

ENERGETICS

- 5.1 Exothermic and endothermic reactions
- 5.2 Calculation of enthalpy changes
- 5.3 Hess's law
- 5.4 Bond enthalpies
- 15.1 Standard enthalpy changes of reaction (AHL)
- 15.2 Born-Haber cycle (AHL)
- 15.3 Entropy (AHL)
- 15.4 Spontaneity (AHL)

5

CORE



5.1 EXOTHERMIC & ENDOTHERMIC REACTIONS

- 5.1.1 Define the terms exothermic reaction, endothermic reaction and standard enthalpy change of reaction (ΔH^\ominus).
- 5.1.2 State that combustion and neutralization are exothermic processes.
- 5.1.3 Apply the relationship between temperature change, enthalpy change and the classification of a reaction as endothermic or exothermic.
- 5.1.4 Deduce, from an enthalpy level diagram, the relative stabilities of reactants and products and the sign of the enthalpy change for the reaction.

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Thermochemistry is the study of energy changes associated with chemical reactions. Most chemical reactions absorb or evolve energy, usually in the form of heat, though chemical reactions can also produce light and mechanical energy. Thermochemistry studies the amounts of energy (measured in joules, J) associated with these changes. It is important to note that the energy evolved or absorbed in a reaction is unrelated to the rate of the reaction, which refers to how fast a reaction takes place.

Enthalpy (H , also known as heat content) is the total energy of a system, some of which is stored as chemical potential energy in the chemical bonds. In chemical reactions, bonds are broken and made, but the energy absorbed in breaking bonds is almost never exactly equal to that released in making new bonds. As a result, all reactions are accompanied by a change in the potential energy of the bonds and hence an **enthalpy change**. There is no 'absolute zero' for enthalpy, so absolute enthalpies for particular states cannot be measured, but the change in enthalpy that occurs during a reaction can be measured. This enthalpy change of reaction can be measured and is given the symbol ΔH . It is equal to the difference in enthalpy between the reactants and the products (see

Figure 502) assuming that the reaction occurs with no change in temperature or pressure, or that these conditions are restored to their initial values. If this is the case and any other factors affecting a system's enthalpy do not change, then ΔH is equal to the change in the potential energy of the chemical bonds. Strictly speaking the term enthalpy change only applies to reactions that occur at **constant pressure**, but in the laboratory using open beakers and test tubes, this is most often the case.

A useful comparison may be made with gravitational potential energy. If an object gains gravitational potential energy, then it must absorb energy from its surroundings (for example, from the muscles of the person lifting it) and if this is in the form of heat energy, heat is lost from the surroundings and they cool down. Similarly if a chemical reaction leads to an increase in enthalpy (i.e. the total enthalpy of the products is greater than the total enthalpy of the reactants, so the enthalpy change, ΔH , is positive), then heat energy is absorbed from the surroundings and either they get cooler or heat from an external source must be provided. This is described as an **endothermic reaction**. If the chemicals lose enthalpy (i.e. the enthalpy change, ΔH , is negative), then the heat energy lost by the chemicals is gained by the surroundings and they get hotter. This is described as an **exothermic reaction**. A comparison would be that a falling object loses gravitational potential energy and this is converted into sound (and a little heat) when it hits the floor. Most **spontaneous reactions** (that is, ones that occur, without heating, on mixing the reagents and hence are capable of doing useful work) are exothermic,

but spontaneous endothermic reactions do occur (for example, dissolving ammonium chloride in water). This is summarised in Figure 501:

Enthalpy changes during the course of a reaction may also be represented by **energy level diagrams**. In an exothermic reaction the products are more stable than the reactants (bonds made are stronger than bonds broken), so that ΔH is negative. In an endothermic reaction the opposite is true. This is shown in Figure 502 below for both an exothermic and an endothermic reaction. In these energy level diagrams, the horizontal axis (x-axis) signifies the transition from reactants to products and hence is sometimes referred to as the reaction coordinate.

The numerical value of an enthalpy change for a reaction is best shown by writing the balanced chemical equation for the reaction, with the enthalpy change written alongside it. It is vital to include state symbols in all thermochemical equations because changes of state have their own enthalpy changes associated with them. The enthalpy change will of course vary with the amount of the limiting reagent, so by convention it is given for molar amounts in the equation as it is written. The units may therefore be given as kilojoules per mole, kJ mol^{-1} (to indicate that it refers to molar quantities) or simply as kilojoules, kJ (because it may not be for one mole of all the species involved). The former convention is used throughout this book. Using the thermal decomposition of sodium hydrogencarbonate as an example, a thermochemical equation would be:

Type of reaction	Heat energy change	Temperature change	Relative enthalpies	Sign of ΔH
Exothermic	Heat energy evolved	Becomes hotter	$H_p < H_r$	Negative (-)
Endothermic	Heat energy absorbed	Becomes colder	$H_p > H_r$	Positive (+)

Figure 501 Summary of exothermic and endothermic changes

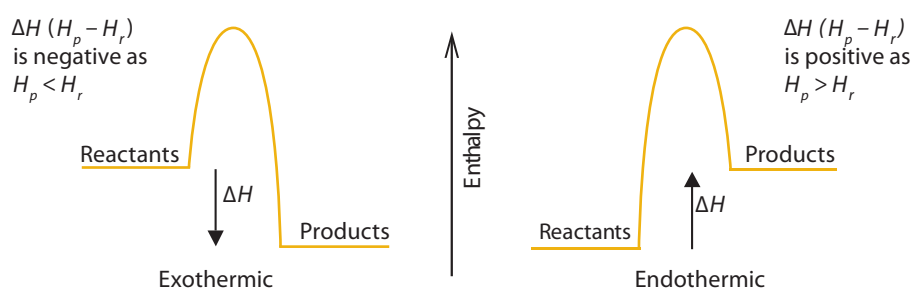
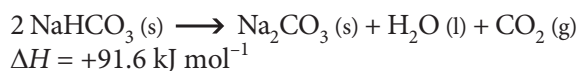
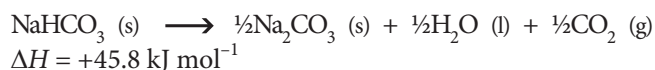


Figure 502 Energy level diagrams of reactions



Note that ΔH is positive, indicating the reaction is endothermic. It is advisable to actually put in the '+' sign rather than just assuming that its absence indicates a positive quantity, as this concentrates the mind on whether the sign should be positive or negative. It is however also correct, though perhaps less common to write:



so as to focus on the amount of sodium hydrogencarbonate. Hence the need to always quote an equation (with state symbols). Note that the basic unit of enthalpy is the Joule (J), but the quantities involved in chemical enthalpy changes are quite large, so that it is more convenient to use kilojoules (kJ, $1 \text{ kJ} = 10^3 \text{ J}$).

By definition an enthalpy change must occur at constant pressure, but the exact numerical value will depend slightly on the exact conditions, such as the pressure and the temperature at which the reaction is carried out. For convenience **thermochemical standard conditions** have been defined as a temperature of $25 \text{ }^\circ\text{C}$ (298 K), a pressure of 101.3 kPa (1 atm) with all solutions having a concentration of 1 mol dm^{-3} . Note that the temperature is different from standard temperature and pressure (s.t.p.) for gases, which is $0 \text{ }^\circ\text{C}$ (273 K); the pressure is however the same. Thermochemical quantities that relate to standard conditions are often indicated by a 'standard' sign (\ominus) as a superscript after the quantity (e.g. ΔH^\ominus), or even more correctly by also including the absolute temperature as a subscript (e.g. ΔH^\ominus_{298}). Frequently however, as in this text, the temperature is omitted.

Exercise 5.1

- If a reaction is endothermic
 - ΔH is negative and heat is absorbed.
 - ΔH is positive and heat is absorbed.
 - ΔH is positive and heat is evolved.
 - ΔH is negative and heat is evolved.
- A reaction gives out heat. This means that
 - the reaction only involves making new bonds.
 - the reaction only involves breaking existing bonds.
 - the bonds made are stronger than the bonds broken.
 - the bonds broken were stronger than the bonds made.
- In the enthalpy level diagram shown

 - the reactants are more stable than the products and the reaction is endothermic.
 - the products are more stable than the reactants and the reaction is endothermic.
 - the reactants are more stable than the products and the reaction is exothermic.
 - the products are more stable than the reactants and the reaction is exothermic.
- When magnesium is added to dilute sulfuric acid, the temperature of the acid rises.
 - Write a balanced equation for the reaction of magnesium with sulfuric acid.
 - Is the reaction exothermic or endothermic?
 - Explain what this implies in terms of the chemical potential energy contained in the reactants and the products.
 - Draw an energy level diagram for this reaction, clearly label on this the enthalpy of reaction.

5. Consider the formation of chlorine monoxide (Cl_2O) from its elements.
- What bonds must be broken? Does this process absorb or release energy?
 - What bonds are made? Does this process absorb or release energy?
 - Explain what is meant by the term “enthalpy change”.
 - In this case the bonds made are less strong than those broken, will the enthalpy change be positive or negative?
 - Will the formation of (Cl_2O) from its elements be an endothermic or exothermic change?

5.2 CALCULATION OF ENTHALPY CHANGES

- 5.2.1 Calculate the heat energy change when the temperature of a pure substance is changed.
- 5.2.2 Design suitable experimental procedures for measuring the heat energy changes of reactions.
- 5.2.3 Calculate the enthalpy change for a reaction using experimental data on temperature changes, quantities of reactants and mass of water.
- 5.2.4 Evaluate the results of experiments to determine enthalpy changes.

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The **temperature** of a system is a measure of the average kinetic energy of the particles present. More specifically the absolute temperature (in Kelvin, K) is proportional to the mean kinetic energy and is independent of the amount of substance present. Heat, on the other hand, is a measure of the total energy in a substance and does depend on the amount of substance present. Thus, to raise the temperature of 100 g water by 1 °C requires five times the heat needed to raise the temperature of 20 g water by 1 °C.

When the temperature of a substance increases, **heat energy** must be absorbed from the surroundings. The amount of heat required will depend on how much of the substance there is to heat (its mass, m), what the substance

is made of (its **specific heat capacity**, c) and the amount by which its temperature is being increased (ΔT). The amount of heat energy released when a substance cools can be calculated in the same way:

$$\text{Heat energy} = m.c.\Delta T$$

For example the energy required to heat 50.0 g of water (specific heat capacity = $4.18 \text{ J g}^{-1} \text{ K}^{-1}$) from 20.0 °C to 60.0 °C ($\Delta T = 40.0 \text{ °C}$) is:

$$\begin{aligned} \text{Heat energy} &= m.c.\Delta T \\ &= 50.0 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ K}^{-1} \times 40.0 \text{ °C} \\ &= 8360 \text{ J} \text{ or } 8.36 \text{ kJ} \end{aligned}$$

The specific heat capacity depends on the substance whose temperature is being changed, because some materials require more heat energy to bring about a change in temperature. For example from the specific heats of aluminium and gold (Al: $0.90 \text{ J g}^{-1} \text{ °C}^{-1}$; Au: $0.13 \text{ J g}^{-1} \text{ °C}^{-1}$) it can be seen that gold requires about 7 times less energy to raise its temperature than aluminum does. Sometimes the heat capacity of an object is referred to. This is the amount of energy required to increase its temperature by 1 °C (i.e. $m.c$). Thus heating a calorimeter with a heat capacity of 50 J K^{-1} by 12 °C will require $50 \times 12 = 600 \text{ J}$ of energy.

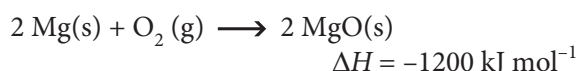
Calorimetry is a technique used to measure the enthalpy associated with a particular change. In this the temperature change of a liquid inside a well insulated container, known as a calorimeter, is measured before and after the change. For many chemical reactions a styrofoam (i.e. expanded polystyrene) cup is a convenient calorimeter because it has a very low (that is, for most purposes, negligible) heat capacity and it is a good insulator. If calorimeters made of other materials are used, for example a copper calorimeter in a combustion experiment, then the heat absorbed by the calorimeter must be added to that absorbed by the liquid:

$$\text{Heat absorbed} = (m.c.\Delta T)_{\text{liquid}} + (m.c.\Delta T)_{\text{calorimeter}}$$

Calorimetry depends on the assumption that all the heat absorbed or evolved changes the temperature of the calorimeter and its contents, that is, that no heat is gained from/lost to the surroundings. That is why it is important that calorimeters are well insulated. Nevertheless heat exchange with the surroundings is the major source of error in all thermochemistry experiments in school laboratories. It may be minimised by increasing the insulation, especially by fitting an insulated lid, but significant errors are inevitable, especially in reactions where a gas is evolved. Errors in combustion experiments, where a hot

gas is being used to heat liquid in a calorimeter, are even greater. This source of error always leads to temperature rises that are less than would be expected and hence to ΔH values that are numerically less than literature values. The thermometer used often has a precision uncertainty of $\pm 0.1^\circ\text{C}$ or greater, so that uncertainty in the value of the temperature change is often the major source of imprecision.

