Extension 16: Entropy and applications Of Gibbs Energy Change

Introduction

In Unit 16:

- The meaning of 'spontaneous process' was explained, with the cautionary note that some spontaneous processes may be extremely slow.
- The idea of entropy was introduced.
- When systems undergo a spontaneous change, G falls.
- The standard change in Gibbs energy for a reaction $\Delta G^\ominus$, was used to calculate the equilibrium constant, K, at that temperature. If $\Delta G^\ominus$ is negative, K > 1.

This extension complements Unit 16, so it will be very useful to have a copy of your textbook to hand so that you can identify where further explanations have been made.

The sections in this extension are as follows:

These topics can be selected in any order with some material deferred for future study as required. The choice of topics is not comprehensive but gives a flavour of what is involved in a more advanced study of this subject.

The idea of entropy and Gibbs energy are not easy to grasp, but there is something special and fundamental about the way that they illuminate the 'goings on' of chemical reactions in particular and for this reason their study can be very rewarding. However, gaining an understanding of these topics only occurs incrementally, with new insight every time they are studied, so be patient!

1. Spontaneous Processes

In Unit 16, we used the following definition of the word 'spontaneous':

A spontaneous process is one which is one which, once started, proceeds naturally in a particular direction without help.

We might add that a spontaneous process means a process on a bulk (macroscopic) scale. As discussed in the book (p.262), chemical equilibrium is dynamic. The fact that the concentrations of reactants and products remain unchanged at equilibrium is a consequence of the fact that the forward and back reactions are proceeding at the same rate. At the molecular level change is constant as reactant molecules are constantly changing to product and vice versa, but macroscopically there is no change. It is at the macroscopic level that the word 'spontaneous' applies.

When we state that a particular change is spontaneous, this is only true under a specific set (or range) of conditions. One such condition is temperature. Ice left out in the garden will spontaneously melt (albeit often slowly) at temperatures above 0°C, but not if the temperature is below 0°C. A protein will not denature at room temperature, demonstrating that this process is not spontaneous, but it is spontaneous at 100°C.

We shouldn't think that changes that are non-spontaneous at room temperature are impossible. A non-spontaneous process can be forced to happen, but it requires work – the expenditure of energy - to do this. Imagine a cylinder of gas which has a piston (Fig. 16.1). Suppose we very rapidly increase the temperature of the gas by placing the cylinder and piston into a vat of boiling water. The gas temperature increases and the piston will be forced upwards as the gas spontaneously expands at the higher temperature. After a minute or so, the gas volume remains constant at its new (equilibrium) value. Provided that the water is kept boiling, the temperature of the gas in the cylinder will not fall and the volume of the gas will not spontaneously change. However, even then we can force the reverse (non-spontaneous) process by 'doing work' e.g. by placing a heavy mass on the piston handle. The gas volume then decreases.
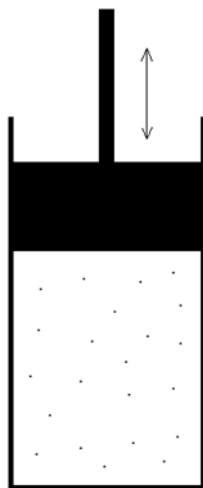

Fig. 16.1 Gas inside a cylinder with a movable piston

The electrolysis of water is another example of bringing about a change that is naturally non-spontaneous at room temperature. Water can be decomposed into hydrogen and oxygen at room temperature by using electricity which is brought into contact with the solution through electrodes,

but without the electricity no decomposition takes place. Here, it is the electricity that 'does the work' and without it, the water would not decompose at room temperature.

The absence of reaction speed in the definition of spontaneous process raises an interesting question. Think of a proposed reaction: the reaction of reactant P with reactant Q. Suppose that we mix P and Q in the lab but notice no reaction. How do we know whether or not the reaction is kinetically slow or simply non-spontaneous at room temperature? The kinetic approach would be to try harder to make the rate visibly fast: use a higher temperature by bringing the reactants in contact with a flame, increase reactant concentration, try a variety of catalysts or use UV light. Yet, if these attempts were unsuccessful, we would still not know the answer to the question. In that case, we have only one course of action: to calculate the change in Gibbs energy, ΔG, of the reaction and see if it is negative at the temperature in question. This will be, of course, dependent on the availability of the enthalpy and entropy data.

2. Examples of Spontaneous Reactions

Most of the examples of spontaneous processes given in the book are chemical reactions, but our conclusions regarding entropy and Gibbs energy apply to all spontaneous processes, including physical changes such as:

- The dissolution of salts in water. Some salts spontaneously dissolve in water.
- The diffusion of gases from higher to lower gas pressure.
- The transfer of heat from a hot body to a cold body.

The third example (Fig. 16.2) occupies a particularly hallowed place in the history of thermodynamics. It is deceptively important and has been the subject of study by some of the greatest scientific minds. It has been known for hundreds of years that the *condition* for heat to flow between two objects is a difference in temperature between those objects: heat always travels from hot to cold and this is the basis of one of many statements of the Second Law of Thermodynamics, due to Rudolf Clausius (1822–1888): 'that heat cannot travel from a cold body to a hot body without external help'. The refrigerator is an important example which helps clarify Clausius' definition. In order to cool food, 'external help' (or work) in the form of an evaporation/condensation cycle is required.
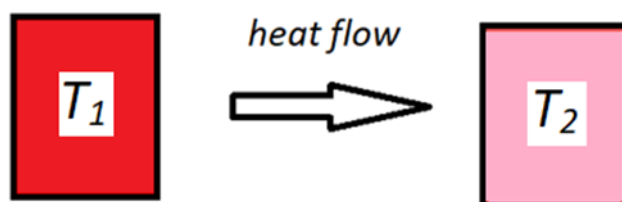
Fig. 16.2 For centuries, scientists have been fascinated by the universal observation that heat flows spontaneously from a hot to a cold body, never from a cold body to a hot body. Here, $T_1 > T_2$

3. Entropy

During a spontaneous process, energy always spreads out so that energy is more dispersed in the final state than in the initial state. This observation, suitably developed and formalised with the type of system specified, is another way of expressing the famous Second Law of Thermodynamics. The degree to which energy is spread out during a process is measured by the quantity named **entropy**, S.

It is fitting that the word 'entropy' comes from a Greek word meaning 'transformation'. Changes in entropy occur if:

1. There is a change in temperature
2. A molecular re-arrangement (a chemical reaction) occurs
3. We mix materials together
4. There is an alteration in volume
5. There is a change in phase (e.g. solid to liquid)

It is useful to be able to predict the sign of an entropy change, ΔS, of a chemical reaction and simple rules to make such predictions are explained in p.284 in the book.

In chemistry, it is convenient to distinguish between the reacting system (e.g. a beaker containing reactants and products) and the 'surroundings', which are normally the laboratory, its fittings and its atmosphere. The overall change in entropy, $\Delta S_{overall}$, that accompanies a chemical change (from start to completion) may then be broken down into two parts:

$$\Delta S_{overall} = \Delta S + \Delta S_{sur} \qquad\qquad (1)$$

where ΔS is the entropy change undergone by the reacting system from its initial state to completion and ΔS_{sur} is the entropy change undergone by the immediate surroundings at a constant temperature. (We might have symbolised the entropy change of the reacting system as ΔS_{react} but the convention is that we use ΔS).

Think of a reaction that takes place in an open beaker. The temperature of the beaker and its contents before reaction started equals the temperature, T, of the laboratory. After the reaction is over, the temperature of the beaker and its contents slowly returns to T. The enthalpy change of the reaction will have a negligible effect upon the temperature of the much more massive lab and its atmosphere, and so the temperature of the surroundings does not change. Therefore, when we state that 'the reaction has taken place at T', we mean that this was the initial temperature of the reactants and, eventually (after heat has been exchanged with the surroundings), the final temperature of the products. T is also the temperature of the surroundings before, during and after the reaction. It is this temperature, T, that we substitute into our equations below and which we use to calculate $\Delta G^{\ominus}$ (see for example s.16.10 in the book, p.289).

The effect of the reaction on the laboratory atmospheric pressure is also negligible and so we may also regard this as unchanging during the reaction. Since the temperature and pressure of the surroundings will be constant during the reaction, we can use enthalpy to represent any energy changes.

