

23 Chemical energetics

This is a continuation of chemical energetics, which you started in [Chapter 5](#). It is worth checking that you are still happy with the material covered in that chapter before moving on, such as endo- and exothermic reactions, and reaction pathway diagrams. Particularly in the first part of this chapter you will see similarities to what you have already studied.

Enthalpy changes

At A Level there is another group of energy changes you need to be familiar with. These are shown in [Table 23.1](#).

Table 23.1

Enthalpy change	Definition	Example
Atomisation $\Delta H^{\ominus}_{\text{at}}$	The enthalpy change for the formation of 1 mole of gaseous atoms from an element under standard conditions	$\frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{O}(\text{g})$
Lattice energy $\Delta H^{\ominus}_{\text{latt}}$	The energy change when 1 mole of solid is formed from its isolated ions in the gas phase	$\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl}(\text{s})$
Hydration $\Delta H^{\ominus}_{\text{hyd}}$	The enthalpy change when 1 mole of gaseous ions become hydrated under standard conditions	$\text{Al}^{3+}(\text{g}) + \text{aq} \rightarrow \text{Al}^{3+}(\text{aq})$
Solution $\Delta H^{\ominus}_{\text{sol}}$	The enthalpy change when 1 mole of a substance is completely dissolved, under standard conditions, so that no further heat change takes place on adding more solvent	$\text{HCl}(\text{g}) + \text{aq} \rightarrow \text{HCl}(\text{aq})$

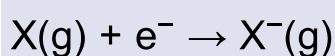
Electron affinity

Ionisation energies are concerned with the formation of positive ions.

Electron affinities are the negative ion equivalent, and their use is generally confined to elements in Groups 16 and 17 of the Periodic Table. Electron affinity is sometimes regarded as the reverse of ionisation energy.

KEY TERM

Electron affinity is defined as the energy change for the addition of one electron to each of one mole of atoms in the gas phase.



Electron affinities have negative values. In other words, energy is released. For example, the first electron affinity of chlorine is -349 kJ mol^{-1}

The first electron affinities of the Group 17 elements are shown in [Table 23.2](#).

Table 23.2

Element	Electron affinity/ kJ mol^{-1}
F	328
Cl	349
Br	325
I	295

There is a trend in [Table 23.2](#) showing that less energy is released as the group is descended. Fluorine is the exception because the electron is being added to a small atom crowded with electrons and there is significant repulsion.

NOW TEST YOURSELF

1 What does the term 'second electron affinity' mean?

2 Give an example of an element for which the second electron affinity is relevant.

Born–Haber cycles

Some energy changes are more complicated than others. Take, for example, the enthalpy of formation of an ionic (electrovalent) solid such as sodium chloride. A number of enthalpy changes are involved in converting the two elements into a solid crystal lattice. These changes can be shown diagrammatically in a **Born–Haber cycle** (Figure 23.1), which uses Hess's law.

Stage 1 is the enthalpy of atomisation of sodium:



Stage 2 is the enthalpy of atomisation of chlorine:



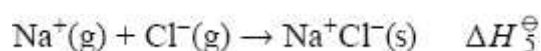
Stage 3 is the first ionisation energy of sodium:



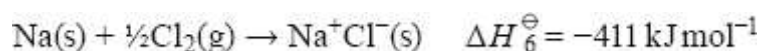
Stage 4 is the electron affinity of chlorine:



Stage 5 is the lattice energy of sodium chloride (to be determined):



Stage 6 is the standard enthalpy of formation of sodium chloride:



Using Figure 23.1 you can see that:

$$+108 + 121 + 496 - 348 + \Delta H_5^\ominus = -411 \text{ kJ mol}^{-1}$$

$$+377 + \Delta H_5^\ominus = -411 \text{ kJ mol}^{-1}$$

$$\Delta H_5^\ominus = -788 \text{ kJ mol}^{-1}$$

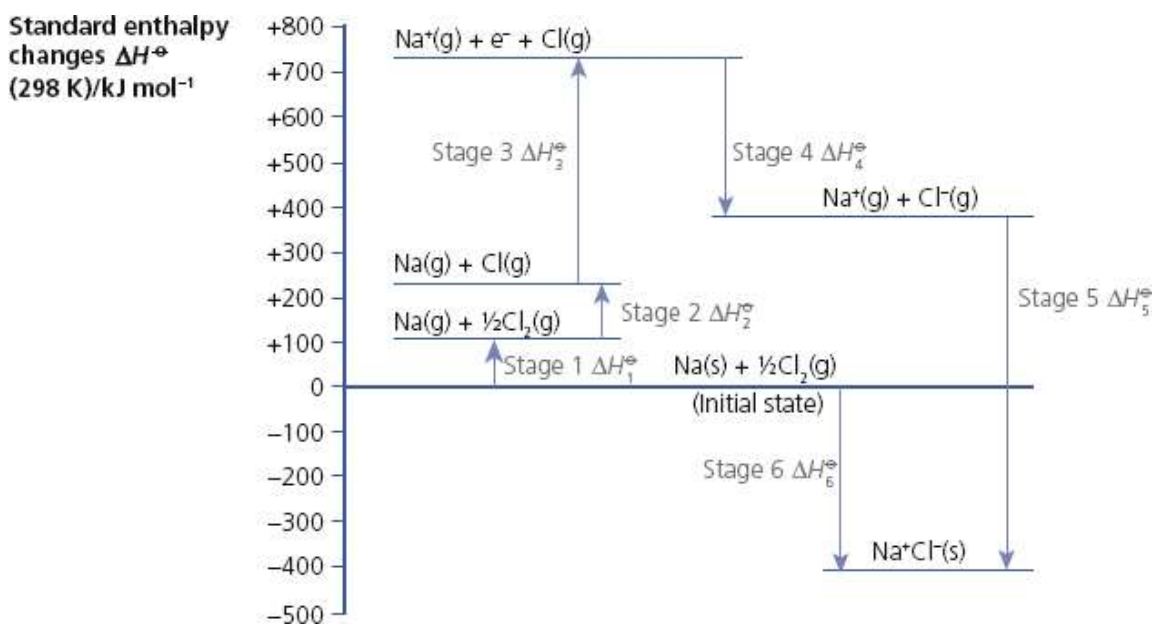


Figure 23.1 Born–Haber cycle for the enthalpy of formation of sodium chloride

You may also be asked to calculate the standard enthalpy of solution of a simple ionic solid. Once again this can be done using a Born–Haber cycle containing the enthalpy changes for the relevant steps.

The magnitude of the lattice energy of an ionic solid depends on several factors:

- the charges on the ions
- the ionic radii of the ions

Magnesium chloride has a much larger lattice energy than sodium chloride ($-2522 \text{ kJ mol}^{-1}$ compared with -788 kJ mol^{-1}). This is because there are more anion-to-cation interactions since there are twice as many chloride ions. In addition, each of these interactions is stronger because the magnesium ion has twice the charge of the sodium ion.

Another factor that influences the lattice energy is the inter-ionic distance (the sum of the ionic radii). [Table 23.3](#) shows two halides from Group 1.

Table 23.3

Compound	Inter-ionic distance/nm	Lattice energy/ kJ mol^{-1}
LiF	0.211	-1036

Compound	Inter-ionic distance/nm	Lattice energy/kJ mol ⁻¹
CsI	0.385	-604

In LiF we have the smallest Group 1 ion and the smallest halide ion whereas in CsI we have a large Group 1 ion and a large halide ion.

We see similar qualitative effects with the enthalpy of hydration of ions. This becomes more negative:

- if the ion is small
- if the ion has more than a single unit of charge

Entropy change, ΔS

- **Entropy** is sometimes explained by saying it is a measure of the ‘disorder’ of a system.

KEY TERM

Entropy is a measure of the number of ways that particles can be arranged in a system and the number of ways in which energy can be shared between the particles in the system.

- Another way of looking at it is to say that a system becomes more stable when its energy is spread out in a more disordered way.

This all sounds rather abstract, so let us look at the idea of entropy changes under different conditions:

- The physical state of a substance affects its entropy, so changing the state will cause a change in entropy (Figure 23.2).
- The particles in a solid just vibrate about fixed positions. There is little randomness in their motion, so they have the lowest entropy.
- By contrast, gas particles move freely around any container and, as a result, show plenty of random arrangements, meaning they have the highest entropy of the three states of matter.
- Dissolving a solid also increases the entropy, because the dissolved particles are no longer held in place and can move randomly.