The enthalpy change that occurs in a reaction is quoted for molar amounts in the chemical equation as it is usually written, so for example the equation



means that 1200 kJ of heat are evolved (as ΔH is negative) when 2 moles of magnesium react completely with 1 mole of oxygen molecules. Thus if 0.600 g of magnesium ($= 0.600/24.3$ moles) is burnt, then the amount of heat produced is:

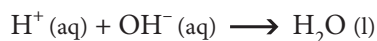
$$\frac{1}{2} \times 0.600/24.3 \times 1200 = 14.8 \text{ kJ}$$

Often chemical reactions occur in aqueous solution and the energy evolved or absorbed alters the temperature of the water the reactants are dissolved in. Water is usually in excess and has a very high specific heat capacity, so that to a first approximation, the heat energy required to change the temperature of the other substances present may be ignored, in comparison to that needed to heat the water.

If for example 20.0 cm^3 of exactly 2 mol dm^{-3} aqueous sodium hydroxide is added to 30.0 cm^3 of hydrochloric acid of the same concentration, the temperature increases by 12.0°C . The total volume of aqueous solution is 50.0 cm^3 ($20.0 + 30.0$) and the density of water (also assumed for dilute aqueous solutions) is 1.00 g cm^{-3} , hence the mass of the aqueous solution is 50.0 g . The amount of heat required to heat the water can be calculated:

$$\begin{aligned} \text{Heat energy} &= m.c.\Delta T \\ &= 50.0 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1} \times 12.0^\circ\text{C} \\ &= 2508 \text{ J or } 2.51 \text{ kJ} \end{aligned}$$

This heat is equal to the heat energy evolved, for the quantities specified, by the reaction:



The hydroxide ion is the limiting reagent (amount of $\text{NaOH} = c.V = 2 \times 0.0200 = 0.0400$ moles, amount of $\text{HCl} = 2 \times 0.0300 = 0.0600$ moles), so the reaction of

0.0400 moles evolved this amount of heat energy. The enthalpy of reaction per mole can therefore be calculated as:

$$2.508 \times 1/0.0400 = 62.7 \text{ kJ mol}^{-1}$$

But as the reaction is exothermic the sign of ΔH must be negative, therefore

$$\Delta H = -62.7 \text{ kJ mol}^{-1}.$$

TOK Experimental and theoretical values

What criteria do we use in judging whether discrepancies between experimental and theoretical values are due to experimental limitations or theoretical assumptions?

I'm much better at chemistry than Charlie. I spend more time reading through my notes, I never miss a chemistry class, I hand in all my assignments on time and I get A-grades for them, whereas Charlie's book is in mint condition, his seat in class is as often empty as it is occupied and as for assignments Just one nagging problem; he always gets a higher mark than me in tests. Our dumb teacher always manages to set questions he knows the answer to, and when it comes to multiple choice he is so lucky with his guesses.

Science is sometimes like that, what should be true sometimes doesn't quite correspond to reality and we have to ask whether the problem lies with "what should be true" (i.e. the theory) how we measure reality (i.e. the experiment) or perhaps both. Probably working out where the problem lies involves looking at both very carefully. With regard to the experimental results we need to consider the precision uncertainty of our measurements and how reproducible they are. If after a number of repetitions the values seem to differ consistently in the same direction to theory we then probably need to carefully examine the method for systematic errors – are we always making the same mistake without realising it. In thermochemical determinations of enthalpy changes of reaction explaining a smaller numerical value, through a smaller than expected temperature change owing to heat exchange with the environment, or not taking into account the specific heat capacity of the container, is easy. Variations in the opposite direction require more imagination. With the theory, what assumptions are we making? Have we evidence regarding their validity? Are there factors we haven't considered, like overlooking state changes if using bond enthalpies?

Exercise 5.2

CORE

In this section, assume the specific heat capacity of water and all dilute aqueous solutions to be $4.18 \text{ kJ dm}^{-3} \text{ K}^{-1}$ (equivalent to $4.18 \text{ J g}^{-1} \text{ K}^{-1}$).

- How much heat energy is required to increase the temperature of 10 g of nickel (specific heat capacity $440 \text{ J kg}^{-1} \text{ K}^{-1}$) from $50 \text{ }^\circ\text{C}$ to $70 \text{ }^\circ\text{C}$?
 - 4.4 J
 - 88 J
 - 4400 J
 - 88000 J
- Copper has a specific heat capacity of $400 \text{ J kg}^{-1} \text{ K}^{-1}$. If a 50 g cylinder of copper absorbs 800 J of energy, by how much will its temperature rise?
 - $5 \text{ }^\circ\text{C}$
 - $20 \text{ }^\circ\text{C}$
 - $40 \text{ }^\circ\text{C}$
 - $320 \text{ }^\circ\text{C}$
- The enthalpy of combustion of ethanol ($\text{C}_2\text{H}_5\text{OH}$) is 1370 kJ mol^{-1} . How much heat is released when 0.200 moles of ethanol undergo complete combustion?
 - 30 kJ
 - 274 kJ
 - 1370 kJ
 - 6850 kJ
- $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l})$
 ΔH for the reaction above is -286 kJ mol^{-1} . What mass of oxygen must be consumed to produce 1144 kJ of energy?
 - 4 g
 - 32 g
 - 64 g
 - 128 g
- When 4.0 g of sulfur is burnt in excess oxygen, 40 kJ of heat is evolved. What is the enthalpy change for the combustion of sulfur?
 - 10 kJ
 - 40 kJ
 - 160 kJ
 - 320 kJ
- In thermochemistry experiments carried out in a school laboratory the major source of error is usually
 - heat losses to the surroundings.
 - accurate measurement of the volumes of liquids.
 - innaccuracies in the concentrations of the solutions.
 - impurities in the reagents.
- When 25 cm^3 of 2 mol dm^{-3} aqueous sodium hydroxide is added to an equal volume of hydrochloric acid of the same concentration, the temperature increases by $15 \text{ }^\circ\text{C}$. What is the enthalpy change for the neutralisation of sodium hydroxide by hydrochloric acid?
 - $25 \times 2 \times 15 \times 4.18 \text{ kJ mol}^{-1}$
 - $50 \times 2 \times 15 \times 4.18 \text{ kJ mol}^{-1}$
 - $\frac{25 \times 15 \times 4.18}{2} \text{ kJ mol}^{-1}$
 - $\frac{50 \times 15 \times 4.18}{2 \times 25} \text{ kJ mol}^{-1}$
- When 8.00 g of ammonium nitrate completely dissolved in 100 cm^3 of water, the temperature fell from 19.0°C to 14.5°C . Calculate the enthalpy of solution of ammonium nitrate.
- In cooking 'Crepe Suzette' a tablespoon of brandy is poured over the pancakes and then it is ignited.
 - If the volume of brandy in a tablespoon is 10 cm^3 and the brandy is 30% ethanol by volume, what volume of ethanol is present?
 - The density of ethanol is 0.766 g cm^{-3} . What mass of ethanol is there in the tablespoon of brandy?
 - The molar mass of ethanol is 46 g mol^{-1} . How many moles of ethanol were there in the tablespoon?
 - Write a balanced equation for the complete combustion of one mole of ethanol.
 - The standard enthalpy change for this reaction is $-1350 \text{ kJ mol}^{-1}$. How much heat is given out when the brandy on the Crepe Suzette burns?
- A camping stove, burning butane, was used to heat 500 g of water from $20 \text{ }^\circ\text{C}$ until it was boiling. Heating this amount of water from $20 \text{ }^\circ\text{C}$ to boiling with an electrical heater requires 168 kJ of energy.

- If the pot was made out of aluminium and it weighed 100 g, how much heat energy was required to heat the pot (the specific heat capacity of aluminium is $875 \text{ J kg}^{-1} \text{ K}^{-1}$)?
- What is the total energy required to heat the pot and water?
- When the water started to boil, the stove weighed 14.5 g less than it had initially. How many moles of butane (C_4H_{10}) were used to heat the pot and water?
- Use these data to calculate the enthalpy of reaction, in kJ mol^{-1} , of butane with air?
- The accepted value for the enthalpy of combustion of butane is 2874 kJ mol^{-1} . Explain why you think the two values are so different.

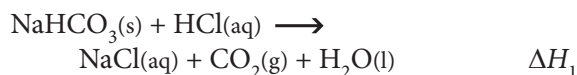
5.3 HESS'S LAW

5.3.1 Determine the enthalpy change of a reaction that is the sum of two or three reactions with known enthalpy changes.

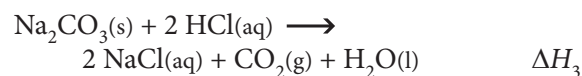
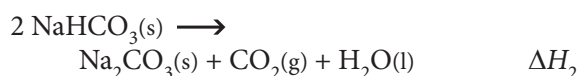
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The principle of **conservation of energy** (which Physicists call the **First Law of Thermodynamics**) states that energy cannot be created or destroyed. In chemistry terms this means that the total change in chemical potential energy (that is, enthalpy change) must be equal to the energy lost or gained by the system. It also means that the total enthalpy change on converting a given set of reactants to a particular set of products is constant, irrespective of the way in which the change is carried out. This is known as **Hess's Law**. This principle holds irrespective of whether a particular reaction could actually be carried out in practice.

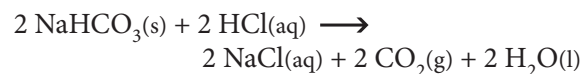
For example sodium hydrogencarbonate can be directly reacted with hydrochloric acid to produce sodium chloride, carbon dioxide and water:



The reaction, to give exactly the same products, could also be carried out by first heating the sodium hydrogencarbonate and then reacting the sodium carbonate produced with the hydrochloric acid:



If these equations are added together, the Na_2CO_3 cancels and the result is equal to twice the overall equation given.



Hess's Law states that the total enthalpy change for the two stage reaction must be equal to the single stage process, i.e.

$$2 \Delta H_1 = \Delta H_2 + \Delta H_3$$

Note the factor of two occurs because the equation for the direct reaction, as usually written involves only one mole of NaHCO_3 being converted to one mole of NaCl , whereas the route via Na_2CO_3 would usually be written for the conversion of two moles.

This may also be shown in the form of an enthalpy cycle.

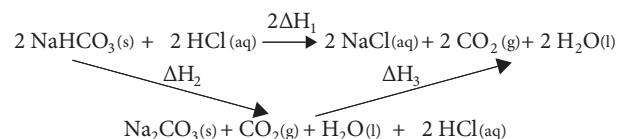


Figure 504 An enthalpy cycle for the direct and indirect reaction of sodium hydrogencarbonate with dilute acid

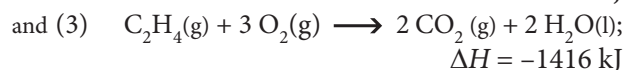
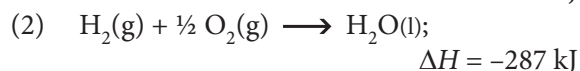
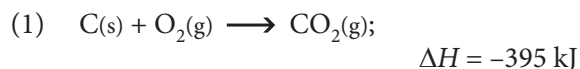
The use of Hess's Law is particularly important in determining the enthalpy change of reactions for which direct measurement is difficult (i.e. not easy in practice) or impossible (i.e. the reaction in question does not occur). In the example considered above, ΔH_2 would be difficult to measure in practice because it involves heating the substance. Both ΔH_1 and ΔH_3 can be easily determined by standard calorimetric methods, and values of -140 kJ mol^{-1} and -370 kJ mol^{-1} can be found respectively. Hence ΔH_2 can be calculated as

$$\begin{aligned} \Delta H_2 &= 2\Delta H_1 - \Delta H_3 &= 2 \times (-140) - (-370) \\ & &= +90 \text{ kJ mol}^{-1} \end{aligned}$$

Another important example is the enthalpy change for the formation of compounds, such as the alkanes, which cannot be formed by the direct combination of the elements. There is an example of this below.

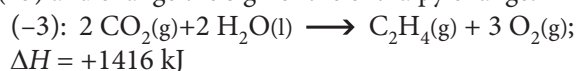
Example

Calculate ΔH_1 for reaction



Solution

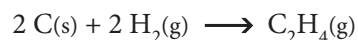
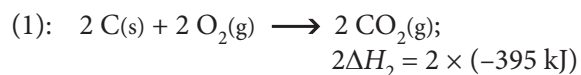
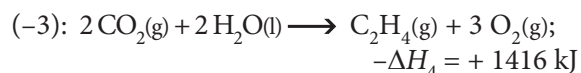
Reverse equation (3) to get C_2H_4 in the product; this gives (-3) and change the sign of the enthalpy change:



(This has to be done since in equation (1) $\text{C}_2\text{H}_4\text{(g)}$ is on the right.)