The only reason that the entropy of the surroundings changes is that it has either received heat from the reaction or lost heat to the reaction. The amount of heat exchanged equals ΔH joules, the enthalpy change of the reacting system. Under these circumstances it can be shown that that the entropy change takes a simple form:

$$\Delta S_{sur} = -\frac{\Delta H}{T} \qquad\qquad (3)$$

Note that T must be constant if we are to use eqn (3) to calculate ΔS_{sur}.

The entropy change for the *reacting system*, ΔS is caused by a change in the molecular structures:

$$\Delta S = \text{(sum of entropy of products)} - \text{(sum of entropy of reactants)}$$

and the size and sign of ΔS depends upon the size and complexity of the reactant and product molecules, which controls the way that energy is stored in the molecules.

We can now re-state equation (1) as:

$$\Delta S_{overall} = \Delta S - \frac{\Delta H}{T} \qquad\qquad (4)$$

This equation is remarkable because it allows us to determine the entropy change overall using ΔH and ΔS of the reacting system. **There is no reference to the entropy change of the surroundings on the RHS of this equation**. T is the temperature of the laboratory in which the reaction is carried out. Later, we will link this equation to the Gibbs energy change of the reaction, ΔG.

4. The Second Law of Thermodynamics

The term **isolated system** means a system in which there is no exchange of energy or matter with its surroundings. An example of an isolated system is a perfectly thermally insulated and tightly stoppered vacuum flask.

We now state the **Second Law of Thermodynamics** in a form that involves spontaneous changes /processes and entropy:

If a spontaneous change occurs in an isolated system, there is an increase in the entropy of the isolated system

We can express this mathematically:

$$\Delta S_{\text{isolated system}} > 0$$

The increase in entropy is maximised when the isolated system reaches equilibrium.

There are no known exemptions to the Second Law. If the system is not isolated, the overall entropy change associated with a process can only be calculated if we know ΔS_{sur} as well as ΔS for the system.

Examples of equilibrium include:

- Thermal equilibrium, as when a sample of metal or gas is heated up to a constant temperature
- Phase equilibrium, as when water, ice and water vapour co-exist under a particular temperature and pressure
- Chemical equilibrium, when reactant and product molecules achieve equilibrium, characterised by the concentrations in an equilibrium expression equalling K, the equilibrium constant, at that temperature.

Assuming that the universe is an isolated system (and we don't know that for sure), allows us to define the **Second Law of Thermodynamics** in another form:

A spontaneous change increases the entropy of the universe i.e. $\Delta S_{uni} > 0$

Although this a catchy statement and it is easy to remember, it does not allow us to make any calculations of entropy changes because the universe is not at thermal equilibrium i.e. it is not at one temperature. For this reason, we cannot equate ΔS_{sur} with ΔS_{uni}. There are many hotspots and coldspots in the universe and it may take 10^{100} years for the universe to attain equilibrium! (For completeness we may also add that since T and P is not constant in the universe the use of enthalpy as energy in equation (3) is inappropriate).

The connection between the spread of energy and entropy is discussed in s.8 below.

5. Calculating overall entropy change as a result of chemical reaction

The applicability of the Second Law to isolated systems at equilibrium only, might appear to render it too impractical to use, but fortunately we have a ready-made practical arrangement that fits the bill – that of a chemical reaction taking place in an open vessel in a lab in which T remains constant. We may safely regard the combination of **a reaction system and the laboratory surroundings as an isolated system**. Consequently, if the chemical or physical change in the beaker is spontaneous and it reaches equilibrium, $\Delta S_{overall}$ must be > 0.

We have previously introduced an expression for the entropy change of the reaction system and that of the immediate surroundings for most 'open vessel' laboratory situations:

$$\Delta S_{overall} = \Delta S - \frac{\Delta H}{T} \qquad\qquad (4)$$

It follows that in order to generate $\Delta S_{overall} > 0$ during a spontaneous process, *either*:

- ΔS and the term $-\frac{\Delta H}{T}$ must be positive; or
- ΔS *or* the term $-\frac{\Delta H}{T}$ must be positive, with the term that is positive being numerically larger than the term that is negative.

Since T is always positive, the sign of the term $-\frac{\Delta H}{T}$ depends upon ΔH. We illustrate this by two examples, both of which appear in Unit 16. In both cases, we predict the sign of ΔS (the entropy change of the reacting system) using the ideas of energy dispersal discussed in the book, p. 284. We then predict the entropy change of the surroundings (something we didn't cover in Unit 16) using equation (4) above.

EXAMPLE 1

Exothermic hydration of copper(II) sulphate

Our first example is that of a spontaneous *exothermic* reaction where ΔS for the system is negative. An example is the reaction of anhydrous copper(II) sulfate with water:

$$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_2O(aq) \qquad\qquad (5)$$
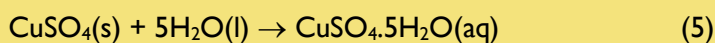
This is easily demonstrated. If white $CuSO_4(s)$ powder is added to a test tube and an equal volume of water added, the mixture gets so hot that test tube cannot be comfortably held with bare hands.

EXAMPLE 1 *(continued)*

Look at equation (4). The first term is ΔS, the entropy change undergone by the reacting system. We cannot calculate an exact value of ΔS using a simple equation, although it can be measured experimentally. From the work done in the book in Unit 16, we can predict the sign of ΔS. Since reaction (4) involves a reduction in the number of species left to right, we predict that ΔS will be negative.

Now we turn to the term for the entropy change of the surroundings as a result of the chemical reaction. Heat is flowing from the reaction to the surroundings and this suggests that the surroundings will undergo an increase in entropy. Inspection of the term:

$$ -\frac{\Delta H}{T} $$

confirms this prediction. T, the temperature of the surroundings does not change during the reaction, but ΔH, the enthalpy change of reaction (4), is negative. Since 'minus times minus is plus', the $-\frac{\Delta H}{T}$ term is positive overall. Since reaction (5) does proceed spontaneously at room temperature, we assume that the $-\frac{\Delta H}{T}$ term is more positive than the ΔH is negative so that overall, $\Delta S_{overall}$ is positive as required by the Second Law for our isolated system of reaction and surroundings.

EXAMPLE 2

Endothermic reaction of barium hydroxide and ammonium chloride

When barium hydroxide solid is mixed with ammonium chloride, the mixture becomes very cold and ammonia gas is evolved:

$$ Ba(OH)_2.8H_2O(s) + 2NH_4Cl(s) \rightarrow 2NH_3(g) + 10H_2O(l) + BaCl_2(s) \qquad (6) $$
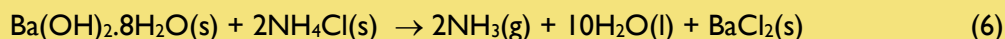
The first term we examine is ΔS, the entropy change undergone by the reacting system. Following the principles discussed in Unit 16, and since there are more product molecules than reactants, including the gas ammonia, we predict that ΔS is positive.

Reaction (6) is endothermic, ΔH is positive and so the term $-\frac{\Delta H}{T}$ is negative overall. Since reaction (6) does proceed spontaneously at room temperature, we assume that the ΔS term is more positive than the $-\frac{\Delta H}{T}$ term is negative, so that overall, $\Delta S_{overall}$ is positive for our isolated system of reaction and surroundings.

We may summarize the effect of ΔH upon the entropy of the *surroundings* as follows:
* If the chemical reaction is **exothermic**, then heats flows outwards and the entropy of the surroundings **increases**
* If the chemical reaction is **endothermic**, then heat flows inwards and the entropy of the surroundings **decreases**

but in every spontaneous process, whether endothermic or exothermic, the overall entropy of the system plus surroundings increases.

Of course, we can easily think of a reaction in which $\Delta S_{overall}$ *would* decrease, but such a reaction would not happen naturally: it would be non-spontaneous.