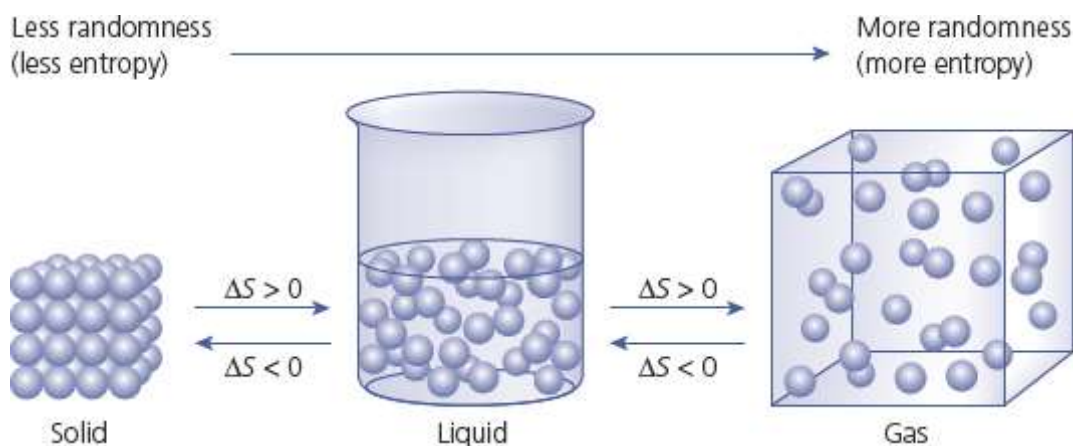


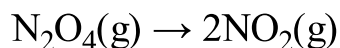
Figure 23.2 How entropy changes with change of state

NOW TEST YOURSELF

3 Explain the change in entropy during:

- a melting wax
- b condensing steam

Now let us suppose you have a chemical reaction in which the number of particles changes on heating. An example might be the decomposition of dinitrogen tetroxide:



The more particles there are, the more ways they and their energy can be arranged and hence the entropy increases.

- There is a general principle that, for a spontaneous change, the total entropy change is positive.
- We know that heat spontaneously flows from a hot body at temperature T_2 to a cooler body at temperature T_1 .
- The removal of energy q at this temperature results in an entropy decrease of $\frac{-q}{T_2}$.
- Similarly, the addition of energy q to the cooler body results in an entropy increase of $\frac{+q}{T_1}$. This is shown in [Figure 23.3](#).

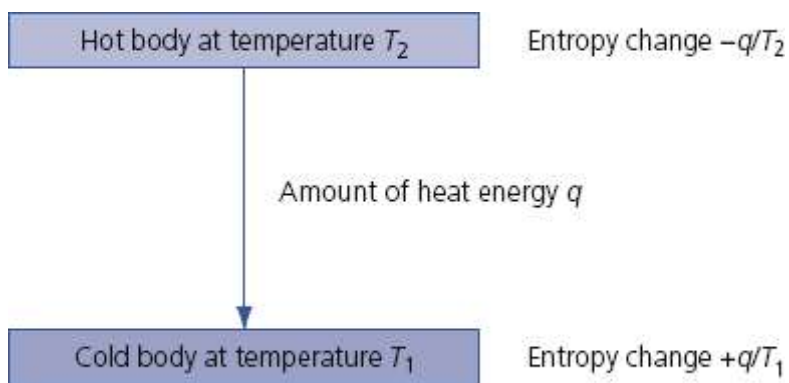
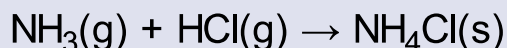


Figure 23.3 Entropy change during heat flow

- The total entropy change is $\frac{-q}{T_2} + \frac{+q}{T_1}$ and, since $T_2 > T_1$ this is positive (as required).

WORKED EXAMPLE

Use standard entropies, S^\ominus , to calculate the entropy change for the reaction between ammonia and hydrogen chloride under standard conditions.



$$S^\ominus(\text{NH}_3(\text{g})) = 192 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S^\ominus(\text{HCl}(\text{g})) = 187 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S^\ominus(\text{NH}_4\text{Cl}(\text{s})) = 95 \text{ J K}^{-1} \text{ mol}^{-1}$$

Answer

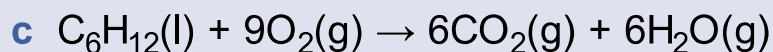
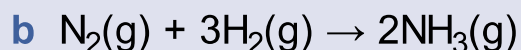
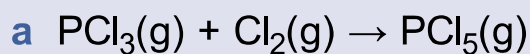
The entropy change of the system is:

$$\begin{aligned} \Delta S^\ominus &= S^\ominus_{\text{products}} - S^\ominus_{\text{reactants}} \\ &= 95 - (192 + 187) \\ &= -284 \text{ J K mol}^{-1} \end{aligned}$$

That is the calculation done, but how does it relate to the chemistry? We had two gases reacting to form a solid, so you might have expected a *decrease* in entropy. However, the reaction is exothermic so the surroundings now have a *higher* entropy and overall the entropy has *increased*.