Because this involves two moles of both water and carbon dioxide it must be added to twice equation (1) and equation

(2), doubling the enthalpy change in each case, to produce the required equation:



Therefore according to Hess's law:

$$\begin{aligned} \Delta H &= 2\Delta H_1 + 2\Delta H_2 - \Delta H_3 \\ &= 2 \times (-395) + 2 \times (-287) + 1416 \text{ kJ} \\ &= +52 \text{ kJ mol}^{-1} \end{aligned}$$

As ΔH is positive this must be, an endothermic process.

The above exercise can be represented as a simple enthalpy cycle as shown in Figure 505

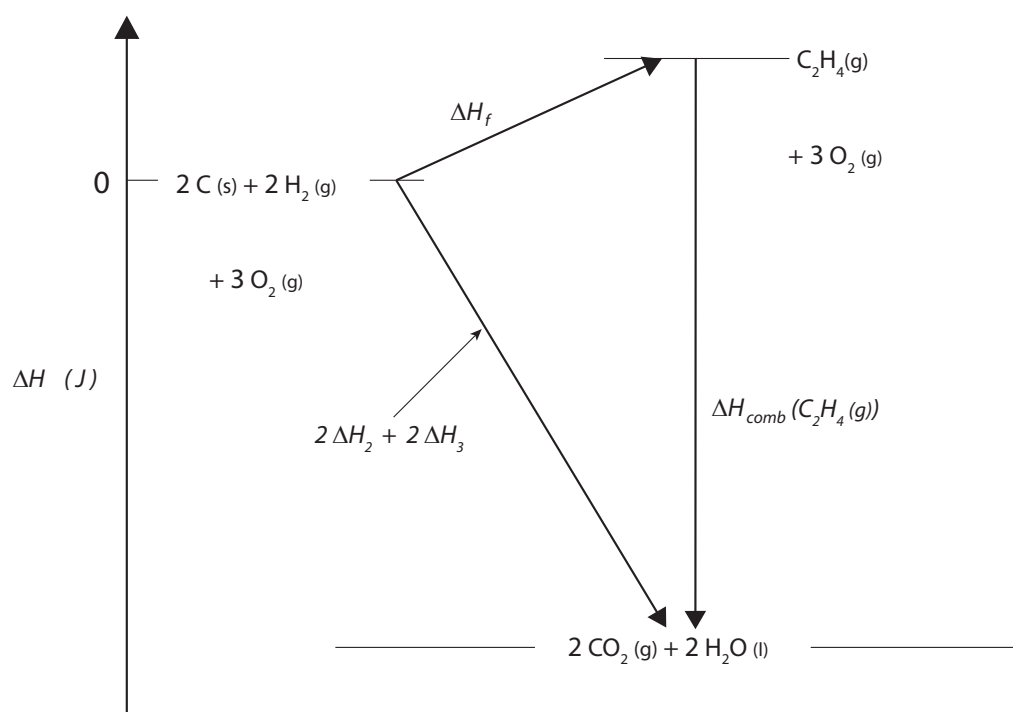
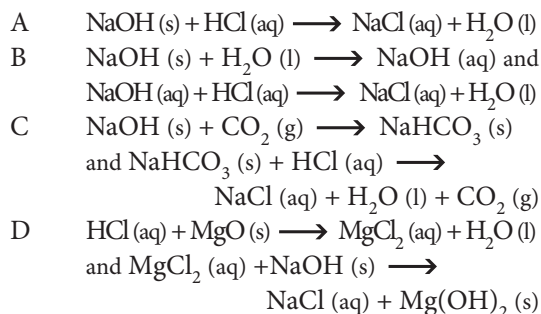


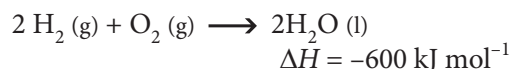
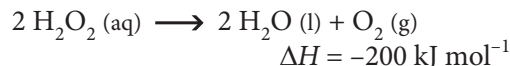
Figure 505 Illustration of the enthalpy example

Exercise 5.3

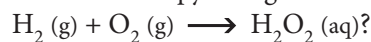
1. Below are four reactions, or series of reactions. Which of these would have an overall enthalpy change different from the others?



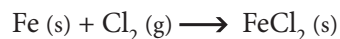
2. Given the enthalpy changes of the reactions below



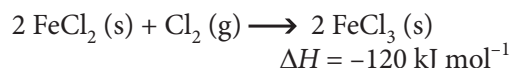
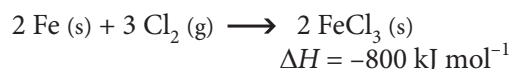
what will be the enthalpy change for



- A -200 kJ mol^{-1}
 B -400 kJ mol^{-1}
 C -600 kJ mol^{-1}
 D -800 kJ mol^{-1}
3. Iron and chlorine react directly to form iron(III) chloride, not iron(II) chloride, so that it is not possible to directly measure the enthalpy change for the reaction



The enthalpy changes for the formation of iron(III) chloride from the reaction of chlorine with iron and with iron(II) chloride are given below. Use these to calculate the enthalpy change for the reaction of iron with chlorine to form iron(II) chloride.



4. The enthalpies of combustion of ethene, ethane and hydrogen are $-1390 \text{ kJ mol}^{-1}$, $-1550 \text{ kJ mol}^{-1}$ and

-286 kJ mol^{-1} respectively. Use these data to calculate the enthalpy of hydrogenation of ethene (i.e. the reaction of ethene with hydrogen to form ethane).

5. The decomposition of calcium carbonate to calcium oxide and carbon dioxide only takes place at very high temperatures, making the direct measurement of the enthalpy change, ΔH for this reaction difficult. Both calcium carbonate and calcium oxide react readily with dilute hydrochloric acid at room temperature.
- Describe an experiment to find out the enthalpy change of these reactions, describing what you would do and stating what measurements you would make.
 - Which of these two experiments is likely to give the more accurate result? Explain why?
 - What further piece of data would you need so that you could use your results to find the enthalpy change for the decomposition of calcium carbonate?
 - Given this further information, describe how you would calculate the enthalpy change for this decomposition.

TOK The Unification of Ideas

As an example of the conservation of energy, this illustrates the unification of ideas from different areas of science.

When ideas from one part of science seem to explain apparently unrelated phenomena elsewhere, then you get the feeling things are really falling in place and you are on to something fairly fundamental. Newton probably experienced this when he found he could use his theory of gravity to explain the motion of the planets. Similarly Mendeleev's periodic table, originally drawn up to show regular patterns of chemical properties seems to fit in beautifully with later evidence about electron structure, which in its turn relates amazingly to quantum mechanics through the Schrödinger wave equation.

Another interesting trick is to say, suppose this wasn't true? Suppose if when I converted reactants A into products B by a different route I found that the energy change wasn't the same as for the direct conversion, what would be the consequences? It is said that Einstein started research into his theory of relativity by saying let's assume that when a light source is moving towards us and when it is moving away from us, the speed of light from the source is just the same.

5.4 BOND ENTHALPIES

5.4.1 Define the term average bond enthalpy.

5.4.2 Explain, in terms of average bond enthalpies, why some reactions are exothermic and others are endothermic.

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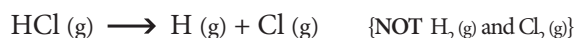
All chemical reactions involve the making and breaking of bonds. **Bond enthalpies** are a measure of the strength of a covalent bond: the stronger the bond, the more tightly the atoms are joined together. The breaking of a chemical bond requires energy and is therefore an endothermic process. Conversely the formation of chemical bonds is an exothermic process. The amount of energy associated with the formation/breaking of a particular covalent bond is to a large extent independent of the bonding in the rest of the molecule, that is, the energy bonding a carbon atom to a hydrogen atom is about 413 kJ mol^{-1} in both methane and ethanol. This means that the average bond enthalpy may be defined as the mean of the enthalpy required to break a particular covalent bond in a range of molecules. Using this concept, approximate enthalpy changes for reactions involving only covalent bonds may be calculated by considering the bonds being broken and the bonds being made in a reaction:

ΔH = the sum of the energy of bonds broken – the sum of the energy of bonds made:

$$\Delta H_{\text{reaction}}^{\circ} = \sum \text{BE}_{\text{bonds broken}} - \sum \text{BE}_{\text{bonds made}}$$

Note that if the bonds being broken are weaker (thus requiring less energy) than those being made (thus producing more energy), the reaction will be exothermic (ΔH is negative) and *vice versa*.

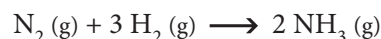
Bond enthalpies are for the conversion of a mole of gaseous molecules (not necessarily the normal state of the compound) into gaseous atoms (not the element in its standard state). The H–Cl bond energy is the enthalpy change for the reaction:



The fact that they refer to gases, coupled with the fact that bond enthalpy values are the average of that bond in a range of compounds and hence are only approximately constant, means that enthalpy changes calculated using bond energies are less precise than those obtained by other methods. Nevertheless, apart from a few exceptional cases such as benzene (which is resonance stabilized), the

values are within about 10% of other more accurate values and hence this is a useful way of calculating approximate enthalpy changes.

Consider the formation of ammonia from nitrogen and hydrogen:



The enthalpies of the bonds involved are:

$$\text{N}\equiv\text{N} \ 945 \text{ kJ mol}^{-1}; \text{H}-\text{H} \ 436 \text{ kJ mol}^{-1}; \text{N}-\text{H} \ 391 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \text{The bonds broken are: } & (\text{N}\equiv\text{N}) + 3 (\text{H}-\text{H}) \\ & = 945 + (3 \times 436) = 2253 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{The bonds made are: } 6 (\text{N}-\text{H}) = 6 \times 391 = 2346 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta H &= (\sum \text{BE}_{\text{bonds broken}} - \sum \text{BE}_{\text{bonds made}}) \\ &= 2253 - 2346 \\ &= -93 \text{ kJ mol}^{-1} \end{aligned}$$

The bond enthalpy concept can be used to explain various observations. For example the enthalpies of combustion of successive alkanes, which form a homologous series increase in a regular manner with the number of carbon atoms as shown in Figure 506 below.

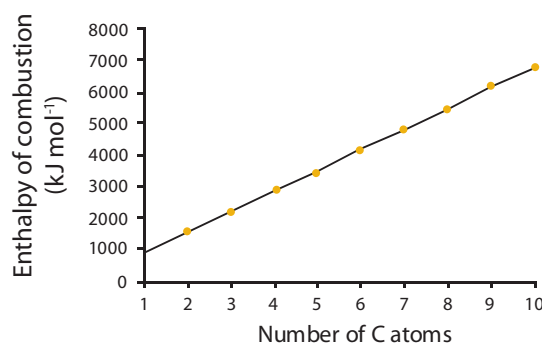


Figure 506 The enthalpies of combustion of the alkanes

This can be explained by the fact that each successive member of the series contains one more methylene group ($-\text{CH}_2-$) than the previous one. When it is burnt there will be one extra C–C bond (347 kJ mol^{-1}) and two extra C–H bonds ($2 \times 413 \text{ kJ mol}^{-1}$) and $1\frac{1}{2}$ extra O=O bonds (for the extra oxygen required; $1\frac{1}{2} \times 499 \text{ kJ mol}^{-1}$) to break. There will however be two more C=O bonds ($2 \times 805 \text{ kJ mol}^{-1}$) and two more O–H bonds ($2 \times 464 \text{ kJ mol}^{-1}$) made from the extra carbon dioxide molecule and water molecule formed respectively. This means, taking into

account that bond breaking is endothermic (positive ΔH) and bond making is exothermic (negative ΔH), that the difference in enthalpy of combustion between successive hydrocarbons will be:

$$[(347) + (2 \times 413) + (1 \times 499)] - [(2 \times 805) - (2 \times 464)] \\ = -616 \text{ kJ mol}^{-1}$$

approximately in keeping with the values in the graph.

Usually covalent bonds formed by smaller atoms are stronger than those of larger atoms (e.g. C—C = 348 kJ mol⁻¹ and Si—Si = 226 kJ mol⁻¹). Bonds to very electronegative elements also tend to be very strong (C—C = 348 kJ mol⁻¹, C—O = 360 kJ mol⁻¹ and C—F = 484 kJ mol⁻¹). Bonds between two very electronegative elements tend to be unusually weak (O—O = 146 kJ mol⁻¹ and F—F = 158 kJ mol⁻¹) and the fission of bonds such as this will often be the initiation step of a chain reaction, such as the halogenation of the alkanes. Indeed if a substance has several different bonds, it is the weakest bond that is likely to break first allowing predictions to be made with regard to the reaction mechanism.

Bond strength increases from single bonds, through double bonds to triple bonds of the same element: N—N, 163 kJ mol⁻¹; N=N, 409 kJ mol⁻¹ and N≡N, 944 kJ mol⁻¹. Similarly the bond enthalpy for carbon carbon bonds increases from C—C, 348 kJ mol⁻¹; C=C, 612 kJ mol⁻¹ and C≡C, 837 kJ mol⁻¹ and as the bonds become stronger they also become shorter. This is because the electron density in the bond increases the attraction of the nuclei for these electrons, pulling the nuclei closer together.

