is always in balance (the external and internal pressures are only infinitesimally different) and so essentially in equilibrium.

irreversible processes (spontaneous):
• *go at finite rate*
• *not at equilibrium*
• *do less than the maximum work*

4.4.2   Reversible isothermal expansion of an ideal gas

If we assume that we have an ideal gas and that it is expanding reversibly we can integrate Eq. 4.2 on p. 20, $\delta w' = p_{ext}\,dV$, to find out the work done *by* the gas. To make the process reversible the external pressure is essentially equal to the internal pressure, $p_{ext} = p_{int}$, so

$$w' = \int_{V_i}^{V_f} p_{int}\,dV. \tag{4.4}$$

For an ideal gas

$$p_{int}V = nRT;$$

rearranging this gives us an expression for p_{int} in terms of V

$$p_{int} = \frac{nRT}{V}.$$

This can then be substituted into Eq. 4.4 and integrated

$$\begin{aligned}
w' &= \int_{V_i}^{V_f} \frac{nRT}{V}\,dV \\
&= nRT \int_{V_i}^{V_f} \frac{1}{V}\,dV \\
&= nRT\Big[\ln V\Big]_{V_i}^{V_f} \\
&= nRT \ln \frac{V_f}{V_i}.
\end{aligned}$$

On the second line we have imposed the condition of constant temperature, and so have taken the T outside the integral. So, the work done in the reversible, isothermal expansion of an ideal gas is

$$\boxed{w' = nRT \ln \frac{V_f}{V_i}} \qquad \text{isothermal, reversible, ideal gas.} \tag{4.5}$$

4.5   Heat changes in gas expansions

Having calculated the work done in a gas expansion, we can use the First Law to say something about the heat involved. For any gas expansion ΔU will be a certain fixed value, regardless of whether or not the expansion is reversible or irreversible (recall that U is a state function). Hence from the First Law

$$\Delta U = q + w \qquad \text{or} \qquad \Delta U = q - w'$$

it follows that if w' is a maximum in a reversible change, so too must q be a maximum (the signs get a bit confusing here – it is best to think of the absolute values of q and w' both being a maximum).
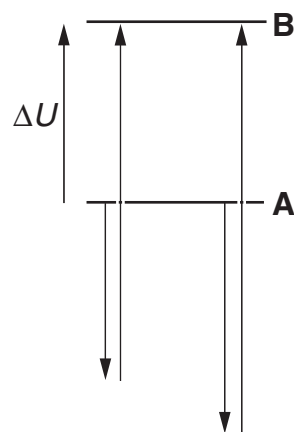
For the special case of an ideal gas, it turns out that U only depends on temperature. At a molecular level, this is because the internal energy of an ideal gas is present entirely as kinetic energy of the molecules (section 3.3 on p. 15). If the gas is heated, that is given energy, the only place that the energy can be stored is in the motion of the molecules. As there are no interactions between the molecules, altering the pressure or volume at constant temperature does not affect the internal energy.

So, for an isothermal expansion of an ideal gas $\Delta U = 0$, and hence from the First Law $0 = q - w'$ or $w' = q$. In section 4.4.2 we have calculated the value of w' so we immediately know the value of q.

What is happening in this isothermal expansion is that the work done in the expansion is exactly compensated for by the heat flowing in. If no heat flowed in, some of the internal energy would have to be converted to work, and as a result the temperature of the gas would drop. However, we specified that the process had to be isothermal, so heat must be supplied in order to maintain the temperature (internal energy) of the gas.

4.6 Entropy and the reversible heat

We can now understand more about the definition of entropy given in section 2.5 on p. 10:

$$\mathrm{d}S = \frac{\delta q_{\text{rev}}}{T}.$$

As we have seen, q is a path function so its value depends on the path taken. Entropy is defined in terms of the *reversible* heat, even if the process itself is not reversible.

This is a subtle point which it is worth spelling out again. If we have an irreversible process taking us from A to B, then, in order to calculate the entropy change, we need to work out what the heat would be *if* we were to go from A to B by a *reversible* path.

You can see that calculating entropy directly from the above definition is not very easy as we have to keep constructing imaginary reversible processes and then determining the heat involved. There are various ways of getting round this awkward point, which we will come to in due course.

The one exception to this is when calculating the entropy change of the surroundings. Recall from p. 12 that, from the point of view of the surroundings, any heat exchanged with it is reversible; hence we can write

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T_{\text{surr}}}.$$

Now that we have seen more precisely what a reversible process is, it is clearer why this heat exchange with the very large surroundings is reversible. The surroundings are essentially unaffected by the heat and so are indifferent to the direction of flow of heat. An infinitesimal change (for example in the temperature) will cause the direction to change: this is the characteristic of a reversible process.

4.6.1 Entropy change in an isothermal expansion of an ideal gas

Recall from the section 4.5 that for an isothermal change of an ideal gas $\Delta U = 0$, so that $q = w'$. It therefore follows from Eq. 4.5 that the heat ab-

sorbed in a reversible, isothermal expansion of an ideal gas is

$$q_{rev} = nRT \ln \frac{V_f}{V_i}.$$

The entropy change of the gas as a result of this expansion is, by definition, q_{rev}/T, so

$$\Delta S = nR \ln \frac{V_f}{V_i} \qquad \text{isothermal, ideal gas.}$$

Since entropy is a state function, this expression for the entropy change is valid for *any* isothermal expansion of an ideal gas from V_i to V_f, *whether or not the expansion is carried out reversibly*. Our expression for ΔS shows that the entropy increases as the volume increases, which is precisely the result we anticipated using statistical arguments (see section 2.4.5 on p. 8).

5 Internal energy, enthalpy and heat capacity

This section extends the discussion of the First Law (section 3 on p. 15) in some ways which will be very useful for us when it comes to discussing chemical equilibrium. The first thing we will do is to introduce a new state function called the *enthalpy*, H. You are already familiar with this from talking about 'ΔH' values for chemical reactions.

We shall see that the enthalpy and the internal energy are complementary functions which have the important properties that:

- the internal energy change, ΔU, is equal to the heat under *constant volume* conditions;

- the enthalpy change, ΔH, is equal to the heat under *constant pressure* conditions.

This section closes with a discussion of *heat capacities*. Unpromising though these quantities seem to be, they turn out to be the key to many important calculations. Not least of these is that heat capacities provide us with a practical way of determining the entropies of substances – an exceptionally important application which we will discuss in the next section.

5.1 Differential forms

So far we have written the First Law as $\Delta U = q + w$, where the Δ implies a finite change in U. We could just as well have written it for an infinitesimal change in U, using the language of calculus:

$$\mathrm{d}U = \delta q + \delta w.$$

We have been careful here to write δq and not $\mathrm{d}q$. This is because $\mathrm{d}q$ would imply 'a small change in the heat', but heat is not a state function so we cannot talk of a 'change in heat'. Rather, all we can do is talk of a small *amount* of heat, which is what δq implies. The same is true for work, so we write δw.

In section 4.2 on p. 19 we found that the work of expanding a gas was $\delta w = -p\mathrm{d}V$, so, if this is the only kind of work done, the First Law can be written

$$\mathrm{d}U = \delta q - p\,\mathrm{d}V. \qquad pV \text{ work only} \qquad (5.1)$$

Unless we say otherwise, we will assume that the only kind of work done is that due to gas expansions, and so use the form of the First Law given in Eq. 5.1.

Work can take many forms, such as that due to gas expansions, due to moving charges (a current) in an electrical field or due to expanding a surface. Work due to gas expansions is sometimes called 'pV work'.

5.2 Constant volume processes
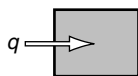
If we imagine a process taking place in a sealed container, that is at constant volume, then no work can be done as the gas cannot expand. In terms of

Eq. 5.1 the $p\,dV$ term is zero ($dV = 0$ as the volume does not change) and so

$$dU = \delta q_{\text{const. vol}} \qquad \text{constant volume}$$

This says that the heat absorbed under conditions of constant volume is equal to the change in internal energy; in other words, all the heat goes into internal energy. If we want to measure ΔU, therefore, all we have to do is measure the heat change under constant volume conditions.

It is important to realize that, for a given change, ΔU has a certain value because U is a state function. In the special case of a constant volume process ΔU is equal to the heat absorbed, but under other conditions although ΔU is no longer equal to the heat it still has a well defined value.

5.2.1 Heat capacities

When heat is supplied to an object its temperature usually increases; the more heat that is supplied the greater the temperature rise. The relationship between the heat supplied, q, and the temperature rise, ΔT, is

$$q = c\Delta T$$

where c is the *heat capacity* of the object. For infinitesimal quantities this relationship becomes $\delta q = c\,dT$.

The larger the object the greater the heat capacity. If we are talking about chemical substances it is convenient to use the molar heat capacity, C, which is the amount of heat needed to raise one mole of the substance through one degree. C has units of J K^{-1} mol^{-1}. Using this molar quantity the above equation becomes

$$q = nC\Delta T$$

where n is the number of moles.

For a process taking place at constant volume, we have seen in the previous section that the heat is equal to the change in internal energy: $\Delta U = q_{\text{const. vol}}$, so we can write

$$\Delta U = n\,C_V\,\Delta T$$

where C_V is the *molar heat capacity at constant volume*.

Writing this in the differential form we obtain

$$dU = C_V\,dT \qquad \text{constant volume} \qquad (5.2)$$

where we are now assuming that dU is the change in internal energy per mole (i.e. $n = 1$). Equation 5.2 can be rearranged to

$$C_V = \left(\frac{dU}{dT}\right)_{\text{constant volume}}. \qquad (5.3)$$

We have written 'constant volume' to remind ourselves that this only applies to constant volume processes. Mathematically, Eq. 5.3 can be expressed as a partial derivative:

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V} \qquad \text{definition of } C_V \qquad (5.4)$$

The 'curly d', ∂, indicates that only the variation of U with T is being considered, and the subscript V indicates that volume is to be held constant. Equation 5.4 is taken as the definition of the constant volume heat capacity.

5.3 Constant pressure processes – enthalpy

Processes taking place under constant pressure conditions are more common, especially in chemistry, where open apparatus 'on the bench' can be considered to be at constant pressure.

If we heat a gas at constant external pressure it will expand and by doing so it will do work. Thus, some of the heat is converted into work and some is converted to internal energy. For a given amount of heat, the increase in the internal energy will be less in a constant pressure process than in a constant volume one on account of part of the heat being converted to work.

It will be convenient to have a state function whose value is equal to this heat supplied at constant pressure; this function will be the constant pressure analogue of U.

The function we need is called the *enthalpy*, H and it is defined as

$$\boxed{H = U + pV} \qquad \text{definition of } H. \qquad (5.5)$$

Supplying heat to a gas held at constant pressure (here held in a cylinder by a piston) results in the gas expanding and so doing work against the external pressure. Some of the heat supplied increases the internal energy and some appears as work of expansion.

From this it follows that H is a state function as it is defined in terms of other state functions (U) and variables (p and V) which define the state of the system. It will be useful to alter the form of Eq. 5.5 so that it is expressed in terms of the *change* in H, dH.

The procedure is as follows: suppose that p changes by a small amount dp giving a new value ($p + dp$), likewise V changes by a small amount dV giving a new value ($V + dV$), and likewise U changes by a small amount dU giving a new value ($U + dU$). As a result of the changes in p, V and U, it is clear that H will also change by a small amount dH giving a new value ($H + dH$). So, from Eq. 5.5 we have

$$(H + dH) = (U + dU) + (p + dp)(V + dV).$$

Multiplying this out gives

$$H + dH = U + pV + dU + p\,dV + V\,dp + dp\,dV.$$

We ignore the last term, $dp\,dV$, because it is the square on an infinitesimal quantity; we also note that, as $H = U + pV$, the term H on the left and ($U + pV$) on the right will cancel to give

$$dH = dU + p\,dV + V\,dp. \qquad (5.6)$$

Equation 5.6 is called the complete differential of Eq. 5.5.

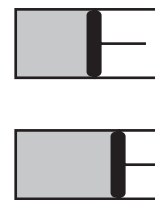Another way of thinking about how to take the complete differential is just to differentiate both sides of Eq. 5.5

$$dH = dU + d(pV)$$

and recognise that pV is a product of two functions and so needs to be differentiated using the usual rule

$$dH = dU + p\,dV + V\,dp.$$

Once we have seen how this works we can go straight from relationships like Eq. 5.5 to their complete differentials without doing the intermediate steps.

Now we substitute in the First Law, $dU = \delta q - p \, dV$ (Eq. 5.1 on p. 25), into Eq. 5.6

$$
\begin{aligned}
dH &= dU + p \, dV + V \, dp \\
&= \delta q - p \, dV + p \, dV + V \, dp \\
&= \delta q + V \, dp.
\end{aligned}
$$

Finally, we impose the condition of constant external pressure, which means that the term $V \, dp$ is zero (the change in p, dp, is zero), to give

$$
dH = \delta q_{\text{const. press.}}. \tag{5.7}
$$

What we have shown is that the enthalpy change is equal to the heat measured under conditions of constant pressure. With hindsight we can see that this is precisely why H is defined as it is (Eq. 5.5) so that it will have this useful property.

Just as with ΔU, we must not forget that ΔH has a defined value for a particular change, regardless of whether or not it is at constant pressure. It is only if the pressure is constant that q is equal to ΔH. Chemists tend to talk of 'heat of reaction' by which they normally mean the enthalpy of reaction. Enthalpies are the quantities which are most commonly tabulated.

5.3.1 Heat capacity at constant pressure

For a process taking place at constant pressure, we have just shown that the heat absorbed is equal to the change in H: $dH = \delta q_{\text{const. press.}}$. Following a similar line of argument as in section 5.2.1 on p. 26, we have

$$
dH = C_p \, dT \qquad \text{constant pressure}
$$

Since in a constant pressure process some of the heat supplied ends up as work of expansion, more heat is needed to raise the temperature of a gas at constant pressure than is needed at constant volume i.e. $C_p > C_V$. For an ideal gas $C_p - C_V = R$.

where C_p is the constant pressure molar heat capacity. Note that in this equation as the heat capacity is expressed per the mole, the enthalpy is also per mole. As with C_V, the usual definition of C_p is as a partial derivative

$$
\boxed{C_p = \left(\frac{\partial H}{\partial T} \right)_p} \qquad \text{definition of } C_p. \tag{5.8}
$$

5.3.2 Variation of enthalpy with temperature

Suppose we know the (molar) enthalpy, $H(T_1)$, of a substance at a particular temperature, T_1, but we want to know its (molar) enthalpy, $H(T_2)$, at another temperature T_2. This is quite a common situation as data are often tabulated at only a few temperatures, and these may not correspond to the temperature of interest.

Heat capacities are the key to finding how H varies with T. We start with Eq. 5.8

$$
C_p = \left(\frac{\partial H}{\partial T} \right)_p
$$

and rearrange this to give

$$
dH = C_p \, dT. \qquad \text{constant pressure} \tag{5.9}
$$

We have dropped the partial derivative symbol and moved to working with normal derivatives, but have made ourselves a mental note that all of what follows is only valid at constant pressure. Both sides of Eq. 5.9 can be integrated. First the left-hand side

$$
\int_{T_1}^{T_2} dH = \left[H \right]_{T_1}^{T_2}
$$
$$
= H(T_2) - H(T_1).
$$

This needs a little explanation. The integral of dx is just x, so in the same way the integral of dH is H. However, the limits of integration are T_1 and T_2, which means we need to evaluate H at these two temperatures. These values are written $H(T_1)$, meaning 'the value of H at temperature T_1', and likewise $H(T_2)$.

The right-hand side of Eq. 5.9 is also integrated, and we make the additional assumption that C_p does not vary with temperature, so it can be taken outside the integral

$$
\int_{T_1}^{T_2} C_p \, dT = C_p \int_{T_1}^{T_2} dT
$$
$$
= C_p \left[T \right]_{T_1}^{T_2}
$$
$$
= C_p \left[T_2 - T_1 \right].
$$

Putting the left- and right-hand sides together we have

$$
H(T_2) - H(T_1) = C_p \left[T_2 - T_1 \right] \quad \text{or} \quad H(T_2) = H(T_1) + C_p \left[T_2 - T_1 \right]. \quad (5.10)
$$

This is a practical relationship: if we know H at one temperature and the heat capacity, we can work out H at any other temperature (assuming that it is valid to consider C_p as constant in this range). Note that as C_p is a molar quantity, Eq. 5.10 gives the change in molar enthalpy. To compute the change for n moles, we simply multiply the term in C_p by n so that the terms becomes $nC_p \left[T_2 - T_1 \right]$.

