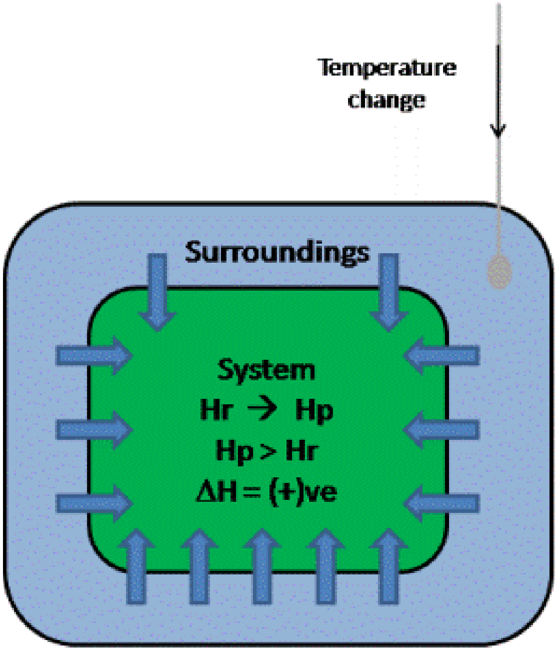
3A Energy

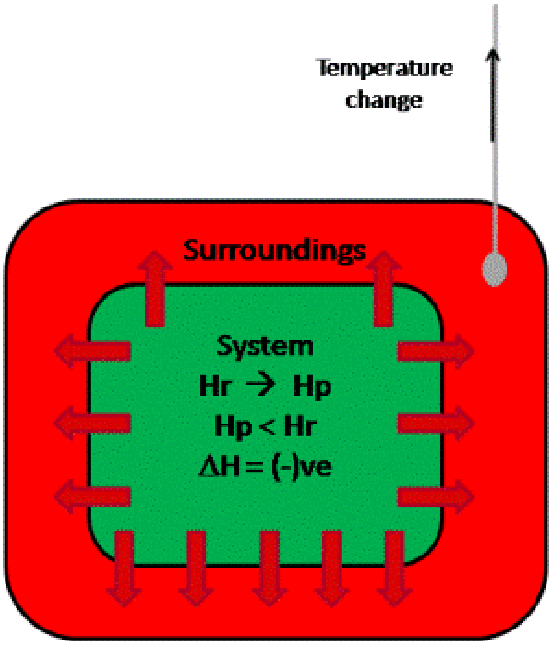
What is chemical energy?

- Chemical energy is a form of potential energy which is stored in chemical bonds.
- Chemical bonds are the attractive forces that bind atoms together.
- As a reaction takes place, bonds break in the reactants and new bonds are formed in the products.
- The difference in energies of the bonds between the atoms of reactants and products is called chemical energy.

Enthalpy, H

- Enthalpy, H, is the heat content that is stored in a chemical **system**, as **reactants or products**.
- It is impossible to measure the enthalpy content of a system directly but we can measure the differences in enthalpy contents.
- The difference in enthalpy contents is the energy either given out or absorbed.





- The energy exchanged with the **surroundings** can be given out as light, sound, electrical but is more usually heat.
- This change in enthalpy content is called **enthalpy change**.

Conservation of energy (First Law of thermodynamics)

Energy cannot be created or destroyed just transferred between the system and the surroundings

- The surroundings, water, tube, air either gains the energy given out by the system (hot)
- Or the surroundings, water, tube, air loses energy to the system (cold) - like ethanol evaporating from your hand
- This means that:

Heat loss in a chemical system	=	**Heat gain to the surroundings**	**Temperature increases**
Heat gain in a chemical system	=	**Heat loss to the surroundings**	**Temperature decreases**

- What your thermometer is measuring is the **surroundings**. That is - the water, tube, air the energy is transferred from / to.

Enthalpy change, ΔH:

- This is the difference between the enthalpy contents of the products and the reactants (at constant pressure):

$\Delta H = H_{products} - H_{reactants}$

- It is rare for enthalpy contents of products and reactants to be exactly equal.
- This means that there is almost always a transfer of energy between the **system** and the **surroundings**.