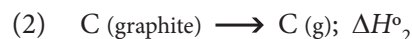
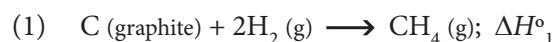
Various uses can therefore be made of bond enthalpy data:

- Comparing the strengths of bonds
- Understanding structure and bonding
- In calculations relating bond enthalpies to enthalpies of reaction
- Making predictions with regard to some reaction mechanisms.

Apart from a few simple molecules, such as hydrogen chloride H—Cl, it is not possible to determine bond enthalpies directly, so they must be determined indirectly. This can be done applying Hess's Law to the fundamental stages involved.

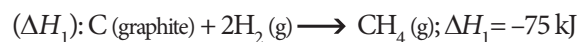
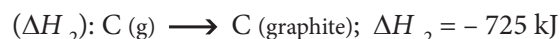
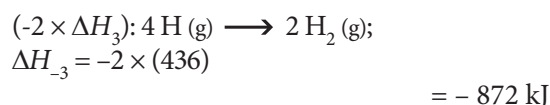
Example

Use the data provided below to obtain the value for the bond enthalpy of the C—H bond.

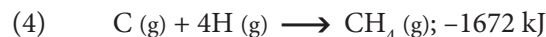


Solution

Doubling equation (3), then reversing it and equation (2) and adding equation (1) gives the equation for the formation of four C—H bonds:



Add equations (-3) + (-2) + (1) gives the equation:



\therefore Forming each C—H bond produces $1672/4 = 418 \text{ kJ}$

See Figure 507 for a graphical illustration of this method.

Note that this is an average value for the four bonds. It does not imply, and it is not true, that this is equal to the enthalpy change for the reaction:



Note also that the standard state of carbon is defined as solid graphite, rather than the less stable allotrope diamond.

This method of determining bond enthalpies can be carried out for a variety of bonds over a large number of compounds and it is by this process that the average bond enthalpies given in data books are deduced.

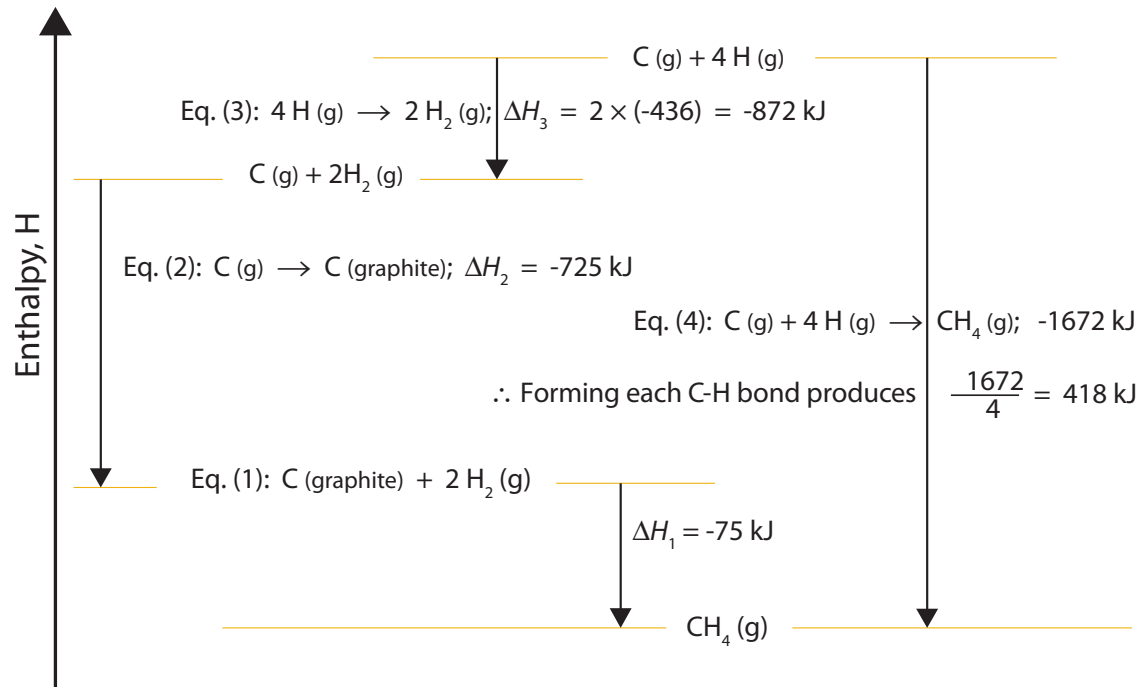


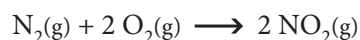
Figure 507 Solution to example illustrated as an enthalpy cycle

Exercise 5.4

1. For which of the following equations is the value of ΔH equivalent to the bond enthalpy for the carbon-oxygen bond in carbon monoxide?

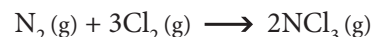
- A $\text{CO(g)} \longrightarrow \text{C(g)} + \text{O(g)}$
 B $\text{CO(g)} \longrightarrow \text{C(s)} + \text{O(g)}$
 C $\text{CO(g)} \longrightarrow \text{C(s)} + \text{O}_2\text{(g)}$
 D $\text{CO(g)} \longrightarrow \text{C(g)} + \text{O}_2\text{(g)}$

2. The bond enthalpy of the bond between nitrogen and oxygen in nitrogen dioxide is 305 kJ mol^{-1} . If those of the bonds in the oxygen molecule and the nitrogen molecule are 496 kJ mol^{-1} and 944 kJ mol^{-1} respectively, what will be the enthalpy change for the reaction?



- A $+716 \text{ kJ mol}^{-1}$
 B $+1135 \text{ kJ mol}^{-1}$
 C $+1326 \text{ kJ mol}^{-1}$
 D $+1631 \text{ kJ mol}^{-1}$

3. Given that the bond enthalpy of the carbon-oxygen bonds in carbon monoxide and carbon dioxide are 1073 kJ mol^{-1} and 743 kJ mol^{-1} respectively, and that of the bond in the oxygen molecule is 496 kJ mol^{-1} , calculate the enthalpy change for the combustion of one mole of carbon monoxide.
4. Given that the enthalpy change for the reaction



is $+688 \text{ kJ mol}^{-1}$, calculate the bond enthalpy of the N-Cl bond, given that the bond enthalpies in the nitrogen molecule and the chlorine molecule are 944 kJ mol^{-1} and 242 kJ mol^{-1} respectively.

5. Use bond enthalpy data to calculate the enthalpy change when cyclopropane reacts with hydrogen to form propane. The actual value found is -159 kJ mol^{-1} . Give reasons why you think this differs from the value you have calculated.

[Bond enthalpies in kJ mol^{-1} : C-C 348; C-H 412; H-H 436]

6. Consider the halogens (Cl_2 , Br_2 , I_2) - the bond enthalpies of the halogens given in the table below. Explain the trend in these. Based on the data in the table below, predict a value for the $\text{F}-\text{F}$ bond. Compare this to the literature value, and explain any discrepancy:

	Cl—Cl	Br—Br	I—I
B.E. / kJ mol^{-1}	243	193	151

HIGHER LEVEL

15.1 STANDARD ENTHALPY CHANGES OF REACTION (AHL)

15.1.1 Define and apply the terms standard state, standard enthalpy change of formation (ΔH_f^\ominus) and standard enthalpy change of combustion (ΔH_c^\ominus).

15.1.2 Determine the enthalpy change of a reaction using standard enthalpy changes of formation and combustion.

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Just as when comparing altitudes it is useful to assign an arbitrary zero point for comparison (for example, mean sea level), so in considering enthalpies it is useful to assign an arbitrary zero. This is taken as the elements in their **standard states** under standard conditions. The enthalpy of formation of any element in its standard state is therefore zero by definition.

The **standard enthalpy change of formation** (ΔH_f^\ominus) is the amount of energy evolved or absorbed in the formation of one mole of the compound, in its standard state, from its constituent elements in their standard states. Standard state refers to the form normally found at a temperature of 25°C (298 K) and a pressure of 101.3 kPa (1 atmosphere pressure). If allotropes exist, then one of these (usually the most stable one) is agreed on as the standard state. For example the standard state of oxygen is $\text{O}_2(\text{g})$, not $\text{O}_3(\text{g})$. The superscript (\ominus) is sometimes placed after a quantity to indicate that its value refers to standard conditions, though this is often omitted.

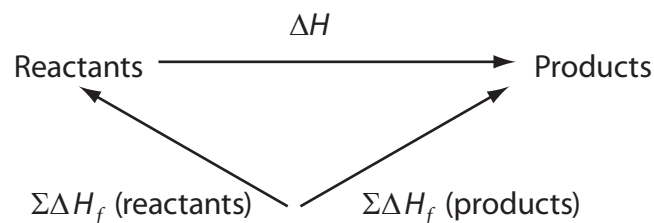
Under standard conditions, sodium chloride is a solid, and the standard states of the elements, from which it is formed are solid sodium metal and gaseous chlorine molecules. The standard enthalpy of formation of sodium chloride (-411 kJ mol^{-1}) is therefore the enthalpy change for the reaction:



The sum of the enthalpies of formation of the reactants will give the total enthalpy change to form the reactants from the component elements in their standard states. Similarly the sum of the enthalpies of formation of the products will give the total enthalpy to form the products. The enthalpy change of the reaction is therefore the difference between these, so that the enthalpy change for any reaction can be calculated using the equation:

$$\Delta H^\ominus = \sum \Delta H_f^\ominus(\text{products}) - \sum \Delta H_f^\ominus(\text{reactants})$$

This same formula also results from a consideration of the appropriate enthalpy cycle:



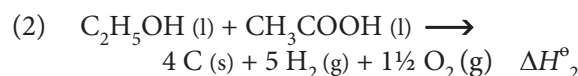
Elements in their standard states

Figure 509 Illustrating the relationship between enthalpy of reaction and standard enthalpies of formation

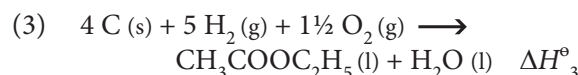
Consider for example the reaction of ethanol and ethanoic acid to form ethyl ethanoate and water:



This could be thought of as the result of two hypothetical reactions, going via the elements:



followed by



ΔH^\ominus_2 is $-\left[\Delta H_f^\ominus(\text{C}_2\text{H}_5\text{OH}(\text{l})) + \Delta H_f^\ominus(\text{CH}_3\text{COOH}(\text{l}))\right]$ as it is the reverse of the formation of the compounds from

the elements, and ΔH°_3 is even more obviously ΔH°_f ($\text{CH}_3\text{COOC}_2\text{H}_5(\text{l}) + \Delta H^\circ_f(\text{H}_2\text{O}(\text{l}))$), as it is the formation of the elements from their compounds. Applying Hess's Law:

$$\begin{aligned}\Delta H^\circ_1 &= \Delta H^\circ_2 + \Delta H^\circ_3 \\ &= -[\Delta H^\circ_f(\text{C}_2\text{H}_5\text{OH}(\text{l})) + \Delta H^\circ_f(\text{CH}_3\text{COOH}(\text{l}))] + \\ &\quad [\Delta H^\circ_f(\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})) + \Delta H^\circ_f(\text{H}_2\text{O}(\text{l}))]\end{aligned}$$

Substituting in appropriate values [$\Delta H^\circ_f(\text{C}_2\text{H}_5\text{OH}(\text{l})) = -1367 \text{ kJ mol}^{-1}$; $\Delta H^\circ_f(\text{CH}_3\text{COOH}(\text{l})) = -874 \text{ kJ mol}^{-1}$; $\Delta H^\circ_f(\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})) = -2238 \text{ kJ mol}^{-1}$; $\Delta H^\circ_f(\text{H}_2\text{O}(\text{l})) = -286 \text{ kJ mol}^{-1}$]:

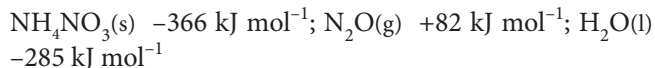
$$\begin{aligned}\Delta H^\circ_1 &= -[(-1367) + (-874)] + [(-2238) + (-286)] \\ &= 2241 - 2524 \\ &= -283 \text{ kJ mol}^{-1}\end{aligned}$$

AHL

It is simpler however just to substitute in the equation relating ΔH° and ΔH°_f values. Consider as a second example the decomposition of ammonium nitrate:



The standard enthalpies of formation of the compounds involved are:

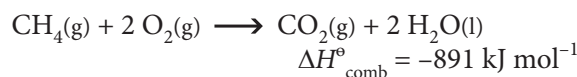


Substituting in the equation:

$$\begin{aligned}\Delta H^\circ_f &= \sum \Delta H^\circ_f(\text{products}) - \sum \Delta H^\circ_f(\text{reactants}) \\ &= [\Delta H^\circ_f(\text{N}_2\text{O}(\text{g})) + 2 \times \Delta H^\circ_f(\text{H}_2\text{O}(\text{l}))] \\ &\quad - [\Delta H^\circ_f(\text{NH}_4\text{NO}_3(\text{s}))] \\ &= [(+82) + 2 \times (-285)] - [(-366)] \\ &= (-488) - (-366) \\ &= -122 \text{ kJ mol}^{-1}\end{aligned}$$

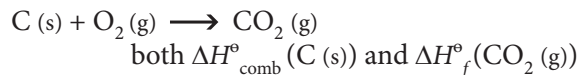
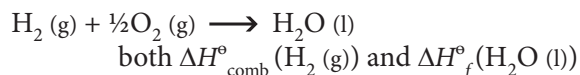
Notice the care taken not to make mistakes with signs.

