8 A Microscopic Approach to Entropy

The thermodynamic approach

Internal energy and enthalpy

When energy is added to a body, its *internal energy* U increases by an amount ΔU. The energy added may be either as heat or work and this is summarised in the equation $\Delta U = q + w$, where q is the energy added as heat and w the energy added as work. This equation assumes that the energy has been added at constant volume but if it is added at constant pressure some additional work may absorbed in expansion, which requires $p\Delta V$ of work. Under these conditions the added heat or work changes a quantity called the *enthalpy* H of the body. If we compare the equations $\Delta U = q + w$ (constant volume) with $\Delta H = q + w$ (constant pressure), we have $\Delta H = \Delta U + p\Delta V$. As chemical reactions are usually done at atmospheric pressure, ΔH is more commonly used than ΔU. In practice ΔU and ΔH have similar values even when there are large changes in volume because the reaction involves a change in the number of moles of gas. For example for the reaction

$$CH_4(g) = C(s) + 2H_2(g),$$

$\Delta U = +72.3$ kJ mol^{-1} and $\Delta H = +74.8$ kJ mol^{-1}. The difference between these two values is $p\Delta V$, the work required to expand one mole of gas at 1 atmosphere and 298 K. The energy required to bring about this expansion is most easily calculated using the ideal gas equation $pV = nRT$. As p, R and T are constants $p\Delta V = \Delta nRT = +1 \times 8.31 \times 298 = +2.5$ kJ mol^{-1}.

Heat and entropy

Heating involves the passage of random kinetic energy, while doing work (for example by compressing a gas or by passing an electric current) involves the passage of ordered energy. As entropy is measure of the degree of disorder of a system, it increases whenever random kinetic energy is added to a body; on the other hand the addition of ordered energy in the form of work will leave the entropy unchanged. So to look at entropy changes, we must first consider what happens to various systems when energy added to them in the form of heat. The following examples illustrate some of the different effects.

An inert gas. If energy is added to an inert gas, it is absorbed by the individual atoms of the gas. As long as the energy is not in packets large enough to excite the electrons in the atoms, the energy appears as translational kinetic energy of the atoms and the temperature of the gas increases.

A polyatomic gas. The absorbed energy can now appear as translational kinetic energy, rotational kinetic energy and as increased vibrational energy of the bonds. Vibrational energy has two components, kinetic energy when the atoms are moving and potential energy when the atoms are momentarily at rest while at their maximum or minimum distance apart. Vibrational energy is absorbed in bigger packets than rotational energy, while energy absorbed as translation is absorbed in packets so small that they appear to be continuous. This means that that most of the energy is absorbed as translational kinetic energy and the temperature of the gas increases.

A crystalline solid. The only type of motion in a crystalline solid such as sodium chloride is vibration and any energy absorbed increases the vibration of the individual ions. As vibration energy is partly kinetic energy, the temperature of the solid increases.

A solid at its melting point. When a solid melts, some of the intermolecular forces are broken. Usually this results in expansion as solid changes to a liquid (water being the obvious exception). Complex changes take place at the molecular level during this melting process as a liquid is composed of solid-like aggregates that are randomly mixed and can move freely over each other. The net result is that the potential energy of the system has increased because some bonds have been broken, while the overall kinetic energy has stayed the same. The energy is absorbed as *latent* heat, a name that indicates that the energy is *hidden* as there is no increase in temperature.

A liquid evaporating. A similar situation occurs when a liquid evaporates. The remaining intermolecular forces are broken so that there is a large increase in potential energy, accompanied by a large increase in volume. The nature of the forces that are broken depends on the material; for a liquid inert gas, they will all be London dispersion forces, while for an ionic liquid they will be the simple electrostatic forces between the ions.

The increase in entropy ΔS of the system depends on the temperature of the system. At high temperatures the system contains a lot of random kinetic energy and the addition of small extra amount has little effect on the total disorder. At low temperatures the amount of random kinetic energy is small and any increase has a big effect on the disorder. A popular analogy, used by Peter Atkins in his books on thermodynamics, is that of a sneeze in a quiet room (ordered, low temperature) is very distracting, while in a busy noisy street (disordered, high temperature) the sneeze passes unnoticed. This dependence on temperature is shown by the equation $\Delta S = q/T$, which relates the increase of entropy ΔS to the amount of heat energy absorbed q when it is transferred to a system at temperature T. This temperature is on the absolute (Kelvin) scale of temperature; on this scale the maximum increase in entropy is at very low temperatures when the system is highly ordered and the minimum at high temperatures when the system is already very disordered.

