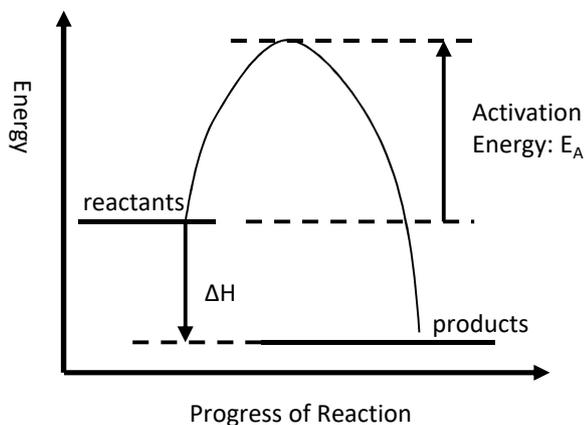


## 5 Chemical Energetics

**Definition: Enthalpy change** is the amount of **heat energy** taken in or given out during any change in a system provided the **pressure is constant**.

In an exothermic change energy is transferred from the system (chemicals) to the surroundings.  
The products have less energy than the reactants.

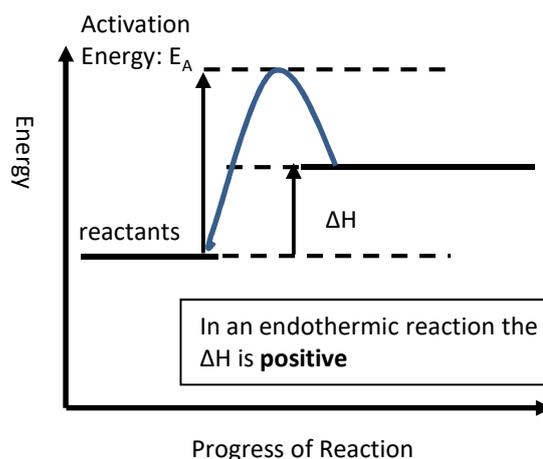


In an exothermic reaction the  $\Delta H$  is **negative**

Common oxidation exothermic processes are the combustion of fuels and the oxidation of carbohydrates such as glucose in respiration.

If an enthalpy change occurs then energy is transferred between **system** and **surroundings**. The system is the chemicals and the surroundings is everything outside the chemicals.

In an endothermic change, energy is transferred from the surroundings to the system (chemicals). They require an input of heat energy e.g. thermal decomposition of calcium carbonate  
The products have more energy than the reactants.



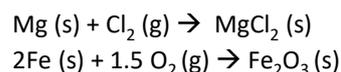
In an endothermic reaction the  $\Delta H$  is **positive**

**Definition: Enthalpy change of reaction**  $\Delta_r H$  is the enthalpy change when the number of moles of reactants as specified in the balanced equation react together

### Standard Enthalpy Change of Formation

The standard enthalpy change of formation of a compound is the **enthalpy change** when **1 mole of the compound** is formed from **its elements** under **standard conditions (298K and 100kPa)**, all reactants and products being in their standard states.

Symbol  $\Delta_f H$

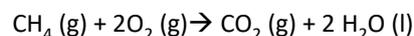


The enthalpy of formation of an element =  $0 \text{ kJ mol}^{-1}$

### Standard Enthalpy Change of Combustion

The standard enthalpy of combustion of a substance is defined as the **enthalpy change** that occurs when **one mole of** a substance is **combusted completely in oxygen** under **standard conditions. (298K and 100kPa)**, all reactants and products being in their standard states.

Symbol  $\Delta_c H$



**Incomplete combustion** will lead to soot (carbon), carbon monoxide and water. It will be **less exothermic** than complete combustion.

Enthalpy changes are normally quoted at **standard** conditions.

Standard conditions are:

- 100 kPa pressure
- 298 K (room temperature or 25°C)
- Solutions at  $1 \text{ mol dm}^{-3}$
- all substances should have their normal state at 298K

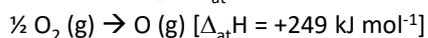
When an enthalpy change is measured at standard conditions the symbol  $\Delta$  is used

Eg  $\Delta H$

## Definitions of enthalpy changes

### Enthalpy of atomisation

The enthalpy of atomisation of an element is the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state



The enthalpy change for a solid metal turning to gaseous atoms can also be called the **Enthalpy of sublimation** and will numerically be the same as the enthalpy of atomisation

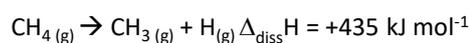


### Bond dissociation enthalpy (bond energy)

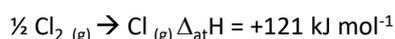
The bond dissociation enthalpy is the standard molar enthalpy change when one mole of a covalent bond is broken into two gaseous atoms (or free radicals)



Or

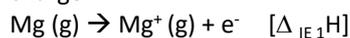


For diatomic molecules the  $\Delta_{\text{diss}}\text{H}$  of the molecule is the same as  $2 \times \Delta_{\text{at}}\text{H}$  of the element



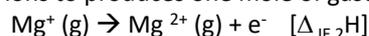
### First Ionisation enthalpy

The first ionisation enthalpy is the enthalpy change required to remove 1 mole of electrons from 1 mole of gaseous atoms to form 1 mole of gaseous ions with a +1 charge



### Second Ionisation enthalpy

The second ionisation enthalpy is the enthalpy change to remove 1 mole of electrons from one mole of gaseous 1+ ions to produce one mole of gaseous 2+ ions.



### First Electron affinity

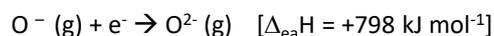
The first electron affinity is the enthalpy change that occurs when 1 mole of gaseous atoms gain 1 mole of electrons to form 1 mole of gaseous ions with a -1 charge



The first electron affinity is exothermic for atoms that normally form negative ions because the ion is more stable than the atom and there is an attraction between the nucleus and the electron

### second electron affinity

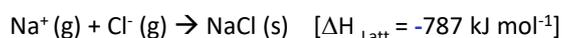
The second electron affinity is the enthalpy change when one mole of gaseous 1- ions gains one electron per ion to produce gaseous 2- ions.



The second electron affinity for oxygen is **endothermic** because it takes energy to overcome the **repulsive force** between the **negative ion and the electron**

### Enthalpy of lattice formation

The Enthalpy of lattice formation is the standard enthalpy change when **1 mole** of an ionic crystal lattice is formed from its constituent **ions in gaseous form**.



### Enthalpy change of Neutralisation

The standard enthalpy change of neutralisation is the enthalpy change when solutions of an acid and an alkali react together under standard conditions to produce 1 mole of water.

### Enthalpy of Hydration $\Delta_{\text{hyd}}\text{H}$

Enthalpy change when **one mole of gaseous ions** become **aqueous ions**.



or



This always gives out energy (exothermic, -ve) because bonds are made between the ions and the water molecules

### Enthalpy of solution

The enthalpy of solution is the standard enthalpy change when one mole of an ionic solid dissolves in a large enough amount of water to ensure that the dissolved ions are well separated and do not interact with one another



## Measuring the Enthalpy Change for a Reaction Experimentally

### Calorimetric method

For a reaction in solution we use the following equation

**energy change = mass of solution x heat capacity x temperature change**

$$Q \text{ (J)} = m \text{ (g)} \times c_p \text{ (J g}^{-1}\text{K}^{-1}) \times \Delta T \text{ (K)}$$

This equation will only give the energy for the actual quantities used. Normally this value is converted into the energy change per mole of one of the reactants. (The enthalpy change of reaction,  $\Delta H_r$ )

### Calorimetric method

### Practical

One type of experiment is one in which substances are mixed in an insulated container and the temperature rise measured.

This could be a solid dissolving or reacting in a solution or it could be two solutions reacting together

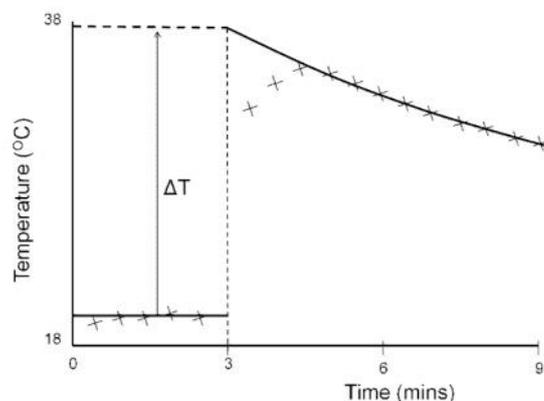
#### General method

- washes the equipment (cup and pipettes etc) with the solutions to be used
- dry the cup after washing
- put polystyrene cup in a beaker **for insulation and support**
- Measure out desired volumes of solutions with volumetric pipettes and transfer to insulated cup
- clamp thermometer into place making sure the thermometer bulb is immersed in solution
- measure the initial temperatures of the solution or both solutions if 2 are used. Do this every minute for 2-3 minutes
- At minute 3 transfer second reagent to cup. If a solid reagent is used then add the solution to the cup first and then add the solid weighed out on a balance.
- If using a solid reagent then use 'before and after' weighing method
- stirs mixture (**ensures that all of the solution is at the same temperature**)
- Record temperature every minute after addition for several minutes

If the reaction is slow then the exact temperature rise can be difficult to obtain as cooling occurs simultaneously with the reaction

To counteract this we take readings at regular time intervals and extrapolate the temperature curve/line back to the time the reactants were added together.