The **standard enthalpy change of combustion** ($\Delta H^\circ_{\text{comb}}$) is the enthalpy change when one mole of the compound undergoes complete combustion in excess oxygen under standard conditions. For example the standard enthalpy change of combustion for methane is ΔH for the reaction:



The standard enthalpy change of combustion is always exothermic. Note that the enthalpies of formation of many oxides (e.g. H_2O and CO_2) are equivalent to the enthalpies

of combustion of the element, because both refer to the same thermochemical equation, e.g.:



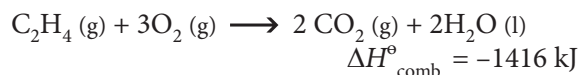
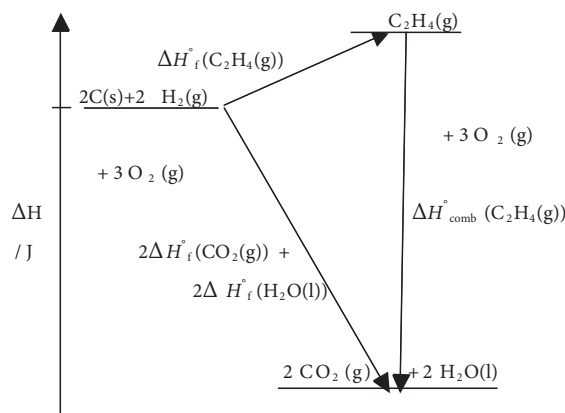
Many covalent compounds will undergo combustion and hence it is often easy to determine the standard enthalpy change of combustion for molecules. An enthalpy cycle, similar to that for enthalpy of formation can be constructed using enthalpies of combustion, as shown in the example below, and this can be used to calculate a value for the enthalpy of formation:

Example

Calculate $\Delta H^\circ_f(\text{C}_2\text{H}_4(\text{g}))$, given: $\Delta H^\circ_f(\text{CO}_2(\text{g})) = -395 \text{ kJ mol}^{-1}$, $\Delta H^\circ_f(\text{H}_2\text{O}(\text{l})) = -287 \text{ kJ mol}^{-1}$ and $\Delta H^\circ_{\text{comb}}(\text{C}_2\text{H}_4(\text{g})) = -1416 \text{ kJ mol}^{-1}$.

Solution

The enthalpy diagram for this example is illustrated below



$$\Delta H^\circ = \sum \Delta H^\circ_f(\text{products}) - \sum \Delta H^\circ_f(\text{reactants})$$

$$\begin{aligned}\therefore \Delta H^\circ_{\text{comb}}(\text{C}_2\text{H}_4(\text{g})) &= [2\Delta H^\circ_f(\text{CO}_2(\text{g})) + 2\Delta H^\circ_f(\text{H}_2\text{O}(\text{l}))] \\ &\quad - [\Delta H^\circ_f(\text{C}_2\text{H}_4(\text{g})) + 3\Delta H^\circ_f(\text{O}_2(\text{g}))]\end{aligned}$$

Since ΔH of $(\text{O}_2(\text{g})) = 0$, this may be rearranged to give:

$$\Delta H_f^\circ(\text{C}_2\text{H}_4(\text{g})) = 2\Delta H_f^\circ(\text{CO}_2(\text{g})) + 2\Delta H_f^\circ(\text{H}_2\text{O}(\text{l})) - \Delta H_{\text{comb}}^\circ(\text{C}_2\text{H}_4(\text{g}))$$

Substituting:

$$\Delta H_f^\circ(\text{C}_2\text{H}_4(\text{g})) = 2(-395) + 2(-287) - (-1416) = +52 \text{ kJ mol}^{-1}$$

Note that standard enthalpy of combustion data can be used to calculate values for the enthalpy of reaction directly using the enthalpy cycle below:

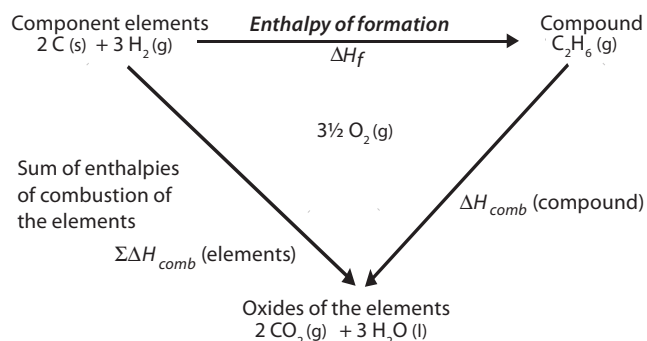


Figure 511 Finding enthalpies of reaction from enthalpies of combustion

This can be summarised by the equation:

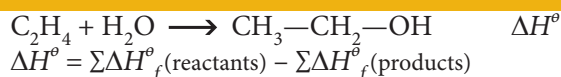
$$\Delta H^\circ = \sum \Delta H_{\text{comb}}^\circ(\text{reactants}) - \sum \Delta H_{\text{comb}}^\circ(\text{products})$$

Note that the position of products and reactants in this is the opposite of that for the equation using the enthalpy of formation because the enthalpy change being used is in the opposite direction (combustion is from the compound whereas formation is to the compound).

Example

Calculate the enthalpy change for the hydration of ethene, given that the enthalpy of combustion of ethene and ethanol are $-1409 \text{ kJ mol}^{-1}$ and $-1371 \text{ kJ mol}^{-1}$ respectively.

Solution



$$\Delta H^\circ = -1409 - (-1371) = -38 \text{ kJ mol}^{-1}$$

(n.b. ΔH_c for water is zero)

Again notice the care taken to avoid making mistakes with signs.

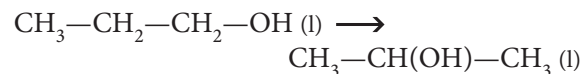
Similarly enthalpies of combustion can be used to find the enthalpy change of other reactions, in which the reactants and products can all be readily converted to the oxides, even if the changes cannot occur in practice.

Example

Calculate the relative stabilities of propan-1-ol and propan-2-ol from their enthalpies of combustion.

Solution

Consider the reaction:

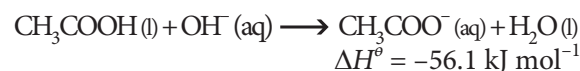


$$\Delta H^\circ = \Delta H_{\text{comb}}^\circ(\text{propan-1-ol}) - \Delta H_{\text{comb}}^\circ(\text{propan-2-ol})$$

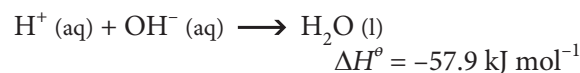
$$\Delta H^\circ = -2021 - (-2006) = -15 \text{ kJ mol}^{-1}$$

Hence, as the conversion of propan-1-ol to propan-2-ol is exothermic, propan-2-ol is the more energetically stable of the two isomers.

One other notable enthalpy change is the standard enthalpy change of neutralisation, $\Delta H_{\text{neut}}^\circ$, the enthalpy change when one mole of the acid (base) undergoes complete neutralisation with a strong base (acid) under standard conditions. For example the standard enthalpy change of neutralisation for ethanoic acid is ΔH° for the reaction:



Again, this also is always exothermic. Note also that the enthalpy of neutralisation of any strong acid by any strong base is always the same because it is equal to the enthalpy change for the reaction:



In the case of ethanoic acid the enthalpy of neutralisation is less exothermic as it is a weak acid and the dissociation of the acid is an endothermic process.

Exercise 15.1

1. Which one of the following is not a 'standard state' condition?

A A temperature of 298 K
 B A pressure of 101.3 kPa
 C All substances in the gaseous state
 D Elements present as the standard allotrope

2. The standard enthalpy change of formation for hydrogen chloride is the enthalpy change for

A $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{HCl}(\text{g})$
 B $\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) \longrightarrow \text{HCl}(\text{g})$
 C $\text{H}(\text{g}) + \text{Cl}(\text{g}) \longrightarrow \text{HCl}(\text{g})$
 D $\text{H}^+(\text{g}) + \text{Cl}^-(\text{g}) \longrightarrow \text{HCl}(\text{g})$

3. Given the standard enthalpy of formation data:

$\text{NaHCO}_3(\text{s})$: -948; $\text{Na}_2\text{CO}_3(\text{s})$: -1131;
 $\text{CO}_2(\text{g})$: -395; $\text{H}_2\text{O}(\text{l})$: -286; all in kJ mol^{-1}

what is the enthalpy change for the reaction

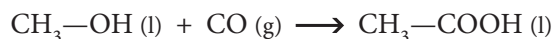


A +84 kJ mol^{-1}
 B +864 kJ mol^{-1}
 C -864 kJ mol^{-1}
 D -84 kJ mol^{-1}

4. Which one of the following is the reaction for which the enthalpy change is equal to the enthalpy change of combustion for ethyne?

A $\text{C}_2\text{H}_2(\text{g}) + 2\frac{1}{2}\text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
 B $\text{C}_2\text{H}_2(\text{g}) + 1\frac{1}{2}\text{O}_2(\text{g}) \longrightarrow 2\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{l})$
 C $2\text{C}_2\text{H}_2(\text{g}) + 5\text{O}_2(\text{g}) \longrightarrow 4\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
 D $\text{C}_2\text{H}_2(\text{g}) + 2\frac{1}{2}\text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$

5. What value would you expect for the enthalpy change of the reaction



Given that $\Delta H_{\text{comb}}^\circ(\text{CH}_3\text{—OH}) = -715 \text{ kJ mol}^{-1}$,
 $\Delta H_{\text{comb}}^\circ(\text{CO}) = -283 \text{ kJ mol}^{-1}$ and
 $\Delta H_{\text{comb}}^\circ(\text{CH}_3\text{—COOH}) = -876 \text{ kJ mol}^{-1}$?

A +161 kJ mol^{-1}
 B +122 kJ mol^{-1}
 C -122 kJ mol^{-1}
 D -405 kJ mol^{-1}

6. Which one of the following enthalpy terms is not required to calculate the enthalpy of the nitrogen-fluorine bond in nitrogen trifluoride?

A The electron affinity of fluorine.
 B The fluorine-fluorine bond enthalpy.
 C The enthalpy of atomisation of nitrogen.
 D The enthalpy of formation of nitrogen trifluoride.

7. Given the enthalpies of atomisation of phosphorus and hydrogen (+354 kJ mol^{-1} and +218 kJ mol^{-1} respectively) and the phosphorus-hydrogen bond enthalpy (321 kJ mol^{-1}), calculate the approximate enthalpy of formation of a hypothetical compound PH_5 .

8. Write balanced equations for the following reactions and use standard enthalpy of formation data to calculate the standard enthalpy change associated with each:

a) Zinc and chlorine reacting to form zinc chloride.
 b) Hydrogen sulfide and sulfur dioxide reacting to form sulfur and water.
 c) Lead(II) nitrate decomposing to lead(II) oxide, nitrogen dioxide and oxygen.

[Standard enthalpy of formation data, in kJ mol^{-1} :
 $\text{ZnCl}_2(\text{s})$ -416; $\text{H}_2\text{S}(\text{g})$ -21; $\text{SO}_2(\text{g})$ -297;
 $\text{H}_2\text{O}(\text{l})$ -286; $\text{Pb}(\text{NO}_3)_2(\text{s})$ -449; $\text{PbO}(\text{s})$ -218;
 $\text{NO}_2(\text{g})$ +34.]

9. Depending on whether you consider the chlorine to be converted to the element or to hydrogen chloride, it is possible to write two different equations for the combustion of dichloromethane (CH_2Cl_2). Use enthalpy of formation data to calculate the enthalpy changes of these two reactions. If the experimental value is -578 kJ mol^{-1} , what conclusions can you draw?

[Standard enthalpy of formation data, in kJ mol^{-1} :
 $\text{CH}_2\text{Cl}_2(\text{l}) -121$; $\text{HCl}(\text{g}) -92$;

$\text{CO}_2(\text{g}) -395$; $\text{H}_2\text{O}(\text{l}) -286$]

10. In the Apollo project, the engines of the lunar module mixed methylhydrazine ($\text{CH}_3\text{—NH—NH}_2$) and dinitrogen tetroxide (N_2O_4), which ignite spontaneously, as fuel for the rocket.