Exercise 6
Exercise 7

It turns out that we can only measure changes in enthalpy rather than the absolute values of the enthalpies of substances. However, we will see in section 8.5 on p. 41 how a modified form of Eq. 5.10 can be used to convert ΔH values from one temperature to another.

5.4   Measurement and tabulation of heat capacities

Heat capacities turn out to be surprisingly useful when it comes to manipulating various thermodynamic quantities. They are easy to measure, as all we need to do is measure the temperature rise for a know heat input. The heat capacities of a great many substances have been measured and are available in tabulated form.

It is found that the heat capacity does vary with temperature, although generally not too strongly. To get around this, heat capacities are often expressed in the parametrized form
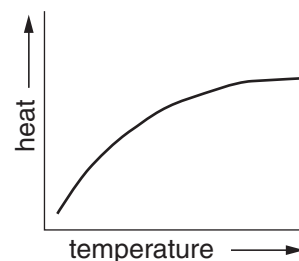
The heat capacity at a particular temperature is the slope at that temperature of a plot of heat supplied against temperature.

$$
C(T) = a + bT + \frac{c}{T^2}.
$$

We have written the heat capacity as $C(T)$, meaning that 'C is a function of T'. Armed with the values of the parameters a, b and c (which are tabulated), the heat capacity can be evaluated at any temperature.

6 Measuring entropy

We mentioned right at the start that the values of entropies of substances could be measured and were available in tabulated form. We are in a position to describe how this is done using the heat capacities introduced in the previous section.

6.1 Absolute entropies

Entropies can be evaluated from measurements of heat capacities in the following way. The definition of entropy is, in differential form

$$dS = \frac{\delta q_{\text{rev}}}{T}.$$

If we think about a process at constant pressure, the heat is equal to the enthalpy change: $\delta q_{\text{const. press.}} = dH$ (Eq. 5.7 on p. 28), so

$$dS = \frac{dH}{T}. \tag{6.1}$$

We do not need to specify 'reversible' as H is a state function and takes the same value for any path. Next we use the definition of the constant pressure heat capacity to express dH in terms of C_p (Eq. 5.8 on p. 28):

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \quad \text{hence} \quad dH = C_p \, dT.$$

Substituting this into Eq. 6.1 gives

$$dS = \frac{C_p \, dT}{T} \quad \text{or} \quad \frac{dS}{dT} = \frac{C_p}{T} \qquad \text{const. pressure} \tag{6.2}$$

To find the entropy at temperature T^* both sides are integrated from $T = 0$ up to T^*

$$\int_0^{T^*} dS = \int_0^{T^*} \frac{C_p(T)}{T} \, dT$$

$$S(T^*) - S(0) = \int_0^{T^*} \frac{C_p(T)}{T} \, dT. \tag{6.3}$$

In principle there are other ways of finding entropies, but this method is the one most commonly used as heat capacities are relatively simple to measure.

To evaluate the left-hand side a similar line of argument has been used as in section 5.3.2 on p. 28. We have written the heat capacity as $C_p(T)$ to remind ourselves that C_p depends on T. Over a small temperature range it may be acceptable to assume that it is constant, but not over a wide range.

6.1.1 Practical evaluation of entropies

The right-hand side of Eq. 6.3 has to be evaluated graphically. We make measurements of C_p as a function of temperature and then plot $C_p(T)/T$ against T all the way from 0 to T^*. The area under the curve is $S(T^*) - S(0)$.

Evaluating entropy: the shaded area is $S(T^*) - S(0)$.

By convention, the entropy at absolute zero is set to zero. In fact this is not an arbitrary choice, but is founded on an understanding of entropy as a statistical concept, as discussed in section 2.4 on p. 5.

At absolute zero, kT goes to zero and so all the molecules must be in the lowest energy level (the ground state). There is thus only one way of arranging them, $W = 1$ and hence, from $S = k \ln W$, the entropy is zero. This is the reason for choosing S at absolute zero to be zero.

Having this zero point enables us to determine absolute entropies. In contrast, there is no such natural zero for enthalpy or internal energy, so we cannot determine these quantities absolutely.

Measuring heat capacities right down to absolute zero (or, in practice, as close as we can get) is not a particularly easy task but it has been done for many substances. The entropy values determined in this way are called *absolute entropies*.

There may well be phase changes (solid to liquid, for example) over the range of temperature for which we want to plot the graph. At the precise temperature of the phase change the heat capacity goes to infinity (supplying heat does not change the temperature) and it is also commonly observed that there is a jump in the plot. It turns out that the entropy associated with a phase change, ΔS_{pc}, is related to the enthalpy of the phase change, ΔH_{pc}, by

$$\Delta S_{\mathrm{pc}} = \frac{\Delta H_{\mathrm{pc}}}{T_{\mathrm{pc}}}.$$

A phase change at temperature T_{pc} results in a discontinuity in the C_p/T against T plot. The entropy change due to the phase change needs to be added to the shaded area in order to find $S(T^*)$.

These extra entropy changes need to be included in the calculation of absolute entropies.
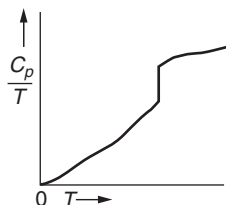
$$S(T^*) = \int_0^{T^*} \frac{C_p(T)}{T} \, dT \; + \sum_{\text{phase changes}} \frac{\Delta H_{\mathrm{pc}}}{T_{\mathrm{pc}}}$$

where the summation symbol, $\sum$, means to sum over all phase changes. Usually, entropies are tabulated as molar quantities, in units J K^{-1} mol^{-1}.

6.1.2   Converting entropies from one temperature to another

Absolute entropies vary with temperature but tend to be tabulated at just one or two temperatures. It will therefore be convenient to have a way of converting the value of the entropy from one temperature to another, just as we did for enthalpies in section 5.3.2 on p. 28.

The starting point is Eq. 6.2 on p. 31. As before we integrate this but this time just between T_1 and T_2. Provided that these two temperatures are not too different, we can assume that C_p will be constant and so take it out of the integrand:

$$\int_{T_1}^{T_2} dS \;\; = \;\; \int_{T_1}^{T_2} \frac{C_p}{T} \, dT$$

$$S(T_2) - S(T_1) \;\; = \;\; C_p \int_{T_1}^{T_2} \frac{1}{T} \, dT$$

$$= \;\; C_p \big[\ln T \big]_{T_1}^{T_2}$$

$$S(T_2) - S(T_1) = C_p \ln \frac{T_2}{T_1} \qquad \text{or} \qquad S(T_2) = S(T_1) + C_p \ln \frac{T_2}{T_1} \quad (6.4)$$

Equation 6.4 is a practical relationship for converting entropies from one temperature to another. Note that, as C_p is a molar quantity, Eq. 6.4 gives us the change in the molar entropy. To compute the change for n moles we simply multiply the term in C_p by n: $nC_p \ln(T_2/T_1)$.

7   Gibbs energy

The Second Law gives us a criterion for which processes are spontaneous, and which are at equilibrium (reversible) – that is $\Delta S_{univ} > 0$ for a spontaneous process and $\Delta S_{univ} = 0$ for a process which has come to equilibrium. However, it is not convenient to have to calculate the entropy change of the Universe each time we want to think about a chemical or physical process.

We will show in this section that the *Gibbs energy*, *G*, is a convenient way of using the Second Law. *G* is defined as

$$\boxed{G = H - TS} \qquad \text{definition of G} \qquad (7.1)$$

and we will see that in a spontaneous process *G* of the system *decreases* and reaches a minimum at equilibrium. The convenience is that by employing the Gibbs energy we only have to think about the system, and not the Universe.

Sometimes the Gibbs energy is called 'the Gibbs free energy', 'the Gibbs function' or simply 'the free energy'.

7.1   Gibbs energy and the Universal entropy

Starting from the definition of *G*, Eq. 7.1, we can form the complete differential as we did on p. 27

$$dG = dH - T\,dS - S\,dT$$

Now, we consider a process at constant temperature, so that the $S\,dT$ term is zero. Then, we divide each side by $-T$ to give

$$-\frac{dG_{sys}}{T_{sys}} = -\frac{dH_{sys}}{T_{sys}} + dS_{sys} \qquad \text{const. temperature} \qquad (7.2)$$

To remind ourselves that all these quantities refer to the system the subscript 'sys' has been added.

Now, consider the expression for the Universal entropy found in section 2.6.1 on p. 12

$$\Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys} = -\frac{q_{sys}}{T_{surr}} + \Delta S_{sys}.$$

Writing this in differential form we have

$$dS_{univ} = -\frac{\delta q_{sys}}{T_{surr}} + dS_{sys}.$$

We impose the further two conditions that: (1) the process is taking place at constant pressure, so $\delta q_{sys} = dH$; and (2) the system and the surroundings are at the same temperature; then

$$dS_{univ} = -\frac{dH_{sys}}{T_{sys}} + dS_{sys}. \qquad (7.3)$$

Comparing Eqs. 7.2 and 7.3 we see that $-dG_{sys}/T$ is exactly the same thing as dS_{univ}.

It therefore follows that as S_{univ} increases in a spontaneous process, dS_{univ} must be positive and so must $(-dG_{sys}/T)$. Therefore dG_{sys} must be negative, i.e. G decreases in a spontaneous process. For reversible (equilibrium) processes dS_{univ} is 0, and so is dG_{sys}. All of this is true under conditions of constant pressure and temperature, as these are restrictions we have introduced earlier in this argument.

In summary, at constant temperature and pressure:

G falls in a spontaneous process i.e. $dG < 0$;
at equilibrium G reaches a minimum, i.e. $dG = 0$

The usual units for G are kJ mol^{-1}, i.e. it is an energy, just as U and H. We can write Eq. 7.2 for finite changes as

$$-\frac{\Delta G_{sys}}{T_{sys}} = -\frac{\Delta H_{sys}}{T} + \Delta S_{sys} \tag{7.4}$$

$-\Delta G_{sys}/T_{sys}$ is the entropy change of the Universe and $-\Delta H_{sys}/T_{sys}$ is the entropy change of the surroundings. For a process to be spontaneous, ΔS_{univ} must be positive so ΔG_{sys} must be negative.

Equation 7.4 can be written another way by multiplying both sides by $-T$

$$\boxed{\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys};} \tag{7.5}$$

this is the form of ΔG we usually quote. The 'sys' subscripts are usually left off, it being taken as implied that we are talking about the system.

We commented in section 2.6.2 on p. 12 that a process which is endothermic can be spontaneous provided ΔS_{sys} is sufficiently positive to compensate for the reduction in entropy of the surroundings. In terms of Eq. 7.5 we would say that an endothermic process can be spontaneous provided the ΔS_{sys} term is large enough that the $-T\Delta S_{sys}$ term overcomes the positive ΔH_{sys} and so makes ΔG_{sys} negative.

Likewise, a process which has a negative ΔS_{sys} can be spontaneous provided it is sufficiently exothermic that the negative ΔH_{sys} term overcomes the positive $-T\Delta S_{sys}$ term. Thinking about ΔG_{sys} is really equivalent to thinking about ΔS_{univ}.

Exercise 9

From now on, we will frame all of our discussion of equilibria in terms of the Gibbs energy.

7.2 How the Gibbs energy varies with pressure and temperature

When we come to discussing chemical equilibrium we will need to know how the Gibbs energy varies with pressure and temperature. To find this out, we first need to introduce the so-called *Master Equations*.

7.2.1 The Master Equations

In section 5.1 on p. 25 we wrote the First Law in its differential form for the case that only 'pV' work is done as (Eq. 5.1 on p. 25)

$$dU = \delta q - p \, dV.$$

Imagine, for the moment, a reversible process: by definition, $dS = \delta q_{\text{rev}}/T$ (Eq. 2.2 on p. 10), so it follows that $\delta q_{\text{rev}} = T dS$. Substituting this into the above expression for dU we have

$$dU = T\, dS - p\, dV. \qquad (7.6)$$

Now, U is a state function, so dU is the same for a given change, regardless whether or not is takes place reversibly, so Eq. 7.6 is true for all changes. This seems a bit paradoxical, as Eq. 7.6 appears to have been derived under the assumption that we are thinking about a reversible process. The point is that if the process is reversible, $T\, dS$ is δq and $-p\, dV$ is δw; if the process is irreversible then the two terms cannot be identified directly with δq and δw, but their sum is still equal to dU.

Equation 7.6 is some times called the *First and Second Laws combined*, and it is the first of the thermodynamic *Master Equations*. We will find that these Master Equations are very useful in relating one thermodynamic quantity to another.

The second Master Equation is developed by starting with the definition of enthalpy (Eq. 5.5 on p. 27), $H = U + pV$, and then taking its complete differential, as we did on p. 27 to give

$$dH = dU + p\, dV + V\, dp. \qquad (7.7)$$

Equation 7.6, the first Master Equation, is used to substitute for dU in Eq. 7.7 to give

$$
\begin{aligned}
dH &= T\, dS - p\, dV + p\, dV + V\, dp \\
&= T\, dS + V\, dp. \qquad (7.8)
\end{aligned}
$$

Equation 7.8 is the second of the Master Equations.

The next Master Equation is found by taking the definition of G, Eq. 7.1 on p. 34, forming the complete differential and them substituting in for dH from Eq. 7.8

$$
\begin{aligned}
G &= H - TS \\
\text{thus } dG &= dH - T\, dS - S\, dT \\
dG &= T\, dS + V\, dp - T\, dS - S\, dT
\end{aligned}
$$

hence

$$dG = V\, dp - S\, dT. \qquad (7.9)$$

Equation 7.9 is the most useful of the Master Equations we will derive. We will use it immediately to find out how G varies with pressure and temperature.

7.2.2 Variation of G with p (and V), at constant T

We start with Eq. 7.9 and impose the condition of constant temperature, so that $dT = 0$

$$dG = V\, dp \qquad \text{const. } T. \qquad (7.10)$$

which can be written, using the notation of partial derivatives, as

$$\left(\frac{\partial G}{\partial p}\right)_T = V.$$

To integrate Eq. 7.10, and hence find a useful equation for how G varies with p, we need to recognise that V varies with p according to the ideal gas equation

$$pV = nRT \qquad \text{so} \qquad V = \frac{nRT}{p}.$$

Substituting this expression for V into the right-hand side of Eq. 7.10 and integrating gives

$$dG = \frac{nRT}{p} \, dp$$

$$\int_{p_1}^{p_2} dG = \int_{p_1}^{p_2} \frac{nRT}{p} \, dp$$

$$\left[G\right]_{p_1}^{p_2} = nRT \int_{p_1}^{p_2} \frac{1}{p} \, dp$$

$$G(p_2) - G(p_1) = nRT \left[\ln p\right]_{p_1}^{p_2}$$

$$G(p_2) - G(p_1) = nRT \ln \frac{p_2}{p_1}$$

where we have written $G(p)$ to indicate that G depends on pressure. On the third line we have used the fact that T is constant, so it can be taken outside the integral.

The usual way of writing the final expression is to take p_1 as the standard pressure, p°, of 1 bar and to write $G(p^\circ)$ as G°, the Gibbs energy at standard pressure

$$G(p) = G^\circ + nRT \ln \frac{p}{p^\circ}. \qquad \text{const. } T \qquad (7.11)$$

For one mole, $n = 1$, the quantities all become molar quantities, indicated by a subscript m:

$$\boxed{G_\mathrm{m}(p) = G_\mathrm{m}^\circ + RT \ln \frac{p}{p^\circ}.} \qquad \text{const. } T \qquad (7.12)$$

The pressures can be in any units we like, as the only important thing is the ratio between them. If we choose to write them in bar, $p^\circ = 1$ and it is tempting to write $G_\mathrm{m}(p) = G_\mathrm{m}^\circ + RT \ln p$. Apart from the objection that we appear to be taking the logarithm of a dimensioned quantity, this form can also lead us into difficulties so it is best to use Eq. 7.12.

Since, for an ideal gas, pressure is inversely proportional to volume (at constant temperature), it follows that $p_2/p_1 = V_1/V_2$ and so

$$G(V_2) - G(V_1) = nRT \ln \frac{V_1}{V_2}.$$

The important take home message of this section is that the Gibbs energy *falls* as the pressure falls (at constant temperature); such a process will therefore be spontaneous.