Exothermic reactions:

- This means that the enthalpy content of the **products** is **smaller** than the **reactants**.
- The excess energy is **transferred from the system to the surroundings - hot**

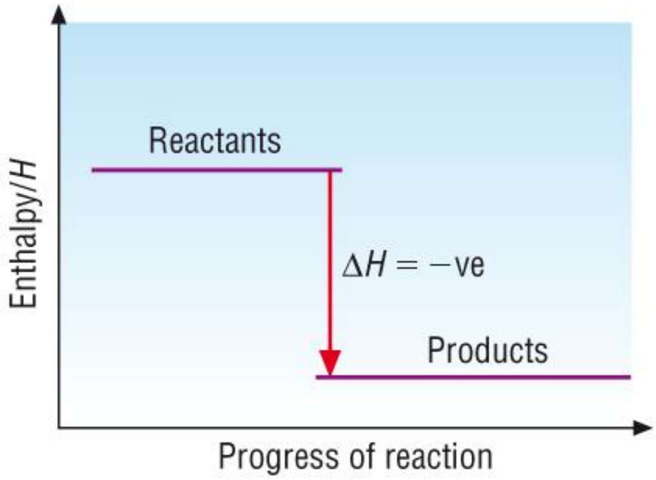
$H_{products} < H_{reactants}$

$\Delta H = H_{products} - H_{reactants}$

$\Delta H =$ **Small - Large**

$\Delta H =$ **Negative value**

Energy is released from the system to the surroundings



Endothermic reactions:

- This means that the enthalpy content of the **products** is **greater** than the **reactants**.
- The excess energy is **transferred to <u>system</u> from the surroundings - cold**

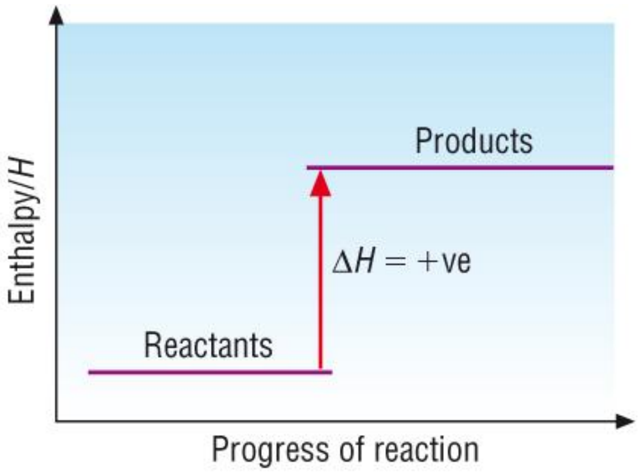
$H_{products} > H_{reactants}$

$\Delta H = H_{products} - H_{reactants}$

$\Delta H =$ Large - Small

$\Delta H =$ Positive value

Energy is transferred to the <u>system</u> from surroundings



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<u>Exothermic and endothermic reactions</u>

1) Oxidation of fuels:

- The most common example is the oxidation of methane forming carbon dioxide and water:

$$CH_{4(g)} + O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(g)} \quad \Delta H = -890 \text{ Kj mol}^{-1}$$

- The negative sign means that the reaction is **exothermic**.
- This means that $H_{products} < H_{reactants}$
- The units tell you that **890 Kj** of energy is given out per **mole** of methane.
- Changes in enthalpy are given in molar quantities:

Environmental impact - Example:

- A small car travelling 2 miles uses 200 - 250g of petrol, C_8H_{18}, $\Delta H = -5470$ KJ mol^{-1}.
- How much energy is needed and how much CO_2 is produced?

$$C_8H_{18(l)} + 12.5O_{2(g)} \rightarrow 8CO_{2(g)} + 9H_2O_{(g)} \quad \Delta H = -5470 \text{ Kj mol}^{-1}$$

200g

Moles = m / Mr

Moles = 200 / 114

Moles = 1.75 **1:8**

Moles ~ 2 → **Moles = 16**

Energy used = 2 x 5470

Volume = 16 x 24

Volume = 384 dm^3

2) Respiration:

- An important exothermic reaction providing energy for all living things:

$$C_6H_{12}O_{6(aq)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)} \quad \Delta H = -2801 \text{ Kj mol}^{-1}$$

Endothermic reactions:

1) Photosynthesis:

- An important endothermic reaction without which there would be no life.
- This reaction makes 'food', the starting point for all foods, and oxygen for respiration.
- Energy from the sun provides the energy to transfer from surroundings to system.

$$6CO_{2(g)} + 6H_2O_{(l)} \rightarrow C_6H_{12}O_{6(aq)} + 6O_{2(g)} \quad \Delta H = +2801 \text{ Kj mol}^{-1}$$

- The reverse reaction of respiration.