Some entropy changes.

Heat flowing from a hot to a cold body. If a body at temperature T_2 is placed in contact with another at a lower temperature T_1, a quantity of heat q flows from the hot body to the cold. The gain in entropy of the cold body is q/T_1 and the loss in entropy of hot body is q/T_2. As $T_2 > T_1$, there is an overall gain in entropy. This is quite general; processes that take place *spontaneously* (that is can take place on their own accord) are always accompanied by an overall increase in entropy. Under special circumstances it is possible for the change to take place *reversibly* when the overall entropy change is zero. This must be the case for a reversible change which can go either way. If a reversible change has an entropy increase in one direction it would have an entropy decrease in the other (which is impossible); the only way to avoid an entropy decrease in one direction is to have the entropy changes in both direction equal to zero. This entropy condition is called the *Second Law of Thermodynamics* and may be expressed in the form $\Delta S \geq 0$.

A solid melting at its melting point. At 273 K, ice melts and becomes water. In doing so it absorbs 6000 J mol^{-1} so there is an entropy decrease of 6000/273 = 22.0 J mol^{-1} K^{-1} (note the units). This entropy decrease arises from the amount of heat absorbed from the *surroundings* and must be balanced by an entropy increase of at least the same amount if the process is to be spontaneous. The entropy increase comes from the *system* and arises because water is far more disordered than ice. We can measure this entropy increase ΔS_{system} by using the equation

$$\Delta S_{\text{total}} = \Delta S_{\text{surroundings}} + \Delta S_{\text{system}}.$$

At 273 K, the system is in equilibrium so that $\Delta S_{\text{total}} = 0$. Thus

$$0 = -6000/273 + \Delta S_{\text{system}}$$

and $\Delta S_{\text{system}} = +22.0$ J mol^{-1} K^{-1}. In chemistry we pay attention to changes in the system, rather than to changes in the surroundings and ΔS_{system} is often written just ΔS. This can cause confusion when it has a negative value as it appears to violate the Second Law of Thermodynamics, but we must remember that any entropy decrease in the system must be balanced (or overcome) by an entropy increase of the surroundings; this is a common situation in chemistry for it implies that the reaction is exothermic.

If the temperature is slightly above 273 K, $\Delta S_{\text{surroundings}} < \Delta S_{\text{system}}$ and under these conditions $\Delta S_{\text{total}} > 0$ and all the ice turns to water. A similar argument shows that below 273 K, $\Delta S_{\text{total}} > 0$ for the reverse process (water to ice).

Liquid to vapour

In the presence of air, a liquid can be in equilibrium with its vapour at a range of temperatures, but there is only one temperature at which its vapour pressure is one atmosphere (namely at its boiling point T_b). At this temperature, there are entropy changes similar to those at the melting point of a solid. For most liquids, at their boiling points, their change in disorder when they change to the vapour is very similar, which implies that ΔS_b has a fixed value. This entropy change is equal to the latent enthalpy change of boiling ΔH_b divided by the boiling pointT_b; experimentally it has been shown that this has a value of ~88 J mol^{-1} K^{-1}. This constant value of ΔS_b is known as Trouton's Rule and is a useful way of estimating molar latent enthalpy changes. However, some liquids, such as water, have values of ΔS_b much larger than 88 J mol^{-1} K^{-1} which indicates that the liquid at its boiling point is more ordered than usual, probably because of hydrogen bonding.

Entropy and heat capacity.

If a substance is heated from T to $T + \delta T$, it absorbs an amount of heat $C_p\delta T$, where C_p is the molar heat capacity of the substance (the amount of heat needed to raise the temperature of one mole of the substance one Kelvin). The entropy change associated with this absorption of heat is $C_p\delta T/T$. If the temperature change is from T_1 to T_2, the overall entropy change is given by

$$\Delta S = \int_{T_1}^{T_2} C_p \mathrm{d}T/T.$$

If we know how C_p varies with temperature we can plot a graph of C_p/T against T and the entropy change can then be found by measuring the area of the graph between T_1 and T_2. Experiment (and theory) shows that C_p approaches zero as T approaches zero (Figure 1). This does not necessarily mean that C_p/T also approaches zero as T approaches zero, but measurements at very low temperatures suggest that this is the case (Figure 2). This is the basis of the Third Law of Thermodynamics, which states that ‘the entropy of a pure, crystalline substance is zero at absolute zero’. Thus S, unlike U and H, has an absolute value.