A rather trivial example is the expansion of a gas into a vacuum. For an ideal gas, such a process involves no change in temperature; all that happens is that the pressure falls. We have seen that such a fall in pressure results in a reduction in the Gibbs energy and so is a spontaneous process, as expected.

We will see a much less trivial application of Eq. 7.12 when we come to discuss chemical equilibrium.

1 bar is 10^5 N m^2.

These relationships apply at 'constant temperature'. This does not mean that they apply at one unique temperature; rather it means that they apply at any temperature, provided that it remains constant during the change. At different temperatures G and G° will be different, but they are still related by Eq. 7.12.

7.2.3   Variation of G with T, at constant p

Again we start with the Master Equation, Eq. 7.9, but this time impose the condition of constant pressure, so that $dp = 0$:

$$dG = -S \, dT \qquad \text{const. } p. \tag{7.13}$$

which can be written, using the notation of partial derivatives, as

$$\left(\frac{\partial G}{\partial T}\right)_p = -S. \tag{7.14}$$

We have already seen in section 6.1 on p. 31 that S itself varies with temperature, so integrating Eq. 7.13 is not straightforward.

In fact there is a special relationship, called the *Gibbs–Helmholtz* equation, which we can derive using Eq. 7.13 and which we will need later on. The derivation starts by considering the derivative of the function G/T with respect to T. As G depends on T, to find the derivative we have to recognize that we are differentiating a product of two functions

$$\frac{d}{dT}\left(GT^{-1}\right) = T^{-1}\frac{dG}{dT} - T^{-2}G. \tag{7.15}$$

At constant pressure, which we will assume from now on, Eq. 7.14 tells us that $dG/dT = -S$; we substitute this on the right of Eq. 7.15. We also know that, by definition, $G = H - TS$; we substitute this for G on the right of Eq. 7.15. The result is

$$
\begin{aligned}
\frac{d}{dT}\left(GT^{-1}\right) &= T^{-1}(-S) - T^{-2}(H - TS) \\
&= -T^{-1}S - T^{-2}H + T^{-1}S \\
&= -T^{-2}H.
\end{aligned}
$$

Exercise 10

Tidying this up gives the Gibbs–Helmholtz equation

$$\frac{d}{dT}\left(\frac{G}{T}\right) = -\frac{H}{T^2}. \qquad \text{const. pressure} \tag{7.16}$$

Later on, we will use this odd-looking relationship to good effect!

8   Chemical changes

We need to extend the ideas we have developed so far to cover chemical reactions and then chemical equilibrium. The idea of talking about the 'ΔH of a reaction' is a familiar one, but we need to be more careful about exactly what this means and to define the equivalent quantities for the entropy and Gibbs energy change. In the following section we will introduce the symbol Δ_r which we need to describe the changes accompanying chemical reactions.

8.1   The Δ_r symbol

It is easiest to describe what is meant by $\Delta_r H$ etc. by thinking about a particular balanced chemical equation

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g).$$
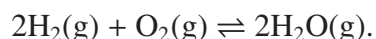
This says that two moles of H_2 react with one mole of O_2 to give two moles of H_2O.

Imagine that we have a mixture of H_2, O_2 and H_2O in a particular ratio – this need not be the equilibrium mixture. The term used to describe a particular ratio of reactants and products is *composition*.

Imagine also that we have a very large amount of this mixture. Now, out of this large amount, we allow two moles of H_2 to react with one mole of O_2 to give two moles of H_2O. The resulting change in enthalpy is written $\Delta_r H$.

The reason that we have to think about having a large amount of the reaction mixture is so that, when the two moles of H_2O are formed, the ratio of H_2 to O_2 to H_2O *does not change* i.e. the composition remains the same. This is important since, as we shall see later, some thermodynamic quantities depend on the composition.

In short, $\Delta_r H$ is the enthalpy change when *one mole of reaction* takes place at the specified (and constant) composition. In a similar way we can define $\Delta_r G$ and $\Delta_r S$ as the Gibbs energy and entropy changes under the same circumstances.

The quantity known as the *standard enthalpy change* ($\Delta_r H^\circ$) is more commonly encountered (and similarly for the entropy and Gibbs energy). We will see how these standard changes are defined in the next section.

8.2   Standard states and standard changes

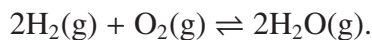**The standard state of a substance is the *pure* form at a pressure of *one bar* and at the *specified temperature***

1 bar is a pressure of 10^5 N m^{-2} which is very close to, but not quite the same as, a pressure of 1 atmosphere.

The standard state is usually denoted by adding a superscript ∘ or the 'underground' symbol (a Plimsoll line) ⦵ e.g. $S^\circ(H_2)$ denotes the standard entropy of H_2.
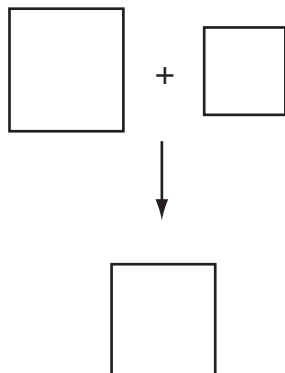
It is often thought, erroneously, that the standard state implies a certain temperature; this is not the case. The value that the standard entropy, Gibbs energy or enthalpy takes depends on the temperature, which must be stated.

Referring again to our example reaction

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g).$$

$\Delta_r H^\circ$ is the enthalpy change when two moles of H_2 reacts with one mole of O_2 to give two moles of H_2O, *all species being in their standard states*. It is important to realise that as the standard state implies the *pure* substance, this standard enthalpy change is for *pure* (unmixed) reactants going to *pure* (unmixed) products.

$\Delta_r S^\circ$ and $\Delta_r G^\circ$ are defined in a similar way.
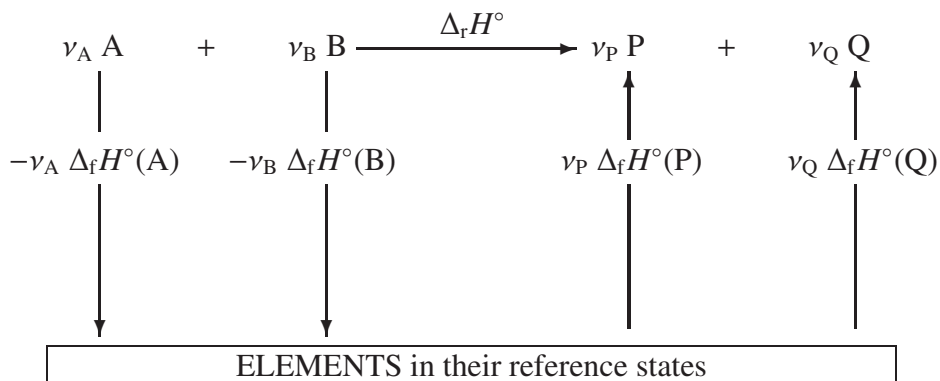
8.3 Enthalpies of formation

It is common to tabulate standard enthalpies of formation of compounds, as from these it is possible to work out the standard enthalpy change for any reaction.

The *standard enthalpy of formation* of a compound, $\Delta_f H^\circ$, is the standard enthalpy change for a reaction in which one mole of the compound is formed from its constituent elements, each in their *reference states*. As noted above, the temperature must be stated.

The *reference state* is the most stable state of that element at a pressure of 1 bar.

For example, at 298 K the reference state of nitrogen is N_2 gas (as opposed to nitrogen atoms) and the reference state of carbon is graphite. With this definition the standard enthalpy of formation of elements in their reference states is zero.

The standard enthalpy change for any reaction can be computed from standard enthalpies of formation in a way which is best visualized as a cycle:

The arrows on the left show the conversion of the reactants to their elements in their reference states. The enthalpies are therefore minus the standard enthalpies of formation; note that these have to be multiplied by the stoichiometric coefficients ν_i. The arrows on the right show the formation of the products from the elements in their reference states.

It follows from the cycle that

$$\Delta_r H^\circ = \nu_P \Delta_f H^\circ(P) + \nu_Q \Delta_f H^\circ(Q) - \nu_A \Delta_f H^\circ(A) - \nu_B \Delta_f H^\circ(B).$$

Visualization of the meaning of $\Delta_r H^\circ$ for the reaction
$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

8.4   Standard entropy and Gibbs energy changes for reactions

As we have seen in section 6.1 on p. 31 it is possible to determine the absolute entropies of substances; usually these are tabulated as standard entropies, S°. Using these data, $\Delta_r S^\circ$ for the general reaction

$$\nu_A A + \nu_B B \longrightarrow \nu_P P + \nu_Q Q$$
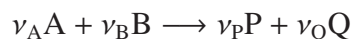
can be computed as

$$\Delta_r S^\circ = \nu_P S^\circ(P) + \nu_Q S^\circ(Q) - \nu_A S^\circ(A) - \nu_B S^\circ(B).$$

Once we have $\Delta_r H^\circ$ and $\Delta_r S^\circ$ for a reaction, it is simple to calculate $\Delta_r G^\circ$ using Eq. 7.5 on p. 35:

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

Sometimes you will find values tabulated for the *standard Gibbs energy of formation*, $\Delta_f G^\circ$, of a substance; as with standard enthalpies of formation, $\Delta_f G^\circ$ for elements in their reference phases are zero. From these $\Delta_f G^\circ$ values, $\Delta_r G^\circ$ can be computed directly in the same way that $\Delta_r H^\circ$ is computed from $\Delta_f H^\circ$ values.

Example 5

8.5   Variation of $\Delta_r H^\circ$ with temperature

We were at pains to point out above that $\Delta_r H^\circ$ may well vary with temperature. Typically, values are tabulated at 298 K, which gives us something of a problem if we want to know $\Delta_r H^\circ$ at another temperature. The rather un-promising heat capacities come to our rescue and allow us to convert $\Delta_r H^\circ$ values from one temperature to another.

In section 5.3.2 on p. 28 we saw that enthalpy varies with temperature in a way which depends on the heat capacity.

$$\frac{dH}{dT} = C_p.$$

We now recall that $\Delta_r H^\circ$ is just the enthalpy of the products minus the en-thalpy of the reactants, everything being under standard conditions. It thus follows that

$$\frac{d\Delta_r H^\circ}{dT} = \Delta_r C_p{}^\circ$$

where, for the general reaction

$$\nu_A A + \nu_B B \longrightarrow \nu_P P + \nu_Q Q$$

$\Delta_r C_p{}^\circ$ is defined as

$$\boxed{\Delta_r C_p{}^\circ = \nu_P C_p{}^\circ(P) + \nu_Q C_p{}^\circ(Q) - \nu_A C_p{}^\circ(A) - \nu_B C_p{}^\circ(B).}$$

$C_p{}^\circ(A)$ is the molar heat capacity (at constant pressure and under standard conditions) of substance A, and so on; these values are tabulated.

We saw before that if we assume that the heat capacity does not vary with temperature in the range T_1 to T_2 then the enthalpies at the two temperatures are related by (Eq. 5.10 on p. 29)

$$H(T_2) = H(T_1) + C_p\,[T_2 - T_1].$$

Similarly, the $\Delta_r H°$ values at the different temperatures are related by

$$\Delta_r H°(T_2) = \Delta_r H°(T_1) + \Delta_r C_p°\,[T_2 - T_1].$$ (8.1)

With the aid of tabulated values of $C_p°$ we can therefore convert $\Delta_r H°$ values from one temperature to another.

8.6   Variation of $\Delta_r S°$ with temperature

The argument here is just the same as it was in the previous section. We start with Eq. 6.4 on p. 32

$$S(T_2) = S(T_1) + C_p \ln \frac{T_2}{T_1}$$

and simply rewrite it for $\Delta_r S°$ as

$$\Delta_r S°(T_2) = \Delta_r S°(T_1) + \Delta_r C_p°\,\ln \frac{T_2}{T_1}.$$

Example 6
Exercises 11 to 14

9 Mixtures

Ultimately we want to use thermodynamics to understand chemical equilibrium, which means that we must deal with the thermodynamic properties of mixtures of substances (reactants and products). However, none of the tools we have discussed so far are directly applicable to mixtures, so this is an area where we need to develop our understanding. The mixing of ideal gases will be used to illustrate the key concepts.

9.1 The mixing of ideal gases

We know that ideal gases mix spontaneously, so mixing must be accompanied by a reduction in the Gibbs energy. Our first task will be to understand how this reduction arises and then calculate the Gibbs energy change of mixing.

Consider two gases, A and B, separated by a partition but both at the same temperature and pressure, p; let there be n_A moles of A and n_B moles of B. When the partition is removed the gases mix completely. The final pressure is still p and the temperature does not change.

What have changed are the *partial pressures* of the gases, and it is this change which is responsible for the reduction in Gibbs energy and hence for the mixing process being spontaneous.

9.1.1 Partial pressures

The partial pressure of gas i in a mixture is the pressure that it would exert *if it occupied the whole volume on its own*. For a mixture of ideal gases, the partial pressure of i, p_i is given by

$$p_i = x_i \, p_{tot}$$

where p_{tot} is the total pressure and x_i is the *mole fraction* of i.

The mole fraction of i is given by

$$x_i = \frac{n_i}{n_{tot}} \qquad n_{tot} = n_1 + n_2 + \ldots = \sum_i n_i$$

where n_i is the number of moles of i, and n_{tot} is the total number of moles of all species, found by adding together all of the n_i. It is clear from these definitions that the sum of all the mole fractions of the substances in a mixture is = 1.

Before mixing, when gas A is in its separate compartment, its partial pressure is p. After mixing, the mole fraction of A, x_A, is $n_A/(n_A + n_B)$, so the partial pressure of A, p_A, is

$$p_A = \frac{n_A}{n_A + n_B} \, p$$

and similarly for B

$$p_B = \frac{n_B}{n_A + n_B} \, p.$$
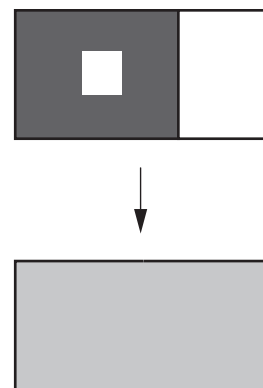
As a result of its definition, the mole fraction of A in the mixture is always less than one, and so the partial pressure of A in the mixture is always less than the pressure before mixing. We will show that it is this reduction in pressure which leads to the favourable change in Gibbs energy.

9.1.2 Gibbs energy of the components in a mixture

In section 7.2.2 on p. 36 we saw that the molar Gibbs energy of a pure gas varies with pressure according to Eq. 7.12 on p. 37

$$G_{\mathrm{m}}(p) = G_{\mathrm{m}}^{\circ} + RT \ln \frac{p}{p^{\circ}} \qquad \text{const. } T \qquad (9.1)$$

If we are considering ideal gases, then there is no difference between a pure gas at pressure p and the same gas at partial pressure p in a mixture; this is because ideal gases do not interact. Thus, we can say that the molar Gibbs energy of i in a mixture depends on its partial pressure, p_i, in exactly the same way as in Eq. 9.1:

$$\boxed{G_{\mathrm{m},i}(p_i) = G_{\mathrm{m},i}^{\circ} + RT \ln \frac{p_i}{p^{\circ}}} \qquad (9.2)$$

where $G_{\mathrm{m},i}(p_i)$ is the molar Gibbs energy of substance i present at partial pressure p_i and $G_{\mathrm{m},i}^{\circ}$ is the standard molar Gibbs energy of i.

Exercise 15

Exercise 16

From this relationship we see that the Gibbs energy *falls* as the partial pressure *falls*. So, the Gibbs energy of A in the mixture is less than its Gibbs energy before mixing; the same is true of B. The lowering of the partial pressures of the gases which takes place on mixing results in a reduction of the Gibbs energy of each gas and hence of the mixture as a whole; this is why gases mix.

cyclopropane   propene
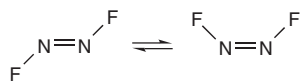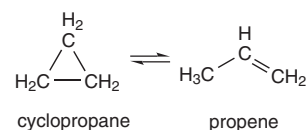
Examples of A ⇋ B equilibria involving two isomers.

9.2 Reacting mixtures

So far, we have established that two ideal gases will always mix, as the process is accompanied by a reduction in the Gibbs energy. The next question we want to answer is what would happen if the two species A and B could interconvert chemically, according to the equilibrium

$$A \rightleftharpoons B$$
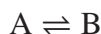
Such a situation would occur if A and B were two isomers of the same compound.