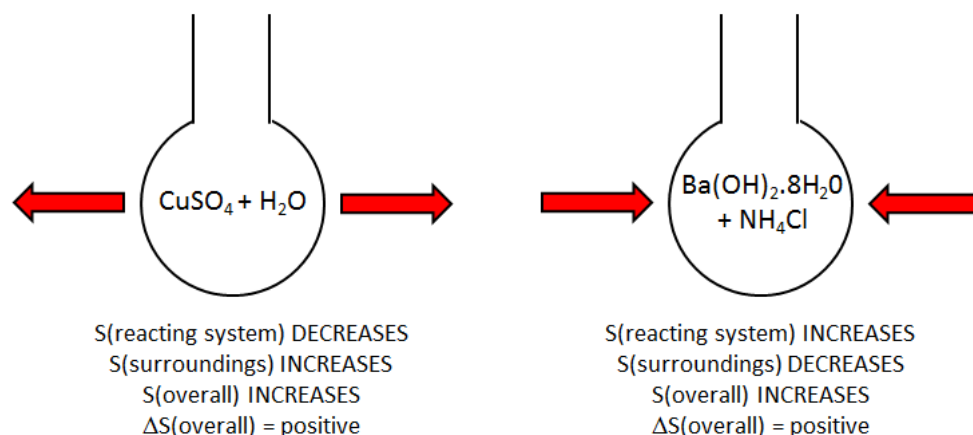| CuSO$_4$ + H$_2$O	Ba(OH)$_2$.8H$_2$O + NH$_4$Cl
S(reacting system) DECREASES	S(reacting system) INCREASES
S(surroundings) INCREASES	S(surroundings) DECREASES
S(overall) INCREASES	S(overall) INCREASES
ΔS(overall) = positive	ΔS(overall) = positive

Fig. 16.3 Entropy changes for two spontaneous reactions, with the arrows showing the direction of heat flow. **(a)** The reaction of anhydrous copper sulfate and water is an exothermic reaction in which the reacting mixture undergoes a fall in entropy. **(b)** The reaction of barium hydroxide with ammonium chloride is an endothermic reaction in which the reacting mixture ('the reacting system') undergoes an increase in entropy. In both cases, the overall entropy of the reaction system plus surroundings increases, in accordance with the Second Law of Thermodynamics.

BOX 1: The Detonation of Nitrogylcerine

There are also examples of spontaneous chemical reactions which are exothermic *and* in which there are more product molecules than the reactants. An example is the explosive decomposition of the dangerous compound nitroglycerine (see the book, Box 13.2, p.231) which is sensitive to shock even at room temperature:

$$4C_3H_5(NO_3)_3(l) \rightarrow 12CO_2(g) + 10H_2O(g) + 6N_2(g) + O_2(g) \qquad (7)$$
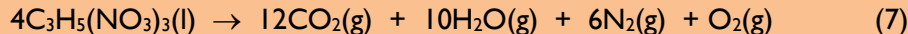
Reaction (7), is enormously exothermic, with $\Delta H^{\ominus}(6)$ = - 8620 kJ mol^{-1}. Unfortunately, the standard entropy of one mol of nitrogycerine, ($S^{\ominus}$(nitroglycerine)), is unknown and so $\Delta S^{\ominus}$ for reaction (7) cannot be calculated, but since the reaction produces so many gaseous products we can predict that it is large and positive. The entropy of both reaction mixture and the surroundings both increase and reinforce each other, so that the overall entropy change is very large and positive.

Fig. 16.4 In an explosion, gases are produced so rapidly that a pressure wave is produced in the surrounding air.
Photograph © PhotoDisc/Getty Images.

6. Gibbs Energy change, ΔG

We start with equation (4).

$$\Delta S_{\text{overall}} = \Delta S - \frac{\Delta H}{T} \qquad (4)$$

If we multiply both sides of this equation by $-T$ and re-arrange the order of the right-hand terms, the equation becomes:

$$-T\Delta S_{\text{overall}} = \Delta H - T\Delta S \qquad (8)$$

We now give $-T\Delta S_{\text{overall}}$ a new symbol, ΔG:

$$\Delta G = -T\Delta S_{\text{overall}} \qquad (9)$$

Substitution of (8) into (7) gives the famous Gibbs energy equation:

$$\Delta G = \Delta H - T\Delta S \qquad (10)$$

In order to apply this equation, the system in question must be at constant pressure and temperature during the change, requirements that apply in most laboratory ('open beaker') experiments.

As with equation (4), the RHS of this equation involves only the thermodynamic quantities of the reacting system, ΔH and ΔS – **not of the surroundings**. When the chemical species are in their standard states, equation (9) takes the familiar form:

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} \qquad (11)$$

On carrying out calculations of $\Delta G^{\ominus}$ (page 292 of the book) we consider the two components of equation (10), $\Delta H^{\ominus}$ and $-T\Delta S^{\ominus}$. Sometimes the terms reinforce each other and sometimes they are in opposition. When they are opposition, it is tempting to see $\Delta G^{\ominus}$ as the outcome of a 'fight' between the two terms. The importance of equation (7) is that it reminds us that $\Delta G^{\ominus}$ is not simply the result of a 'contest' between terms, but that it is itself an entropy term, albeit overall entropy change $\Delta S_{\text{overall}}$, as opposed to the entropy change for the system.

In order to calculate $\Delta G^{\ominus}$ for a reaction we require both $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$, both of which are calculated from individual standard enthalpies of formation and standard entropies of the reactants and products of the reaction. Enthalpies of formation and standard entropies are to be found in the NIST chemical database (https://webbook.nist.gov/chemistry/). An example calculation is shown in Extension 15 (Appendix 1) of this website.

7. Microstates and the Boltzmann interpretation of entropy

The entropy (S) of 'something' is a measurement of how spread out energy is within 'that something'. (This is easy to remember: '**S** is for **s**preading'). In Unit 16, we rationalized increases in entropy during a spontaneous reaction in terms of the increase in spreading of energy, either among more particles or in a greater volume of space. A more exact microscopic description of entropy involves the idea of **microstates**.

A microstate is the way that energy is distributed among a collection of molecules at an instant. If we have N molecules in a sample, we would specify the microstate by listing the energy of each molecule at that instant. A collection of molecules can only be in one microstate at a time, but the microstate will change an instant later as one or more molecules collide and exchange energy.

Think of a single molecule that can exist with only four possible energies, 0, 1, 2 and 3 energy units respectively. The energies are represented by a ladder (Fig. 16.5(a)) and the precise energy level occupied by the molecule is indicated by a red circle. If the molecule possesses no energy (Fig. 16.5(b)) it is assigned a molecular energy value of 0 units. The energy levels are equally spaced, and if the molecule occupies the first energy level (Fig. 16.5(c)) it has an energy of 1 unit, if it occupies the second level (Fig. 16.5(d)) an energy of 2 units and if the molecule occupies the third energy level (Fig. 16.5(e)) an energy of 3 units.
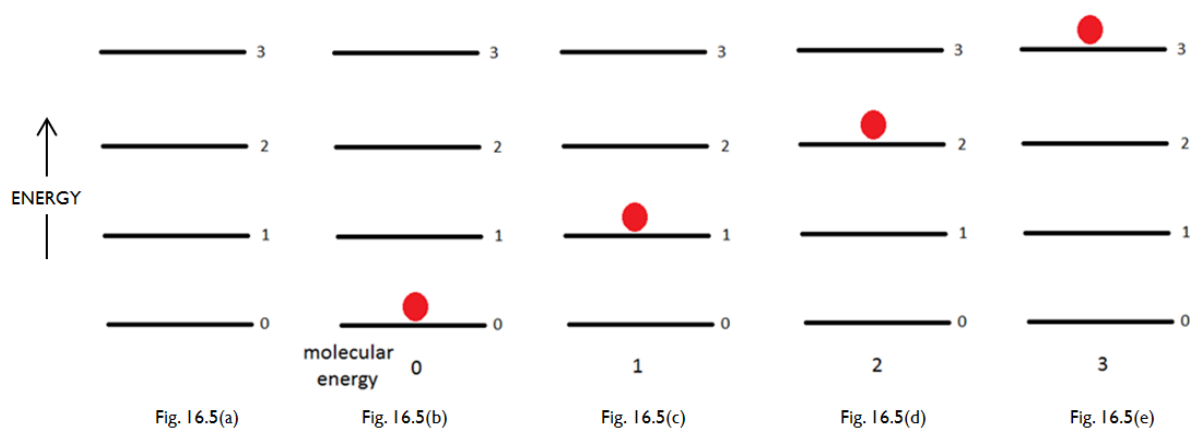

Fig. 16.5: 16.5(b), 16.55(c), 16.5(d) and 16.5(e) show the four ways in which energy could be stored in a single molecule.