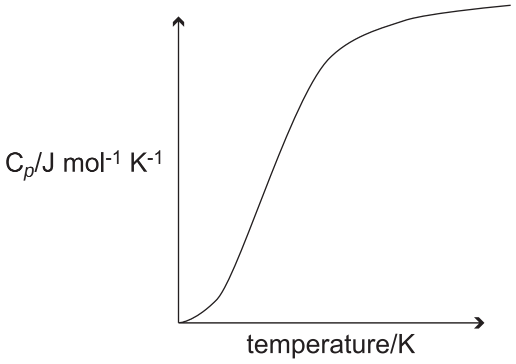

Figure 1. Variation of C_p with temperature.

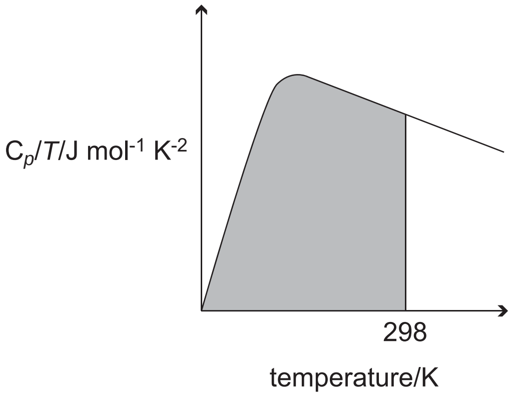

Figure 2. Variation of C_p/T with temperature. The area under the graph gives the value of the absolute entropy of the substance S^{θ}.

As shown by Figure 1, the value of C_p at high temperatures becomes nearly constant. Under these conditions, we can calculate the entropy change when a substance is heated from T_1 to T_2. If C_p is constant, we can evaluate the integral in the expression

$$\Delta S = \int_{T_1}^{T_2} C_p \mathrm{d}T/T.$$

and this leads to $\Delta S = C_p \ln T_2/T_1$.

Molar heat capacities and absolute entropies of solids.

Table 1 lists some values of molar heat capacities and absolute entropies under standard conditions S^{θ}_{298}.

Substance	C_p/mol^{-1} K^{-1}	S^{θ}_{298}/J mol^{-1} K^{-1}
Diamond	6.2	2.4
Pb	26	65
LiF	42	36
CsI	52	126
$BaCl_2$	75	126
$CaCO_3$	82	93
Naphthalene $C_{10}H_8$	166	167

Table 1. Molar heat capacities and absolute entropies of some solids at 298 K.

In a solid, heat is absorbed in the form of increased vibrational energy. If the atoms in the solid vibrate slowly, the energy is easily absorbed as energy levels are close together (remember $E = hf$). This is the case with heavy atoms, weakly attracted to each other. The reverse is true for light atoms, strongly attracted to each other. Thus lead can absorb heat easily and its heat capacity and entropy are large, while the reverse is the case for diamond and its heat capacity and entropy are low. The same effect is shown by LiF (light ions attracted strongly to each other) and CsCl (heavy ions less strongly attracted). A mole of each of these two ionic substances have two moles of particles that can vibrate so that in order to compare one solid substance with another we ought to look at the values per mole of particles, rather than per mole of substance. We should note that per mole of atoms, the values of C_p for Pb, CsI and $BaCl_2$ are very similar and we shall come back to this point later on. The entropy of crystalline $CaCO_3$ is much larger as it contains 5 moles of particles which can vibrate; the vibrations will be of two types; those between the Ca^{2+} ions and CO_3^{2-} ions and those between the Ca and O atoms in the CO_3^{2-} ion. The complexity of this situation makes it difficult to calculate its actual value, but the value suggests that the average bond vibration is intermediate between that for diamond and that for lead. The situation in naphthalene is even more complicated as it has vibrations within the naphthalene molecule and much weaker vibrations between the naphthalene molecules.

Absolute entropies of liquids

The absolute entropy of a liquid is made up of three parts; the entropy of the solid up to its melting point, the entropy change at its melting point and the entropy change of the liquid to 298 K. These individual terms can be measured so that absolute entropies of liquids can be found (Table 2).