Qualitatively we know that A and B would interconvert until the equilibrium mixture is reached, at which point there would be no further change. This approach to equilibrium is a spontaneous process and so must be accompanied by a reduction in the Gibbs energy. At the equilibrium point, the Gibbs energy will be a minimum.

Suppose that we have n_A moles of A and n_B moles of B present, and that the total pressure is p. The Gibbs energy of the mixture can be computed from

the molar Gibbs energies of A and B in the following way:

$$
\begin{aligned}
G_{\text{mixed}} &= n_A G_{\text{m,A}}(p_A) + n_B G_{\text{m,B}}(p_B) \\
&= n_A \left(G_{\text{m,A}}^\circ + RT \ln \frac{p_A}{p^\circ} \right) + n_B \left(G_{\text{m,B}}^\circ + RT \ln \frac{p_B}{p^\circ} \right) \\
&= n_A \left(G_{\text{m,A}}^\circ + RT \ln x_A \frac{p}{p^\circ} \right) + n_B \left(G_{\text{m,B}}^\circ + RT \ln x_B \frac{p}{p^\circ} \right).
\end{aligned}
$$

To go to the second line we have used Eq. 9.2 for $G_{\text{m,A}}(p_A)$ and $G_{\text{m,B}}(p_B)$, and to go to the last line we have used $p_A = x_A p_{\text{tot}}$ and similarly for B. Note that here $p_{\text{tot}} = p$.

It is easier to understand the final expression if we divide both sides by $(n_A + n_B)$

$$
\begin{aligned}
\frac{G_{\text{mixed}}}{n_A + n_B} &= \left(\frac{n_A}{n_A + n_B} \right)\left(G_{\text{m,A}}^\circ + RT \ln x_A \frac{p}{p^\circ} \right) + \left(\frac{n_B}{n_A + n_B} \right)\left(G_{\text{m,B}}^\circ + RT \ln x_B \frac{p}{p^\circ} \right) \\
&= x_A \left(G_{\text{m,A}}^\circ + RT \ln x_A \frac{p}{p^\circ} \right) + x_B \left(G_{\text{m,B}}^\circ + RT \ln x_B \frac{p}{p^\circ} \right).
\end{aligned}
$$

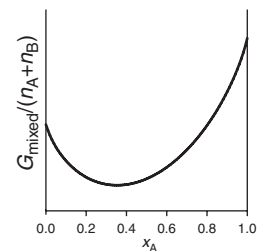where on the second line we have used the definition of x_i.

Remember that as A and B interconvert, both $(n_A + n_B)$ and p remain constant. A plot of $G_{\text{mixed}}/(n_A + n_B)$ as a function of x_A is shown opposite; to make this plot we have used the fact that $(x_A + x_B) = 1$ and have arbitrarily made $G_{\text{m,A}}^\circ$ greater than $G_{\text{m,B}}^\circ$. The key thing about the plot is that it shows a *minimum* in G_{mixed}; as we shall see, this minimum corresponds to the equilibrium mixture of A and B.

In the plot, the minimum is at around $x_A = 0.4$. What this means is that if A and B are mixed at an initial composition of $x_A = 0.2$ the conversion of B into A will be spontaneous as it is accompanied by a decrease in Gibbs energy; the result in an increase in x_A. This process goes on until the minimum is reached; from this point no further increase in x_A is possible as this would result in an increase in G.

If the initial composition is $x_A = 0.6$ the conversion of A into B is spontaneous, and so x_A decreases until the minimum is reached. Either way, the system ends up at the composition of the minimum. The point to notice is that even though the Gibbs energy of pure B is less than that of pure A, a mixture of A and B can have even lower Gibbs energy than pure B.

It is not difficult to show that at the minimum (the equilibrium position) the ratio x_B/x_A depends *only* on $\Delta_r G^\circ$, the change in standard Gibbs energy between A and B: $\Delta_r G^\circ = G_{\text{m,B}}^\circ - G_{\text{m,A}}^\circ$. Of course, the equilibrium ratio x_B/x_A is the equilibrium constant, so what we have found is that the value of the equilibrium constant depends only on $\Delta_r G^\circ$.

We will not pursue this important point in more detail here, but now proceed to a more general derivation of the relationship between $\Delta_r G^\circ$ and the equilibrium constant for any reaction. However, before doing this we need to introduce the concept of *chemical potential*

9.3 Chemical potential

As ideal gases do not, by definition, interact, it is possible to work out the Gibbs energy of a mixture of such gases simply by using the molar Gibbs

$G_{\text{mixed}}/(n_A + n_B)$ plotted as a function of x_A. It has been assumed, arbitrarily, that $G_{\text{m,A}}^\circ > G_{\text{m,B}}^\circ$.

Exercise 17

energies:

$$G = n_A G_{m,A}(p_A) + n_B G_{m,B}(p_B) + n_C G_{m,C}(p_C) + \dots \tag{9.3}$$

where the molar Gibbs energy of A at partial pressure p_A, $G_{m,A}(p_A)$, can be found using Eq. 9.2 on p. 44:

$$G_{m,A}(p_A) = G^\circ_{m,A} + RT \ln \frac{p_A}{p^\circ}$$

and so on for B, C ....

Once we move away from ideal gases things become much more complex as there will be specific interactions between the species present. In such a situation it will no longer be the case that the molar Gibbs energy of A depends simply on its partial pressure; rather, the identity and amounts of the other species present will influence the Gibbs energy. Equation 9.3 will no longer be valid.

To deal with non-ideal mixtures this situation we need to introduce the *chemical potential*, given the symbol μ_i for substance i. The Gibbs energy of a mixture can be computed from a knowledge of these chemical potentials:

$$G = n_A \mu_A + n_B \mu_B + n_C \mu_C + \dots \tag{9.4}$$

where μ_A is the chemical potential of A when present in the mixture at partial pressure p_A.

Eq. 9.4 looks just the same as Eq. 9.3 with the molar Gibbs energies replaced by the chemical potentials. However, the important point is that the chemical potential of A is, in principle, a function of composition of the entire mixture, not just of the partial pressure of A.

In this course we are only going to consider the theory of reactions involving ideal gases and solutions, so we do not need chemical potential as such. However, for compatibility with later courses we will use chemical potentials in our derivations.

9.3.1   The chemical potential of gases, solutions and solids
Gases
For mixtures of ideal gases the chemical potential is identical to the molar Gibbs energy at the relevant partial pressure i.e. Eq. 9.2 on p. 44

$$\boxed{\mu_i(p_i) = \mu_i^\circ + RT \ln \frac{p_i}{p^\circ}.} \tag{9.5}$$

In this equation μ_i° is the chemical potential of i under standard conditions i.e. pure and 1 bar pressure; do not forget that, like the Gibbs energy, μ_i° will be a function of temperature. For an ideal gas, μ_i° is the same as the molar standard Gibbs energy, $G^\circ_{m,i}$.

Solutions
If species i is a solute, we will simply assert that its chemical potential varies according to

$$\boxed{\mu_i(c_i) = \mu_i^\circ + RT \ln \frac{c_i}{c^\circ}.} \tag{9.6}$$

Here c_i is the concentration of solute i and c° is the standard concentration; μ_i° is the standard chemical potential of i i.e. when the concentration is equal to c°. Usually concentrations are given in mol dm^{-3}, so $c^\circ = 1$ mol dm^{-3}.

In fact Eq. 9.6 only applies to ideal solutions, which are ones in which there are no significant interactions. In practice, solutions are rarely ideal, especially when the solutes are ions. Dealing with non-ideal solutions is a complex matter which is beyond the scope of this course, so we will simply have to assume that our solutions are ideal and used Eq. 9.6.

Solids and liquids

A solid is always present in the standard state, so its chemical potential is simply equal to its standard chemical potential, μ_i°.

Similar considerations apply to pure liquids.

10 Equilibrium

In the section 9.2 on p. 44 we found that for the simple $A \rightleftharpoons B$ equilibrium the Gibbs energy is minimised at a particular ratio of A to B which depended only on $\Delta_r G^\circ$. This minimum corresponds to the position of equilibrium to which the reaction will move and, of course, the ratio of B to A at this point is the equilibrium constant.

In this section we will find the position of equilibrium, and hence the equilibrium constant, for a general chemical reaction. First, though, we will discuss how equilibrium constants are defined.

10.1 Equilibrium constants

If we take a balanced chemical equation

$$\nu_A A + \nu_B B \ldots \rightleftharpoons \nu_P P + \nu_Q Q \ldots$$
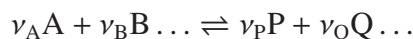
then the equilibrium constant, K, is given by 'products over reactants'

$$K = \frac{[P]^{\nu_P}[Q]^{\nu_Q}\ldots}{[A]^{\nu_A}[B]^{\nu_B}\ldots} \tag{10.1}$$

where [A] means the concentration of A and so on; note that the concentrations are raised to the power of the stoichiometric coefficients.

The point about the equilibrium constant is that it has a fixed value for a given reaction at a given temperature. A reaction mixture at equilibrium will always have concentrations such that the right hand side of Eq. 10.1 is equal to the particular value of K for that reaction, regardless of the initial concentration of the reagents.

There are different ways in which concentration can be expressed, and hence different equilibrium constants. Also, we will find that we need to define K in way which makes it *dimensionless*.

One way to write the equilibrium constant is in terms of *partial pressures*; for gases, these are measures of concentrations. Each partial pressure is divided by the standard pressure, p°, so as to make the whole expression dimensionless. The resulting equilibrium constant is called K_p.

$$K_p = \frac{\left(\frac{p_P}{p^\circ}\right)^{\nu_P}\left(\frac{p_Q}{p^\circ}\right)^{\nu_Q}\ldots}{\left(\frac{p_A}{p^\circ}\right)^{\nu_A}\left(\frac{p_B}{p^\circ}\right)^{\nu_B}\ldots} \tag{10.2}$$

Another commonly encountered form is K_c, the equilibrium constant in terms of concentrations; again, division by c°, the standard concentration, make the equilibrium constant dimensionless; typically, c° is 1 mol dm^{-3}.

$$K_c = \frac{\left(\frac{c_P}{c^\circ}\right)^{\nu_P}\left(\frac{c_Q}{c^\circ}\right)^{\nu_Q}\ldots}{\left(\frac{c_A}{c^\circ}\right)^{\nu_A}\left(\frac{c_B}{c^\circ}\right)^{\nu_B}\ldots} \tag{10.3}$$

The convention is that any solids involved in the equilibrium do *not* contribute a term to the equilibrium constant. For example, for the reaction

$$H_2O(g) + C(s) \rightleftharpoons CO(g) + H_2(g)$$
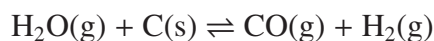
the equilibrium constant K_p is writen

$$
\begin{aligned}
K_p &= \frac{(p_{CO}/p^\circ)(p_{H_2}/p^\circ)}{(p_{H_2O}/p^\circ)} \\
&= \frac{p_{CO}p_{H_2}}{p_{H_2O}p^\circ}.
\end{aligned}
$$

Why solids do not appear in expressions for the equilibrium constant, and indeed why there is such a thing as the equilibrium constant, is the subject of the next section.

10.2 Condition for chemical equilibrium

We will discuss equilibrium for our general chemical reaction

$$\nu_A A + \nu_B B \rightleftharpoons \nu_P P + \nu_Q Q$$
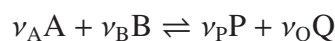
Imagine that we have an arbitrary mixture of the reactants (A and B) and the products (P and Q); this need not be the equilibrium mixture. Imagine also that we have a large amount of this mixture and that we let 'one mole of reaction' take place. By one mole of reaction we mean ν_A moles of A reacting with ν_B moles of B to give ν_P moles of P and ν_Q moles of Q according to the above stoichiometric equation. As we have a large amount of mixture, the composition is unchanged by one mole of reaction taking place.

Using Eq. 9.4 on p. 46 we can work out the change in Gibbs energy, $\Delta_r G$, when this mole of reaction takes place

$$\boxed{\Delta_r G = \nu_P \mu_P + \nu_Q \mu_Q - \nu_A \mu_A - \nu_B \mu_B.} \tag{10.4}$$

The first two terms are positive as when the reaction proceeds we gain ν_P moles of P and ν_Q moles of Q; the second two terms are negative as ν_A moles of A are lost, as are ν_B moles of B.

Remember that the values of the chemical potentials, μ_A etc., depend on the partial pressures (or concentrations) of the species present (section 9.3.1 on p. 46). So the size and sign of $\Delta_r G$ will depend on the composition of the mixture.

If, for given concentrations, it turns out that $\Delta_r G$ is negative then the reaction will proceed from left to right, as this is associated with a decrease in Gibbs energy and is thus spontaneous. If $\Delta_r G$ is positive, then the reaction will proceed from right to left as this direction will have a negative $\Delta_r G$.

Of course in practice we do not have an infinitely large amount of the reaction mixture so as the reaction proceeds one way or the other the concentrations will change. The key thing is that the change in these concentrations will be such as to lead to a reduction in the Gibbs energy. Eventually we will reach the composition at which the Gibbs energy becomes a minimum; at this point $\Delta_r G = 0$ so no further spontaneous change is possible. This is the position of equilibrium.

$$\boxed{\text{at equilibrium:} \quad \Delta_r G = 0.} \tag{10.5}$$

So we can write, *at equilibrium*,

$$(\nu_P\mu_P + \nu_Q\mu_Q - \nu_A\mu_A - \nu_B\mu_B)_{eq} = 0.$$

where the subscript has been added to remind us that this relationship only holds at the equilibrium point.

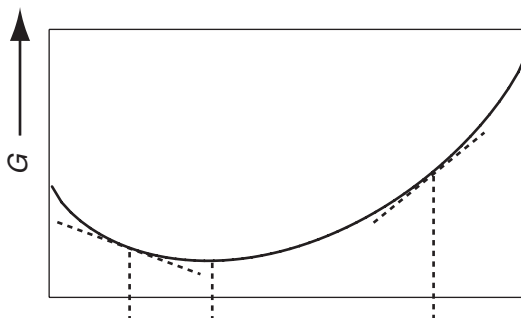These ideas are illustrated in the diagram below.

Illustration of how the sign of $\Delta_r G$ varies as a function of composition. At composition *a*, the slope of the graph of *G* against composition is negative and so therefore is $\Delta_r G$. The spontaneous direction of the reaction will therefore be towards the products. At composition *b*, the slope and $\Delta_r G$ are positive; the reaction thus proceeds towards the reactants. Finally at point *c*, the slope is zero: this is the equilibrium point. Once reached, there will be no further change in composition.