We also take the temperature of the reactants for a few minutes before they are added together to get a better average temperature. If the two reactants are solutions then the temperature of both solutions need to be measured before addition and an average temperature is used.



#### Errors in this method

- energy transfer from surroundings (usually loss)
- approximation in specific heat capacity of solution. The method assumes all solutions have the heat capacity of water.
- neglecting the specific heat capacity of the calorimeter- we ignore any energy absorbed by the apparatus.
- reaction or dissolving may be incomplete or slow.
- density of solution is taken to be the same as water.

Read question carefully. It may be necessary to describe:

- Method
- Drawing of graph with extrapolation
- Description of the calculation

## Calculating the enthalpy change of reaction, $\Delta H$ , from experimental data

### General method

1. Using  $q = m \times c_p \times \Delta T$  calculate energy change for quantities used
2. Work out the moles of the reactants used
3. Divide  $q$  by the number of moles of the reactant not in excess to give  $\Delta H$
4. Add a sign and unit (divide by a thousand to convert  $\text{J mol}^{-1}$  to  $\text{kJ mol}^{-1}$ )

The heat capacity of water is  $4.18 \text{ J g}^{-1}\text{K}^{-1}$ . In any reaction where the reactants are dissolved in water we assume that the heat capacity is the same as pure water.

Also assume that the solutions have the density of water, which is  $1 \text{ g cm}^{-3}$ . Eg  $25 \text{ cm}^3$  will weigh  $25 \text{ g}$

**Example 1.** Calculate the enthalpy change of reaction for the reaction where  $25 \text{ cm}^3$  of  $0.2 \text{ M}$  copper sulphate was reacted with  $0.01 \text{ mol}$  (excess of zinc). The temperature increased  $7^\circ\text{C}$ .

Step 1: Calculate the energy change for the amount of reactants in the test tube.

$$Q = m \times c_p \times \Delta T$$

$$Q = 25 \times 4.18 \times 7$$

$$Q = 731.5 \text{ J}$$

Note the mass is the mass of the copper sulphate solution only. Do not include mass of zinc powder.

Step 2 : calculate the number of moles of the reactant not in excess.

$$\begin{aligned} \text{moles of CuSO}_4 &= \text{conc} \times \text{vol} \\ &= 0.2 \times 25/1000 \\ &= 0.005 \text{ mol} \end{aligned}$$

If you are not told what is in excess, then you need to work out the moles of both reactants and work out using the balanced equation which one is in excess.

Step 3 : calculate the enthalpy change per mole which is often called  $\Delta H$  (the enthalpy change of reaction)

$$\Delta H = Q / \text{no of moles}$$

$$= 731.5 / 0.005$$

$$= 146300 \text{ J mol}^{-1}$$

$$= 146 \text{ kJ mol}^{-1} \text{ to 3 sf}$$

Remember in these questions: **sign, unit, 3 sig figs.**

Finally add in the sign to represent the energy change: if temp increases the reaction is exothermic and is given a minus sign e.g.  **$-146 \text{ kJ mol}^{-1}$**

**Example 2.**  $25 \text{ cm}^3$  of  $2 \text{ M}$  HCl was neutralised by  $25 \text{ cm}^3$  of  $2 \text{ M}$  NaOH. The Temperature increased  $13.5^\circ\text{C}$  What was the energy change per mole of HCl?

Step 1: Calculate the energy change for the amount of reactants in the test tube.

$$Q = m \times c_p \times \Delta T$$

$$Q = 50 \times 4.18 \times 13.5$$

$$Q = 2821.5 \text{ J}$$

Note the mass equals the mass of acid + the mass of alkali, as they are both solutions.

Step 2 : calculate the number of moles of the HCl.

$$\begin{aligned} \text{moles of HCl} &= \text{conc} \times \text{vol} \\ &= 2 \times 25/1000 \\ &= 0.05 \text{ mol} \end{aligned}$$

Step 3 : calculate  $\Delta H$  the enthalpy change per mole which might be called the enthalpy change of neutralisation

$$\Delta H = Q / \text{no of moles}$$

$$= 2821.5 / 0.05$$

$$= 56430 \text{ J mol}^{-1}$$

$$= -56.4 \text{ kJ mol}^{-1} \text{ to 3 sf}$$

Exothermic and so is given a minus sign

Remember in these questions: **sign, unit, 3 sig figs.**

## Measuring Enthalpies of Combustion using Calorimetry

Enthalpies of combustion can be calculated by using calorimetry. Generally the fuel is burnt and the flame is used to heat up water in a metal cup.

**Example 3.** Calculate the enthalpy change of combustion for the reaction where 0.65g of propan-1-ol was completely combusted and used to heat up 150g of water from 20.1 to 45.5°C

Step 1: Calculate the energy change used to heat up the water.

$$Q = m \times c_p \times \Delta T$$

$$Q = 150 \times 4.18 \times 25.4$$

$$Q = 15925.8 \text{ J}$$

Note the mass is the mass of water in the calorimeter and not the alcohol

Step 2 : calculate the number of moles of alcohol combusted.

$$\begin{aligned} \text{moles of propan-1-ol} &= \text{mass} / M_r \\ &= 0.65 / 60 \\ &= 0.01083 \text{ mol} \end{aligned}$$

Step 3 : calculate the enthalpy change per mole which is called  $\Delta H_c$  (the enthalpy change of combustion)

$$\begin{aligned} \Delta H &= Q / \text{no of moles} \\ &= 15925.8 / 0.01083 \\ &= 1470073 \text{ J mol}^{-1} \\ &= 1470 \text{ kJ mol}^{-1} \text{ to 3 sf} \end{aligned}$$

Remember in these questions: **sign, unit, 3 sig figs.**

Finally add in the sign to represent the energy change: if temp increases the reaction is exothermic and is given a minus sign eg **-1470 kJ mol<sup>-1</sup>**

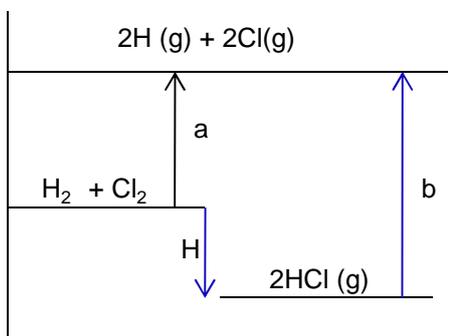
### Errors in this method

- Energy losses from calorimeter
- Incomplete combustion of fuel
- Incomplete transfer of energy
- Evaporation of fuel after weighing
- Heat capacity of calorimeter not included
- Measurements not carried out under standard conditions as H<sub>2</sub>O is gas, not liquid, in this experiment

## Hess's Law

Hess's law states that total **enthalpy change** for a reaction is **independent of the route** by which the chemical change takes place

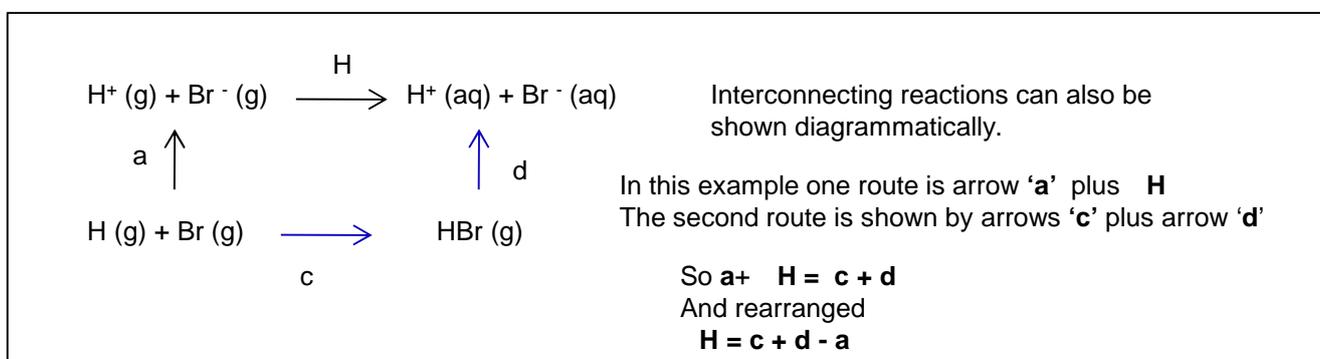
Hess's law is a version of the first law of thermodynamics, which is that energy is always conserved.



