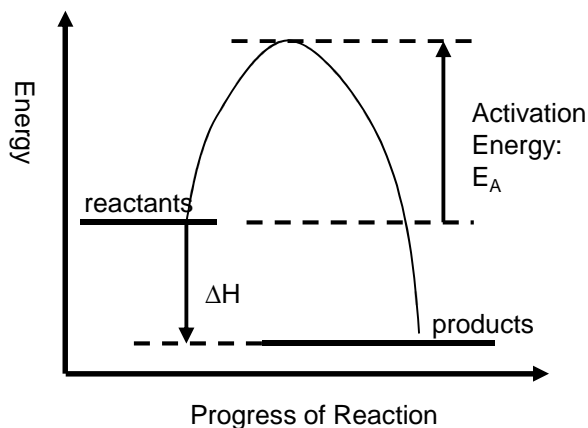


## 2. Enthalpy changes

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

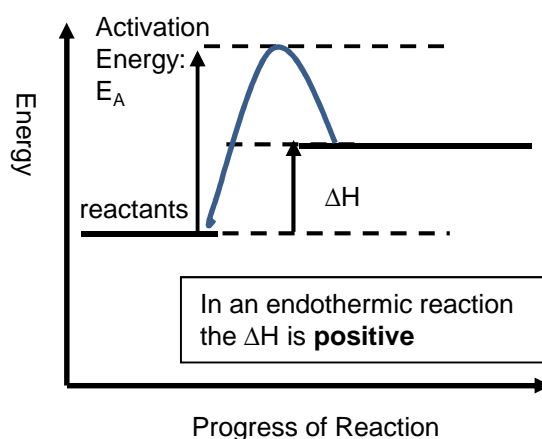


In an exothermic reaction the  $\Delta H$  is **negative**

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

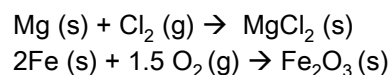


In an endothermic reaction the  $\Delta H$  is **positive**

### 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  $\Delta H_f^\ominus$

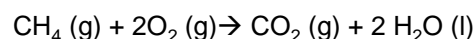


The enthalpy of formation of an element = 0 kJ mol<sup>-1</sup>

### 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  $\Delta H_c^\ominus$



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

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

When an enthalpy change is measured at standard conditions the symbol  $\ominus$  is used  
Eg  $\Delta H^\ominus$

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

Standard conditions are :

- 100 kPa pressure
- 298 K (room temperature or 25°C)
- Solutions at 1 mol dm<sup>-3</sup>
- all substances should have their normal state at 298K

## 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 changes of neutralisation are always exothermic. For reactions involving strong acids and alkalis, the values are similar, with values between  $-56$  and  $-58 \text{ kJ mol}^{-1}$

### Enthalpy of atomisation

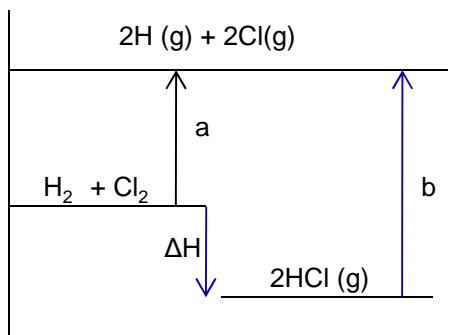
The enthalpy of atomisation of an element is the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state



## 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

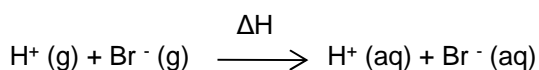
Hess's law is a version of the first law of thermodynamics, which is that energy is always conserved.



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  $\Delta H$  plus arrow 'b'

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



a ↑



c

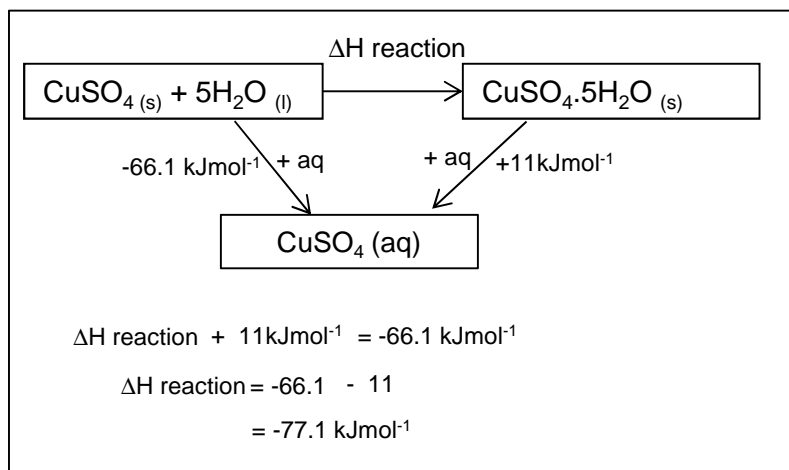
↑ d

Interconnecting reactions can also be shown diagrammatically.