Now think of a collection of just three molecules among which the energy is distributed. The molecules are identical (e.g. three argon atoms) but to distinguish their energies we label them A, B and C. Any molecule is allowed to possess zero energy. In order to simplify things, we apply a restriction: the sum of the energies of A, B and C totals 3 units of energy in every case. Each particular combination of energy held by all three atoms is a possible *microstate*. There are ten possible microstates – ten ways of distributing the energy among the three molecules within the total energy limit of 3 units of energy - and these are shown in Table 1. We will also take for granted one of the fundamental assumptions of molecular thermodynamics: no one microstate is preferred and each is equally likely.

The microstates in Table 1 have been organized into three groups, which are known as **configurations**. The three configurations are combinations of microstates with a common arrangement of energy and the microstates in a configuration are said to be 'energetically equivalent'. The term 'energetically equivalent' means that the microstates in that group (configuration) have the same number of molecules with the same energy, and differ only in the identity of the molecules possessing that energy. For example, there are six microstates of configuration (i), which might be called the '2, 1 and 0 type of configuration' because each of its microstates involve one molecule having zero energy, one molecule having one unit of energy and one molecule of two units of energy respectively; the difference between the microstates lies simply in the identity (A, B or C) of the molecule having those values. There are three microstates of configuration (ii), in each of which one molecule has all the available energy (3 units) with the other molecules having zero energy. There is only one microstate of configuration (iii), and in it each molecule has one unit of energy.

Table 1 The ten possible microstates for a collection of three molecules. Each microstate has the same total energy (three units). The microstates are organised into groups, known as configurations. Since the molecules A, B, and C are indistinguishable except in energy, each configuration contains energetically equivalent microstates.

Microstate	Molecule A	Molecule B	Molecule C	Total energy	Configuration	Random probability that a microstate will have the configuration shown
m1	0	1	2	3	(i)	60%
m2	0	2	1	3		
m3	1	0	2	3		
m4	1	2	0	3		
m5	2	0	1	3		
m6	2	1	0	3		
m7	0	0	3	3	(ii)	30%
m8	0	3	0	3		
m9	3	0	0	3		
m10	1	1	1	3	(iii)	10%

Suppose that we were able to look inside the container holding our three molecules, A, B and C ('the system') and that we were able to measure their energy at an instant. Which of the microstates (m1 to m10) would the system be in? The system might be in m8 at one instant and in m2 a millionth of a second later. Since there are ten possible microstates and each are equally likely, the random probability of any one microstate occurring is 1/10. However, since the molecules are indistinguishable except in energy and there are six microstates of configuration (i), the probability of a microstate having *configuration* (i) is 6/10 or 60%. In other words, microstates of the '2, 1 and 0' type of configuration represent the most probable arrangement of energy for our three molecules. In summary, **the most probable configuration of molecular energies is the one with the largest number of energetically equivalent microstates**.

The reason that there are more microstates of configuration 1 than there are of group 2 is that there are more ways of distributing energy between any two molecules than there are ways of distributing energy in any single molecule. If we think of entropy as a measure of how much energy is spread out, we conclude that microstates of configuration 1 are of lower entropy than those of configuration 2. Microstates of configuration 3 are of the lowest entropy but there is only one microstate so that configuration is less probable.

If we increase the number of molecules with 0, 1, 2, or 3 units of energy from 3 to 150, there are 570 000 possible microstates. If we increase the number of molecules to $N = 10^{23}$ and repeat the above exercise, we would need an expanded version of table 1 with 10^{23} columns to register the molecules present from 1 to 1×10^{23}. This generates an astonishingly vast number of possible microstates, much bigger than 10^{100} (10 followed by 100 zeros). It can be shown mathematically that as a result of this vast number there is one single configuration of energetically equivalent microstates that is so highly probable that it is extremely unlikely – to the point of practical impossibility - that the energy of the collection of molecules will be distributed in any other way[1]. In

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[1] 10^{23} 'real' molecules will have even more possible microstates because molecular energy is not limited to a few values of energy. A molecule possesses electronic, vibrational, rotational and translational energy. All the types of energy are quantised, but in the case of translational energy (the kinetic energy of a molecule moving through space), there are a huge number of energy levels that are extremely close together and this vastly increases the number of possible microstates.

other words, and for all practical purposes and at a particular temperature, **the energy of a large number of molecules always exists in the most probable configuration**.

Think of a gas sample containing 10^{23} molecules which have achieved thermal equilibrium amongst each other by collision. The energy we are interested in here is the translational (kinetic) energy of movement of the molecules through space. Once again, the most probable configuration is a distribution of energies that, statistically, will be followed by the whole collection of 10^{23} molecules. Although the energy of individual molecules will vary from one instant to another, the most probable configuration dictates that at a particular temperature, P_1 % of the molecules will possess energy ε_1, P_2 % of the molecules will possess energy ε_2, P_3 % of the molecules will possess energy ε_3, P_4 % of the molecules will possess energy ε_4, and so on. The overall distribution of kinetic energies amongst this vast number of molecules is remarkably reproducible and provided that N is large the distribution does not change perceptibly as the number of molecules changes. Since for a gas, 'energy means speed', the distribution of molecular speeds[2] for gases is also entirely reproducible at a particular temperature (Fig. 16.6). The meaning of 'reproducible' in this context may be illustrated as follows. If every laboratory in the world were asked to experimentally measure the distribution of molecular speed in chlorine gas at 300 K, and such experiments were repeated hourly for a billion years, they would always – without exception – produce exactly the same curve as in Fig 16.6.
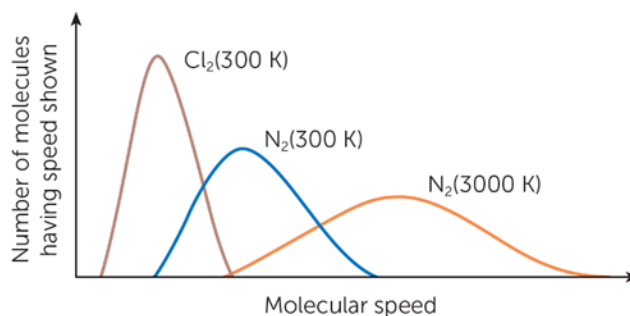

Fig. 16.6 The spread of molecular speeds in chlorine and nitrogen gases

8. Using microstates to rationalise the changes in entropy for spontaneous processes

We now examine an imaginary spontaneous process. Suppose that we start with 10^{23} molecules and that magically one third of the molecules possesses three units of energy (as in the microstate of configuration group (ii) in Table 1); the other molecules possess zero energy. This is our imaginary starting system – our 'reactant'. The molecules are now allowed to collide with each other and the exchange of energy between them occurs extremely rapidly. This results in a spontaneous re-distribution of energy. The reason for the distribution is sheer chance: there are many more microstates in which molecules may share the available energy more widely than there are microstates in which molecules may only possess three units of energy. The 'product' of this spontaneous process is that all the molecules take up the most probable configuration of energetically equivalent microstates, and such a distribution would be of lower entropy than the system we started with. Macroscopically, we describe this by stating that the system has reached **equilibrium**. Equilibrium is the end product of the spontaneous process but it is simply the bulk manifestation of the fact that the molecules have reached the most probably energy distribution. The movement towards equilibrium is **statistically driven**, meaning that molecules will spread

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[2] See p. 163, Unit 10, in the book.

themselves over more microstates simply because they are available and it is more likely for them to do this.