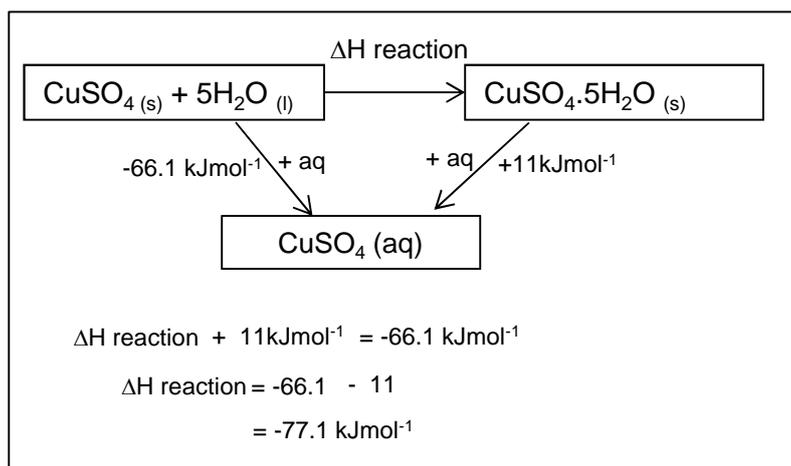
On an energy level diagram the directions of the arrows can show the different routes a reaction can proceed by.

In this example one route is arrow 'a'  
The second route is shown by arrows **H** plus arrow 'b'

$$\begin{aligned} \text{So } a &= H + b \\ \text{And rearranged} \\ H &= a - b \end{aligned}$$



Often Hess's law cycles are used to measure the enthalpy change for a reaction that cannot be measured directly by experiments. Instead alternative reactions are carried out that can be measured experimentally.

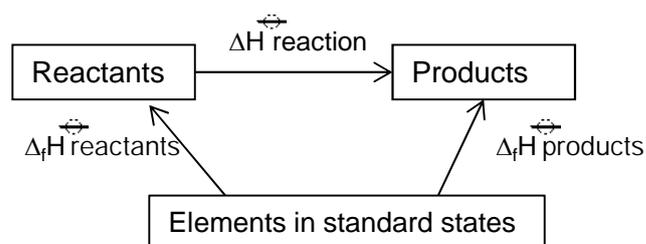


This Hess's law is used to work out the enthalpy change to form a hydrated salt from an anhydrous salt.

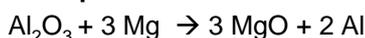
This cannot be done experimentally because it is impossible to add the exact amount of water and it is not easy to measure the temperature change of a solid.

Instead both salts are dissolved in excess water to form a solution of copper sulphate. The temperature changes can be measured for these reactions.

## Using Hess's law to determine enthalpy changes from enthalpy changes of formation.



**Example 4.** What is the enthalpy change for this reaction ?



$$\Delta H = \Delta_f H \text{ products} - \Delta_f H \text{ reactants}$$

$$\Delta H = 3 \times \Delta_f H (\text{MgO}) - \Delta_f H (\text{Al}_2\text{O}_3)$$

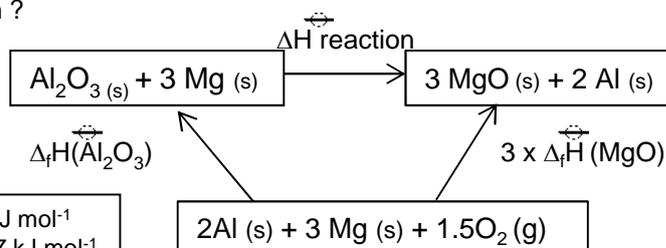
$$\Delta H = (3 \times -601.7) - -1675.7$$

$$= -129.4 \text{ kJ mol}^{-1}$$

Remember  
elements have  
 $\Delta H_f = 0$

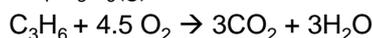
$$\Delta_f H (\text{MgO}) = -601.7 \text{ kJ mol}^{-1}$$

$$\Delta_f H (\text{Al}_2\text{O}_3) = -1675.7 \text{ kJ mol}^{-1}$$



**Example 5.** Using the following data to calculate the heat of combustion of propene

$$\Delta_f H \text{ C}_3\text{H}_6(\text{g}) = +20 \text{ kJ mol}^{-1} \quad \Delta_f H \text{ CO}_2(\text{g}) = -394 \text{ kJ mol}^{-1} \quad \Delta_f H \text{ H}_2\text{O}(\text{g}) = -242 \text{ kJ mol}^{-1}$$

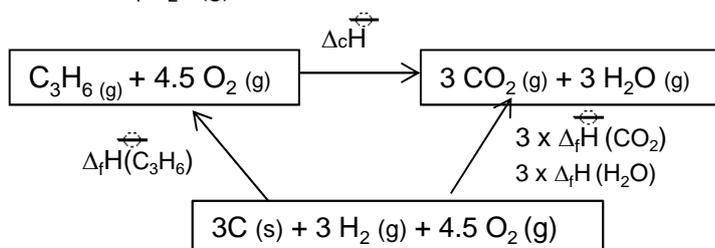


$$\Delta_c H = \Delta_f H \text{ products} - \Delta_f H \text{ reactants}$$

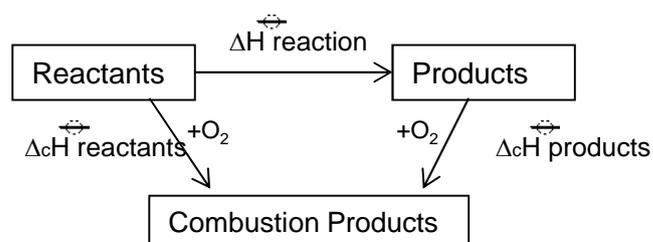
$$\Delta_c H = [3 \times \Delta_f H (\text{CO}_2) + 3 \times \Delta_f H (\text{H}_2\text{O})] - \Delta_f H (\text{C}_3\text{H}_6)$$

$$\Delta_c H = [(3 \times -394) + (3 \times -242)] - 20$$

$$= -1928 \text{ kJ mol}^{-1}$$



## Using Hess's law to determine enthalpy changes from enthalpy changes of combustion.



**Example 6.** Using the following combustion data to calculate the heat of reaction



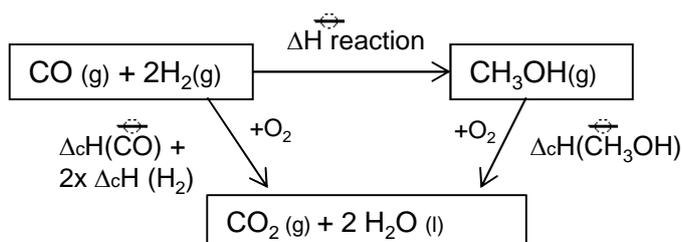
$$\Delta_c H \text{ CO}(\text{g}) = -283 \text{ kJ mol}^{-1} \quad \Delta_c H \text{ H}_2(\text{g}) = -286 \text{ kJ mol}^{-1} \quad \Delta_c H \text{ CH}_3\text{OH}(\text{g}) = -671 \text{ kJ mol}^{-1}$$

$$\Delta H \text{ reaction} = \sum_c H \text{ reactants} - \sum_c H \text{ products}$$

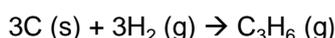
$$\Delta H = \Delta_c H (\text{CO}) + 2 \times \Delta_c H (\text{H}_2) - \Delta_c H (\text{CH}_3\text{OH})$$

$$\Delta H = -283 + 2 \times -286 - -671$$

$$= -184 \text{ kJ mol}^{-1}$$



**Example 7.** Using the following combustion data to calculate the heat of formation of propene



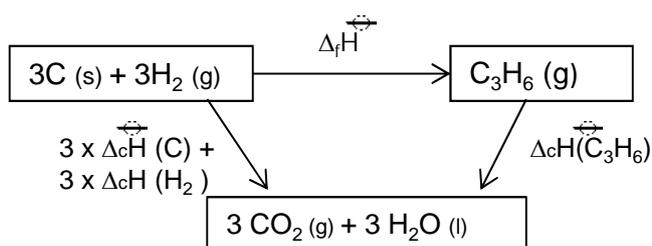
$$\Delta_c\text{H C (s)} = -393\text{kJ mol}^{-1} \quad \Delta_c\text{H H}_2\text{(g)} = -286\text{ kJ mol}^{-1} \quad \Delta_c\text{H C}_3\text{H}_6\text{(g)} = -2058\text{ kJ mol}^{-1}$$

$$\Delta\text{H} = \Delta_c\text{H reactants} - \Delta_c\text{H products}$$

$$\Delta_f\text{H} = 3 \times \Delta_c\text{H (C)} + 3 \times \Delta_c\text{H (H}_2) - \Delta_c\text{H (C}_3\text{H}_6)$$

$$\Delta_f\text{H} = 3 \times -393 + 3 \times -286 - -2058$$

$$= +21\text{ kJ mol}^{-1}$$



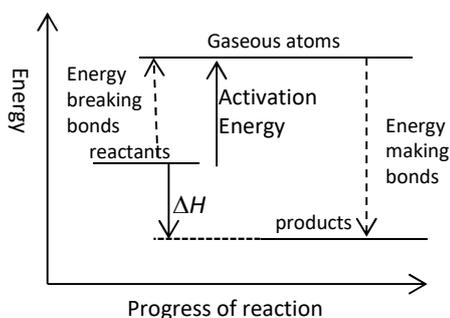
### Mean Bond energies

Definition: The Mean bond energy is the enthalpy needed to break the **covalent** bond into **gaseous atoms**, **averaged over different** molecules

We use values of **mean** bond energies because every single bond in a compound has a slightly different bond energy. E.g. In  $\text{CH}_4$  there are 4 C-H bonds. Breaking each one will require a different amount of energy. However, we use an average value for the C-H bond for all hydrocarbons.