10.3   Relation between $\Delta_r G^\circ$ and the equilibrium constant

Assuming for the moment that all of the species in the reaction are gases, each chemical potential can be written using Eq. 9.5 on p. 46

$$\mu_i(p_i) = \mu_i^\circ + RT \ln \frac{p_i}{p^\circ}. \tag{10.6}$$

We can rewrite Eq. 10.4 to make it explicit that the chemical potentials depend on the partial pressures:

$$\Delta_r G = \nu_P\mu_P(p_P) + \nu_Q\mu_Q(p_Q) - \nu_A\mu_A(p_A) - \nu_B\mu_B(p_B).$$

We now substitute each $\mu_i(p_i)$ in this equation using Eq. 10.6:

$$
\begin{aligned}
\Delta_r G = {} & \nu_P\left(\mu_P^\circ + RT \ln \frac{p_P}{p^\circ}\right) + \nu_Q\left(\mu_Q^\circ + RT \ln \frac{p_Q}{p^\circ}\right) \\
& -\nu_A\left(\mu_A^\circ + RT \ln \frac{p_A}{p^\circ}\right) - \nu_B\left(\mu_B^\circ + RT \ln \frac{p_B}{p^\circ}\right).
\end{aligned}
$$

Now we gather together the standard chemical potentials

$$
\begin{aligned}
\Delta_r G = {} & \left[\nu_P\mu_P^\circ + \nu_Q\mu_Q^\circ - \nu_A\mu_A^\circ - \nu_B\mu_B^\circ\right] \\
& +\nu_P RT \ln \frac{p_P}{p^\circ} + \nu_Q RT \ln \frac{p_Q}{p^\circ} - \nu_A RT \ln \frac{p_A}{p^\circ} - \nu_B RT \ln \frac{p_B}{p^\circ}.
\end{aligned}
$$

The quantity in the square bracket *is* the standard Gibbs energy change for the reaction, $\Delta_r G^\circ$

$$\Delta_r G^\circ = \nu_P\mu_P^\circ + \nu_Q\mu_Q^\circ - \nu_A\mu_A^\circ - \nu_B\mu_B^\circ.$$

This is because $\Delta_\mathrm{r}G^\circ$ is defined as 'products minus reactants' under standard conditions; μ_P° is the Gibbs energy of P under standard conditions, and so on for the other species. Using this, and taking the ν_P etc. inside the ln terms, we have

$$\Delta_\mathrm{r}G = \Delta_\mathrm{r}G^\circ + RT \ln\left(\frac{p_\mathrm{P}}{p^\circ}\right)^{\nu_\mathrm{P}} + RT \ln\left(\frac{p_\mathrm{Q}}{p^\circ}\right)^{\nu_\mathrm{Q}} - RT \ln\left(\frac{p_\mathrm{A}}{p^\circ}\right)^{\nu_\mathrm{A}} - RT \ln\left(\frac{p_\mathrm{B}}{p^\circ}\right)^{\nu_\mathrm{B}}.$$

Finally, we bring all of the ln terms together

$$\Delta_\mathrm{r}G = \Delta_\mathrm{r}G^\circ + RT \ln \frac{\left(\frac{p_\mathrm{P}}{p^\circ}\right)^{\nu_\mathrm{P}} \left(\frac{p_\mathrm{Q}}{p^\circ}\right)^{\nu_\mathrm{Q}}}{\left(\frac{p_\mathrm{A}}{p^\circ}\right)^{\nu_\mathrm{A}} \left(\frac{p_\mathrm{B}}{p^\circ}\right)^{\nu_\mathrm{B}}}. \tag{10.7}$$

Given a certain composition, i.e. certain values of the partial pressures p_A etc., we can use Eq. 10.7 to compute the value (and sign) of $\Delta_\mathrm{r}G$ (recall that the value of $\Delta_\mathrm{r}G^\circ$ can be determined from tables, as described in section 8.4 on p. 41).

We can also use Eq. 10.7 to find the position of equilibrium since at this point $\Delta_\mathrm{r}G = 0$:

$$0 = \Delta_\mathrm{r}G^\circ + RT \ln \left[\frac{\left(\frac{p_\mathrm{P}}{p^\circ}\right)^{\nu_\mathrm{P}} \left(\frac{p_\mathrm{Q}}{p^\circ}\right)^{\nu_\mathrm{Q}}}{\left(\frac{p_\mathrm{A}}{p^\circ}\right)^{\nu_\mathrm{A}} \left(\frac{p_\mathrm{B}}{p^\circ}\right)^{\nu_\mathrm{B}}}\right]_{\mathrm{eq.}}.$$

We have added the subscript 'eq.' to remind ourselves that this is only true when the partial pressures are at their equilibrium values.

The quantity in the square bracket is, of course, the equilibrium constant for the reaction (in fact it is K_p, as defined in Eq. 10.2 on p. 48). So, we can write

$$\boxed{\Delta_\mathrm{r}G^\circ = -RT \ln K_p.} \tag{10.8}$$

This is the exceptionally important relationship which we have been working towards for some time now. It shows that the value of the equilibrium constant is determined *only* by the value of $\Delta_\mathrm{r}G^\circ$. Remember that we can determine $\Delta_\mathrm{r}G^\circ$ from tabulated data, so using Eq. 10.8 we are able to compute the equilibrium constant of *any* reaction we care to think of. It is indeed a powerful relationship.

We could just as well have carried through the calculation assuming that the species were present in solution at concentration c_i. In this case we would have found

$$\Delta_\mathrm{r}G^\circ = -RT \ln K_c$$

where $\Delta_\mathrm{r}G^\circ$ is the Gibbs energy change under standard concentration conditions (rather than standard pressure).

10.3.1 Equilibria involving solids
Suppose we have an equilibrium involving solids as well as gases, for example

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \,.$$

From Eq. 10.4 on p. 49 we can write

$$\Delta_r G = \mu(CO_2) + \mu(CaO) - \mu(CaCO_3).$$

As we noted on p. 47, the chemical potentials of solids are always equal to their standard values. For CO_2 we can write the chemical potential in terms of the partial pressure (Eq. 10.6 on p. 50), just as we did before:

$$\Delta_r G = [\mu^\circ(CO_2) + \mu^\circ(CaO) - \mu^\circ(CaCO_3)] + RT \ln \frac{p_{CO_2}}{p^\circ}$$

The quantity in the square bracket is $\Delta_r G^\circ$ so we have, at equilibrium,

$$\Delta_r G^\circ = -RT \ln \frac{p_{CO_2,eq.}}{p^\circ}.$$

For this reaction equilibrium constant (the quantity in the ln) is simply $p_{CO_2,eq.}/p^\circ$.

We see that the reason that solids (and liquids) do not contribute to the expression for the equilibrium constant is that their chemical potentials are always equal to their standard chemical potentials. It is important not to forget that such species *do* contribute to $\Delta_r G^\circ$, and so affect the value of the equilibrium constant.

Example 7

10.4   Interpretation of $\Delta_r G^\circ = -RT \ln K$
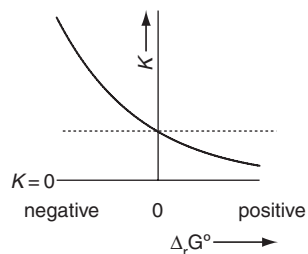
$$\boxed{\Delta_r G^\circ = -RT \ln K} \qquad\qquad \boxed{\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ}$$

These two relationships are so important that it is worthwhile spending some time exploring their interpretation.

The first thing to notice is that the sign of $\Delta_r G^\circ$ is very important. This is perhaps best seen by rewriting the relationship for K using exponentials:

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

From the properties of the exponential function we can see that


These points are illustrated in the graph opposite.

It is very important to realize that a reaction with *positive* $\Delta_r G^\circ$ will still go to products to some extent; it is just that at equilibrium the reactants will be favoured. Sometimes this can cause confusion as $\Delta_r G$ must be negative for a spontaneous process. The plot below should help to clarify this.
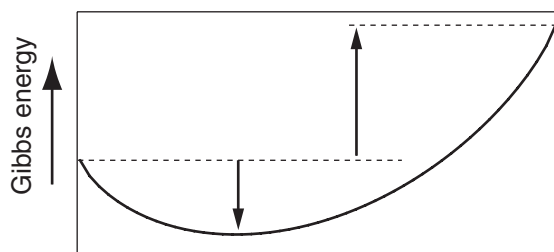
From the plot above we can see that going from pure reactants to pure products results in an increase in the Gibbs energy; such a process would not be spontaneous. However, if we start from pure reactants, and then increase the proportion of the products, to start with the Gibbs energy falls: such a process is spontaneous. In fact, the Gibbs energy falls all the way until we reach the equilibrium composition. So, although $\Delta_r G^\circ$ is positive, the reaction can still proceed to some extent.

Due to the exponential relationship between $\Delta_r G^\circ$ and the equilibrium constant, quite small changes in $\Delta_r G^\circ$ cause large changes in the equilibrium constant. This is illustrated on the graph below where K is plotted on a logarithmic scale (the temperature is taken as 298 K).
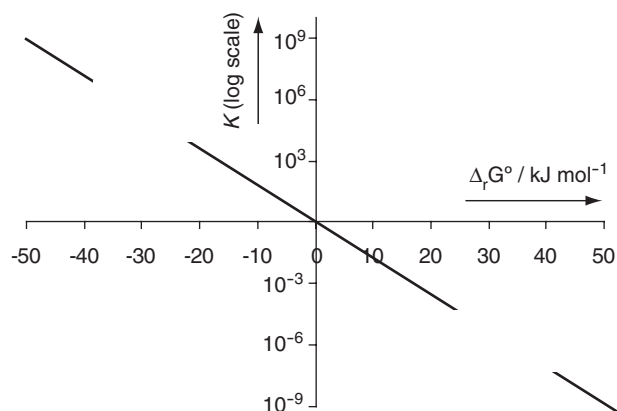
Once $\Delta_r G^\circ$ is more negative than about -40 kJ mol^{-1}, the equilibrium constant has become so large that the reaction goes essentially completely to products. Similarly, once $\Delta_r G^\circ$ is more positive that about $+40$ kJ mol^{-1}, the equilibrium constant is so small that essentially no products are formed.

10.5   Influencing equilibrium

10.5.1   Le Chatelier's principle

You may have come across *Le Chatelier's principle*, one statement of which is

> When a system in equilibrium is subjected to a change, the composition of the equilibrium mixture will alter in such a way as to counteract that change.

Various kinds of changes can be envisaged, such as concentration, pressure and temperature.

With the tools we have developed so far we are now able both to explain how Le Chatelier's principle arises and put is on a quantitative basis.

10.5.2 Changing concentration

We can think about the effect of changing concentration using the diagram opposite which is a typical profile of Gibbs energy against extent of reaction, from 100% reactants on the left, to 100% products on the right. The minimum in the plot corresponds to the position of equilibrium.
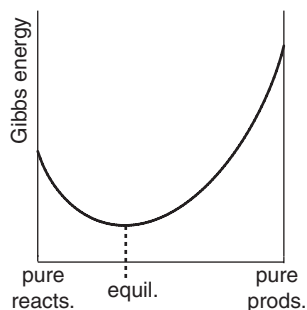
Suppose that we first allow the reaction to come to equilibrium. Then, by some means, we remove some of the product; this will increase the proportion of the reactants in the mixture, taking us to point **a**. The Gibbs energy at **a** is higher than at the equilibrium point, so moving towards equilibrium will be a spontaneous process; as a result of this process, some of the reactants will be converted to products.

Overall, we see that removing some of the products causes the system to react in such a way as to increase the amount of the products. This is just what Le Chatelier's principle predicts: the system moves in such a way as to oppose the change.

We can also move from equilibrium to point **a** by adding more of the reactants; the system will return to equilibrium by increasing the amount of the products. Once again, this is in accord with Le Chatelier's principle.

It is important to realise that the value of the equilibrium constant is not being changed. On the contrary, the concentrations of the species are altering in order to bring the ratio of the concentrations to the equilibrium value.

This idea of forcing the reaction one way or the other by removing or adding a reactant or product is used very often in chemistry. For example, the reaction in which an ester (**E**) is formed from a carboxylic acid (**C**) and an alcohol (**A**) is in fact a readily reversible equilibrium
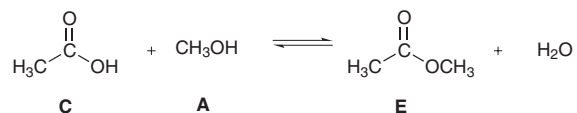
If we want to increase the yield of the ester we need to remove the products as they are formed, for example by distilling off the ester (if it is more volatile than the reactants) or by using a dehydrating agent which will sequestrate the water. Increasing the concentration of the reactants will also increase the amount of the ester at equilibrium; one common trick is to use the alcohol as the solvent. On the other hand, if we want the favoured reaction to be the reverse one (i.e. hydrolysis of the ester) then we could promote this my adding more water.

10.5.3 Effect of temperature

$$\boxed{\Delta_r G^\circ = -RT \ln K} \qquad\qquad \boxed{\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ}$$

From these equations we can see that $\Delta_r G^\circ$ is strongly temperature dependent (on account of the $T\Delta_r S^\circ$ term) and so the equilibrium constant is definitely temperature dependent. It is important to realise that this temperature dependence is *not* given by $\Delta_r G^\circ = -RT \ln K$ alone as $\Delta_r G^\circ$ is temperature dependent.

The quick approach

The temperature dependence of K can be found by starting with $\Delta_r G^\circ = -RT \ln K$ and then substituting in $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$:

$$-RT \ln K = \Delta_r G^\circ$$
$$-RT \ln K = \Delta_r H^\circ - T\Delta_r S^\circ$$
$$\ln K = \frac{-\Delta_r H^\circ}{R}\frac{1}{T} + \frac{\Delta_r S^\circ}{R} \qquad (10.9)$$

where to get to the last line we have divided both sides by $-RT$.

In interpreting Eq. 10.9 we need to be careful to remember that $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are temperature dependent (see sections 8.5 and 8.6 on p. 41). However, over a modest temperature range it is often the case that this variation is slight and so we may interpret Eq. 10.9 under assumption that $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are temperate independent.
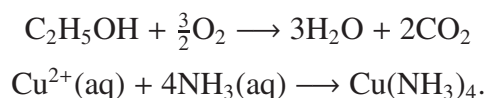
What Eq. 10.9 says is that the way in which K varies with temperature is determined by the *sign* of $\Delta_r H^\circ$.

These are the familiar results that for an endothermic reaction increasing the temperature shifts the equilibrium to the right (to products, increase in K) and that for an exothermic reaction the equilibrium shifts to the left (decrease in K).
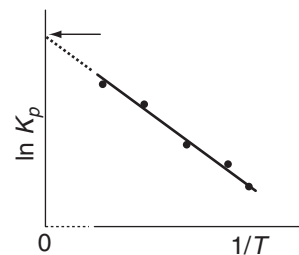
Indirect determination of $\Delta_r H^\circ$

Equation 10.9 implies that a plot of $\ln K$ against $1/T$ will be straight line of slope $-\Delta_r H^\circ/R$ and intercept $\Delta_r S^\circ/R$ (assuming that $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are independent of temperature). This proves to be a convenient way of determining $\Delta_r H^\circ$, as it is often quite straightforward to measure equilibrium constants (you will see several examples in the practical class).

Recall that ΔH is equal to the heat absorbed, at constant pressure. So $\Delta_r H^\circ$ for a reaction will be the heat absorbed when the reactants, in their standard states, are completely converted to the products, also in their standard states. It will thus only be possible to use heat measurements to determine $\Delta_r H^\circ$ for reactions which go *completely* to products. Examples of such reactions are the combustion of organic compounds and the formation of some transition metal complexes:

Graphical method for determining $\Delta_r H^\circ$ from the variation of K with temperature. A long extrapolation is needed to find $\Delta_r S^\circ$ from the intercept, so it may be preferable to compute $\Delta_r G^\circ$ from the measured values of K and then use $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$ to find $\Delta_r S^\circ$.

$$C_2H_5OH + \tfrac{3}{2}O_2 \longrightarrow 3H_2O + 2CO_2$$
$$Cu^{2+}(aq) + 4NH_3(aq) \longrightarrow Cu(NH_3)_4.$$

However, it is not possible to measure $\Delta_r H^\circ$ directly for a reaction such as the dimerization of NO_2 in the gas phase

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$
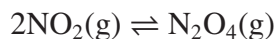
for which the equilibrium constant is about 1; the reaction simply does not go to completion.

Variation of the equilibrium constant with temperature: the van't Hoff isochore

A more formal method of finding how the equilibrium constant varies with temperature starts from the Gibbs–Helmholtz equation, Eq. 7.16 derived in section 7.2.3 on p. 38

$$\frac{d}{dT}\left(\frac{G}{T}\right) = -\frac{H}{T^2}. \qquad \text{const. pressure}$$

This is equally valid if we replace G by $\Delta_r G^\circ$ and H by $\Delta_r H^\circ$:

$$\frac{d}{dT}\left(\frac{\Delta_r G^\circ}{T}\right) = -\frac{\Delta_r H^\circ}{T^2}. \qquad (10.10)$$

$\Delta_r G^\circ = -RT \ln K$ can be rearranged to $\Delta_r G^\circ / T = -R \ln K$ and then this can be substituted in for the left-hand side of Eq.10.10 to give

$$\frac{d}{dT}(-R \ln K) = -\frac{\Delta_r H^\circ}{T^2}.$$

which can be rearranged to give the *van't Hoff isochore*

$$\boxed{\frac{d \ln K}{dT} = \frac{\Delta_r H^\circ}{RT^2}.} \qquad (10.11)$$

This equation says that if $\Delta_r H^\circ$ is positive, i.e. an endothermic reaction, $d \ln K/dT$ is positive and so the equilibrium constant *increases* with temperature. On the other hand, an exothermic reaction has a negative $\Delta_r H^\circ$ and so $d \ln K/dT$ is negative, meaning that the equilibrium constant decreases with increasing temperature. These are exactly the conclusions we reached earlier in this section.