NOW TEST YOURSELF

4 State the sign of the entropy change in these reactions:



Gibbs free energy change, ΔG

As you have seen, both the change in enthalpy (ΔH) and the change in entropy (ΔS) are important in deciding whether or not a physical or chemical change will take place.

KEY TERM

The **Gibbs free energy** (G) is the energy associated with a chemical reaction that can be used to do work.

You can link the two factors and the temperature using the **Gibbs free energy** of the system, G .

$$G = H - TS$$

Because you are looking at *changes* in enthalpy and entropy, this is more usefully written as:

$$\Delta G = \Delta H - T\Delta S$$

If the change takes place under standard conditions, then the free energy change is equal to the standard free energy change, ΔG^\ominus :

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

For any change to be spontaneous it has to happen in the direction that leads to a *decrease* in free energy. In other words, ΔG must be negative. Note that any reaction for which ΔG is negative is feasible, but this tells us nothing about the *rate* of the reaction.

WORKED EXAMPLE

Calculate the change in free energy at 420 K and 1000 K for the reaction:



	MgCO ₃ (s)	MgO(s)	CO ₂ (g)
$\Delta H^\ominus_f/\text{kJ mol}^{-1}$	-1113	-602	-394
$S^\ominus/\text{J K}^{-1} \text{ mol}^{-1}$	66	27	214

Answers

For the enthalpy change:

$$\Delta H^\ominus = (-602) + (-394) - (-1113) = +117 \text{ kJ mol}^{-1}$$

For the entropy change:

$$\Delta S^\ominus = 27 + 214 - 66 = 175 \text{ J K}^{-1} \text{ mol}^{-1} \text{ or } 0.175 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

For the free energy change:

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

$$\Delta G_{420} = +117 - (420 \times 0.175) = +43.5 \text{ kJ K mol}^{-1}$$

$$\Delta G_{1000} = +117 - (1000 \times 0.175) = -58 \text{ kJ mol}^{-1}$$

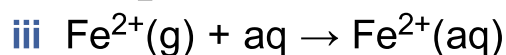
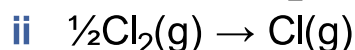
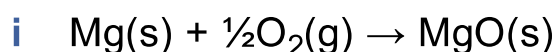
At 420 K the value of ΔG is positive and so the reaction will not occur, whereas at 1000 K the value of ΔG is negative and the reaction takes place. We have assumed that ΔH and ΔS do not change with temperature.

STUDY TIP

Notice that entropy values are typically quoted in $\text{J K}^{-1} \text{ mol}^{-1}$. Before substituting them into $\Delta G = \Delta H - T\Delta S$ they must be converted to $\text{kJ K}^{-1} \text{ mol}^{-1}$. Also T must be in Kelvin.

REVISION ACTIVITY

a Identify the types of enthalpy changes shown in these equations:



b Sketch a Hess's law cycle to show how you could work out the enthalpy of combustion, ΔH_c^\ominus , of ethane, C_2H_6 .

c Use the following data to calculate the enthalpy of combustion, ΔH_c^\ominus , of ethane:

$$\Delta H_f^\ominus[\text{CO}_2] = -393.5 \text{ kJ mol}^{-1}; \Delta H_f^\ominus[\text{H}_2\text{O}] = -241.8 \text{ kJ mol}^{-1};$$

$$\Delta H_f^\ominus[\text{C}_2\text{H}_6] = -84.7 \text{ kJ mol}^{-1}.$$

d How would you expect the enthalpy of combustion to change if ethene, C_2H_4 , was used instead of ethane, C_2H_6 ?

END OF CHAPTER CHECK

By now you should be able to:

- define and use the terms enthalpy change of atomisation, lattice energy, first electron affinity
- explain the factors affecting electron affinities and the trends in these for Group 16 and 17 elements
- construct, use and carry out calculations using Born–Haber cycles
- define and use enthalpy change of hydration and solution; explain the effect of ionic charge and ionic radius on the size of lattice energy and enthalpy change of hydration
- define entropy and predict and explain the sign of the entropy changes that occur during a change of state, during a temperature change and during a reaction in which there is a change in the number of gaseous molecules
- calculate the entropy change for a reaction given the standard entropies of the reactants and products
- state, use and perform calculations using the Gibbs equation, $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

- predict the feasibility of a reaction from the sign of ΔG and the effect of temperature change on its feasibility given standard enthalpy and entropy changes