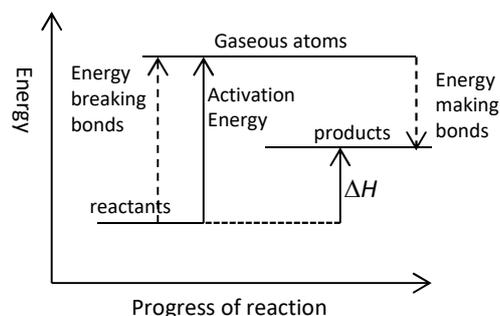
These values are positive because energy is required to break a bond.

The definition only applies when the **substances start and end in the gaseous state**.



Reaction profile for an EXOTHERMIC reaction

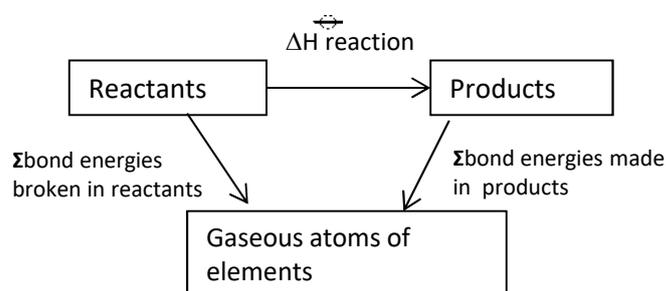
In an exothermic reaction the sum of the bonds in the reactant molecules will be less than the sum of the bonds in the product molecules.



Reaction profile for an ENDOTHERMIC reaction

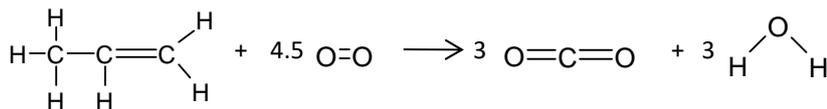
**In general** (if all substances are gases)

$$\Delta\text{H} = \Sigma \text{bond energies broken in reactants} - \Sigma \text{bond energies made in products}$$



$\Delta\text{H}$  values calculated using this method will be less accurate than using formation or combustion data because the mean bond energies are not exact

**Example 8.** Using the following mean bond enthalpy data to calculate the heat of combustion of propene

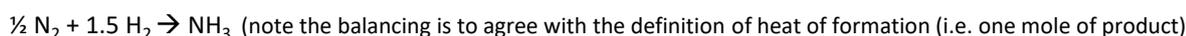


$U_H = \text{d bond energies broken} - \text{d bond energies made}$

$$\begin{aligned}
 &= [E(\text{C}=\text{C}) + E(\text{C}-\text{C}) + 6 \times E(\text{C}-\text{H}) + 4.5 \times E(\text{O}=\text{O})] - [6 \times E(\text{C}=\text{O}) + 6 E(\text{O}-\text{H})] \\
 &= [612 + 348 + (6 \times 412) + (4.5 \times 496)] - [(6 \times 743) + (6 \times 463)] \\
 &= -1572 \text{ kJ mol}^{-1}
 \end{aligned}$$

Bond	Mean enthalpy (kJ mol <sup>-1</sup> )
C=C	612
C-C	348
O=O	496
O=C	743
O-H	463
C-H	412

**Example 9.** Using the following mean bond enthalpy data to calculate the heat of formation of NH<sub>3</sub>



$$E(\text{N}\equiv\text{N}) = 944 \text{ kJ mol}^{-1} \quad E(\text{H}-\text{H}) = 436 \text{ kJ mol}^{-1} \quad E(\text{N}-\text{H}) = 388 \text{ kJ mol}^{-1}$$

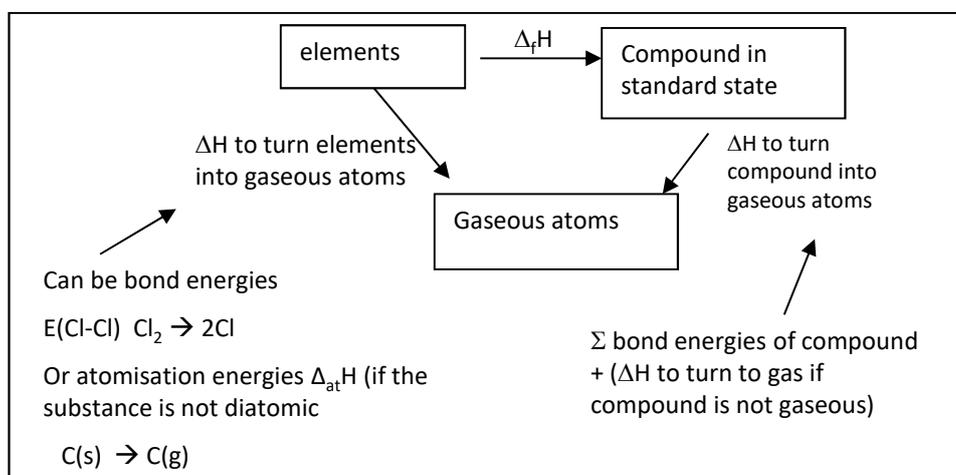
$U_H = \text{d bond energies broken} - \text{d bond energies made}$

$$\begin{aligned}
 &= [0.5 \times E(\text{N}\equiv\text{N}) + 1.5 \times E(\text{H}-\text{H})] - [3 \times E(\text{N}-\text{H})] \\
 &= [(0.5 \times 944) + (1.5 \times 436)] - [3 \times 388] \\
 &= -38 \text{ kJ mol}^{-1}
 \end{aligned}$$

### A more complicated example that may occur at A - Level

Working out  $\Delta_f H$  of a compound using bond energies and other data

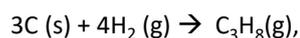
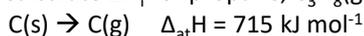
This is a more complicated example of the type in example 9



The  $\Delta H$ 's can be combinations of different data

### Example 10

Calculate  $\Delta_f H$  for propane, C<sub>3</sub>H<sub>8</sub>(g), given the following data.



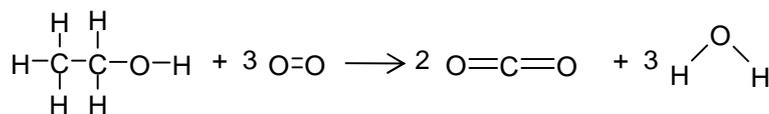
Bond	C-C	C-H	H-H
kJ mol <sup>-1</sup>	348	412	436

$$U_{H_f} = \Sigma \Delta H \text{ to turn elements into gaseous atoms} - \Sigma \Delta H \text{ to turn compound into gaseous atoms}$$

$$\begin{aligned}
 \Delta_f H &= (3 \times U_{\text{at}} H [\text{C}] + 4 \times E[\text{H}-\text{H}]) - (2 \times E[\text{C}-\text{C}] + 8 \times E[\text{C}-\text{H}]) \\
 &= (3 \times 715 + 4 \times 436) - (2 \times 348 + 8 \times 412) \\
 &= -103 \text{ kJ mol}^{-1}
 \end{aligned}$$

## Enthalpies of Combustion in a Homologous Series

When comparing the enthalpies of combustion for successive members of a **homologous series** such as alkanes or alcohols there is a **constant rise** in the size of the enthalpies of combustion as the number of **carbon atoms increases**.