Substance	S^{θ}_{298}/J mol^{-1} K^{-1}
Pentane	261.2
Hexane	295.9
Heptane	328.5
Octane	361.1
Nonane	393.7
Decane	425.9
2-Methylpentane	290.6
2-Methylhexane	323.3
2-Methylheptane	356.4
Methanol	127.2
Ethanol	159.9
Propan-1-ol	192.8
Propan-2-ol	180.6

Table 2. Absolute entropies of some liquids.

While it is difficult to calculate values of absolute entropies for individual liquids, some trends are easy to see; for example absolute entropies become larger in a regular fashion as we ascend a homologous series. Another trend is that straight chain molecules have higher entropies than their branched chain isomers as the straight chain form can adopt more different molecule configurations. This is more easily understood when the statistical (rather than the heat) approach to thermodynamics is used. Statistics also enables us to calculate absolute entropies of gases.

The statistical approach

The Boltzmann equation

The interpretation of entropy as a measure of disorder in a system suggests that it should be related to how probable the state is. As an ordered state has fewer ways of being arranged than a disordered state, it should have a lower probability and a smaller entropy.

The connection between entropy and probability is given by the Boltzmann equation $S = R/N \ln W$, where W is the number of ways the microstates of the system can be arranged, R is the gas constant and N the Avogadro constant. (A microstate is a distinct way in which a particle can be made distinguishable from another, either because it is in a different position or because it has a different amount of energy.)

There is much evidence to support this equation and we will look at some of it.

(1).At the absolute zero, all the atoms in a crystal are fixed in position and are in their lowest energy state; this means there is only one arrangement of the microstates. As ln1 = 0, this leads to the Third Law of Thermodynamics, namely that the entropy of a pure crystalline substance is zero at absolute zero.

(2).If we go from a state with entropy S_1 that has W_1 arrangements to a state S_2 that has W_2 arrangements, the entropy change is $S_2 – S_1$ but the probabilities of these arrangements change by the factor W_2/W_1. This suggests that there should be a logarithmic relationship between S and W.

(3).If we expand a gas reversibly against a piston at constant pressure p from volume V_1 to volume V_2, the work done is given by the expression

$$w = \int_{V_1}^{V_2} p\mathrm{d}V.$$

If at the same time as the expansion takes place the temperature is kept constant by allowing a quantity of heat q to flow into the system we can, using the gas equation, make the substitution $p = RT/V$ and then

$$w = RT \int_{V_1}^{V_2} \mathrm{d}V/V = RT \ln V_2/V_1.$$

The absorption of this quantity of heat q is accompanied by an entropy *decrease* of q/T. In order that the overall entropy change is zero (the expansion is under reversible conditions), the expansion of the gas will have an equivalent entropy *increase* of $R \ln V_2/V_1$.

We can show that the equation $S = R/N \ln W$ leads to a similar result If we consider gas contained in a volume V_1 that expands to a volume V_2, each molecule is now more likely to be in the whole volume V_2 rather than in the smaller volume V_1; that is it has a V_2/V_1 chance of being found in the bigger container. For N molecules, all initially in volume V_1, the chance they will be spread out into the larger volume V_2 is $(V_2/V_1)^N$. The entropy change associated with this expansion is $R/N \ln(V_2/V_1)^N = R \ln V_2/V_1$. (This argument ignores that fact that gas molecules have a range of molecular speeds. A more rigorous derivation, which makes allowance for the distribution of molecular speeds, can be done and leads to the same result.)

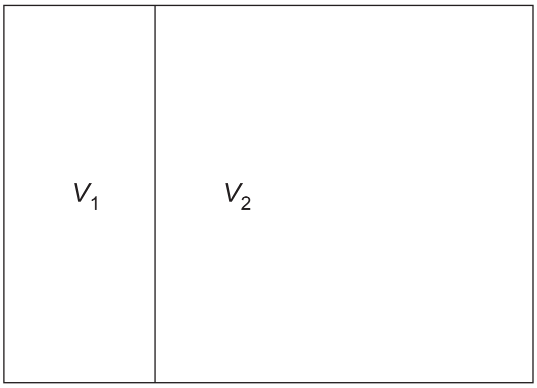

Figure 3. A box of volume V_2 contains a partition enclosing a volume V_1. When the partition is removed, a molecule originally in V_1 as a V_2/V_1 chance of being found anywhere in the box. For N molecules, all originally in V_1, the chance that they are spread throughout V_2 is $(V_2/V_1)^N$.