Although our example is imaginary, since the starting energy distribution described could never be achieved in practice, it is believed this is the mechanism by which all spontaneous processes achieve equilibrium. During a physical or chemical change, **the number of available microstates increases and energy becomes more spread out and so, overall, the entropy increases.**

9. Why raising the temperature of a material raises its entropy

In the book we stated that increases in temperature always increases entropy and we can now understand this by looking at the molecular level. Consider the heating of a substance, which causes a rise in temperature. When a substance is heated, the average energy of its molecules increases. This increases the number of energy levels that the molecules in the substance are now able to occupy. In other words, the number of possible microstates increases. This is simplistically shown in Fig 16.7, where only one type of energy is shown. At the higher temperature, some of the ten molecule molecules represented can occupy higher energy levels in addition to the lower ones: they can occupy more energy levels (i.e. the molecules can occupy a greater range of microstates) and it is statistically probable that they will do so. The average energy of the molecules and the spread of that energy in the most probable configuration is greater at the higher temperature. Entropy, an index of such energy dispersion, is therefore greater at the higher temperature.
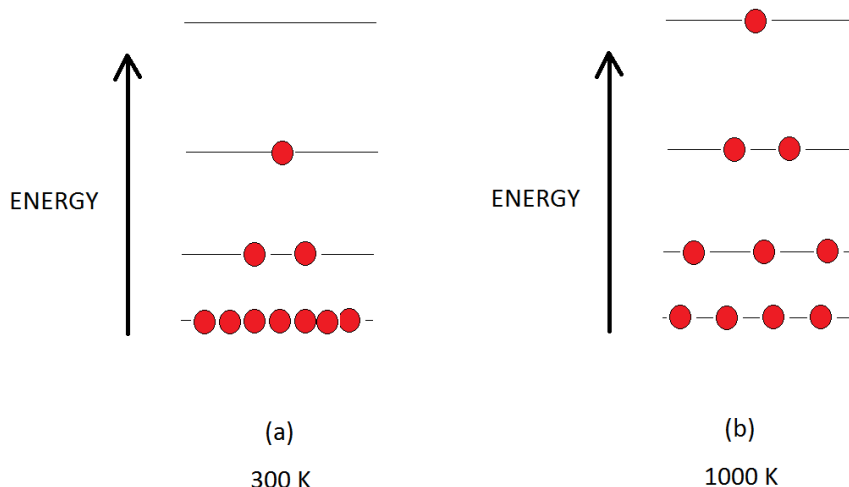

Fig. 16.7 Simplified explanation for the increase in entropy of a substance that arises from an increase in temperature. At the higher temperature, (b), more of the molecules have enough energy to occupy higher levels. The range (the spread) of energy levels accessible to molecules is therefore much greater at higher temperature.

10. Why increasing the volume in which molecules are contained increases entropy

In the book, we also stated that increases in volume increase entropy and our next example relates to the expansion of a gas. Take one of the simplest cases of expansion: a gas which spontaneously expands from one container into a second (previously evacuated) container at constant temperature (Fig. 16.8). (The constant temperature might be achieved by placing the containers in a tank of water maintained at constant temperature by a thermostatically controlled heater). The gas expands into the second container, but its temperature (and therefore its total energy) remains constant.

Therefore, the explanation of the increase in entropy is different from that of a material which undergoes an increase in temperature.

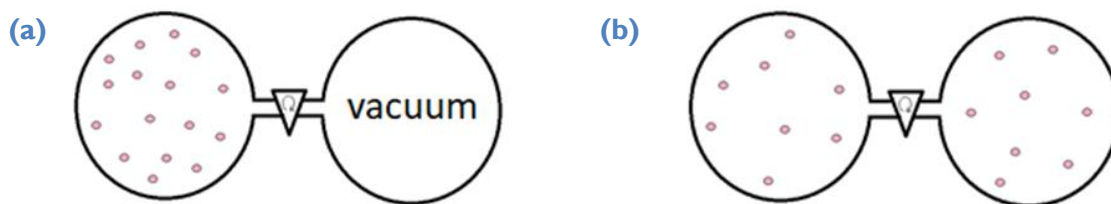**(a)**   **(b)**

Fig. 16.8 Expansion of a gas under constant temperature (isothermal) conditions. **(a)** Flask filled with gas; the right-hand flask is evacuated. **(b)** The tap connecting the two flasks is opened. Very quickly, the gas spreads out into the right-hand flask.

Once the tap in Fig. 16.8 is opened, the gas molecules are no longer held back and this allows them to spread out rapidly because the molecules are travelling at high speed. The increase in entropy associated with this expansion may then be explained in terms of the same amount energy being spread out in a greater volume.

In section (8), we have explained entropy changes in terms of the availability of more microstates. But why should molecules being dispersed over a greater volume result in an increase in the number of microstates for the 'end system'? The answer to this question is very surprising. Perhaps contrary to our intuition, it can be shown theoretically that when the volume of a collection of molecules increases, the energy levels of the molecules get closer together (Fig. 16.9) so that many more levels are available to be occupied by molecules for the same total energy. This results in trillions of molecules spontaneously occupying a greater variety of new energy levels simply because it is overwhelmingly probable for them to do so. Gas molecules spread into the second flask and in doing so the energy they carry spreads out more. Once again, the spreading out of the collective energy of the molecules *microscopically* results in the *macroscopic* observation that the entropy increases overall. In practice, this means that the gas will spread out spontaneously throughout the two containers to assume the new most probable configuration of molecular energies, and it extremely unlikely (to the point of practical impossibility) that the molecules will assemble in one container more than the other.
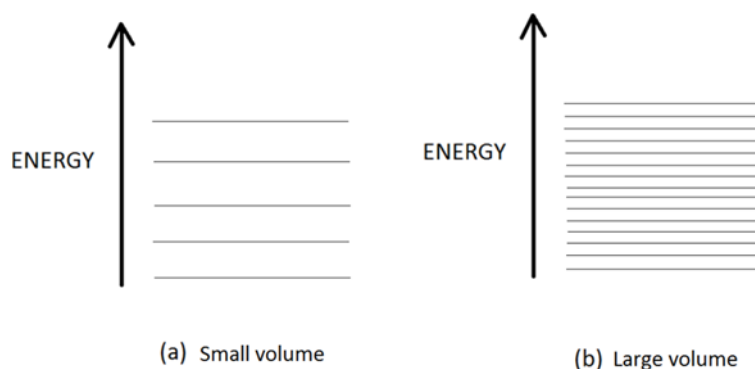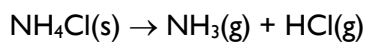

Fig. 16.9 The increase in the number of possible microstates during the expansion of a gas. The 'density' or packing of energy levels of molecules in a gas increases with volume. This means that molecules have 'a choice' of many more energy levels within their 'energy budget'.

Gas expansion may also result from chemical reaction, as when more molecules in the gaseous state are produced than we started with, as in the dissociation of ammonium chloride:

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

The volume of the system increases so once again, the number of possible microstates increases.

BOX 1: Boltzmann and Entropy

It was Ludwig Boltzmann (b.1844), an Austrian physicist, who established that the greater the number of microstates (W) the greater the entropy (S). This is formally expressed in the famous Boltzmann equation:

$$S = k \ln W \qquad (12)$$

where k is the Boltzmann constant and $\ln W$ is the natural log of W. This equation has been adapted and applied to many different systems. Boltzmann's work founded a new subject known as statistical mechanics and his students included Svante Arrhenius and Walter Nernst. Sadly, Boltzmann suffered from depression and he committed suicide in 1906. His gravestone bears the famous Boltzmann equation.

11. The Gibbs energy change, ΔG and spontaneous change

As we have seen, there is a simple relationship between the change in Gibbs energy change of a process, ΔG, and the overall entropy change of system plus surroundings:

$$\Delta G = -T\Delta S_{overall} \qquad (9)$$

This relationship is not often practically useful, but it does allow us to come to the two important conclusions about Gibbs energy changes stated (but not derived) in s.16.6 (p. 285) in the book.