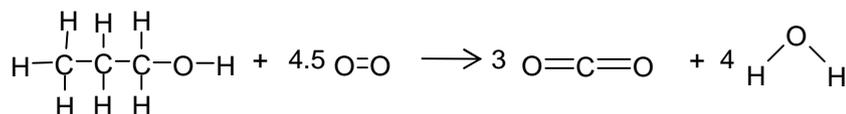


ethanol

**1 C-C, 5C-H 1C-O 1O-H and 3 O=O**  
bonds are broken

**4 C=O and 6 O-H** bonds are made

$$H_c = -1365 \text{ kJ mol}^{-1}$$

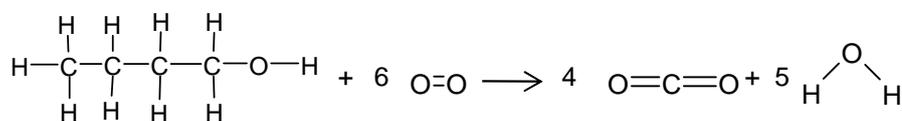


Propan-1-ol

**2C-C, 7C-H 1C-O 1O-H and 4.5 O=O**  
bonds are broken

**6 C=O and 8 O-H** bonds are made

$$H_c = -2016 \text{ kJ mol}^{-1}$$



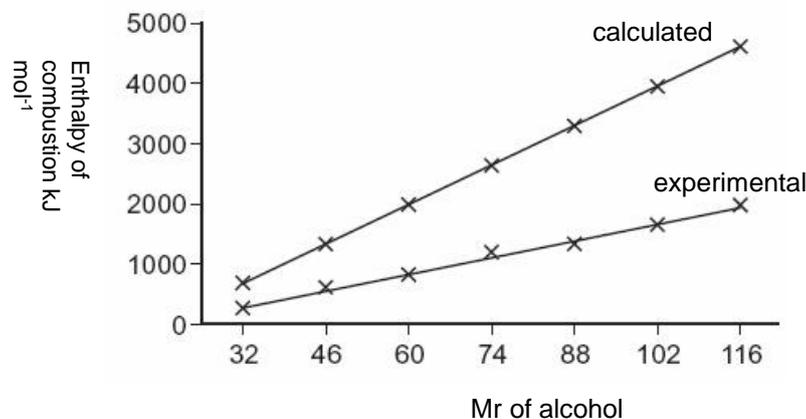
Butan-1-ol

**3C-C, 9C-H 1C-O 1O-H and 6 O=O**  
bonds are broken

**8 C=O and 10 O-H** bonds are made

$$H_c = -2677 \text{ kJ mol}^{-1}$$

As one goes up the homologous series there is a constant amount and type of extra bonds being broken and made e.g. 1C-C, 2C-H and 1.5 O=O extra bonds broken and 2 C=O and 2 O-H extra bonds made, so the enthalpy of combustion increases by a constant amount.

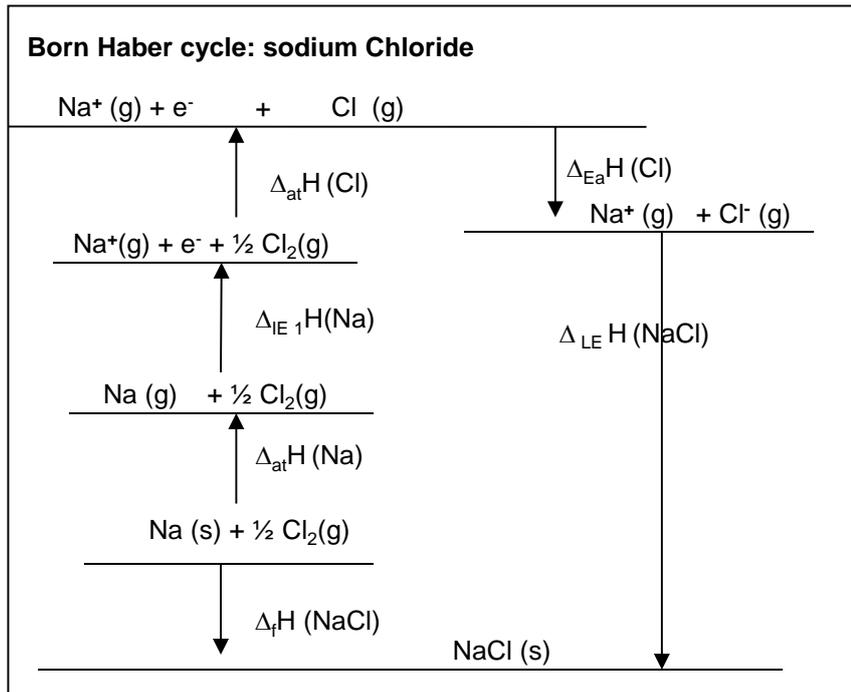


If the results are worked out experimentally using a calorimeter the experimental results will be much lower than the calculated ones because there will be significant heat loss. There will also be incomplete combustion which will lead to less energy being released.

Remember that calculated values of enthalpy of combustions will be more accurate if calculated from enthalpy of formation data than if calculated from average bond enthalpies. This is because average bond enthalpy values are averaged values of the bond enthalpies from various compounds.

## Born Haber cycles

The lattice enthalpy cannot be determined directly. We calculate it indirectly by making use of changes for which data are available and link them together in an enthalpy cycle the Born Haber cycle



Pay attention to state symbols and direction of arrows.

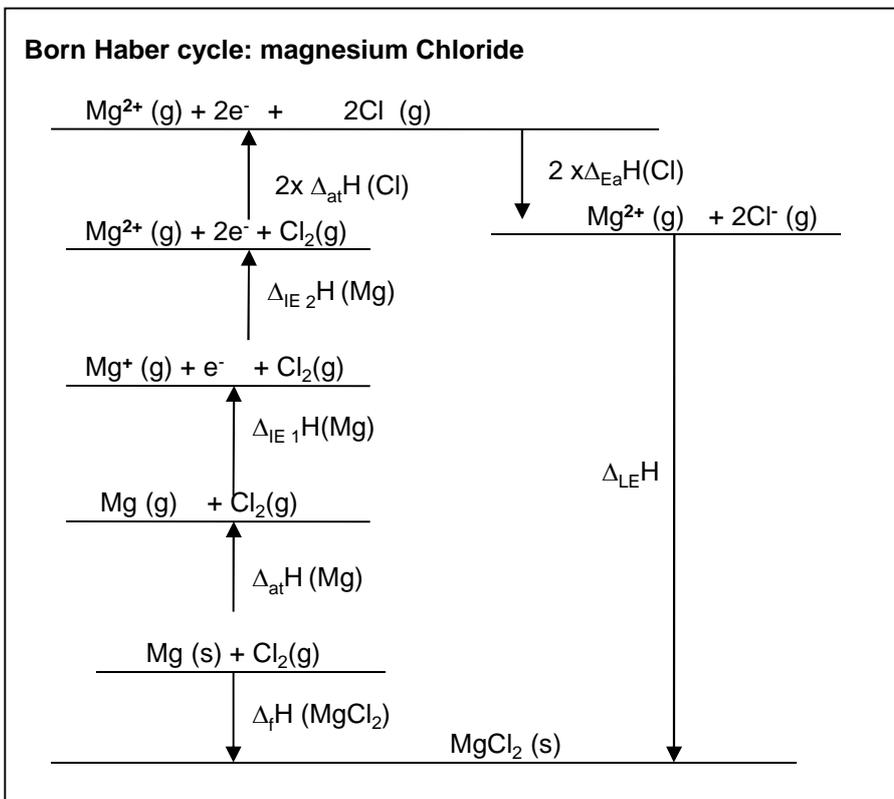
Usually all pieces of data are given except the one that needs to be calculated

By applying Hess's law the heat of formation equals to the sum of everything else

$$\Delta_f H = \Delta_{at} H(\text{Na}) + \Delta_{IE} H(\text{Na}) + \Delta_{at} H(\text{Cl}) + \Delta_{Ea} H(\text{Cl}) + \Delta_{LE} H$$

Rearrange to give  $\Delta_{LE} H = \Delta_f H - (\Delta_{at} H(\text{Na}) + \Delta_{IE} H(\text{Na}) + \Delta_{at} H(\text{Cl}) + \Delta_{Ea} H(\text{Cl}))$

$$\Delta_{LE} H = -411 - (+107 + 496 + 122 + -349) = -787 \text{ kJmol}^{-1}$$



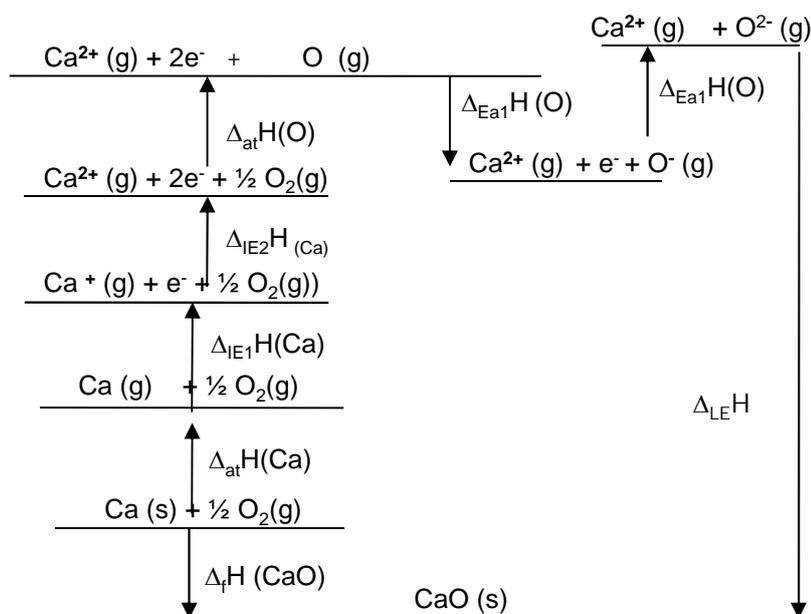
The data for the  $\Delta_{at} H(\text{Cl})$  could also be given as the bond energy for  $E(\text{Cl}-\text{Cl})$  bond.