In this example one route is arrow 'a' plus  $\Delta H$   
The second route is shown by arrows 'c' plus arrow 'd'

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

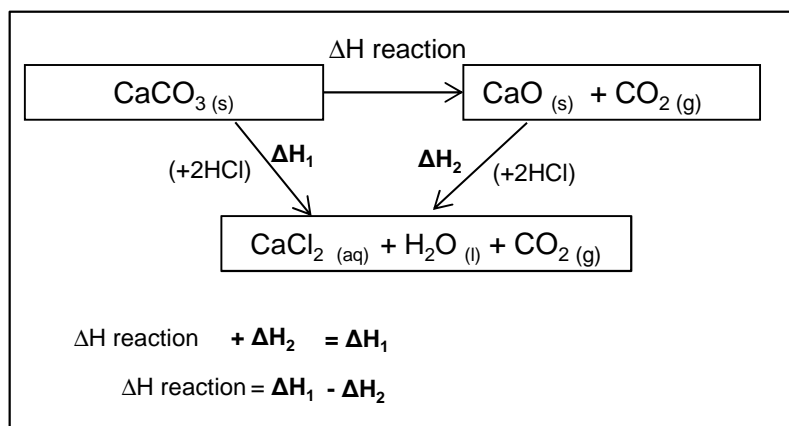
Often Hess's law cycles are used to measure the enthalpy change for a reaction that cannot be measured directly by experiments. Instead alternative reactions are carried out that can be measured experimentally.



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.



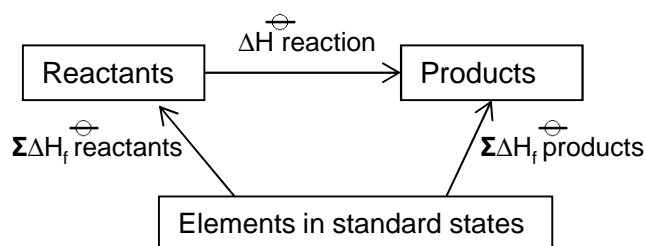
This Hess's law is used to work out the enthalpy change for the thermal decomposition of calcium carbonate.

This cannot be done experimentally because it is impossible to add the heat required to decompose the solid and to measure the temperature change of a solid at the same time.

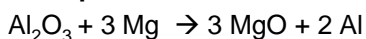
Instead both calcium carbonate and calcium oxide are reacted with hydrochloric acids to form a solution of calcium chloride. The temperature changes can be measured for these reactions.

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

$$\Delta H_{\text{reaction}} = \sum \Delta H_f^{\ominus} \text{ products} - \sum \Delta H_f^{\ominus} \text{ reactants}$$



**Example 1 .** What is the enthalpy change for this reaction ?



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

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

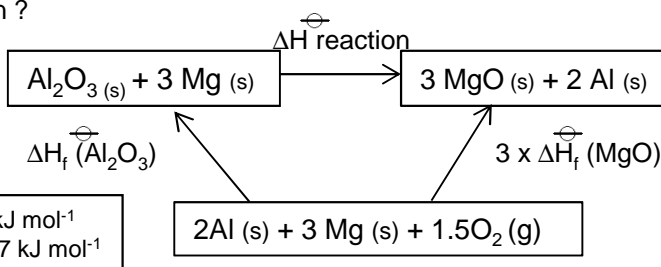
$$\Delta H = (3 \times -601.7) - -1675.7$$