- Write the most probable equation for the reaction. (It forms common simple molecules).
- Use enthalpy of formation data to calculate the enthalpy change for this reaction.
- What factors, apart from the reaction being highly exothermic, would have made this combination of fuels suitable for this application?

[Standard enthalpy of formation data, in kJ mol^{-1} :
 $\text{CH}_3\text{NHNH}_2(\text{l}) +13.0$; $\text{N}_2\text{O}_4(\text{g}) +9$;
 $\text{H}_2\text{O}(\text{g}) -244$; $\text{CO}_2(\text{g}) -395$]

11. a) How could you attempt to measure the enthalpy change for the hypothetical isomerisation of butan-1-ol ($\text{C}_4\text{H}_9\text{OH}$) to ethoxyethane ($\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$) experimentally?
- Use bond energy data to calculate a value for this enthalpy change.
 - Use enthalpy of formation data to calculate a value for this enthalpy change.
 - Which would you expect to give the best agreement with your experimental value? Why?

[Standard enthalpy of formation data, in kJ mol^{-1} :
 $\text{H}_2\text{O}(\text{l}) -286$; $\text{CO}_2(\text{g}) -395$; $\text{C}_4\text{H}_9\text{OH}(\text{l}) -327$;
 $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5(\text{l}) -280$.

Bond energies in kJ mol^{-1} : C—C 346; C—H 413;
 H—H 436; C—O 360; O—H 464]

12. The enthalpy of combustion data for cyclohexene, cyclohexane and benzene in the gaseous state, in kJ mol^{-1} , are -3752 , -3924 and -3273 .

- Write balanced equations for the gas phase hydrogenation of cyclohexene to cyclohexane and for benzene to cyclohexane.

- Use the data given, along with the enthalpy of formation of water (-286 kJ mol^{-1}) to calculate the enthalpy change for these two reactions.
- Explain the relationship that might have been expected between these two values.
- Explain why this relationship is not in fact found.

15.2 BORN-HABER CYCLE (AHL)

15.2.1 Define and apply the terms lattice enthalpy and electron affinity.

15.2.2 Explain how the relative sizes and the charges of ions affect the lattice enthalpies of different ionic compounds.

15.2.3 Construct a Born–Haber cycle for group 1 and 2 oxides and chlorides and use it to calculate an enthalpy change.

15.2.4 Discuss the difference between theoretical and experimental lattice enthalpy values of ionic compounds in terms of their covalent character.

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AHL

The formation of an ionic compound can be considered as the sum of a number of individual processes converting the elements from their standard states into gaseous atoms, losing and gaining electrons to form the cations and anions respectively and finally these gaseous ions coming together to form the solid compound. The diagrammatic representation of this, shown in Figure 512, is known as the **Born–Haber cycle**.

The **standard enthalpy change of atomisation** is the enthalpy change required to produce one mole of gaseous atoms of an element from the element in the standard state. For example for sodium it is the enthalpy change for:



Note that for diatomic gaseous elements, such as chlorine, it is numerically equal to half the bond enthalpy, because breaking the bond between the atoms of one molecule produces two atoms. Considering chlorine as the example:

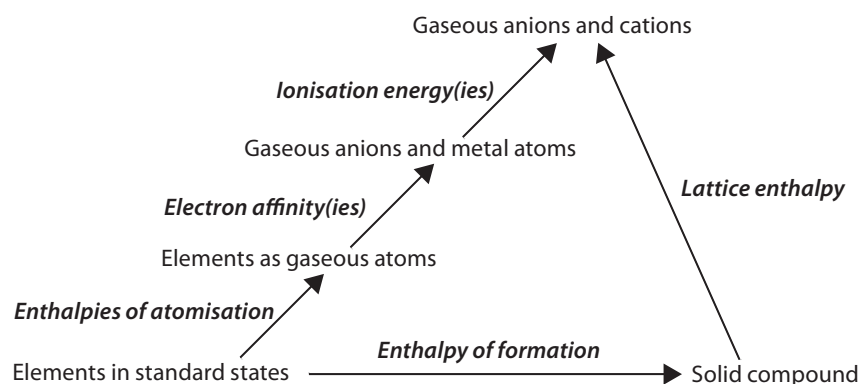
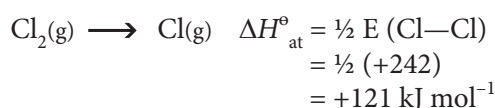
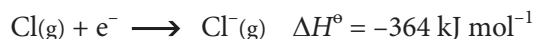


Figure 512 The Born-Haber cycle



The **electron affinity** is the enthalpy change when one mole of gaseous atoms or anions gains electrons to form a mole of negatively charged gaseous ions. For example the electron affinity of chlorine is the enthalpy change for



For most atoms this change is exothermic, but gaining a second electron (e.g. $\text{O}^{-}(\text{g}) + \text{e}^{-} \longrightarrow \text{O}^{2-}(\text{g})$) is endothermic, due to the repulsion between the electron and the negative ion.

The ionisation energy, the enthalpy change for one mole of a gaseous element or cation to lose electrons to form a mole of positively charged gaseous ions, has been met before.

Notice the **lattice enthalpy** is the energy required to convert one mole of the solid compound into gaseous ions. Using sodium chloride as the example it is the enthalpy change for:

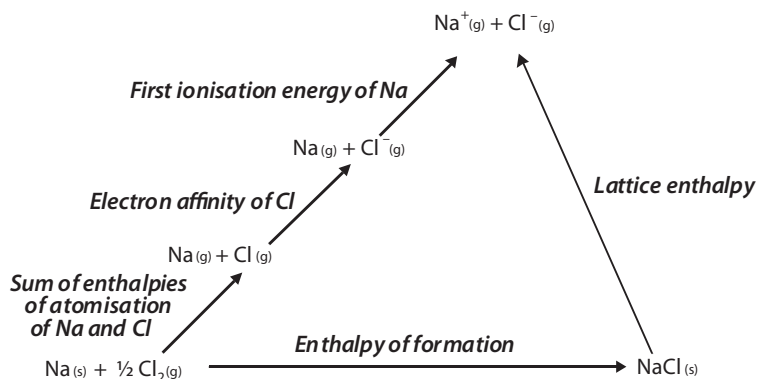


Figure 513 The theoretical steps in the formation of sodium chloride from its elements in their standard states

The lattice enthalpy is therefore very highly endothermic.

The direct determination of lattice enthalpies is not possible since gaseous ions are involved, but values are obtained indirectly using the Born-Haber cycle, a special case of Hess's law for the formation of ionic compounds. The Born-Haber cycle for the formation of sodium chloride is illustrated in Figure 513.

In the Born-Haber cycle, if the magnitude of every term except one is known, then the remaining value may be calculated. The lattice enthalpy of sodium chloride can therefore be calculated knowing the other terms in the cycle:

Enthalpy of formation of NaCl	= -411 kJ mol ⁻¹
Enthalpy of atomisation of Na	= +103 kJ mol ⁻¹
Enthalpy of atomisation of Cl	= +121 kJ mol ⁻¹
Electron affinity of Cl	= -364 kJ mol ⁻¹
Ionisation energy of Na	= +500 kJ mol ⁻¹

$$\begin{aligned} &\text{Enthalpies of atomisation} + \text{Electron affinity} + \\ &\text{Ionisation energy} \\ &= \text{Enthalpy of formation} + \text{Lattice enthalpy} \end{aligned}$$

$$(+103) + (+121) + (-364) + (+500) = (-411) + \text{L.E.}$$

$$\begin{aligned} \therefore \text{L.E.} &= 411 + 103 + 121 - 364 + 500 \\ &= +771 \text{ kJ mol}^{-1} \end{aligned}$$

The magnitude of the lattice enthalpy depends upon the nature of the ions involved:

- The greater the charge on the ions, the greater the electrostatic attraction and hence the greater the lattice enthalpy, and *vice versa*.
- The larger the ions, then the greater the separation of the charges and the lower the lattice enthalpy, and *vice versa*.

These trends are illustrated in Figure 514, which compares the lattice enthalpies of sodium chloride, magnesium oxide and potassium bromide, all of which crystallise with a similar lattice:

Compound	Lattice enthalpy (kJ mol ⁻¹)	Change from NaCl
MgO	3889	Increased ionic charge
NaCl	771	—
KBr	670	Larger ions

Figure 514 Comparison of the lattice enthalpies of some compounds

As illustrated above, the Born–Haber cycle provides a way in which lattice enthalpies can be indirectly measured through experimental techniques (an empirical value). It is also possible to calculate theoretical lattice enthalpies for ionic compounds. This is done by assuming the ionic model, then summing the electrostatic attractive and repulsive forces between the ions in the crystal lattice. As can be seen from Figure 515, this gives excellent agreement for many compounds, implying that the ionic model provides an appropriate description of the bonding in these compounds. For others however, such as the silver halides, the agreement is less good. This is interpreted as evidence for a significant degree of covalent character in the bonding of such compounds (difference in electronegativities < ~1.7). The presence of covalent character in a bond always leads to an increase in the lattice enthalpy. In the case of silver halides this increased lattice enthalpy helps to explain their insolubility and the fact that silver fluoride (the most ionic; difference in electronegativities = 2.1) is in fact soluble.

Compound	Empirical value (kJ mol ⁻¹) [Born-Haber]	Theoretical value (kJ mol ⁻¹) [Electrostatic summing]
Sodium chloride	766	766
Potassium bromide	672	667
Potassium iodide	632	631
Silver iodide	865	736

Figure 515 Experimental and theoretical lattice enthalpies for some compounds

Another enthalpy cycle that involves the lattice enthalpy is that for the formation of an aqueous solution from a solid ionic compound. The **enthalpy change of solution** (ΔH_{sol} ; i.e. the enthalpy change when one mole of the substance is dissolved in water to form a dilute aqueous solution) is equal to the lattice enthalpy of the compound plus the sum of the hydration enthalpies of the component ions. The **enthalpy change of hydration** (ΔH_{hyd}) for an ion is the enthalpy change (always exothermic) when one mole of the gaseous ion is added to excess water to form a dilute solution - the term solvation is used in place of hydration for solvents other than water. This is illustrated below using calcium chloride as an example:

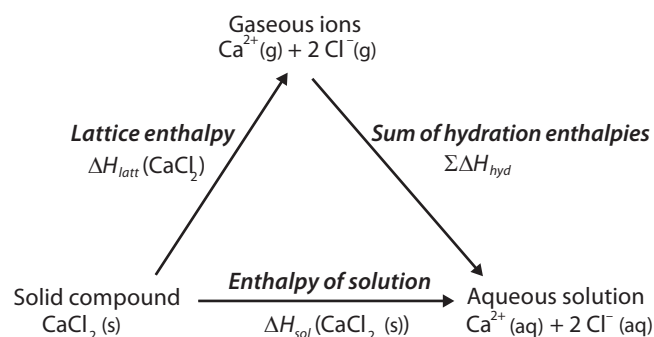


Figure 516 The enthalpy of hydration for calcium chloride

Again, if all the terms are known except one, then this one may be calculated. For example the above cycle will be used to calculate the enthalpy of solution using the lattice enthalpy for calcium chloride (+2258 kJ mol⁻¹) and the hydration enthalpies of the ions ($\Delta H_{\text{hyd}}(\text{Ca}^{2+}) = -1650 \text{ kJ mol}^{-1}$ and $\Delta H_{\text{hyd}}(\text{Cl}^-) = -364 \text{ kJ mol}^{-1}$).

Enthalpy of solution = Lattice enthalpy + Sum of hydration enthalpies

$$\Delta H_{\text{sol}}(\text{CaCl}_2) = \Delta H_{\text{lat}}(\text{CaCl}_2) + \Delta H_{\text{hyd}}(\text{Ca}^{2+}) + 2 \Delta H_{\text{hyd}}(\text{Cl}^-)$$

$$\begin{aligned} \Delta H_{\text{sol}}(\text{CaCl}_2) &= +2258 + (-1650) + 2(-364) \\ &= -120 \text{ kJ mol}^{-1} \end{aligned}$$

Note that the enthalpy of solution, being the sum of two very large terms, one of which is always endothermic the other always exothermic, is usually quite small and may be either positive (endothermic) or negative (exothermic). If it is large and positive, then the compound in question will almost certainly be insoluble. Because the entropy change for the formation of a solution is always positive, this is the explanation for the lack of solubility of many inorganic compounds.

Exercise 15.2

1. The lattice enthalpy is dependent on two main factors, the size of the ions and the charge on the ions. Which combination of these would lead to the greatest lattice enthalpy?