The mathematics of using the Boltzmann formula is complicated as we are dealing with a very large number of molecules distributed among an even larger number of microstates. In practice, the very large number of particles means we can use approximations in the statistical calculations, which yield extremely accurate results. We can, for example, work out the distribution of energy among molecules and can calculate absolute entropies for a variety of solids and gases. For simple solids, such as metals, it is possible to calculate the variation of C_p with temperature by using equations derived by Einstein and Debye; this then enables us to calculate their absolute entropies without having to use a graphical method. Theory predicts that for substances with low vibration frequencies (for example Pb, CsI and $BaCl_2$) C_p per mole of particles is $3R$ (24.9 J mol^{-1} K^{-1}) at room temperature (Table 1). As the values are slightly higher than this, there must be some additional disorder in the lattice to account for the difference.

It is also possible to calculate absolute entropies of gases. The value for a monoatomic gas depends solely on its relative molecular mass M_r and it can be shown that $S^{\theta} = 108.7 + 12.5 \ln M_r$. Calculations for other gases are more complicated as they require information about bond lengths and vibrational frequencies. The values for some gases at 298 K are shown in Table 3.

Gas	M_r	S^{θ}_{298}/J mol^{-1} K^{-1}
He	4.0	126.0
Ne	20.2	146.2
Ar	39.9	154.7
HF	20.0	173.7
HCl	36.5	186.8
HBr	80.9	198.6
HI	127.9	206.5
H_2O	18.0	188.7
NH_3	17.0	192.3
CH_4	16.0	186.2
C_4H_{10}	58.1	310.1

Table 3. Absolute entropies for some gases.

Calculations using absolute entropies

When doing calculations using Δ*H* or Δ*G*, we ignore the values for the elements as they are zero (by definition). Entropies, however, have absolute values and so the values for the elements has to be included in the calculation. For example in the reaction

$$\mathrm{Na(s)} + \tfrac{1}{2}\mathrm{C}l_2\mathrm{(g)} \rightarrow \mathrm{NaC}l\,\mathrm{(s)}$$

$$\Delta H^{\theta} = \Delta H^{\theta}_{f}(\mathrm{NaC}l) - \Delta H^{\theta}_{f}(\mathrm{Na}) - \Delta H^{\theta}_{f}(\mathrm{C}l_2)$$

$$= -411.2 \quad - 0 \quad - 0 \quad = -411.2\ \mathrm{kJ\ mol^{-1}}.$$

Similarly the value of ΔG^{θ} = -384.2 – 0 – 0 = -384.2 kJ mol^{-1}.
The value of ΔS^{θ}, however, must include the values for Na(s) and ½Cl_2(g); thus

$$\mathrm{Na(s)} + \tfrac{1}{2}\mathrm{C}l_2\mathrm{(g)} \rightarrow \mathrm{NaC}l\,\mathrm{(s)}$$

$$\Delta S^{\theta} = S^{\theta}(\mathrm{NaC}l) - S^{\theta}(\mathrm{Na}) - S^{\theta}(\tfrac{1}{2}\mathrm{C}l_2)$$

$$72.1 \quad - 51.2 \quad - 111.5 \quad = -90.6\ \mathrm{J\ mol^{-1}\ K^{-1}}.$$

At 298 K, $-T\Delta S^{\theta}$ = +90.6 × 298/1000 = +27.0 kJ mol^{-1}, the difference between the values of ΔG^{θ} and ΔH^{θ}.

(Note that the absolute entropy of ½Cl_2(g) is larger than that of Cl (g) as ½Cl_2(g) includes a contribution from the rotational and vibrational energy associated with bond.

Equilibrium constants and ΔG^{θ}

The criterion for a spontaneous reaction is that ΔG is negative; this is equivalent to an overall entropy increase in the system and the surroundings. The equation $\Delta G^{\theta} = -RT \ln K$, which relates ΔG^{θ} to the equilibrium constant *K* appears to be violate the principle for spontaneity as it predicts that some equilibrium reactions proceed to a certain extent, even when ΔG^{θ} is positive. A positive value of ΔG^{θ} means that the equilibrium constant of the reaction is less than one and the position of equilibrium is towards the reactant side, rather than the product side, of the equation.