Remember :

$$E(\text{Cl}-\text{Cl}) = 2 \times \Delta_{at} H(\text{Cl})$$

Note in this example the first and second ionisation energies of magnesium are needed as Mg is a +2 ion

## Born Haber cycle: calcium oxide



Notice the second electron affinity for oxygen is **endothermic** because it takes energy to overcome the **repulsive force** between the **negative ion and the electron**

## Trends in Lattice Enthalpies

The strength of an enthalpy of lattice formation depends on the following factors

### 1. The sizes of the ions:

The larger the ions, the less negative the enthalpies of lattice formation (i.e. a weaker lattice). As the ions are larger the charges become further apart and so have a weaker attractive force between them.

### 2. The charges on the ion:

The bigger the charge of the ion, the greater the attraction between the ions so the stronger the lattice enthalpy (more negative values).

The lattice enthalpies become less negative down any group.  
e.g. LiCl, NaCl, KCl, RbCl

e.g. group 1 halides (eg NaF KI) have lattice enthalpies of around -700 to -1000

group 2 halides (eg MgCl<sub>2</sub>) have lattice enthalpies of around -2000 to -3500

group 2 oxides eg MgO have lattice enthalpies of around -3000 to -4500 kJmol<sup>-1</sup>

## Perfect Ionic Model

Theoretical lattice enthalpies assume a **perfect ionic model** where the ions are **100% ionic** and **spherical** and the attractions are **purely electrostatic**.

## Differences between theoretical and Born Haber (experimental) lattice enthalpies

The Born Haber lattice enthalpy is the real experimental value. When a compound shows covalent character, the theoretical and the Born Haber lattice enthalpies differ. The more the covalent character the bigger the difference between the values.

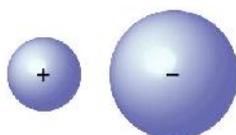
There is a tendency towards covalent character in ionic substances when

- the positive ion is small
- the positive ion has multiple charges
- the negative ion is large
- the negative ion has multiple negative charges.

When a compound has some covalent character - it tends towards giant covalent so the lattice is stronger than if it was 100% ionic. Therefore the Born Haber value would be larger than the theoretical value.

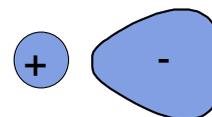
When the negative ion becomes distorted and more covalent we say it becomes polarised. The metal cation that causes the polarisation is called more polarising if it polarises the negative ion.

100% ionic



When 100% ionic the ions are spherical. The theoretical and the Born Haber lattice enthalpies will be the same

Ionic with covalent character



The charge cloud is distorted. The theoretical and the experimental Born Haber lattice enthalpies will differ

## Why does Calcium chloride have the formula $\text{CaCl}_2$ and not $\text{CaCl}$ or $\text{CaCl}_3$ ?

It is useful to draw out the born haber cycles for each potential case.

We need to calculate an enthalpy of formation for each case.

The one with the **most exothermic enthalpy of formation** will be the one that forms as it will be the most thermodynamically stable

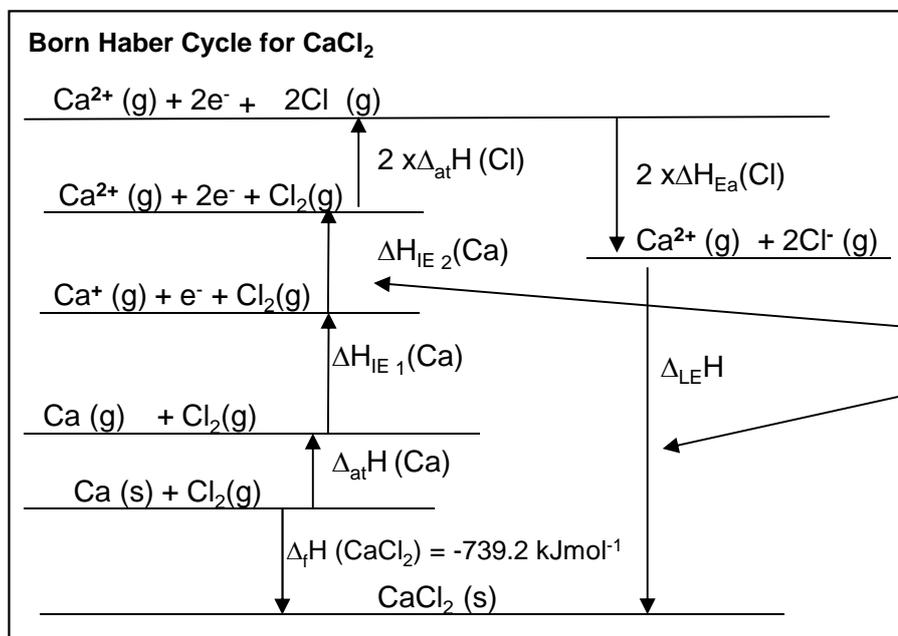
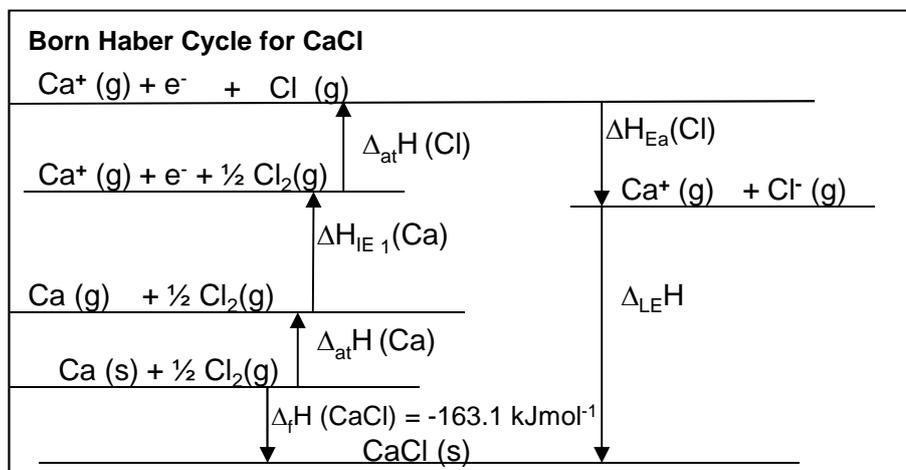
Theoretical lattice enthalpies have been calculated for each case

Theoretical lattice enthalpies  
 $\Delta H_{\text{latt}} \text{CaCl} = -719 \text{ kJ mol}^{-1}$   
 $\Delta H_{\text{latt}} \text{CaCl}_2 = -2218 \text{ kJ mol}^{-1}$   
 $\Delta H_{\text{latt}} \text{CaCl}_3 = -4650 \text{ kJ mol}^{-1}$

These get larger as the positive charge on the calcium ion becomes bigger.