	Size of ions	Charge on ions
A	Large	Large
B	Large	Small
C	Small	Large
D	Small	Small

2. Which one of the following quantities is not directly involved in the Born–Haber cycle?
- A Ionisation energy
B Lattice enthalpy
C Electronegativity
D Enthalpy of formation
3. Which one of the following ionic solids would you expect to have the greatest lattice enthalpy?
- A RbCl
B CaS
C BaI₂
D LiF

4. Calculate the lattice enthalpy of sodium chloride given the following data:

$$\Delta H_{\text{sol}}(\text{NaCl}) = -4 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{hyd}}(\text{Na}^+) = -406 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{hyd}}(\text{Cl}^-) = -364 \text{ kJ mol}^{-1}$$

- A +774 kJ mol⁻¹
B +766 kJ mol⁻¹
C +46 kJ mol⁻¹
D +38 kJ mol⁻¹
5. Which one of the following enthalpy terms will always have a different sign to the others?
- A Ionisation enthalpy
B Enthalpy of hydration
C Lattice enthalpy
D Enthalpy of atomisation
6. Use the data below, relating to the formation of barium chloride, to calculate a value of the electron affinity of the chlorine atom.

$$\begin{aligned} \text{Enthalpy of atomisation of barium} \\ +175 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Enthalpy of atomisation of chlorine} \\ +121 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{First ionisation energy of barium} \\ +502 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Second ionisation energy of barium} \\ +966 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Lattice enthalpy of barium chloride} \\ +2018 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Enthalpy of formation of barium chloride} \\ -860 \text{ kJ mol}^{-1} \end{aligned}$$

7. It would be theoretically possible for calcium to form a fluoride CaF containing Ca⁺ ions and the F⁻ ions in equal numbers. Assuming that the lattice enthalpy of the hypothetical compound is similar to that of NaF (+891 kJ mol⁻¹), use a Born–Haber cycle to calculate its enthalpy of formation using the data below.

Enthalpy of atomisation of calcium
+193 kJ mol⁻¹

F—F bond enthalpy
+158 kJ mol⁻¹

First ionisation energy of calcium
+590 kJ mol⁻¹

Electron affinity of fluorine
-348 kJ mol⁻¹

The enthalpy of formation of CaF₂ is -1214 kJ mol⁻¹. Use this to explain why it is not possible to produce CaF even if two moles of calcium are reacted with one mole of fluorine gas.

8. a) Use the data below to calculate an empirical value for the lattice enthalpy of silver bromide:

Enthalpy of atomisation of silver
+285 kJ mol⁻¹

Enthalpy of atomisation of bromine
+112 kJ mol⁻¹

First ionisation energy of silver
+732 kJ mol⁻¹

Electron affinity of bromine
-342 kJ mol⁻¹

Enthalpy of formation of silver bromide
-100 kJ mol⁻¹

- b) If the electrostatic interactions in the lattice are summed to give a theoretical ionisation energy, a value of +758 kJ mol⁻¹ is found for the lattice enthalpy of silver bromide. Compare this to the value obtained in the first part of the question and comment on its significance
9. The theoretical and experimentally determined lattice enthalpies for silver chloride are +833 kJ mol⁻¹ and +905 kJ mol⁻¹ respectively. Combine these, with the enthalpy of hydration of the component ions ($\Delta H_{hyd}(Ag^+) = -464$ kJ mol⁻¹ and $\Delta H_{hyd}(Cl^-) = -364$ kJ mol⁻¹) to calculate two values for the enthalpy of solution of the compound. Use these to explain the fact that silver chloride is insoluble in water, yet sodium chloride is readily soluble, given that the entropy change for the formation of a solution is similar for both solid salts.

15.3 ENTROPY (AHL)

15.3.1 State and explain the factors that increase the entropy in a system.

15.3.2 Predict whether the entropy change (ΔS) for a given reaction or process is positive or negative.

15.3.3 Calculate the standard entropy change for a reaction (ΔS^\ominus) using standard entropy values (S^\ominus).

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Some states are inherently more probable than others, in the same way that the probability of rolling '7' on a pair of dice (1+6, 2+5, 3+4, 4+3, 5+2, 6+1) is much greater than that of rolling '12' (6+6 only). The probability of a state existing is known as its entropy and it is given the symbol *S*. In general terms the less order there is in a state, the greater the probability of the state and the greater its entropy. The **entropy** of a system is therefore a measure of the degree of disorder or randomness in a system. Thus, other factors being equal, there is an increase in entropy on changing state from solid to liquid to gas, as illustrated by the values for the states of water below:

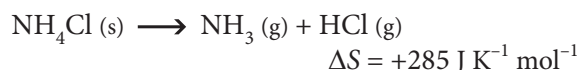
	solid	⇌ liquid	⇌ gas
	(ice)	(water)	(steam)
Entropy	48.0	69.9	188.7 J K ⁻¹ mol ⁻¹

Figure 518 Entropies of water

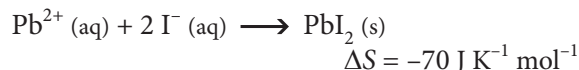
A solid, with a regular arrangement of particles, has a low entropy. When it melts, the particles can move more easily. The system has become more disordered and its entropy increases. Gas molecules move fast and independently of one another since inter-particle forces are negligible and gases have high entropy. Entropy decreases as gas pressure increases, because higher pressure reduces the volume for gas particles to move in, resulting in less disorder. When a solid or a liquid dissolves in a solvent, the entropy of the substance generally increases, however when a gas dissolves in a solvent its entropy decreases. Complex molecules, with more atoms to vibrate and move about, have higher entropies than simple ones. Hard solids with well ordered crystals, such as diamond, have lower entropy than soft, less-ordered ones such as potassium or lead.

The entropy of a perfectly ordered crystal at absolute zero is zero (that is there no randomness in the crystal or from the movement of the particles) hence, unlike enthalpy (H), absolute values of the entropy of a substance in a particular state can be measured relative to this. Real substances always have a greater randomness than this theoretical stationary perfect crystal, hence standard molar entropies of substances are always positive. The units of entropy are $\text{J K}^{-1} \text{mol}^{-1}$.

As a result, in any conversion, as well as the enthalpy change (ΔH), there is also an entropy change (ΔS). This entropy change is likely to be positive if there is a decrease in order through a decrease in the number of moles of solid, or an increase in the number of moles of gas, for example:



Conversely if the number of moles of gas decreases, or the number of moles of solid increases, there is an increase in order and the change in entropy is likely to be negative:



An increase in temperature and an increase in the number of particles (for example by a dissociation reaction), especially if some of these are of a different type, also increase entropy. The latter is, for example, the reason why, even if a reaction is slightly endothermic, a small amount of product will exist at equilibrium. This is dealt with more fully in the next section. The mixing of different types of particles (such as formation of a solution), also increases entropy, but the change in the number of particles in the gaseous state usually has a greater influence on the entropy change than any other factor.

The exact value of the entropy change can be calculated from absolute entropies using the formula:

$$\Delta S = \sum S (\text{Products}) - \sum S (\text{Reactants})$$

Consider the complete combustion of methane:



$$S(\text{CH}_4 \text{ (g)}) = 186, S(\text{O}_2 \text{ (g)}) = 205, \\ S(\text{CO}_2 \text{ (g)}) = 214, S(\text{H}_2\text{O (l)}) = 70 \text{ (all in } \text{J K}^{-1} \text{ mol}^{-1}\text{)}$$

$$\Delta S = [(2 \times 70) + (214)] - [(2 \times 205) + (186)] \\ = -242 \text{ J K}^{-1} \text{ mol}^{-1}$$

As expected, because of the decrease in the number of moles of gas (3 to 1), there is an increase in the order of

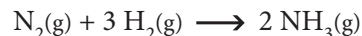
the system so the entropy change is negative. Note that, in contrast to standard enthalpies of formation, the entropy of elements, such as oxygen, is not zero.

Exercise 15.3

1. Which one of the following does not generally lead to an increase in the entropy of a system?

- A An increase in the total number of moles of particles.
 B The formation of a solution.
 C The formation of gaseous products.
 D The formation of solid products.

2. What is the entropy change associated with the Haber process?



[Standard entropies in $\text{J K}^{-1} \text{mol}^{-1}$: $\text{N}_2 \text{ (g)}$, 191; $\text{H}_2 \text{ (g)}$, 131; $\text{NH}_3 \text{ (g)}$, 193]

- A $-129 \text{ J K}^{-1} \text{mol}^{-1}$
 B $-198 \text{ J K}^{-1} \text{mol}^{-1}$
 C $+129 \text{ J K}^{-1} \text{mol}^{-1}$
 D $+198 \text{ J K}^{-1} \text{mol}^{-1}$

3. For each of the following state what kind of entropy change you would expect and briefly give your reasons.

- a) $\text{Br}_2 \text{ (l)} \longrightarrow \text{Br}_2 \text{ (g)}$
 b) $\text{Ag}^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)} \longrightarrow \text{AgCl (s)}$
 c) $2 \text{ NO}_2 \text{ (g)} \longrightarrow \text{N}_2\text{O}_4 \text{ (g)}$
 d) $2 \text{ OH}^- \text{ (aq)} + \text{CO}_2 \text{ (g)} \longrightarrow \text{H}_2\text{O (l)} + \text{CO}_3^{2-} \text{ (aq)}$
 e) $\text{H}_2 \text{ (g)} + \text{Cl}_2 \text{ (g)} \longrightarrow 2 \text{ HCl (g)}$

4. Calculate the enthalpy change for each of the following reactions and comment on how you could have predicted its sign without any need to perform the calculation.

- a) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O (s)} \longrightarrow \text{CuSO}_4 \text{ (s)} + 5 \text{ H}_2\text{O (l)}$
 [ΔS values, in $\text{J K}^{-1} \text{mol}^{-1}$: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O (s)}$, 300; $\text{CuSO}_4 \text{ (s)}$, 109; $\text{H}_2\text{O (l)}$, 70]

- b) $\text{FeCl}_2 \text{ (s)} + \text{Cl}_2 \text{ (g)} \longrightarrow \text{FeCl}_3 \text{ (s)}$
 [ΔS values, in $\text{J K}^{-1} \text{mol}^{-1}$: $\text{FeCl}_2 \text{ (s)}$, 118; $\text{FeCl}_3 \text{ (s)}$, 142; $\text{Cl}_2 \text{ (g)}$, 83]

- c) $\text{Ba}^{2+} \text{ (aq)} + \text{SO}_4^{2-} \text{ (aq)} \longrightarrow \text{BaSO}_4 \text{ (s)}$
 [ΔS values, in $\text{J K}^{-1} \text{mol}^{-1}$: $\text{Ba}^{2+} \text{ (aq)}$, 80.0; $\text{SO}_4^{2-} \text{ (aq)}$, 90.0; $\text{BaSO}_4 \text{ (s)}$, 132]

15.4 SPONTANEITY (AHL)

15.4.1 Predict whether a reaction or process will be spontaneous by using the sign of ΔG° .

15.4.2 Calculate ΔG° for a reaction using the equation

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

and by using values of the standard free energy change of formation ΔG_f° .

15.4.3 Predict the effect of a change in temperature on the spontaneity of a reaction, using standard entropy and enthalpy changes and the equation.

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

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Nature tends to greater disorder, hence any change may occur spontaneously (like water flowing downhill, sodium chloride ('salt') dissolving in water or a gas expanding to fill a container) if the final state is more probable than the initial state, that is, if as a result of the change the final entropy of the universe is greater than the initial entropy of the universe (Physicists call this the Second Law of Thermodynamics). The entropy of the universe depends on both the entropy of the system and the entropy of the surroundings.

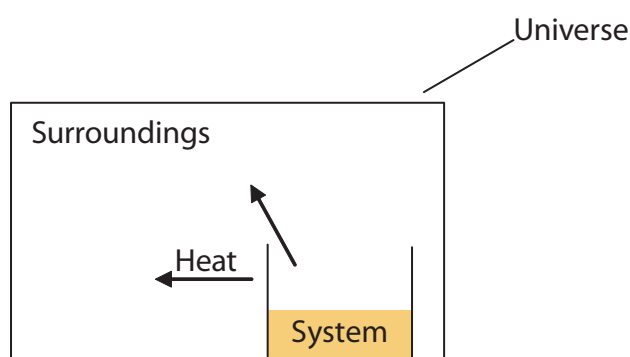


Figure 519 Illustrating the division into system and surroundings

ΔS measures the change in the entropy of the system. The major effect of chemical changes on the entropy of the surroundings results from the gain and loss of heat energy. If chemical potential energy is converted to heat energy which is then transferred to the universe (i.e. an exothermic change), then this results in an increase in the entropy

of the surroundings and *vice versa* for an endothermic change. The magnitude of this entropy change is $-\Delta H^\circ/T$, where T is the absolute temperature. The condition for a spontaneous change to occur is therefore that $\Delta S_{\text{universe}}$ is positive, where $\Delta S_{\text{universe}}$ is given by:

$$\Delta S_{\text{universe}} = \Delta S_{\text{surroundings}} + \Delta S_{\text{system}} = -\Delta H^\circ/T + \Delta S_{\text{system}}^\circ$$

In other words a change will be spontaneous if:

- the final state has a lower enthalpy than the initial state (ΔH° is negative)
- and
- the final state is more disordered than the initial state (ΔS° is positive).