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

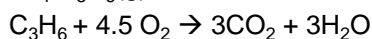
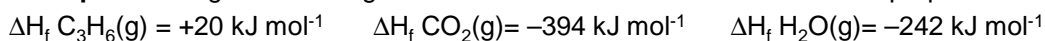
Remember elements have  $\Delta H_f^{\ominus} = 0$

$$\Delta H_f^{\ominus} (\text{MgO}) = -601.7 \text{ kJ mol}^{-1}$$

$$\Delta H_f^{\ominus} (\text{Al}_2\text{O}_3) = -1675.7 \text{ kJ mol}^{-1}$$



**Example 2.** Using the following data to calculate the heat of combustion of propene

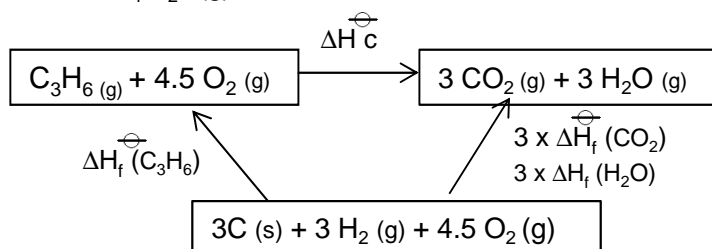


$$\Delta H_c = \sum \Delta H_f \text{ products} - \sum \Delta H_f \text{ reactants}$$

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

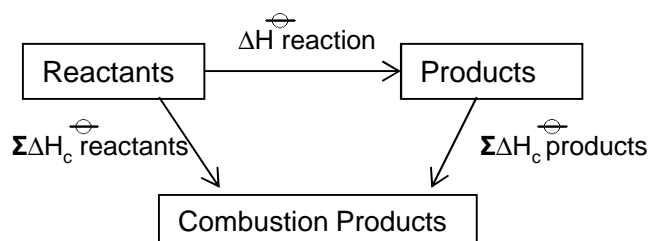
$$\Delta H_c = [(3 \times -394) + (3 \times -242)] - 20$$

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

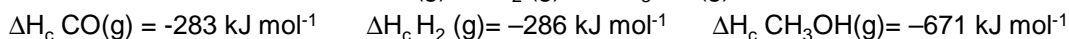
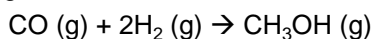


**Using Hess's law to determine enthalpy changes from enthalpy changes of combustion.**

$$\Delta H_{\text{reaction}} = \sum \Delta H_c \text{ reactants} - \sum \Delta H_c \text{ products}$$



**Example 3.** Using the following combustion data to calculate the heat of reaction

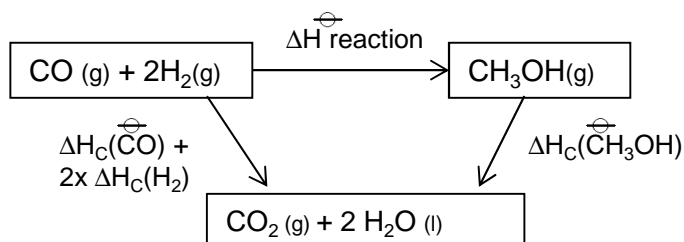


$$\Delta H_{\text{reaction}} = \sum \Delta H_c \text{ reactants} - \sum \Delta H_c \text{ products}$$

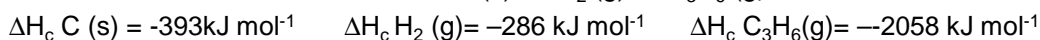
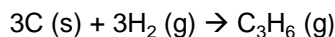
$$\Delta H = \Delta H_c(\text{CO}) + 2 \times \Delta H_c(\text{H}_2) - \Delta H_c(\text{CH}_3\text{OH})$$

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

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



**Example 4.** Using the following combustion data to calculate the heat of formation of propene

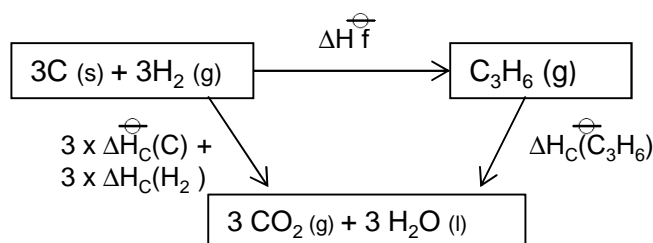


$$\Delta H = \sum \Delta H_c \text{ reactants} - \sum \Delta H_c \text{ products}$$

$$\Delta H_f = 3 \times \Delta H_c(\text{C}) + 3 \times \Delta H_c(\text{H}_2) - \Delta H_c(\text{C}_3\text{H}_6)$$