We can go further and integrate Eq. 10.11 to find explicitly how the equilibrium constant varies with temperature

$$\frac{d \ln K}{dT} = \frac{\Delta_r H^\circ}{RT^2}$$

$$d \ln K = \frac{\Delta_r H^\circ}{RT^2} dT$$

$$\int_{T_1}^{T_2} d \ln K = \frac{\Delta_r H^\circ}{R} \int_{T_1}^{T_2} \frac{1}{T^2} dT$$

$$\left[\ln K\right]_{T_1}^{T_2} = \frac{\Delta_r H^\circ}{R} \left[\frac{-1}{T}\right]_{T_1}^{T_2}$$

$$\ln K(T_2) - \ln K(T_1) = -\frac{\Delta_r H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad (10.12)$$

On the third line we have assumed that $\Delta_r H^\circ$ does not vary with temperature and so can be taken outside the integral. As we have commented on above,

this is probably an acceptable approximation over a small temperature range. As usual, we have written $K(T)$ to remind ourselves that the equilibrium constant varies with temperature.

Equation 10.12 is a practical recipe for converting the equilibrium constant from one temperature to another. Alternatively, if we have measured values of the equilibrium constant at two temperatures we can determine a value of $\Delta_r H^\circ$.

If, rather than integrating between two temperatures, we simply compute the indefinite integral, we find

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

As we found in Eq. 10.9 on p. 55, this implies that a plot of $\ln K$ against $1/T$ will be a straight line of slope $-\Delta_r H^\circ/R$.

Example 8

Exercise 20

10.5.4 Variation of equilibrium with pressure

For a reaction in which all of the species are in solution altering the pressure will not have a significant effect. In contrast, for reactions involving gases we do expect there to be a direct effect.

Since, for a gas phase reaction, K_p and $\Delta_r G^\circ$ are related via $\Delta_r G^\circ = -RT \ln K_p$, and $\Delta_r G^\circ$ is defined under standard conditions (a pressure of 1 bar), it follows that K_p *does not* vary with the actual pressure. This does not mean that the *composition* of the equilibrium mixture does not change when the pressure is altered – quite the contrary.

For example, in a reaction such as

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$
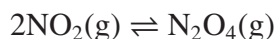
increasing the pressure moves the equilibrium to the right, as this is associated with a reduction in the number of moles of gas (an application of Le Chatelier's principle). One way of viewing what happens is to say that when the pressure is changed, the composition changes in order to keep K_p constant.

We can understand this quantitatively by thinking about a simple equilibrium, such as the dissociation of a dimer, A_2:

$$A_2(g) \rightleftharpoons 2A(g)$$
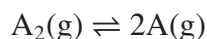
The extent to which this reaction has gone to products can be characterised by a parameter α, the *degree of dissociation*. If $\alpha = 1$, the dimer is completely dissociated; if $\alpha = 0$, there is no dissociation. α can be described as the *fraction* of A_2 molecules which have dissociated.

Suppose that we start out with n_0 moles of A_2 in a reaction vessel whose pressure can be controlled (for example by pushing in or pulling out a piston). The system is allowed to come to equilibrium at a pressure p_{tot}; at equilibrium the degree of dissociation is α.

It follows that the number of moles of A_2 at equilibrium is $(1 - \alpha)n_0$, and the number of moles of A is $2\alpha n_0$; the factor of two arises because each A_2 molecule dissociates into two A molecules. The total number of moles is thus $(1 + \alpha)n_0$.

We now need to work out the partial pressures of the species, and this is done using

$$p_i = x_i p_{tot}$$

where p_i is the partial pressure of species i and x_i is the mole fraction of i, given by n_i/n_{tot}, where n_{tot} is the total number of moles in the system.

Using this, the partial pressures of A_2 and A, p_{A_2} and p_A, are:

$$p_{A_2} = \frac{n_0(1-\alpha)}{n_0(1+\alpha)} p_{tot} = \frac{(1-\alpha)}{(1+\alpha)} p_{tot}$$

$$p_A = \frac{2n_0\alpha}{n_0(1+\alpha)} p_{tot} = \frac{2\alpha}{(1+\alpha)} p_{tot}.$$

Hence the equilibrium constant can be written

$$\begin{aligned} K_p &= \frac{(p_A/p^\circ)^2}{(p_{A_2}/p^\circ)} = \frac{4\alpha^2}{(1+\alpha)^2} \frac{(1+\alpha)}{(1-\alpha)} \frac{p_{tot}^2}{p_{tot}} \frac{p^\circ}{(p^\circ)^2} \\ &= \frac{4\alpha^2}{(1-\alpha^2)} \frac{p_{tot}}{p^\circ}. \end{aligned}$$

When p_{tot} is varied, we have already seen that K_p does not vary, so it must be that α varies i.e. the degree of dissociation varies. We could solve this equation to find how explicitly how α varies with pressure. To make this solution easier, we will assume that α is small, $\alpha << 1$, so $(1-\alpha^2) \approx 1$ and hence

$$K_p = 4\alpha^2 \frac{p_{tot}}{p^\circ}$$

$$\text{hence } \alpha = \sqrt{\frac{K_p p^\circ}{4p_{tot}}}.$$

It is clear from this that as the pressure is increased, the degree of dissociation, α falls i.e. increasing the pressure moves the equilibrium towards the reactants, just as we would expect from Le Chatelier's principle.

11 Applications in biology

We are familiar with the idea that living organisms need 'energy' in order to carry out the chemical processes which are the basis of life. However, from our understanding of the Second Law and Gibbs energy, we now see that the key characteristic of these reactions is that they must be accompanied by a reduction in *Gibbs energy*.

For many organisms the source of Gibbs energy is the oxidation of glucose to water and carbon dioxide – a reaction which has $\Delta_r G^\circ = -2880$ kJ mol^{-1}, a substantial quantity. It is this reduction in Gibbs energy which is used to drive chemical reactions which would not otherwise 'go'.

The way Nature does this is to couple two reactions together. The reaction we want to promote, which is accompanied by an *increase* in the Gibbs energy, is coupled to a second reaction in which the Gibbs energy *decreases*. Provided that this decrease is larger in size than the increase in Gibbs energy of the first reaction, the two reactions taken together result in a decrease in Gibbs energy and therefore 'go'.

The difficult part is coupling the two reactions together: Nature does this by arranging for an intimate connection between the two reactions, for example by arranging that both take place at the active site of an enzyme. Nature has had a long time to develop ways of coupling reactions, and we can only marvel at complexity and subtlety of how such coupling is achieved.

ATP

In biological systems the molecule adenosine triphosphate (ATP) plays an important role in supplying the Gibbs energy which is used to drive other reactions, such a protein synthesis and active transport.
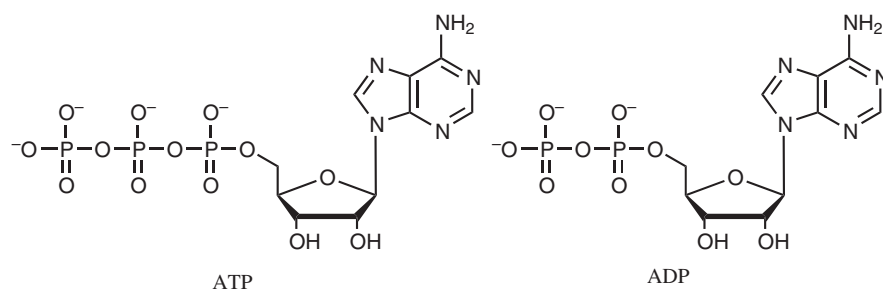

ATP releases Gibbs energy through a hydrolysis reaction involving breaking one of the phosphate bonds to give ADP. The reaction is
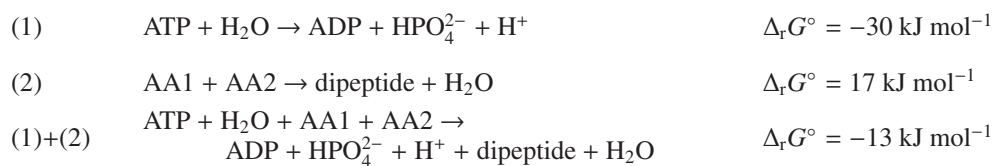
$$ATP(aq) + H_2O(l) \rightarrow ADP(aq) + HPO_4^{2-}(aq) + H^+(aq)$$
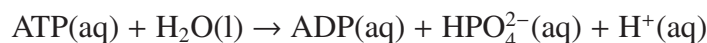
At physiological pH (about 7) and body temperature (37 °C), this reaction has $\Delta_r G^\circ = -30$ kJ mol^{-1}, $\Delta_r H^\circ = -20$ kJ mol^{-1}, $\Delta_r S^\circ = +34$ J K^{-1} mol^{-1} and $-T\Delta_r S^\circ = -10$ kJ mol^{-1}. The reaction is thus favoured, both energetically through the $\Delta_r H^\circ$ term, and entropically through the $\Delta_r S^\circ$ term.

Protein synthesis

Proteins are synthesised by coupling together amino acids, a reaction which has an unfavourable $\Delta_r G°$ of about 17 kJ mol^{-1}.

amino acid 1   amino acid 2   dipeptide
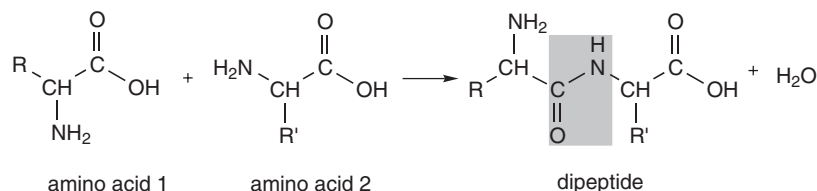
The reaction can be made to 'go' by coupling it with the hydrolysis of ATP:

(1)	$ATP + H_2O \rightarrow ADP + HPO_4^{2-} + H^+$	$\Delta_r G° = -30$ kJ mol^{-1}
(2)	$AA1 + AA2 \rightarrow$ dipeptide $+ H_2O$	$\Delta_r G° = 17$ kJ mol^{-1}
(1)+(2)	$ATP + H_2O + AA1 + AA2 \rightarrow$ $ADP + HPO_4^{2-} + H^+ +$ dipeptide $+ H_2O$	$\Delta_r G° = -13$ kJ mol^{-1}

The result is that $\Delta_r G°$ is negative for the coupled reactions, which means that the equilibrium lies well towards the products i.e. the reaction 'goes'. The hard part is to make sure that the two reactions are physically coupled – it is no use hydrolysing some ATP in one part of the cell and trying to make a peptide bond in another part! As we mentioned above, Nature has crafted carefully designed enzymes to ensure this coupling of the reactions.

Synthesis of ATP: respiration

Of course, if ATP is to be used as a source of Gibbs energy, there has to be a way of converting the ADP back to ATP within the cell. This is done by coupling the reverse of the hydrolysis of ATP to a reaction whose $\Delta_r G°$ is more negative than -30 kJ mol^{-1}.

Many organisms utilize glucose as their primary energy source, and the Gibbs energy is derived from the conversion of glucose into water and carbon dioxide. The complete conversion of glucose to $H_2O + CO_2$ yields a $\Delta_r G°$ of -2880 kJ mol^{-1}. Nature has developed a set of reactions which couple the formation of no less than 38 ATP molecules (from ADP) to the complete oxidation of one glucose molecule.

Photosynthesis

Another example of coupling is photosynthesis, which plants use to produce glucose from water and carbon dioxide. The chemical reaction has $\Delta_r G° = +2880$ kJ mol^{-1}, so clearly cannot take place on its own. However, Nature has developed a method of coupling this reaction to the energy available from light. The apparatus which a plant has to achieve this coupling, and achieve it in an efficient way, is very complex.

12 Electrochemistry

Chemical reactions involving reduction and oxidation can be thought of as involving the transfer of electrons. For example, the reaction

$$Cu^{2+}(aq) + Zn(m) \rightarrow Cu(m) + Zn^{2+}(aq)$$
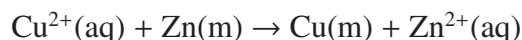
can be thought of as taking place by two electrons being transferred from the zinc metal to the copper cation.

If we just mix the reactants there is no way to 'trap' these electrons, but if the reaction is set up in an electrochemical cell we can arrange for the electron transfer to take place through an external circuit. A suitable cell is shown opposite.

A schematic cell which 'captures' the electrons from the redox reaction between Cu^{2+} and Zn and results in the flow of electrons round an external circuit. The two compartments are separated by a porous barrier.

The key to capturing the electrons is to keep the Cu and Zn species separate in what are called two *half cells*. In the right-hand half cell Zn dissolves from the electrode to form Zn^{2+} ions; the two electrons then move round the external circuit where, on arrival at the Cu electrode, they pick up a Cu^{2+} ion from the left-hand half cell. Overall the reaction is as above, but the electrons travel round the external circuit rather than between the reacting ions.

The same cell, but this time wired to measure the potential (voltage) produced. Modern electronic voltmeters are able to measure the voltage without drawing significant current from the cell.

This cell turns the energy available from the chemical reaction (in fact the Gibbs energy) into an electrical current; this is of great practical importance as this principle is the basis of electrical batteries. However, we will be more interested not in the current that we can extract from the cell but the electric potential (sometimes called the electromotive force, EMF, or loosely the 'voltage') that the cell develops between its electrodes under conditions of zero current flow.

We will show that this potential is directly related to $\Delta_r G$ for the cell reaction. This is exceptionally useful, as it gives us a direct measurement of $\Delta_r G$, something which is rarely achieved by other methods. Using cells we can therefore determine the thermodynamic parameters of ions in solution and other related species. We will also find that there is a relatively simple relationship (the *Nernst Equation*) between the cell potential and the concentration of the species in the solutions. Thus concentrations can be determined from measurements of the cell potential. This has very important practical applications in the construction of non-invasive sensors for measuring the concentration of ions in solution.

A further application of these ideas is in assessing the redox stability of chemical species, particularly metals and their ions. We will see that, simply by comparing two electrode potentials, it is possible to determine whether one species will be oxidized or reduced by another. For example, in the case copper and zinc, simply by referring to tables of electrode potentials it can be determined that Zn will reduce Cu^{2+}, whereas Cu will not reduce Zn^{2+}.

This approach is very useful in understanding the redox reactions of such species as transition metal ions, which have many possible oxidation states. Similarly, electrode potentials are important for understanding redox chemistry in biological systems, where enzyme-bound metal ions often play a crucial role.
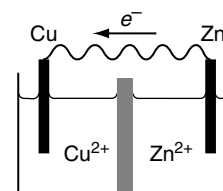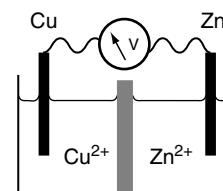
12.1   Cell conventions

When we specify $\Delta_r S$ for a chemical reaction we understand that this means 'entropy of products minus entropy of reactants'. The fact we calculate it in this way is simply a convention; we must adhere to this convention if we want our values to agree with what every one else obtains. In the same way, there are certain conventions for dealing with cells which we must adhere to.

12.1.1   Half-cell reactions and couples

We usually think of a cell in terms of two half cells. For example, in the cell described above the right-hand half cell consists of Zn(m) in contact with Zn^{2+}(aq), and the left-hand half cell consists of Cu(m) in contact with Cu^{2+}(aq). The reactions that take place in these half cells include electrons in the balanced chemical equations. So, in the case of the left-hand half cell, the reaction is

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(m)$$
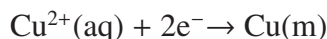
Note that the charges as well as the chemical species balance. Such a reaction is called a *half-cell reaction*. In this reaction, Cu^{2+} is the *oxidized* form and Cu is the *reduced* form. These two forms of Cu, the oxidized and the reduced, are said to form a *couple*. So, we talk about the 'Cu^{2+}/Cu couple'.

   Similarly, the Zn^{2+}/Zn couple has the half-cell reaction

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(m)$$
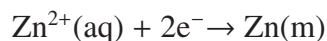
12.1.2   The cell conventions

We will see in due course that the sign of the cell potential is very important, so we need to have an agreed convention about what a positive or negative sign means, and which reaction this refers to. The following set of conventions are adopted in order to remove any ambiguity.

1. The cell is written on paper, thus identifying clearly the left- and right-hand half cells.

RHS: right-hand side; LHS: left-hand side.

2. Each half cell reaction is written as a reduction i.e. with the electrons on the left-hand side of the reaction.

3. Having written the left- and right-hand half cell reactions as reductions involving the same number of electrons, the conventional cell reaction is found by taking (RHS half-cell reaction) − (LHS half-cell reaction).