If only one of these is the case then the outcome will depend on which factor is the dominant one at the temperature being considered.

In chemistry this condition has traditionally been considered in terms of the **Gibbs free energy change**, ΔG . The Gibbs free energy change is equal to $-T\Delta S_{\text{universe}}$. If this quantity is negative, then $\Delta S_{\text{universe}}$ must be positive, so that the process in question may occur spontaneously.

Multiplying through the equation above by $-T$ gives the expression:

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

where ΔH° is the standard enthalpy change, ΔS° the standard entropy change of the system and T is the temperature in Kelvin. Hence for $\Delta S_{\text{universe}}$ to be positive and a change to be spontaneous, ΔG must be negative.

In other words whether a change occurs depends on two fundamental factors:

- whether it results in a product with lower enthalpy (i.e. whether ΔH° is negative)
- whether it results in a product with greater entropy (i.e. an increase in randomness so ΔS° is positive)

As a result a reaction will definitely occur if both the enthalpy change (ΔH°) is negative (i.e. it is exothermic) and the entropy change (ΔS°) is positive (i.e. it gives an increase in randomness). This does not mean that endothermic reactions (ΔH° positive) and reactions in which the randomness of the system decreases (ΔS° negative) or do not occur. Both ΔH° and ΔS° changes must be considered before deciding if a reaction will occur, that is whether it is spontaneous. The Gibbs free energy change (ΔG),

ΔH°	ΔS°	ΔG	Spontaneity
Positive, i.e. endothermic	Positive, i.e. more random products	Depends on T	Spontaneous at high temperatures, when $T\Delta S^\circ > \Delta H$
Positive, i.e. endothermic	Negative, i.e. more ordered products	Always positive	Never spontaneous
Negative, i.e. exothermic	Positive, i.e. more random products	Always negative	Always spontaneous
Negative, i.e. exothermic	Negative, i.e. more ordered products	Depends on T	Spontaneous at low temperatures, when $T\Delta S^\circ < \Delta H$

N.B. This assumes that the effect of temperature on the actual values of ΔH° and ΔS° is negligible

Figure 520 The effect of ΔH and ΔS on the spontaneity of reaction

AHL

defined in the equation above, which is a measure of the driving force of a reaction, is the criterion for predicting the spontaneity of a reaction. The way in which the sign of ΔH° and ΔS° affect the sign of ΔG is summarised in Figure 520:

This may be illustrated graphically as shown in Figure 521 below:

Note that ΔH does not vary much with T (so ΔH° data can be used), but ΔG is strongly temperature dependent hence, because the entropy change (ΔS°) is multiplied by the absolute temperature, the influence of the entropy change is always dominant at high temperature.

Figures 519 and 520 just give the conditions under which a reaction may be spontaneous, they do not actually mean that the reaction will actually take place at a measurable

rate. If the reaction has a high activation energy, then the rate at which the reaction occurs may be infinitesimal, even though it is energetically feasible. For example a mixture of hydrogen and oxygen will not react at a measurable rate at room temperature and pressure, even though the reaction to form water is spontaneous, because virtually none of the molecules have sufficient kinetic energy to overcome the activation energy for the reaction.

The Gibbs free energy (ΔG) for a change is equal to the amount of energy from that system that is available to do useful work. Hence for any system in equilibrium (refer to Chapter 7) ΔG must be exactly zero, i.e. the system can do no useful work. Thus if ΔG for a reaction is zero, then when stoichiometric amounts of both reactants and products are all mixed together there will be no further change. If ΔG is slightly negative there will be a net reaction to increase the amount of products and decrease the amount of reactants.

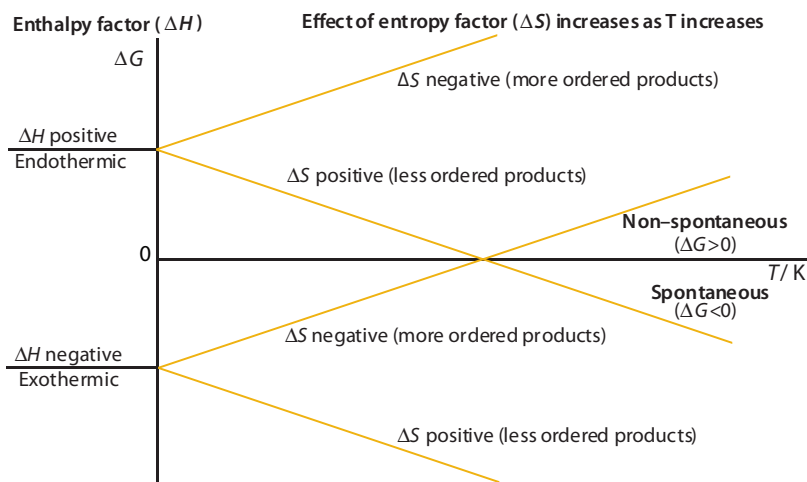


Figure 521 The conditions for spontaneity and the effect of temperature on this

This will continue until ΔG for any further change will be zero (remember standard values only apply to standard conditions, i.e. stoichiometric amounts), at which point equilibrium will be established. If ΔG is very negative then this position will be so far to the right that the reaction will effectively go to completion. Similarly if ΔG is small and positive then an equilibrium favouring the products will occur, but if ΔG is very positive the reaction will not occur.

The value of ΔG can be calculated at any given temperature from values of ΔH and ΔS for the reaction, which are in turn calculated from data about the reactants and products. Consider for example the thermal decomposition of calcium carbonate at 500 K:



The required data are:

Substance	ΔH_f° - kJ mol ⁻¹	S° - J K ⁻¹ mol ⁻¹
CaCO ₃ (s)	-1207	93
CaO(s)	-636	40
CO ₂ (g)	-394	214

Figure 522 Table for the decomposition of CaCO₃

Using these data, values of ΔH° and ΔS° can be calculated for the reaction:

$$\begin{aligned}\Delta H &= \sum H_f(\text{Products}) - \sum H_f(\text{Reactants}) \\ &= [(-636) + (-394)] - [-1207] \\ &= +177 \text{ kJ mol}^{-1} = 177\,000 \text{ J mol}^{-1}.\end{aligned}$$

$$\begin{aligned}\Delta S &= \sum \Delta S(\text{Products}) - \sum \Delta S(\text{Reactants}) \\ &= [(40) + (214)] - [93] \\ &= +161 \text{ J K}^{-1} \text{ mol}^{-1}.\end{aligned}$$

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= 177\,000 - (161 \times 500) \\ &= 96\,500 \text{ J mol}^{-1} = 96.5 \text{ kJ mol}^{-1}.\end{aligned}$$

Note that the units for ΔG_f° and ΔH_f° are usually kJ mol⁻¹. Since the units of ΔS° are J K⁻¹ mol⁻¹, then units of $T\Delta S^\circ$ are J mol⁻¹. Hence it is essential to divide this by 1000 to

convert it to kJ mol⁻¹. Alternatively the whole calculation can be performed in units of J mol⁻¹.

ΔG is positive, therefore at this temperature the reaction is not spontaneous and cannot occur. If the temperature is increased to 2000 K however, assuming ΔH° and ΔS° are both independent of temperature:

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= 177\,000 - (161 \times 2\,000) \\ &= 145\,000 \text{ J mol}^{-1} = 96.5 \text{ kJ mol}^{-1}.\end{aligned}$$

The reaction is now spontaneous so that, provided there is sufficient energy to overcome the activation energy, which is the case for this reaction, the process occurs. The temperature at which the system is in perfect equilibrium (i.e. $K_c = 1$) can be calculated knowing that at equilibrium, because $\Delta G = 0$, $\Delta H^\circ = T \cdot \Delta S^\circ$:

$$\begin{aligned}177\,000 &= T \times 161 \\ T &= \frac{177\,000}{161} = 1\,099 \text{ K}\end{aligned}$$

ΔG° under standard conditions (298 K and 101.3 kPa) can also be calculated using the standard **Gibbs free energy of formation** (ΔG_f°) data in the same way as data on the standard enthalpy of formation (ΔH_f°) data is used to calculate standard enthalpy changes (ΔH°). The Gibbs free energy of elements in their standard state is similarly defined as zero, so that the standard Gibbs free energy change of formation is the free energy change when one mole of a compound is formed from its elements under standard conditions.

Therefore:

$$\Delta G_f^\circ = \sum G_f^\circ(\text{Products}) - \sum G_f^\circ(\text{Reactants})$$

Using this approach for the calcium carbonate example above standard free energy of formation data for the compounds in the appropriate state is:

$$\begin{aligned}\Delta G_f^\circ(\text{CaCO}_3) &= -1120 \text{ kJ mol}^{-1}; \\ \Delta G_f^\circ(\text{CaO}) &= -604 \text{ kJ mol}^{-1}; \\ \Delta G_f^\circ(\text{CO}_2) &= -395 \text{ kJ mol}^{-1}\end{aligned}$$

Hence:

$$\begin{aligned}\Delta G^\circ &= [(-604) + (-395)] - [-1120] \\ &= +121 \text{ kJ mol}^{-1}\end{aligned}$$

Exercise 15.4

1. Which of the following combinations of enthalpy change and entropy change ensures that the position of equilibrium will favour the products under all conditions?

	ΔH	ΔS
A	Positive	Positive
B	Positive	Negative
C	Negative	Positive
D	Negative	Negative

2. For the reaction of liquid phosphorus(III) chloride with chlorine gas to form solid phosphorus(V) chloride at 298 K, the entropy change is $-85 \text{ J mol}^{-1} \text{ K}^{-1}$ and the enthalpy change is -124 kJ mol^{-1} . What is the approximate value of the Gibbs free energy at this temperature?

- A -200 kJ mol^{-1}
 B -100 kJ mol^{-1}
 C -40 kJ mol^{-1}
 D $+40 \text{ kJ mol}^{-1}$

3. Under certain conditions it is possible for three moles of gaseous ethyne (C_2H_2) to polymerise to form liquid benzene (C_6H_6). Use the data provided to calculate:

- a) The entropy change of the system.
 b) The enthalpy change of the system.
 c) The entropy change of the surroundings that would result from the emission of this amount of heat energy at 25°C .
 d) Explain how these factors combine to determine whether a spontaneous reaction is possible and predict the optimum conditions for the formation of benzene.

Data:

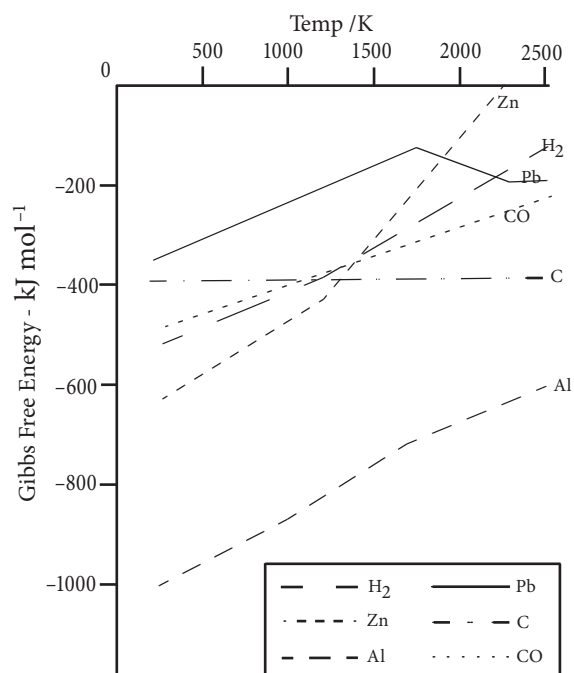
	$\Delta H_f / \text{kJ mol}^{-1}$	$S / \text{J mol}^{-1} \text{ K}^{-1}$
Ethyne	227	201
Benzene	83	269

4. Use values of the Gibbs free energy change of formation, given below, to deduce whether the *cis*- or *trans*- isomer of but-2-ene is the more stable at 25°C . At what temperature will the two isomers have the same stability?

Data:

	$\Delta G_f / \text{kJ mol}^{-1}$	$\Delta H_f / \text{kJ mol}^{-1}$	$S / \text{J mol}^{-1} \text{ K}^{-1}$
<i>cis</i> -but-2-ene	67.1	-5.7	301
<i>trans</i> -but-2-ene	64.1	-10.1	296

5. This question refers to the graph of ΔG against temperature shown.



This shows the variation of ΔG for the reaction of the substance indicated with one mole of oxygen to form the most stable oxide.

- a) The line for the reaction $2\text{Pb} + \text{O}_2 \longrightarrow 2\text{PbO}$ shows two distinct changes of gradient. Explain these.
 b) Is carbon or carbon monoxide the more powerful reducing agent?
 c) Explain what it shows about the potential use of hydrogen as a reductant for:
- Al_2O_3
 - PbO
 - ZnO