$$\Delta H_f = 3 \times -393 + 3 \times -286 - -2058$$

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



## 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,  $\Delta H_r$ )

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

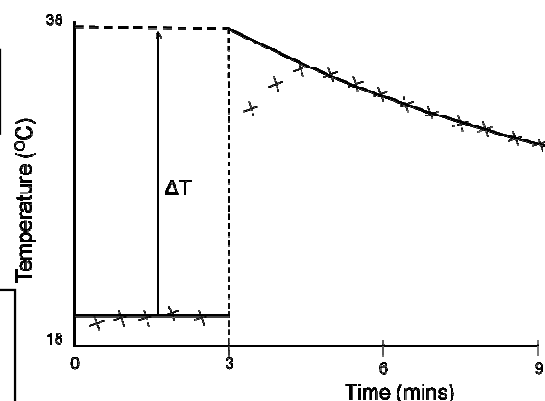
#### General method

- 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
- clamp thermometer into place making sure the thermometer bulb is immersed in liquid
- measure the initial temperatures of the solution or both solutions if 2 are used
- transfers reagents 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.
- stirs mixture
- Measures final temperature

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

- heat 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 heat absorbed by the apparatus.
- reaction or dissolving may be incomplete or slow.
- Density of solution is taken to be the same as water.

## 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 5.** 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 6.**  $25 \text{ cm}^3$  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 7.** 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

- Heat losses from calorimeter
- Incomplete combustion of fuel
- Incomplete transfer of heat
- 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

## Mean Bond energies

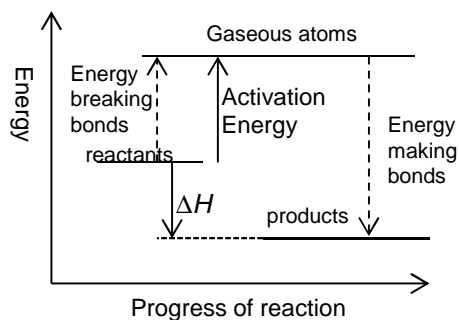
Definition: The Mean bond energy is the enthalpy needed to **break the covalent bond into gaseous atoms, averaged over different molecules**

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.

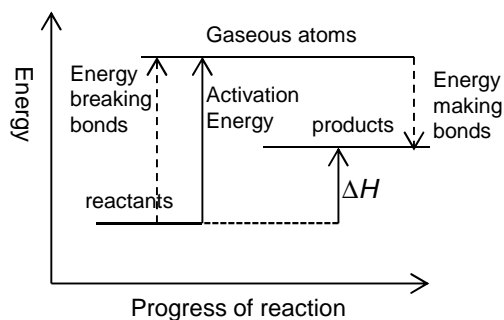
The definition only applies when the **substances start and end in the gaseous state**.

The value for the bond energy for the C-H bond in methane matches this reaction  $\frac{1}{4} \text{CH}_4(\text{g}) \rightarrow \text{C}(\text{g}) + \text{H}(\text{g})$



Reaction profile for an EXOTHERMIC reaction

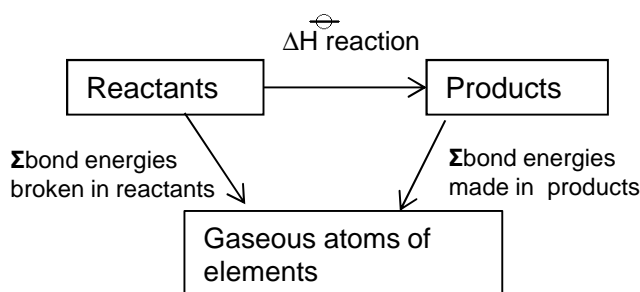
In an exothermic reaction the sum of the bonds in the reactant molecules will be less than the sum of the bonds in the product molecules



Reaction profile for an ENDOTHERMIC reaction

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

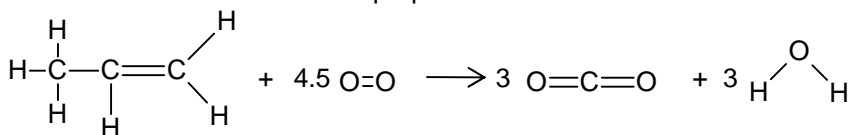
$$\Delta H = \Sigma \text{ bond energies broken} - \Sigma \text{ bond energies made}$$