The Second Law states that for a spontaneous process within an isolated system, $\Delta S_{overall}$ is always positive. T (in K) is always positive (there is no such thing as negative temperature in kelvin) and so the product $-T\Delta S_{overall}$ must always be negative. Since $\Delta G = -T\Delta S_{overall}$, ΔG for a spontaneous change must always be negative. If ΔG is negative, this means that the Gibbs energy of the reacting mixture (G) must fall during a spontaneous reaction and G continues to fall until equilibrium is reached, at which point G remains constant. In summary, we have arrived at our two practically important statements about Gibbs energy which apply at constant temperature and pressure:

- **When a spontaneous reaction is moving towards equilibrium, the total Gibbs energy (*G*) falls and so ΔG is negative**
- **At equilibrium *G* does not change and so ΔG = 0**

Unless a process (such as a chemical reaction) involves a drop in Gibbs energy, it will not be spontaneous (Fig 16.10).
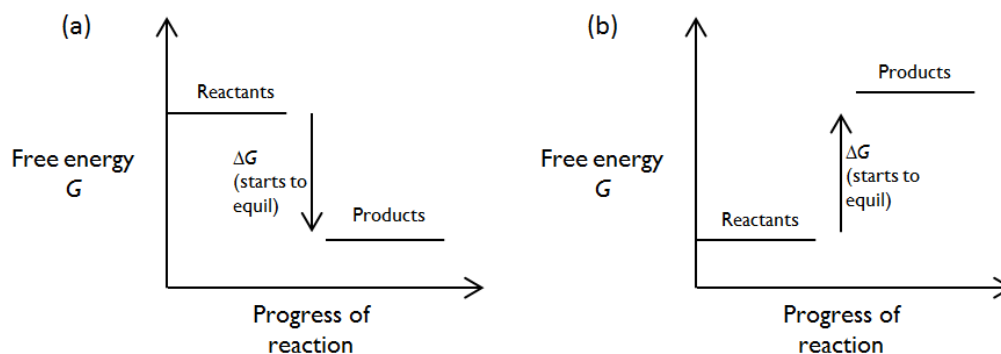
Fig. 16.10 Changes in Gibbs energy during a reaction. **(a)** Spontaneous reaction at temperature T, in which the reacting system moves from a higher Gibbs energy to a lower Gibbs energy. ΔG(start to equilibrium) is negative. (b) Non-spontaneous reaction at temperature T. If the reaction were to take place, ΔG(start to equilibrium) would be positive. Therefore, the proposed reaction is not spontaneous: it does not happen naturally.

Although we didn't mention this in the book, there is new nomenclature that applies here. Reactions (or processes) where ΔG is negative are said to be **exoergic**, just as a reaction for which ΔH is negative is said to be exothermic. A reaction for which ΔG is positive is said to be **endergonic** (compare this to endothermic reactions, when ΔH is positive).

As a footnote, we may note that some scientists do not regard Gibbs energy as a true energy. Although G has the units of energy, Gibbs energy is not conserved like enthalpy, H.

Gibbs energy changes are both convenient and useful, but they are only 'messages' about the changes in entropy that occur below the surface of our laboratory experiments. The requirement that ΔG is negative for a spontaneous process is simply a consequence of the Second Law of thermodynamics and just as we can plot the change in total Gibbs energy of a reaction proceeding to equilibrium (as in Fig. 16.3, p286 in the book) we can produce an equivalent plot of the way that the *entropy of the system plus surroundings* ($S_{overall}$) changes as reaction proceeds (Fig. 16.11). $S_{overall}$ is maximum at equilibrium, the point at which G (for the *reaction system*) reaches a minimum.
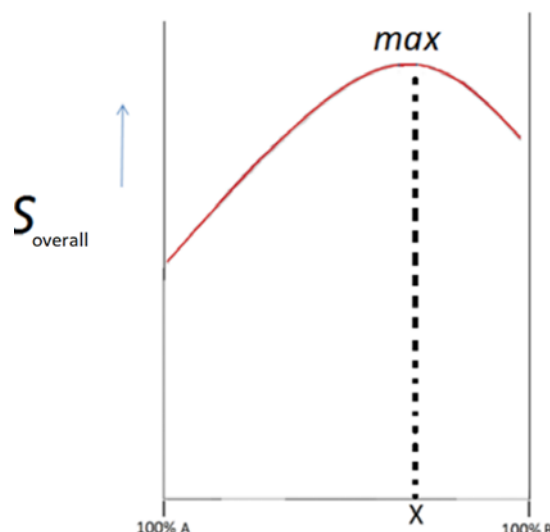

Fig. 16.11 The change in overall entropy of reaction system and surroundings as a reaction moves towards equilibrium X. At equilibrium, $S_{overall}$ is at a maximum but G, the Gibbs energy of the system (not shown), is a minimum.

EXAMPLE 3

Reactions where ΔH^o is zero

The decomposition of silver chlorite is an interesting chemical reaction because its enthalpy change is close to zero:

$$AgClO_2(g) \rightarrow Ag(s) + 1/2Cl_2(g) + O_2(g) \qquad \Delta H^o \approx 0 \qquad (15)$$
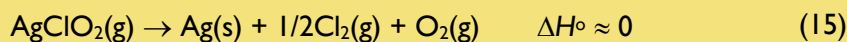
Show that for this reaction $\Delta S^o = \Delta S^o_{overall}$.

Answer

Taking $\Delta H^\ominus$ as zero, the equation $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ reduces to $\Delta G^\ominus = -T\Delta S^\ominus$. Since $\Delta G^\ominus = -T\Delta S^\ominus_{overall}$ (this applies to every reaction), the following applies to the decomposition of silver chlorite:

$-T\Delta S^\ominus = -T\Delta S^\ominus_{overall}$; cancelling temperature on both sides gives:

$\Delta S^\ominus = \Delta S^\ominus_{overall}$

In other words, where there is no enthalpy change, the entropy change of the reaction is also the overall entropy change (of system plus surroundings) caused by the reaction.

12. ΔG^o and spontaneous processes

In the book we have taken great pains to emphasise that the universal criterion for a spontaneous process is that ΔG is negative. Since spontaneous chemical reactions are being driven towards equilibrium, an indicator that ΔG is will be negative as the reaction progresses is that ΔG(start to equilibrium) is negative. The standard change in Gibbs energy accompanying a reaction, $\Delta G^\ominus$, is not a general criterion for spontaneous change and we gave an example of a spontaneous reaction (see p. 288) where $\Delta G^\ominus$ is positive but ΔG(start to completion) is negative. However, we noted that in the case where $\Delta G^\ominus$ for a process is negative, ΔG(start to completion) for that process will also be negative, since (as inspection of Fig. 16.4 in the book shows) ΔG(start to equilibrium) will always be *at least as negative* as $\Delta G^\ominus$. For this reason, some authors use a *negative* value of $\Delta G^\ominus$, the standard change in Gibbs energy, as an indicator of a spontaneous process – whereas in the book, we have used $\Delta G^\ominus$ solely as a means to decide whether or not a reaction has a large equilibrium constant i.e. a reaction for which $K > 1$.

Using $\Delta G^\ominus$ to predict spontaneity has the advantage that it is straightforward to calculate $\Delta G^\ominus$ from thermodynamic data. It is also intuitively correct: a large negative $\Delta G^\ominus$ means a large equilibrium constant, K, and if we start with pure reactants the system has a 'long way to go to reach equilibrium where products dominate reactants'. It is therefore reasonable to expect that reactions for which K is very large will be spontaneous en route to equilibrium. We should remember though, that while a negative value of $\Delta G^\ominus$ for a reaction confirms that the reaction is spontaneous, the reverse does not apply and a positive value of $\Delta G^\ominus$ does not mean it is non-spontaneous.

Extension 15 (Appendix 1) looks at the calculation of the equilibrium constant for the reaction of $2SO_2 + O_2 \rightarrow 2SO_3$ at various temperatures.

13. Is there a driving force of spontaneity?

If someone asks why spontaneous processes happen (and why non-spontaneous processes do not normally happen) what would you say? We can re-phrase this question as a request to identify a 'driving force of spontaneity' – the 'thing' that forces spontaneous processes to move in the direction they do.

One candidate is kinetic energy. Without kinetic energy, molecules could not physically collide or disperse when they are given the opportunity.

If we look back at the topics studied so far in this Extension, other candidates present themselves (Fig. 16.12) and a pause to look at them also gives us a chance to revise some of our previous work.

At the bottom of this hierarchy is the apparent requirement that at constant temperature and pressure, a *reacting system* undergoing spontaneous change must lose Gibbs energy, and this is very useful to chemists who routinely carry out calculations of ΔG on the chemical reaction of interest. However, such a requirement is simply a consequence of the increase in entropy of an isolated system (e.g. a reaction taking place in an open lab) that accompanies a spontaneous change. Since entropy is a measurement of energy dispersion, the tendency of energy to spread out in spontaneous change should occupy a higher level in our hierarchy. Lastly, this dispersion of energy is itself a consequence of the way that vast numbers of atoms, molecules or ions behave statistically: particles distribute their energy in the most statistically probable way and that happens to be one in which they spread out their energy as much as possible across the available microstates.