This means that you connect the positive (red) lead of the voltmeter to the RHS electrode

4. The cell potential is that of the RHS measured relative to the LHS.

12.1.3   Shorthand for cells

There is a commonly used shorthand way for writing cells on paper. The electrodes and species involved are written out on a line, with the left-hand electrode on the left and the right-hand on the right. So, for the cell above the shorthand notation is

$$Cu(m) \mid Cu^{2+}(aq) \parallel Zn^{2+}(aq) \mid Zn(m)$$
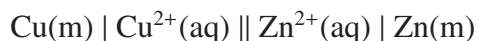
   A vertical line, |, is used to separate different phases (here the solution from the solid), a comma is used to separate species in the same phase, and a double vertical line, ||, indicates a junction between two solutions – often called a liquid junction. An alternative symbol for this is $\mid \times \mid$.

12.1.4 Examples of using the cell conventions

Example 1

For the cell

$$Zn(m)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(m)$$

The RHS half-cell reaction is

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(m)$$
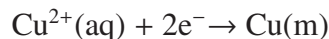
and the LHS half-cell reaction is

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(m)$$
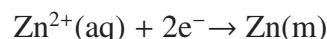
Note that both are written as reductions and both involve the same number of electrons. The conventional cell reaction is thus (RHS − LHS). Remembering that chemical equations can be subtracted just in the same way as algebraic equations, we find
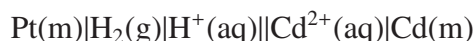
$$
\begin{aligned}
&\quad Cu^{2+}(aq) + 2e^- \rightarrow Cu(m) \\
-&\quad Zn^{2+}(aq) + 2e^- \rightarrow Zn(m) \\
\equiv&\quad Cu^{2+}(aq) + 2e^- - Zn^{2+}(aq) - 2e^- \rightarrow Cu(m) - Zn(m) \\
\equiv&\quad Cu^{2+}(aq) + Zn(m) \rightarrow Cu(m) + Zn^{2+}(aq)
\end{aligned}
$$
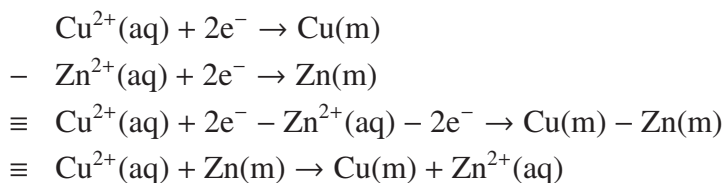
where to get from the third to the fourth line we have moved negative terms to the opposite side. The conventional cell reaction is thus

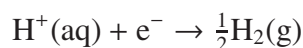$$Cu^{2+}(aq) + Zn(m) \rightarrow Cu(m) + Zn^{2+}(aq)$$

Example 2

The cell

$$Pt(m)|H_2(g)|H^+(aq)||Cd^{2+}(aq)|Cd(m)$$
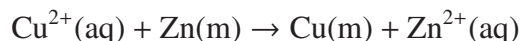
has as hydrogen electrode on the left-hand side. In this electrode the species involved are $H^+(aq)$ and $H_2(g)$; the platinum just acts as in inert conductor to 'pick up' the electrons.
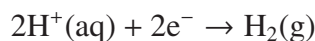
The RHS half cell reaction is

$$Cd^{2+}(aq) + 2e^- \rightarrow Cd(m)$$
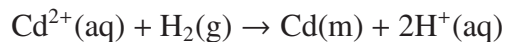
and the LHS is

$$H^+(aq) + e^- \rightarrow \tfrac{1}{2}H_2(g)$$

We note that there are not the same number of electrons involved, so either the RHS equation will have to be halved, or the LHS doubled; we choose the latter, although the former is just as valid a choice. The LHS then becomes

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

Then, taking (RHS − LHS) as before we find the conventional cell reaction is

$$Cd^{2+}(aq) + H_2(g) \rightarrow Cd(m) + 2H^+(aq)$$

Example 9 (a)

We see from these examples that the conventional cell reaction is just a result of how we write the cell down: if we swapped the two sides, the conventional cell reaction would reverse. The conventional cell reaction may not be the same as the reaction which takes place when a current is allowed to flow – called the spontaneous cell reaction; we return to this point in section 12.5 on p. 67.

12.2 Thermodynamic parameters from cell potentials

It can be shown (see appendix section 13.3 on p. 78, but this proof is not required) that, at constant temperature and pressure, the cell EMF is related to $\Delta_r G_{cell}$ for the conventional cell reaction according to:

$$\boxed{\Delta_r G_{cell} = -nFE} \qquad \text{const. } p \text{ and } T. \qquad (12.1)$$

In this relationship, F is the Faraday constant, which is the charge on one mole of fundamental charges; $F = 96{,}485$ C mol^{-1}. n is the number of electrons involved in the cell reaction.

This is an exceptionally important relationship as it relates the cell EMF, which can easily be measured with a voltmeter, to the useful thermodynamic parameter, $\Delta_r G_{cell}$. Such an easy measurement of $\Delta_r G$ is almost unique.

Once we have determined $\Delta_r G_{cell}$ it is easy to find $\Delta_r S_{cell}$. Recall that Eq. 7.14 on p. 38 gives us a relationship between S and the temperature variation of G:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S\,;$$

this applies equally well to $\Delta_r G_{cell}$ and $\Delta_r S_{cell}$. So, using Eq. 12.1, we have

$$
\begin{aligned}
\Delta_r S_{cell} &= -\left(\frac{\partial \Delta_r G_{cell}}{\partial T}\right)_p \\
&= -\left(\frac{\partial (-nFE)}{\partial T}\right)_p \\
&= nF\left(\frac{\partial E}{\partial T}\right)_p. \qquad (12.2)
\end{aligned}
$$

So the entropy change of the cell reaction can be found simply from the temperature coefficient of the cell potential. In practice, all we would need to do is to measure the cell potential over a range of temperatures, plot the graph and then take the slope.

Once we have $\Delta_r G_{cell}$ and $\Delta_r S_{cell}$, $\Delta_r H_{cell}$ is easily found from $\Delta_r G_{cell} = \Delta_r H_{cell} - T\Delta_r S_{cell}$. So, for reactions which can be set up to form an electrochemical cell, it is very straightforward to measure these thermodynamic parameters.

12.3 The Nernst equation

The cell potential changes as the concentration of the species involved in the cell reaction change. We shall see that this comes about because $\Delta_r G_{cell}$ depends on the chemical potentials of the species involved and, as we have already seen, the chemical potential depends on concentration. The Nernst equation predicts this dependence of the cell potential on concentration. Before deriving the Nernst equation we need to consider how chemical potentials depend on concentration.

12.3.1 Chemical potentials and activities

The idea of chemical potential was introduced in section 9.3 on p. 45, and we saw there that the chemical potential of a gas varies with its partial pressure,

p_i, according to

$$\mu_i(p_i) = \mu_i^\circ + RT \ln \frac{p_i}{p^\circ}.$$

We also saw that for solids and liquids the chemical potential is always equal to the standard chemical potential.

For *ideal* solutions, the chemical potential depends on the concentration, c_i

$$\mu_i(c_i) = \mu_i^\circ + RT \ln \frac{c_i}{c^\circ}.$$

The problem with this is that solutions of ions are not ideal, even at very low concentrations, so we really cannot use this expression. Rather, we have to write the chemical potential in terms of a quantity called the *activity*. a_i:

$$\mu_i(a_i) = \mu_i^\circ + RT \ln a_i. \tag{12.3}$$

The activity is a dimensionless quantity whose value is defined by Eq. 12.3. At first, this seems like an odd definition, but it turns out that chemical potentials are experimentally measurable, for example from electrochemical cells.

As the concentration tends to zero, the activity can be approximated by the concentration divided by the standard concentration (to make it a dimensionless ratio)

$$a_i \rightarrow \left(\frac{c_i}{c^\circ}\right) \text{ as } c_i \rightarrow 0$$

For ions in solution, *Debye–Hückel theory* gives reasonable estimates of the activities in terms of concentrations, but this theory lies well beyond the scope of this course. So for now we will simply assume that in any calculations activities can be replaced by concentrations. We will, however, continue to write activities in our expressions.

12.3.2 Derivation of the Nernst equation

Suppose that the conventional cell reaction has the general form

$$\nu_A A + \nu_B B \longrightarrow \nu_P P + \nu_Q Q.$$
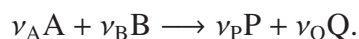
We have already argued (in section 10.2 on p. 49) that $\Delta_r G$ can be written in terms of the chemical potentials

$$\Delta_r G = \nu_P \mu_P + \nu_Q \mu_Q - \nu_A \mu_A - \nu_B \mu_B.$$

In section 10.3 on p. 50 we showed that, as the chemical potentials depend on the partial pressures, $\Delta_r G$ can be written (Eq. 10.7)

$$\Delta_r G = \Delta_r G^\circ + RT \ln \frac{\left(\frac{p_P}{p^\circ}\right)^{\nu_P} \left(\frac{p_Q}{p^\circ}\right)^{\nu_Q}}{\left(\frac{p_A}{p^\circ}\right)^{\nu_A} \left(\frac{p_B}{p^\circ}\right)^{\nu_B}}$$

where

$$\Delta_r G^\circ = \nu_P \mu_P^\circ + \nu_Q \mu_Q^\circ - \nu_A \mu_A^\circ - \nu_B \mu_B^\circ.$$

These relationships work just as well for ions in solution where the chemical potentials depend on the activities, as given by Eq. 12.3, rather than the

partial pressures. So, all we have to do is replace each term $(p_i/p°)$ by a_i to give

$$\Delta_r G_{\text{cell}} = \Delta_r G°_{\text{cell}} + RT \ln \frac{(a_P)^{\nu_P} (a_Q)^{\nu_Q}}{(a_A)^{\nu_A} (a_B)^{\nu_B}} \qquad (12.4)$$

Recall from Eq. 12.1 on p. 64 that $\Delta_r G_{\text{cell}} = -nFE$. Similarly, we can write

$$\Delta_r G°_{\text{cell}} = -nFE°$$

where $E°$ is the *standard cell potential*. It is the potential which the cell will develop when all the species are present under standard conditions (i.e. unit activity, $p = 1$ bar etc.).

Rewriting the $\Delta_r G$ in Eq. 12.4 in terms of cell potentials ($\Delta_r G_{\text{cell}} = -nFE$) we have

$$-nFE = -nFE° + RT \ln \frac{(a_P)^{\nu_P} (a_Q)^{\nu_Q}}{(a_A)^{\nu_A} (a_B)^{\nu_B}};$$

dividing each side by $-nF$ gives the Nernst equation

$$\boxed{E = E° - \frac{RT}{nF} \ln \frac{(a_P)^{\nu_P} (a_Q)^{\nu_Q}}{(a_A)^{\nu_A} (a_B)^{\nu_B}}.} \qquad (12.5)$$

For simplicity we have written the Nernst equation in terms of activities, a_i. However, if a particular species is a gas its activity is replaced by $(p_i/p°)$ as $\mu_i(p_i) = \mu_i° + RT \ln(p_i/p°)$. If a species is a solid or pure liquid, $\mu_i = \mu_i°$ so there is no contribution to the fraction on the RHS of Eq. 12.5.

The fraction on the RHS of the Nernst equation has the same form as an equilibrium constant i.e. 'products over reactants'. However, it is *not* an equilibrium constant as the activities are not necessarily those at equilibrium.

12.3.3   Nernst equation for half cells

As derived, the Nernst equation (Eq. 12.5) refers to the conventional cell reaction which can be thought of as the difference between two half-cell reactions. It is often convenient to think of the potential developed by each half cell on its own, called the half-cell potential. Of course, we cannot measure such a potential directly as any cell necessarily involves two half-cells.

A typical half-cell reaction (written as a reduction in line with the convention described in section 12.1 on p. 62) is

$$\nu_L L + \nu_M M + ne^- \longrightarrow \nu_X X + \nu_Y Y.$$
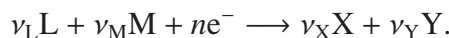
The half-cell potential, $E_{\frac{1}{2}}$, is given by

$$\boxed{E_{\frac{1}{2}} = E°_{\frac{1}{2}} - \frac{RT}{nF} \ln \frac{(a_X)^{\nu_X} (a_Y)^{\nu_Y}}{(a_L)^{\nu_L} (a_M)^{\nu_M}}.} \qquad (12.6)$$

where $E°_{\frac{1}{2}}$ is the *standard half-cell potential* which is defined as the potential generated when all the species are present at unit activity. As before, the fraction in the ln term has the familiar form of 'products over reactants'.

The cell potential is calculated by taking 'RHS − LHS', just as we did when determining the conventional cell reaction in section 12.1 on p. 62:

$$E = E_{\frac{1}{2}}(\text{RHS}) - E_{\frac{1}{2}}(\text{LHS}).$$

In the same way the standard cell potential can be found from the standard half-cell potentials

$$E^\circ = E^\circ_{\frac{1}{2}}(\text{RHS}) - E^\circ_{\frac{1}{2}}(\text{LHS}).$$

Given that standard half-cell potentials are tabulated (see the following section), this is the way in which we can determine the standard potential of any cell.

12.4   Standard half-cell potentials

We noted in the previous section that it is not possible to measure a half-cell potential on its own as the potential of any cell will always be the difference of two half-cell potentials. We can draw up a table of standard half-cell potentials by defining one of the half-cells to have zero potential and then referencing all other half-cell potentials to this. Since all calculations involve a difference in half-cell potentials, this arbitrary choice of a zero point will not cause any problems.

Schematic diagram of a standard hydrogen electrode.

The electrode whose standard potential is take as zero is the *standard hydrogen electrode* (SHE). This consists of H_2 gas at a pressure of 1 bar in contact with an aqueous solution of H^+ at unit activity; an inert Pt electrode is used to make the electrical contact. In the usual notation the cell is

$$\text{Pt(m)} \,|\, H_2(g, p = 1 \text{ bar}) \,|\, H^+(aq, a = 1)$$

and the half-cell reaction is

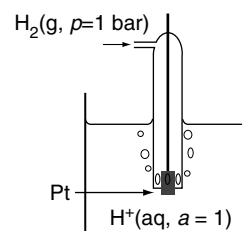$$H^+(aq) + e^- \rightarrow \tfrac{1}{2} H_2(g).$$
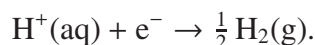
The standard potential of an electrode is defined as the potential developed by a cell in which the left-hand electrode is the standard hydrogen electrode and the right-hand electrode is the one under test; all species are present at unit activity.

Example 9 (b)

12.4.1   Tabulation of standard half-cell potentials

Extensive tabulations of standard half-cell potentials are available (see, for example, the data sections in P W Atkins *Physical Chemistry*). As the cell potential is essentially a value for $\Delta_r G$, we expect it to depend strongly on temperature. Therefore the tabulated data are at a specified temperature, most commonly 298 K.

12.5   The spontaneous cell reaction

In section 12.1 on p. 62 we described the way in which the conventional cell reaction can be determined. It is important to realise that this conventional reaction depends only on how the cell is written down on paper. If we were

to swap the RHS and LHS electrodes, the conventional reaction will be the other way round.

The actual reaction that would take place if current were allowed to flow – called the *spontaneous cell reaction* – is found by inspecting the sign of the cell potential.
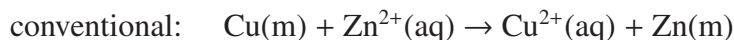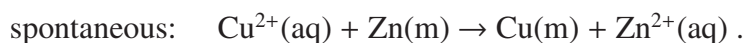
For example, the cell

$$Cu(m) \mid Cu^{2+}(aq, a = 1) \parallel Zn^{2+}(aq, a = 1) \mid Zn(m)$$

in which all species are present at unit activity develops a potential

$$
\begin{aligned}
E &= E^\circ_{\frac{1}{2}}(RHS) - E^\circ_{\frac{1}{2}}(LHS) \\
&= E^\circ(Zn, Zn^{2+}) - E^\circ(Cu, Cu^{2+}) \\
&= -0.76 - (+0.34) = -1.10 \text{ V}.
\end{aligned}
$$

The conventional cell reaction is

$$\text{conventional:} \quad Cu(m) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(m)$$

but as the cell potential is negative the spontaneous reaction is the reverse of this

$$\text{spontaneous:} \quad Cu^{2+}(aq) + Zn(m) \rightarrow Cu(m) + Zn^{2+}(aq).$$
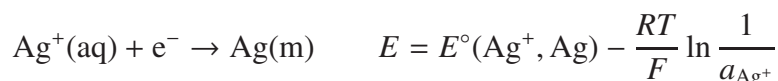
Example 9 (c)

Exercise 26

Note that cell potentials are affected by the concentrations of the species involved, so under some circumstances the direction of the spontaneous cell reaction can be reversed simply by altering the concentrations of the ions.