$\Delta H$  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

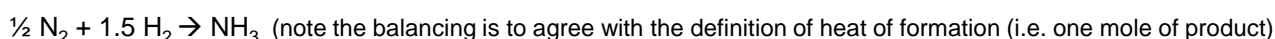


$\Delta H = \Sigma$  bond energies broken -  $\Sigma$  bond energies made

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

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>



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

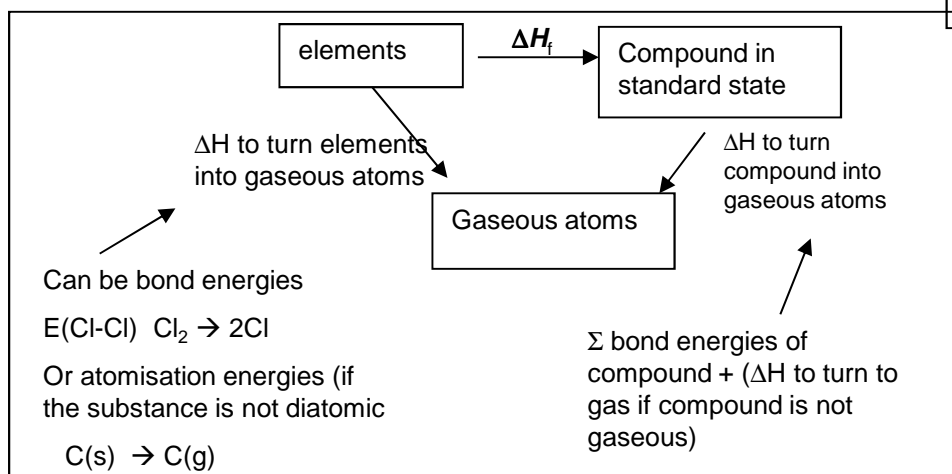
$\Delta H = \Sigma$  bond energies broken -  $\Sigma$  bond energies made

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

### A more complicated example that may occur at AS

Working out  $\Delta H_f$  of a compound using bond energies and other data

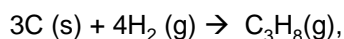
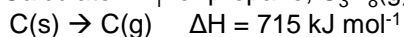
This is a more complicated example of the type in example 9



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

### Example 10

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



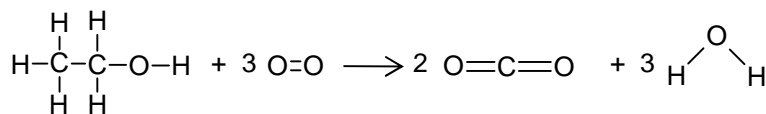
Bond	C-C	C-H	H-H
kJ mol <sup>-1</sup>	348	412	436

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

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

## Enthalpies of combustion in a homologous series

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

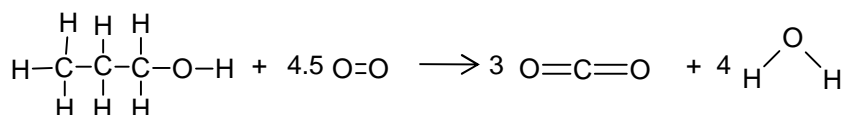


ethanol

**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

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

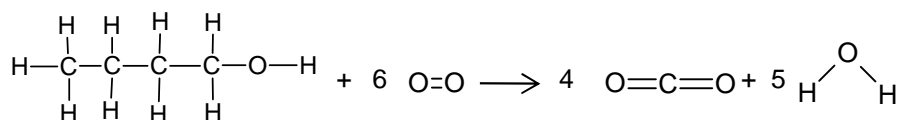


Propan-1-ol

**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

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



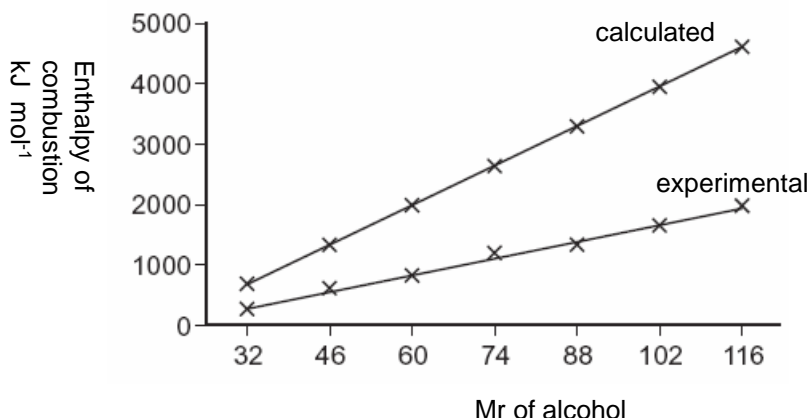
Butan-1-ol

**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

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

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.