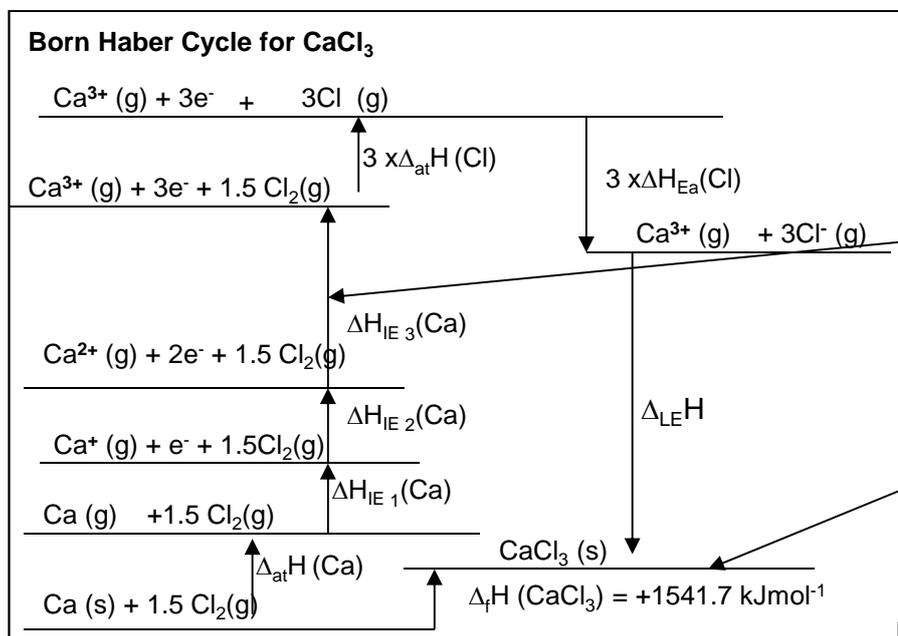
The enthalpy of formation is largely a balance of the ionisation energy and lattice enthalpy.

$\Delta H_f (\text{CaCl})$  is  $-163.1 \text{ kJ mol}^{-1}$ . This is exothermic.



The increased ionisation enthalpy to form  $\text{Ca}^{2+}$  is more than compensated for by the stronger lattice enthalpy of formation

The enthalpy of formation is therefore more exothermic. This is the most stable form



The big increase in ionisation enthalpy to remove the 3<sup>rd</sup> electron is not compensated for by the stronger lattice enthalpy of formation

The enthalpy of formation is therefore endothermic. This is the least stable form

## Free-energy change ( $\Delta G$ ) and entropy change ( $\Delta S$ )

A **SPONTANEOUS PROCESS** (e.g. diffusion) will proceed on its own without any external influence.

### A problem with $\Delta H$

A reaction that is exothermic will result in products that are more **thermodynamically stable** than the reactants. This is a driving force behind many reactions and causes them to be **spontaneous** (occur without any external influence).

Some spontaneous reactions, however, are endothermic.

### How can this be explained?

We need to consider something called **entropy**

### Entropy, $S^\circ$

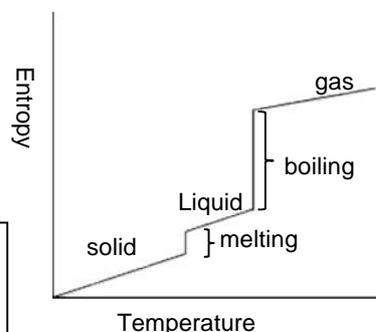
Substances with more ways of arranging their atoms and energy (*more disordered*) have a higher entropy.

Elements	...tend to have lower entropies than...	Compounds
Simpler compounds		Complex compounds
Pure substances		Mixtures

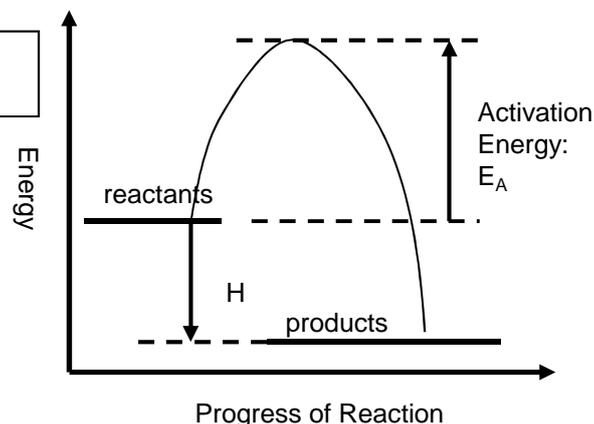
Solids have lower entropies than liquids which are lower than gases. When a solid increases in Temperature its entropy increases as the particles vibrate more.

There is a bigger jump in entropy with boiling than that with melting.

**Gases have large entropies as they are much more disordered**



At 0K substances have zero entropy. There is no disorder as particles are stationary



### Predicting Change in entropy ' $\Delta S^\circ$ ' Qualitatively

An **increase** in disorder and **entropy** will lead to a positive entropy change  $\Delta S^\circ = +ve$

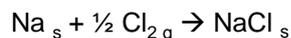
Balanced chemical equations can often be used to predict if  $\Delta S^\circ$  is positive or negative.

**In general**, a significant increase in the entropy will occur if:  
 - there is a **change of state** from **solid or liquid to gas**  
 - there is a significant **increase in number of molecules** between products and reactants.



$\Delta S^\circ = +ve$

- change from solid reactant to gaseous products
  - increase in number of molecules
- both will increase disorder



$\Delta S^\circ = -ve$

- change from gaseous and solid reactant to solid
  - decrease in number of molecules
- both will decrease disorder

### Calculating $\Delta S^\circ$ quantitatively

Data books lists standard entropies ( $S^\circ$ ) **per mole** for a variety of substances. It is not possible for a substance to have a standard entropy of less than zero.

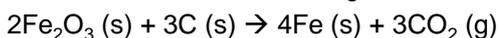
The unit of entropy is  $\text{J K}^{-1} \text{ mol}^{-1}$

$$\Delta S^\circ = S^\circ_{\text{products}} - S^\circ_{\text{reactants}}$$

Elements in their standard states do *not* have zero entropy. **Only perfect crystals at absolute zero ( $T = 0 \text{ K}$ ) will have zero entropy:**

### Example 11

Calculate  $S^\circ$  for the following reaction at 25°C:



$$\begin{aligned} S^\circ &= S^\circ_{\text{products}} - S^\circ_{\text{reactants}} \\ &= (3 \times 213.6 + 4 \times 27.3) - (2 \times 87.4 + 3 \times 5.7) \\ &= +558.1 \text{ J K}^{-1} \text{ mol}^{-1} = \underline{\underline{+558 \text{ J K}^{-1} \text{ mol}^{-1}}} \text{ (3 S.F.)} \end{aligned}$$

$$S[\text{Fe}_2\text{O}_3] = 87.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S[\text{C}] = 5.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S[\text{Fe}] = 27.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S[\text{CO}_2] = 213.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

Note: the entropy change is very positive as a large amount of gas is being created increasing disorder

### Gibbs Free Energy Change, $G$

The balance between entropy and enthalpy determines the feasibility of a reaction.

This is given by the relationship:

$$G = H - T S$$

For any spontaneous change,  $G$  will be **negative**.

Gibbs free energy is a term that combines the effect of enthalpy and entropy into one number

A reaction that has increasing entropy (+ve  $S$ ) and is exothermic (-ve  $H$ ) will make  $G$  be **negative** and will always be feasible

Convert from °C to K (+ 273)

$$G = H - T S$$

Units:  $\text{KJ mol}^{-1}$       Units:  $\text{KJ mol}^{-1}$       Unit of  $S = \text{J K}^{-1} \text{ mol}^{-1}$       Need to convert to  $\text{KJ K}^{-1} \text{ mol}^{-1}$  ( $\div 1000$ )

If  $G$  is negative there is still a possibility, however, that the reaction will not occur or will occur so slowly that effectively it doesn't happen. If the reaction has a high activation energy the reaction will not occur.

**Example 12:** Data for the following reaction, which represents the reduction of aluminium oxide by carbon, are shown in the table.



Calculate the values of  $H^\circ$ ,  $S^\circ$  and  $G^\circ$  for the above reaction at 298 K

#### 1. Calculate $S^\circ$

$$\begin{aligned} S^\circ &= S^\circ_{\text{products}} - S^\circ_{\text{reactants}} \\ &= (2 \times 28 + 3 \times 198) - (51 + 3 \times 6) \\ &= +581 \text{ J K}^{-1} \text{ mol}^{-1} \text{ (3 S.F.)} \end{aligned}$$

#### 2. Calculate $H^\circ$

$$\begin{aligned} H^\circ &= \sum H^\circ_{\text{products}} - \sum H^\circ_{\text{reactants}} \\ &= (3 \times -111) - (-1669) \\ &= +1336 \text{ kJ mol}^{-1} \end{aligned}$$

#### 3. Calculate $G^\circ$

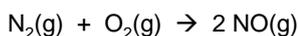
$$\begin{aligned} G^\circ &= H^\circ - T S^\circ \\ &= +1336 - 298 \times 0.581 \\ &= +1163 \text{ kJ mol}^{-1} \end{aligned}$$

$G^\circ$  is positive. The reaction is not feasible

Substance	$H^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{JK}^{-1} \text{ mol}^{-1}$
$\text{Al}_2\text{O}_3(\text{s})$	-1669	51
$\text{C}(\text{s})$	0	6
$\text{Al}(\text{s})$	0	28
$\text{CO}(\text{g})$	-111	198

### Calculating the temperature a reaction will become feasible

Example 13: Calculate the temperature range that this reaction will be feasible



$$H = 180 \text{ kJ mol}^{-1} \quad S = 25 \text{ J K}^{-1} \text{ mol}^{-1}$$

The reaction will be feasible when  $G = 0$

Make  $G = 0$  in the following equation  $G = H - T S$

$$0 = \Delta H - T \Delta S$$

$$\text{So } T = H / S$$

$$\begin{aligned} T &= 180 / (25/1000) \\ &= 7200 \text{ K} \end{aligned}$$

The  $T$  must be  $>7200 \text{ K}$  which is a high Temp!