Some scientists do not like the idea of identifying a driving force. For them, a spontaneous process is one where the molecules follow the most probable route. It is sobering to realise that such behaviour has no grand purpose – it is *purposeless*. There is no magic force at work, simply the laws of chance operating on a very large scale.
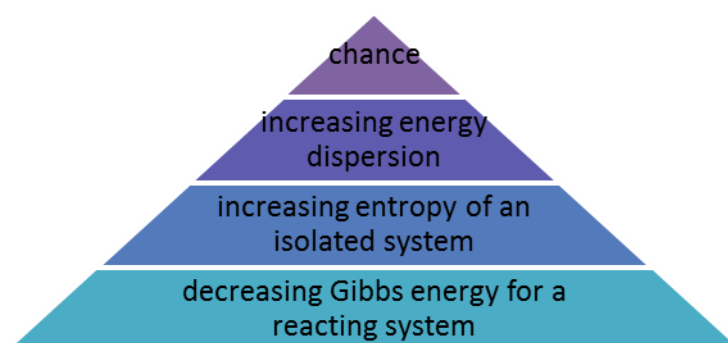

Fig. 16.12 Hierarchy of 'driving forces' for spontaneous processes

14. Gibbs free energy and the thermodynamic stability of substances

Just as the standard enthalpy of formation of a substance is defined as the standard enthalpy change when that substance is formed from its elements in their standard states (see Unit 13) the standard Gibbs free energy of a substance is defined as equal to the **standard Gibbs energy change of formation, $\Delta_f G^\ominus$** of that substance, formed from its elements in their standard states.

Tables of $\Delta_f G^{\ominus}$ are available in reference books, or $\Delta_f G^{\ominus}$ may be calculated from the separate standard entropy and enthalpy changes of formation for that substance.

For example, $\Delta_f G^{\ominus}$ ($H_2O(g)$) is defined as the standard Gibbs energy change for the reaction in which *1 mol* of gaseous water is formed its elements:

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g) \qquad\qquad \Delta G^{\ominus} = \Delta_f G^{\ominus} (H_2O(g)) \quad = -228.6 \text{ kJ mol}^{-1} \text{ at 298 K}$$

If $\Delta_f G^{\ominus}$ is negative, then the reaction in which the substance is formed from its elements has a large equilibrium constant at the temperature at which the data applies (often, 298 K).
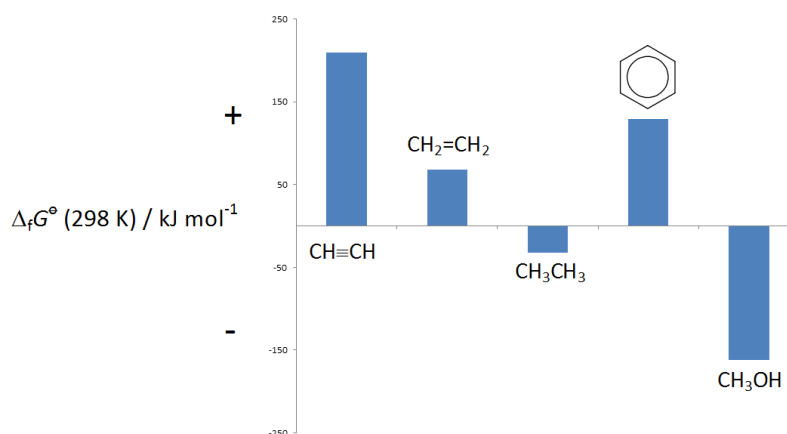

Fig. 16.13 Standard Gibbs energy of formation of selected gaseous organic compounds. From L to R: ethyne (acetylene); ethene (ethylene); ethane; benzene; methanol.

$\Delta_f G^{\ominus}$ values are indicators of the 'thermodynamic stability' of substances. Fig. 16.13 displays $\Delta_f G^{\ominus}$ for several organic compounds, including three (ethyne, ethene and benzene) that contain multiple carbon to carbon bonds. Compounds whose molecules contain multiple bonds are described as 'unsaturated' and for hundreds of years it has been known that unsaturated compounds are 'eager' to react so as replace their multiple CC bonds with single (C-C) bonds. Ethyne, ethene and benzene have positive $\Delta_f G^{\ominus}$ values and so are said to be more thermodynamically unstable than the other compounds.

Ethyne is the least thermodynamically stable compound shown. Ethyne may be converted to ethane in two stages:

$$CH{\equiv}CH(g) + H_2(g) \rightarrow CH_2{=}CH_2(g)$$

followed by:

$$CH_2{=}CH_2(g) + H_2(g) \rightarrow CH_3CH_3(g)$$
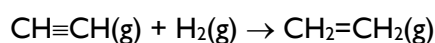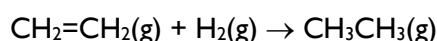
At each stage, $CH{\equiv}CH$ and $CH_2{=}CH_2$ are losing Gibbs energy, finally arriving at ethane, for which $\Delta_f G^{\ominus} = -32$ kJ mol^{-1}.

15. Predicting whether a reaction will occur using standard electrode potentials

In this section we make the link between cell potential and the change in standard Gibbs energy ($\Delta G^{\ominus}$) for a reaction.

In the unit on reduction and oxidation (p.113 in the book), we showed how standard electrode potentials, $E^{\ominus}$, may be used to predict whether or a reaction would occur – although we cannot predict how fast the reaction would proceed. The procedure involved in predicting whether or not an ionic reaction will occur involves writing down the two half reactions involved in the overall reaction. For example, in predicting whether or not the reaction:

$$H_2(g) + Fe^{3+}(aq) \rightarrow 2H^+(aq) + Fe^{2+}(aq) \qquad (16)$$
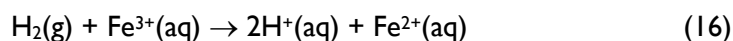
will occur, we first identified the half reactions involved and wrote them down with the most reducing half reaction (the one with the most negative or least positive $E^{\ominus}$) on top:

$2H^+(aq) + 2e^- \rightarrow H_2(g)$ $E^{\ominus} = 0.00$ V
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ $E^{\ominus} = +0.77$ V
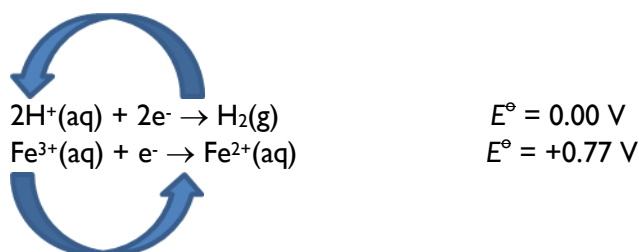
Finally, we drew anticlockwise arrows. The direction in which the arrows pointed showed that the predicted reaction involved the oxidation of $H_2(g)$ and the reduction of $Fe^{3+}(aq)$, so that the reaction (16) does occur.

The meaning of 'occur' here is that the equilibrium constant of the reaction is large. We should not therefore be surprised to be told that $E^{\ominus}$ and $\Delta G^{\ominus}$ are related. Indeed, this is necessary or else they might make different predictions!

Although it is not obvious, the 'anticlockwise arrow' routine works because we are, in effect, predicting whether or not an electrochemical cell consisting of the two electrode systems ($H_2(g)/H^+(aq)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$ respectively) will generate a positive cell potential. In the above example, and following the method of calculating cell potentials given in the book on p.111, an electrochemical cell with the standard $Fe^{3+}(aq)/Fe^{2+}(aq)$ electrode as the cathode and the standard $H_2(g)/H^+(aq)$ electrode as the anode would produce a standard cell voltage of:

$$E^{\ominus}_{cell} = +0.77 - 0.00 = +0.77.$$

It is the fact that the cell voltage is positive that is important. The relationship between between $E^{\ominus}_{cell}$ (the standard *cell* potential) and the change in standard Gibbs energy change ($\Delta G^{\ominus}$, J mol^{-1}) for the overall reaction is that:

$$\Delta G^{\ominus} = - nFE^{\ominus}_{cell} \qquad (17)$$

where n is the number of electrons transferred in the reaction (for reaction 15, $n = 2$) and F is the Faraday constant, with the units of electrical charge (in coulombs) per mole, written as C mol^{-1}. $F =$

96485 C mol⁻¹. Equation (16) is called the Nernst equation. $E^{\ominus}_{cell}$ has the unit of volts. The Nernst equation shows that if $E^{\ominus}_{cell}$, the standard cell potential, is positive, then $\Delta G^{\ominus}$ for the reaction will be negative. Since a negative $\Delta G^{\ominus}$ means a large equilibrium constant, **in predicting a positive $E^{\ominus}_{cell}$ we are predicting $K > 1$.** We are thus reassured that 'anticlockwise' rule is simply an indirect way of calculating the standard Gibbs energy for a reaction.