12.6 Types of half cells

There are many different types of half cells whose potentials are sensitive to a wide variety of different species. For each half-cell electrode illustrated below the half-cell reaction and the Nernst equation is also given.
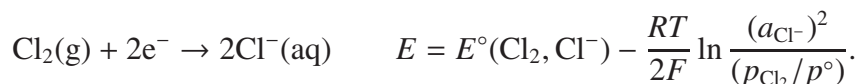
12.6.1 Metal/metal ion

These consist of a metal in contact with a solution of its ions:

$$Ag^+(aq) + e^- \rightarrow Ag(m) \qquad E = E^\circ(Ag^+, Ag) - \frac{RT}{F} \ln \frac{1}{a_{Ag^+}}$$
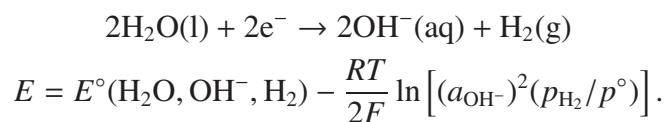
12.6.2   Gas/ion

These consist of the gas in contact with a solution containing related ions; an inert Pt electrode provides the electrical contact. The ions can be anions or cations.

$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq) \qquad E = E^\circ(Cl_2, Cl^-) - \frac{RT}{2F} \ln \frac{(a_{Cl^-})^2}{(p_{Cl_2}/p^\circ)}.$$

The second example is similar to the hydrogen electrode, but instead of there being H^+ in the solution we have OH^-. In order to balance the equation two (solvent) water molecules are needed; we can always use solvent in this way.
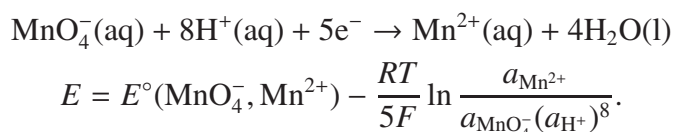
$$2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$$

$$E = E^\circ(H_2O, OH^-, H_2) - \frac{RT}{2F} \ln \left[(a_{OH^-})^2 (p_{H_2}/p^\circ) \right].$$

As the water is the solvent we assume that it is essentially in its pure form and so does not contribute a term to the fraction inside the ln.

12.6.3   Redox

The oxidized and reduced species are both present in solution; an inert Pt electrode provides the electrical contact.

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \qquad E = E^\circ(Fe^{3+}, Fe^{2+}) - \frac{RT}{F} \ln \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}.$$
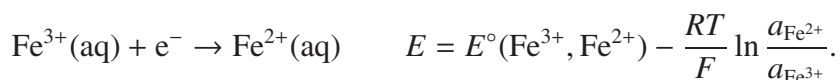
In the second example the solution is acid and solvent (water) is needed to balance the equation

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

$$E = E^\circ(MnO_4^-, Mn^{2+}) - \frac{RT}{5F} \ln \frac{a_{Mn^{2+}}}{a_{MnO_4^-}(a_{H^+})^8}.$$

12.6.4   Metal/insoluble salt/anion

These consist of a metal coated with a layer of the insoluble salt formed by the metal and the anion which is in the solution. The commonest example is the combination silver, silver chloride, chloride anion:

$$AgCl(s) + e^- \rightarrow Ag(m) + Cl^-(aq) \qquad E = E^\circ(AgCl, Ag, Cl^-) - \frac{RT}{F} \ln a_{Cl^-}$$

Another commonly encountered electrode is that between liquid mercury, solid mercurous chloride (mercury(I) chloride) and chloride anions. The mercurous chloride is made up in a paste with liquid mercury and then floated on top of mercury. This electrode is called the *calomel electrode*.
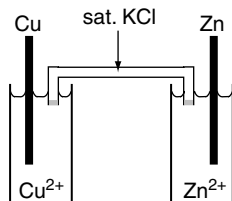
$$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$$

$$E = E^\circ(Hg_2Cl_2, Hg, Cl^-) - \frac{RT}{2F} \ln(a_{Cl^-})^2$$
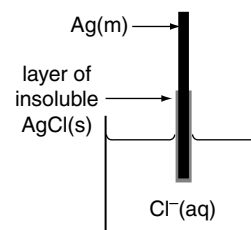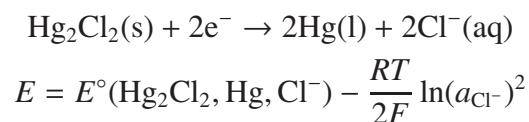
Schematic diagram of an Ag,AgCl electrode.

As in earlier examples, some of the half-cell reactions of this type involve the solvent. For example the lead, lead oxide, hydroxide system

$$PbO(s) + H_2O + 2e^- \rightarrow Pb(m) + 2OH^-(aq)$$
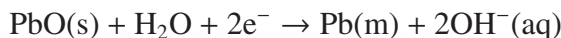
$$E = E^\circ(PbO, Pb, OH^-) - \frac{RT}{2F} \ln(a_{OH^-})^2$$

The point about all of these electrodes is that their half-cell potentials depend on the concentrations of *anions*. The AgCl/Ag electrode is a much more convenient chloride electrode to use that the Cl_2/Cl^- electrode.

12.6.5 Liquid junctions

If it is the case that the solutions in the two half-cells are different, then a problem arises in that for the cell to produce a potential the two solutions must be in contact. However, they must not mix as then the reaction would take place without the electrons moving round the external circuit. The 'join' between the two solutions is called a liquid junction.

Typically such a junction is handled in practice by having a porous barrier between the two solutions; this allows contact but prevents rapid mixing. The problem with this arrangement is that a potential, called a *liquid junction potential*, may be set up across the barrier. It turns out that this potential detracts from the cell potential and so the measured potential will not be correct.

Liquid junction potentials can be minimised by using a salt bridge. This is a tube containing, typically, a concentrated solution of KCl or KNO_3; the ends of the tube dip in the solutions which form the cell and the KCl solution is kept in the tube by glass sinters at each end. Such a salt bridge provides electrical contact between the solutions and minimizes the liquid junction potential.

Schematic of a cell employing a salt bridge to connect the two half cells.

12.7 Redox stability

One very useful application of electrode potentials is in assessing redox reactions. For example, we saw in section 12.5 on p. 67 that, under standard conditions, Zn metal will reduce Cu^{2+} to Cu metal, the zinc being oxidized to Zn^{2+} in the process. We can generalize this approach in the following way.

Suppose that we have a species A which can exist in an oxidized form, A_O, and a reduced form, A_R, related by the half-cell reaction involving n_A electrons:

$$A_O + n_A e^- \longrightarrow A_R;$$
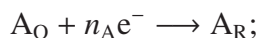
it is supposed that the charges on A_O and A_R are such that this equation is balanced. Let the EMF of this half cell be E_A. Typically, A_O will be a metal ion and A_R will be the metal, or a lower oxidation state of the metal.

Similarly, species B exists in an oxidised and a reduced form, related by the following half cell equation involving n_B electrons:

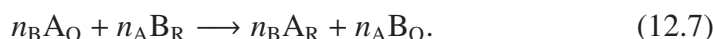$$B_O + n_B e^- \longrightarrow B_R;$$
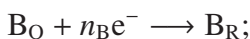
let the half-cell EMF of this reaction be E_B.

Now imagine a cell in which the RHS is formed from the couple A_O/A_R and the LHS from the couple B_O/B_R. We now want to work out the conventional cell reaction, which we do by taking the RHS half cell reaction minus

the LHS. However, first we must ensure that there are the same number of electrons involved in each half cell; this is easily done by multiplying the half-cell reaction for A by n_B and that for B by n_A. This gives

$$\text{RHS} \quad n_B A_O + n_B n_A e^- \longrightarrow n_B A_R$$
$$\text{LHS} \quad n_A B_O + n_A n_B e^- \longrightarrow n_A B_R.$$
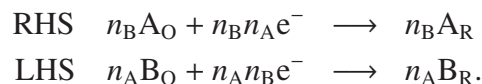
Computing RHS − LHS gives

$$n_B A_O + n_A B_R \longrightarrow n_B A_R + n_A B_O. \tag{12.7}$$

The EMF of the cell is $E_A - E_B$ and so, as the number of electrons is $n_A n_B$, $\Delta_r G_{cell}$ is

$$\Delta_r G_{cell} = -n_A n_B F (E_A - E_B).$$

Recall from section 12.5 on p. 67 that it is the sign of $\Delta_r G_{cell}$ which determines the direction of the spontaneous reaction: if $\Delta_r G_{cell}$ is negative, the conventional cell reaction (Eq. 12.7) is spontaneous in the direction shown i.e. A is reduced and B is oxidized. On the other hand, if $\Delta_r G_{cell}$ is positive, the spontaneous cell reaction is the opposite of the conventional reaction, so B is reduced and A is oxidized.

The really crucial point here is that the sign of $\Delta_r G_{cell}$ is determined *only* by the sign of $(E_A - E_B)$; there is no need to go through all of this palaver of constructing a cell, determining the cell reaction, finding the cell EMF and hence the sign of $\Delta_r G_{cell}$. All we have to do is to compare the two half-cell EMFs.

Using the shortened approach, the conclusions are drawn quite quickly in the following way. Consider the two half-cell reactions:

$$A_O + n_A e^- \longrightarrow A_R \quad E_A$$
$$B_O + n_B e^- \longrightarrow B_R \quad E_B$$
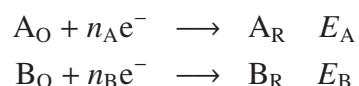
It follows that the oxidized form of a couple with a large positive half-cell EMF will be a powerful oxidizing agent. Conversely, the reduced form of a couple with a larger negative half-cell EMF will be a powerful reducing agent.

Example 10

Remember that, as described in section 12.3.3 on p. 66, the half-cell EMF is affected by the concentration of the species involved. Thus, the sign of $(E_A - E_B)$ is affected not only by the identity of A and B, but also by the relevant concentrations. However, as these EMFs have a logarithmic dependence on concentration, and given that RT/F is of the order of 0.03 V at 298 K, the concentration dependence is not strong.

12.8 Applications

As has already been commented on, the measurement of cell potentials is essentially a measurement of $\Delta_r G$. All we have to do in order to measure $\Delta_r G$ is to set up a cell with the appropriate conventional cell reaction and then measure its potential. Further manipulations can be used to extend the usefulness of such measurements. We will also see that often we can use the standard half cell potentials directly to calculate further thermodynamic parameters without actually setting up an experimental cell.
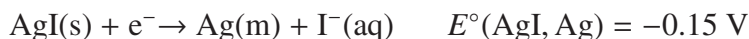
12.8.1 Solubility product of AgI

AgI is a sparingly soluble salt whose solubility is determined by the solubility product, K_{sp}, which is defined as the equilibrium constant for the dissolution reaction

$$\text{AgI(s)} \rightleftharpoons \text{Ag}^+\text{(aq)} + \text{I}^-\text{(aq)} \qquad K_{sp} = a_{\text{Ag}^+} a_{\text{I}^-}$$
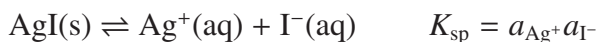
We have written the equilibrium constant using activities rather than concentrations. To find K_{sp} we will first find $\Delta_r G^\circ$ for the above reaction and then use $\Delta_r G^\circ = -RT \ln K$.

From data tables we find the following two standard half-cell potentials (at 298 K):

$$\text{AgI(s)} + \text{e}^- \rightarrow \text{Ag(m)} + \text{I}^-\text{(aq)} \qquad E^\circ(\text{AgI}, \text{Ag}) = -0.15 \text{ V}$$

$$\text{Ag}^+\text{(eq)} + \text{e}^- \rightarrow \text{Ag(m)} \qquad E^\circ(\text{Ag}^+, \text{Ag}) = +0.80 \text{ V}$$

Taking the second of these away from the first gives just the reaction we want

$$\text{AgI(s)} \rightarrow \text{Ag}^+\text{(aq)} + \text{I}^-\text{(aq)} \ .$$
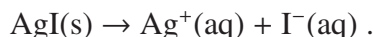
The standard potential is given by

$$E^\circ = E^\circ(\text{AgI}, \text{Ag}) - E^\circ(\text{Ag}^+, \text{Ag}) = -0.15 - (+0.80) = -0.95 \text{ V}$$

which corresponds to a $\Delta_r G^\circ$ value of $-1 \times F \times (-0.95) = 91.6 \text{ kJ mol}^{-1}$ and so the equilibrium constant, K_{sp}, is $\exp(-91.6 \times 10^3/RT) = 8.8 \times 10^{-17}$.

If we assume that the activities can be approximated by concentrations then $K_{sp} = [\text{Ag}^+][\text{I}^-]/(c^\circ)^2$, so the concentration of either Ag^+ or I^- in the solution is $\sqrt{8.8 \times 10^{-17}} = 9.3 \times 10^{-9} \text{ mol dm}^{-3}$ ($c^\circ = 1 \text{ mol dm}^{-3}$). The solubility is indeed very low.

Note that to find the solubility product we did not really use a cell as such, but used the standard half-cell potentials as a source of $\Delta_r G^\circ$ values.
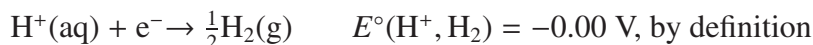
12.8.2 Thermodynamic parameters of ions

We saw in section 8.3 on p. 40 that $\Delta_f H^\circ$ and $\Delta_f G^\circ$ of elements in their reference states are defined as zero. For ions in solution, we introduce the additional conventions that

$$\Delta_f H^\circ(\text{H}^+) = 0 \qquad \Delta_f G^\circ(\text{H}^+) = 0 \ .$$

In any experiment we will only be able to determine the difference of enthalpies or Gibbs energies of ions, so in order to establish values for individual ions we need to fix a zero point of the scale. Assigning the value 0 to H^+ is arbitrary, but as only differences are measurable we are free to choose the origin to be where we like.

Cell potentials can be used to determine the standard Gibbs energies of formation of ions. For example, consider the two half-cell reactions

$$H^+(aq) + e^- \rightarrow \tfrac{1}{2}H_2(g) \qquad E^\circ(H^+, H_2) = -0.00 \text{ V, by definition}$$

$$Ag^+(eq) + e^- \rightarrow Ag(m) \qquad E^\circ(Ag^+, Ag) = +0.80 \text{ V}$$

Taking the second away from the first gives the reaction

$$H^+(aq) + Ag(m) \rightarrow \tfrac{1}{2}H_2(g) + Ag^+(aq)$$
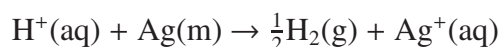
for which $E^\circ = E^\circ(H^+, H_2) - E^\circ(Ag^+, Ag) = 0.00 - (+0.80) = -0.80$ V. The corresponding $\Delta_r G^\circ$ is $-1 \times F \times (-0.80) = 77.2$ kJ mol^{-1}.

For the reaction, we can write $\Delta_r G^\circ$ in terms of standard Gibbs energies of formation, $\Delta_f G^\circ$. Noting that $\Delta_f G^\circ$ of elements in their reference states is defined as zero and that $\Delta_f G^\circ(H^+) = 0$, gives

$$\begin{aligned}
\Delta_r G^\circ &= \tfrac{1}{2}\Delta_f G^\circ(H_2(g)) + \Delta_f G^\circ(Ag^+(aq)) - \Delta_f G^\circ(Ag(m)) - \Delta_f G^\circ(H^+(aq)) \\
&= \Delta_f G^\circ(Ag^+(aq)).
\end{aligned}$$

So, the standard Gibbs energy of formation of $Ag^+(aq)$ is 77.2 kJ mol^{-1}. Using this approach, the $\Delta_f G^\circ$ values of other ions can be found.

As discussed in section 12.2 on p. 64, the entropy (and hence the enthalpy) change can be found from the temperature coefficient of the cell potential.

12.8.3 Concentration cells

A concentration cell has the same electrode on the RHS and LHS, but with different concentrations or pressures of the species involved. The cell produces an EMF which depends on the ratio of the concentrations in the two half cells: see the example for an illustration of this point.

Example 11

Exercises 27 to 34