### $G$ during phase changes

As physical phase changes like melting and boiling are equilibria, the  $G$  for such changes is zero.

Example 14 What temperature would methane melt at?



Make  $G = 0$  in the following equation  $G = H - T S$

$$0 = H - T S$$

$$\text{So } T = H / S$$

$$T = 0.94 / (10.3 \div 1000)$$

$$T = 91 \text{ K}$$

## Effect of Temperature on feasibility

$$G = H - T S$$

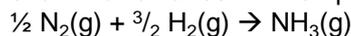
Changing Temperature will change the value of  $-T S$  in the above equation

If the reaction involves an increase in entropy ( $S$  is +ve) then increasing Temperature will make it more likely that **G is negative and more likely that the reaction occurs** e.g.  $\text{NaCl} + \text{aq} \rightarrow \text{Na}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})}$

If the reaction involves a decrease in entropy ( $S$  is -ve) then increasing Temperature will make it more **less likely** that **G is negative and less likely for the reaction to occur**. E.g.  $\text{HCl}(\text{g}) + \text{NH}_3(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$

If the reaction has a **S close to zero** then temperature will not have a large effect on the feasibility of the reaction as  $-T S$  will be **small** and **G won't change much** e.g.  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$

This graph shows how the free-energy change for formation of ammonia varies with temperature above 240 K.



Applying the equation of a straight line

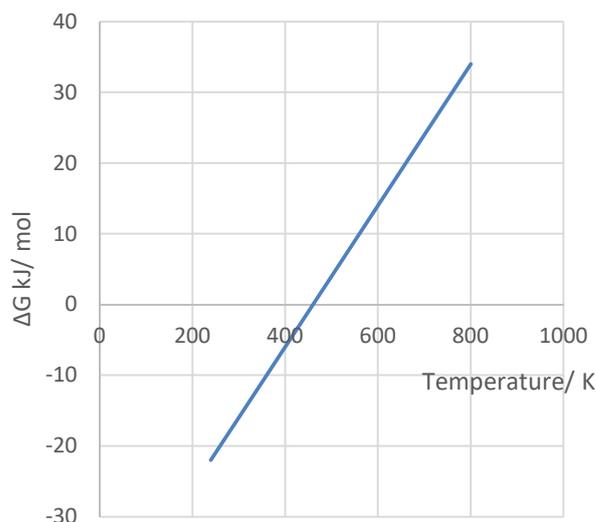
$y = mx + c$  to the  $G = H - T S$  equation.

$$c = H$$

The gradient of this graph is equal to  $-S$

The positive gradient means  $S$  is negative which corresponds to the equation above showing increasing order.

When  $G < 0$  then the reaction is spontaneous. In this case at Temperatures below around 460K



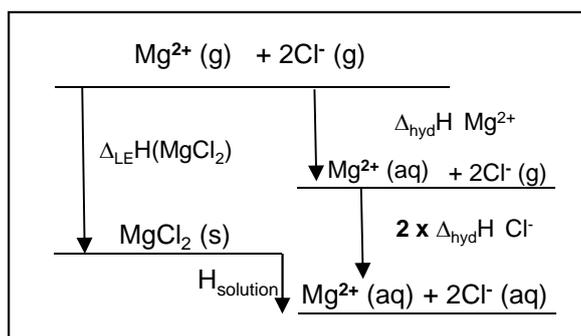
The slope of the line would change below 240K because ammonia would be a liquid and the entropy change would be different

## Enthalpies of solution

### Using Hess's law to determine enthalpy changes of solution

When an ionic lattice dissolves in water it involves breaking up the bonds in the lattice and forming new bonds between the metal ions and water molecules.

For  $\text{MgCl}_2$  the ionic equation for the dissolving is  $\text{MgCl}_2(\text{s}) + \text{aq} \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$



When an ionic substance dissolves the lattice must be broken up. The enthalpy of lattice dissociation is equal to the energy needed to break up the lattice (to gaseous ions). This step is **endothermic**.

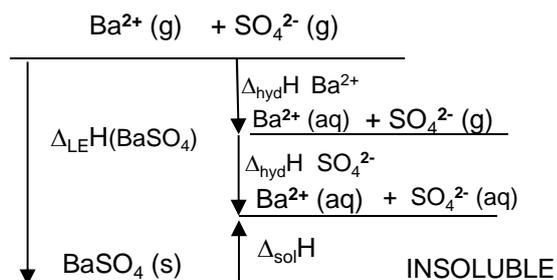
The size of the lattice enthalpy depends on the size and charge on the ion. The smaller the ion and the higher its charge the stronger the lattice

$$\Delta_{\text{sol}} H = -\Delta_{\text{LE}} H + \sum \Delta_{\text{hyd}} H$$

Example 15 . Calculate the enthalpy of solution of NaCl given that the lattice enthalpy of formation of NaCl is  $-771 \text{ kJmol}^{-1}$  and the enthalpies of hydration of sodium and chloride ions are  $-406$  and  $-364 \text{ kJmol}^{-1}$  respectively

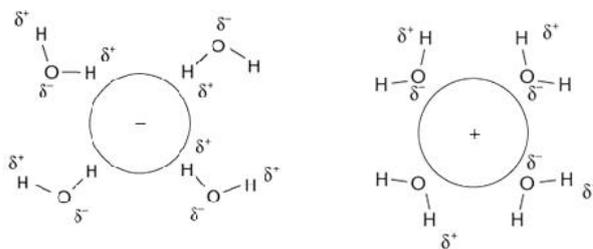
$$\begin{aligned}\Delta_{\text{sol}}H &= -\Delta_{\text{LE}}H + \Sigma\Delta_{\text{hyd}}H \\ &= -(-771) + (-406-364) \\ &= +1 \text{ kJmol}^{-1}\end{aligned}$$

**H solution endothermic.**



Hydration enthalpies are **exothermic** as energy is given out as water molecules bond to the metal ions.

The **negative** ions are attracted to the **+ hydrogens** on the **polar water** molecules and the positive ions are attracted to the **- oxygen** on the polar water molecules.



The higher the **charge density** the greater the hydration enthalpy (e.g. **smaller ions** or **ions with larger charges**) as the ions attract the water molecules more strongly.

e.g. Fluoride ions have more negative hydration enthalpies than chloride ions

Magnesium ions have a more negative hydration enthalpy than barium ions

**What does  $H_{\text{solution}}$  tell us?**

Generally **H solution** is not very exo or endothermic so the hydration enthalpy is about the same as lattice enthalpy.

In general the substance is more likely to **be soluble** if the **H solution is exothermic**.

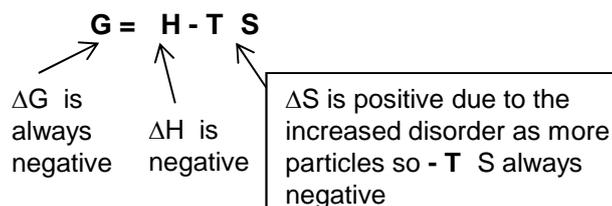
If a substance is insoluble it is often because the lattice enthalpy is much larger than the hydration enthalpy and it is not energetically favourable to break up the lattice, making **H solution endothermic**.

We must consider **entropy**, however, to give us the full picture about solubility.

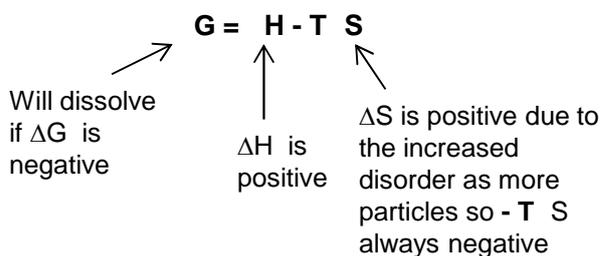
When a solid dissolves into ions the **entropy increases** as there is **more disorder** as solid changes to solution and **number of particles increases**.

This positive  $\Delta S$  can make  $\Delta G$  negative even if  $\Delta H$  solution is endothermic, especially at higher temperatures.

For salts where  $H$  solution is exothermic the salt will always dissolve at all Temperatures



For salts where  $H$  solution is endothermic the salt may dissolve depending on whether the  $-T S$  value is more negative than  $H$  is positive



Increasing the Temperature will make it more likely that  $\Delta G$  will become negative, making the reaction feasible and the salt dissolve