There is only one temperature when water and ice are in equilibrium, namely 273 K. If water is cooled below 273 K it sometimes stays liquid as ‘supercooled’ water. Thermodynamically it should spontaneously change into ice as has been discussed earlier (the total entropy change is positive), but it may stay in this metastable state because there is no nucleus to promote the formation of ice. Scratching the sides of the container or adding a crystal of ice will make the supercooled water change into ice. This releases heat, so that unless this heat is removed the temperature will rise until 273 K is reached when the ice and water are equilibrium. But if the temperature is maintained below 273 K, all the water changes to ice, there is no equilibrium position. Remember that ΔG^{θ} is the free energy change accompanying the conversion of one mole of reactants completely into one mole of products. As the ice and water form two separate phases which do not mix together, the ΔG graph against composition graph is a straight line with a minimum at the ice end (Figure 4)

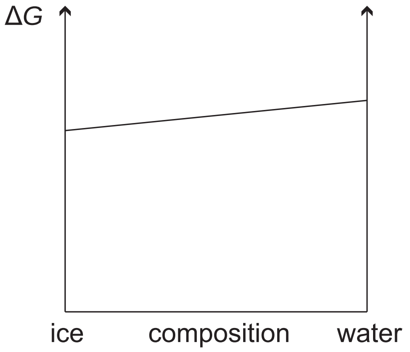

Figure 4. The ΔG against composition graph for ice and water at <273 K.

The situation is different if the products and reactants can mix together. When they mix, there is an additional entropy of mixing term which leads to a minimum in the composition graph. Mixing of reactants and products can be considered as an expansion of the reactants into the volume of the mixture and a similar expansion of the products into the mixture. If we mix together 0.5 mole of gas A with 0.5 mole of gas B, the entropy of mixing will be 1/2 ln 2 (for gas A) + ½ ln 2 (for gas B) =(0.69 J mol^{-1} K-^{1}). If we have two thirds of a mole of gas A mixed with one third of a mol of gas B, the entropy of mixing is 2/3 ln 3/2 (for gas A) + 1/3 ln ln 3 (for gas B) = 0.27 + 0.37 = 0.64 J mol-1 K^{-1} (slightlly smaller than the 0.5/0.5 case).

If we consider how ΔG, at 298 K, for the reaction

$$N_2O_4(g)= \ 2NO_2$$

changes with composition, there is a minimum at about 20% conversion. Although ΔG^{θ} for the reaction is positive (+4.8 kJ mol-1), there is a minimum in the ΔG/composition graph because of the entropy of mixing. This is shown in Figure 5 by the dotted line.

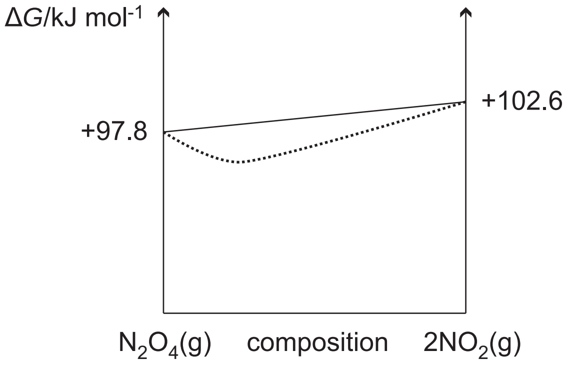

Figure 5. ΔG against composition for the reaction $N_2O_4(g) = 2NO_2(g)$.

Without mixing it would be a straight line. With mixing there is a minimum in the curve even though ΔG^θ is positive.

In practice if ΔG^θ is more negative than -10 kJ mol^{-1}, the minimum is near 100% conversion and we may regard the reaction as having gone to completion. On the other hand, if G^θ is more positive than +10 kJ mol^{-1}, the minimum is near 0% conversion and we may regard the reaction as not having taken place at all.

Summary

The enthalpy of a system may be increased either by adding energy as heat *q* or as work *w*. This heat or work comes from the surroundings; the total amount of energy is unchanged (First Law of Thermodynamics). As heat is random kinetic energy, the addition of heat increases the disorder of the system; this increase in disorder is shown as an increase in entropy ΔS.