To illustrate the use of the Nernst equation, we apply it to equation (16):

$$\Delta G^{\ominus} = - nFE^{\ominus}_{cell} = -2 \times 96485 \times (+0.77) = -148587 \approx -148000 \text{ J mol}^{-1}$$

(Note on units: since 1V = 1 Joule per coulomb, the units of $\Delta G^{\ominus}$ are C mol⁻¹ x J C⁻¹. The coulombs cancel, giving the units as J mol⁻¹)

The standard Gibbs energy change for reaction (15) is thus about -148 kJ mol⁻¹. If $E^{\ominus}_{cell}$ was obtained at 298 K, then the calculated value of $\Delta G^{\ominus}$ also applies to 298 K.

16. Thermodynamically and kinetically controlled reactions

Whether we are in the laboratory or scaling up a chemical reaction on an industrial scale, a good percentage yield of product is always desirable. A good yield of product depends on favourable thermodynamics and kinetics. By thermodynamics we mean a large equilibrium constant. By kinetics we mean the speed at which equilibrium is achieved. If K is small then the rate of reaction is generally irrelevant because the yield will be small anyway[3] at the temperature being used, but equally a slow reaction is not commercially viable.

A study of some reactions in which there are two possible products from the same reactants, brings the thermodynamic and kinetic factors into sharp focus. In these cases, it is possible to use a lower temperature to produce more of a less thermodynamically stable product.

Suppose that two spontaneous reactions are in competition; reactions in which two possible products could be produced from the *same* reactants, such as:
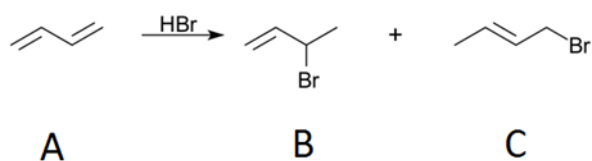
In this example, a mixture (labelled A) of 1,3-butadiene and hydrogen bromide may produce one of two isomers: either B (3-bromo-1-butene) or C (1-bromo-2-butene). To make the molecular structures clearer, we may depict the reaction using 'ball and stick' diagrams in which the bromine atoms are coloured red:

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[3] There is an exception to this rule. It is possible to produce good yields even if K is low, by physically removing the product from the reaction mixture, as in the Haber-Bosch process (book p278) when ammonia is liquified or in some organic chemistry preparations when the product is volatile and is distilled off (book, p271). In these cases, since the product is being removed the reaction mixture, the flask re-establishes equilibria and so produces more product. The cycle is repeated and the product samples collected together.
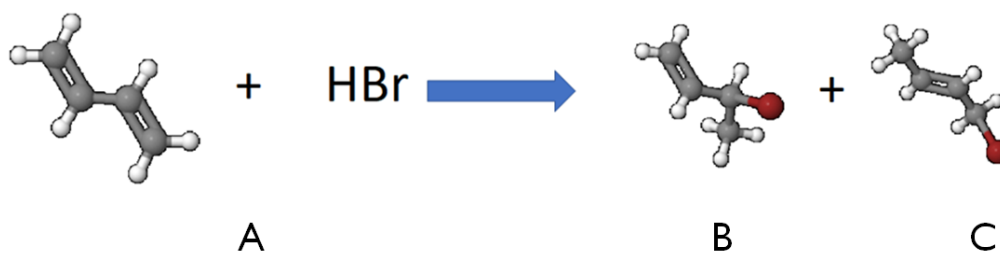
The formation of **C** involves a more negative ΔG over a wide range of temperature (this makes **C** more thermodynamically stable than **B**) and provided that equilibrium is reached, **C** is expected to dominate the product mixture. This is the case at room temperature. The thermodynamics of the reaction are depicted in Fig. 16.14.
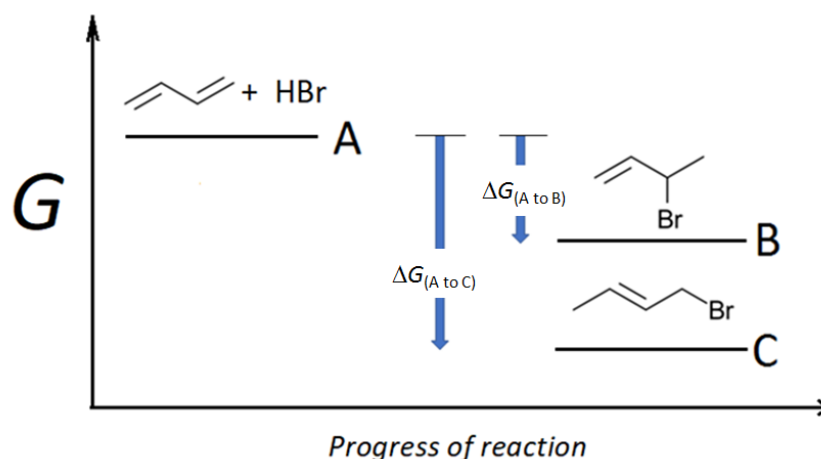

Fig. 16.14 The changes in Gibbs energy for two possible products (**B** and **C**) from the reaction mixture (labelled **A**) of 1,3-butadiene and HBr.

At lower temperature things are different. At -80 °C the **A → C** reaction is much slower than **A →** **B** (which has the lower activation energy) and equilibrium is not achieved over the timescales of the experiment, so even though **C** is thermodynamically preferred, the product mixture contains mostly **B**. If the mixture at -80 °C is allowed to warm up to room temperature, then the product mixture changes: equilibrium is slowly reached and the equilibrium mixture is dominated by C.

This case is expressed as follows: at the low temperature, the reaction of 1,3-butadiene with HBr is **kinetically controlled**, but at higher temperature it is **thermodynamically controlled**.

EXERCISE 16A

When cyclopentadiene and furan react, the resulting mixture contains two isomers, A and B:
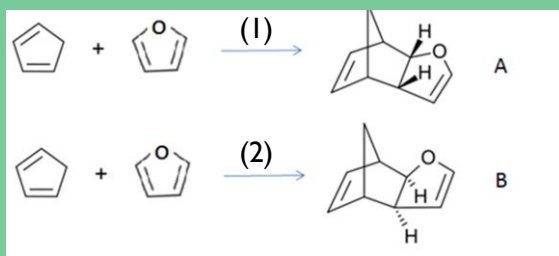
The isomers differ in the position of the hydrogen atoms, either pointing upwards (as in **A**) or downwards (**B**). ΔG for reaction (2) is more negative than for reaction (1) and this is true over a wide range of temperature. Use this information to suggest an explanation for the following:

(a) The product mixture contains more A than B at 25 $^\circ$C, but at 80 $^\circ$C, B dominates.
(b) The mixture at 25 $^\circ$C very slowly converts to a mixture dominated by B.

Answers

(a) This is an example of thermodynamic V kinetic control. The relative ΔG values show that **B** is more stable than **A**. At 25 $^\circ$C, the rate of reaction (1) > rate of reaction (2) presumably because it has the lowest activation energy, E_A. Reaction (2) does not reach equilibrium at 25 $^\circ$C so **A** dominates the product mixture. At 80 $^\circ$C, rate (1) is faster than it was at 25 $^\circ$C, but reaction (2) is now sufficiently fast enough to cause the reaction to reach equilibrium in a reasonable time, an equilibrium in which the more stable isomer (**B**) dominates.

(b) Even at 25 $^\circ$C equilibrium will eventually be achieved and so much of A will break down into B, but it will take very much longer at the lower temperature.

Further reading

1. Elements of Physical Chemistry, by Peter Atkins and Julio De Paula, OUP, 2017. A more advanced textbook which elaborates upon many of the subjects of this unit.

2. There are many websites giving introductions to this subject. For example, Dr Stephen Lower's website, http://www.chem1.com/acad/webtut/thermo/entropy.html