When a quantity of heat *q* is added to a system, ΔS increases by q/T, where *T* is the temperature in kelvins. This heat comes from the surroundings leading to an entropy decrease; if the temperature of the surroundings is maintained at the same temperature *T*, the overall entropy the overall change in entropy, ΔS_{total}, is zero. In order that the heat can flow irreversibly, the temperature of the surroundings must be higher than that of the system; under these conditions the overall entropy change is positive. In general $\Delta S_{\text{total}} \geq 0$ (Second Law of Thermodynamics).

Any change in the chemical structure of system will be accompanied by an entropy change ΔS_{system} (often abbreviated to ΔS). Some examples when ΔS increases are: solid turning to liquid, liquid turning to gas and increase in number of gas molecules.

The entropy of substance can be found by measuring its heat capacity C_p over a wide range of temperatures. The entropy is then found by measuring the area under the C_p/T against *T* graph. Experiment shows that, near absolute zero, the heat capacity of a pure crystalline substance approaches zero (Third law of Thermodynamics). This means that the absolute entropy of a substance S^θ can be found.

Absolute entropies enable us to calculate the Gibbs free energy ΔG from ΔH values, using the equation $\Delta G = \Delta H - T\Delta S$. While free energies and enthalpies of elements are zero (by definition), this is not the case for absolute entropies; they must, therefore, be included in the calculation even when elements are involved in the reaction.

As entropy is a measure of disorder it can be related to the number of microstates W of the system. Microstates are the different ways in which the particles of the system can be arranged and the distribution of different packets of energy among these arrangements. The entropy is connected to the number of microstates by The Boltzmann equation $S = R/N\ln W$.

The Boltzman equation enables us to calculate absolute entropies of simple substances. The increase in entropy when gases (or liquids) are mixed can also be found.

If a system has two separate phases (e.g. ice and water) then the position of minimum free energy is either 100% ice (<273 K) or 100% water.(>273 K). If the system has substances that mix together, the minimum in the free energy against composition graph lies in an intermediate position, which is therefore, the position of equilibrium. If ΔG^θ is more negative than -10 kJ mol^{-1}, the minimum is near 100% conversion; if G^θ is more positive than +10 kJ mol^{-1}, the minimum is near 0% conversion. The G^θ position is related to the equilibrium constant K by the equation $G^\theta = RT\ln K$.

Sample question

The elements of Group 14 can all form monoxides and dioxides. The stabilities of the monoxides, with respect to disproportionation into the element and the dioxide, vary. The equations for the disproportionation reactions are given in Table 3.1 together with some thermodynamic data for the reactions.

Table 3.1

disproportionation equation	$\Delta_r S^\ominus$ (298 K) / J K^{-1} mol^{-1}	$\Delta_r H^\ominus$ (298 K) / kJ mol^{-1}	$\Delta_r G^\ominus$ (298 K) / kJ mol^{-1}
$2CO(g) \longrightarrow C(s) + CO_2(g)$	–175.9	–172.5	–120.1
$2SiO(g) \longrightarrow Si(s) + SiO_2(s)$	–362.9	–711.5	–603.4
$2GeO(s) \longrightarrow Ge(s) + GeO_2(s)$		–126.8	
$2SnO(s) \longrightarrow Sn(s) + SnO_2(s)$	–9.200	–9.100	–6.360
$2PbO(s) \longrightarrow Pb(s) + PbO_2(s)$	–4.000	+157.2	+158.4

(a) Explain why the entropy change for the disproportionation of

(i) SiO is so much bigger than for CO,

....

....

....[2]

(ii) PbO is so close to zero.

....

....

....[2]

(b) Table 3.2 gives the standard molar entropies for germanium and its oxides.

Table 3.2

name	standard molar entropy at 298 K, $S^\ominus$(298 K) / J K^{-1} mol^{-1}
germanium, Ge(s)	31.1
germanium monoxide, GeO(s)	50.0
germanium dioxide, GeO_2(s)	55.3

(i) Calculate the standard entropy change, $\Delta_r S^\ominus$(298 K), for the disproportionation of germanium monoxide.

.... [2]

(ii) Calculate the standard free energy change, $\Delta_r G^\ominus(298\,K)$, for the same reaction.

.... [2]

(c) Use data from Table 3.1 to calculate

(i) the value of the equilibrium constant, K_p, for the disproportionation of carbon monoxide, CO,

.... [2]

(ii) the temperature above which the disproportionation of carbon monoxide ceases to be favourable.

.... [2]

(d) Explain why carbon monoxide does not spontaneously disproportionate at room temperature.

....

....[1]

[Total: 13]