2) Thermal decomposition of limestone:

- Limestone contains calcium carbonate:

$$CaCO_{3(s)} \rightarrow CaCO_{(s)} + CO_{2(g)} \quad \Delta H = +178 \text{ Kj mol}^{-1}$$

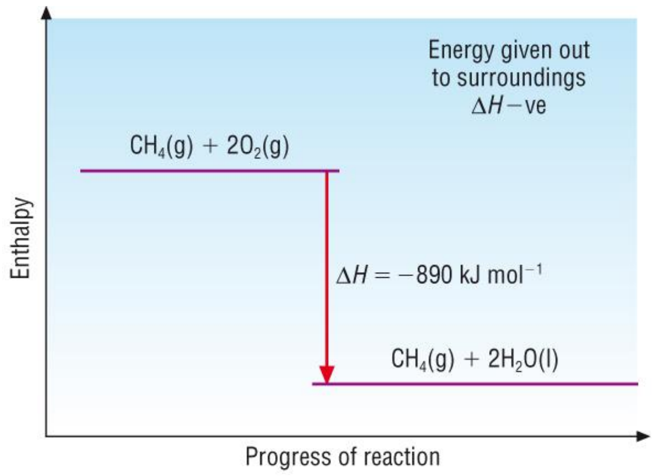
- Calcium oxide is commonly known as lime used in cement and used to treat soils by farmers.
- If water is added to lime, calcium oxide, heat is given off - exothermic reaction.

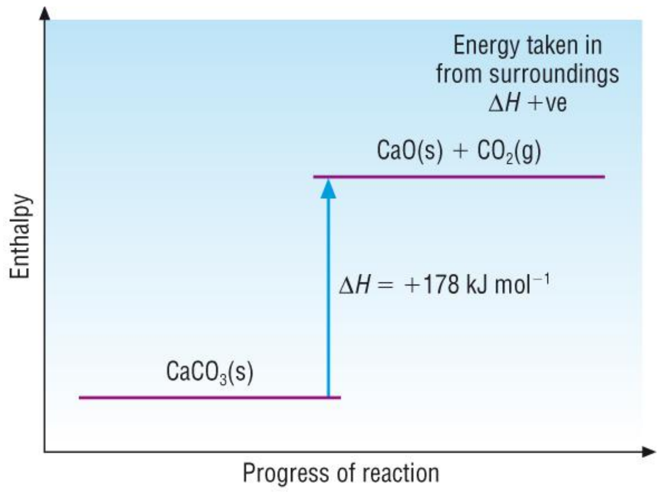
Questions 1 - 2 P187

Enthalpy profile diagrams

Simple enthalpy profile diagrams:

- Reactions and their enthalpy changes have been shown as simple **enthalpy profile diagrams**:





Exothermic reactions:

Where $H_{products} < H_{reactants}$

ΔH = negative

Endothermic reactions:

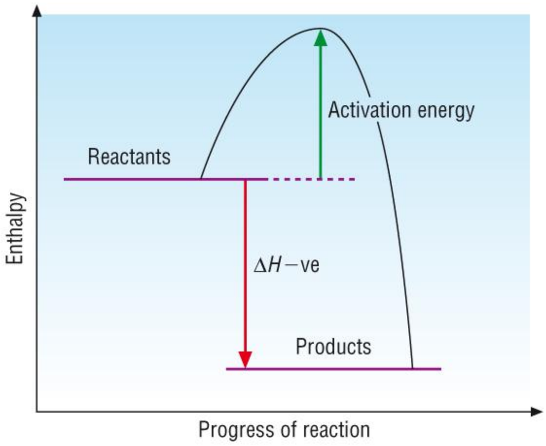
Where $H_{reactants} > H_{products}$

ΔH = positive

Activation energy:

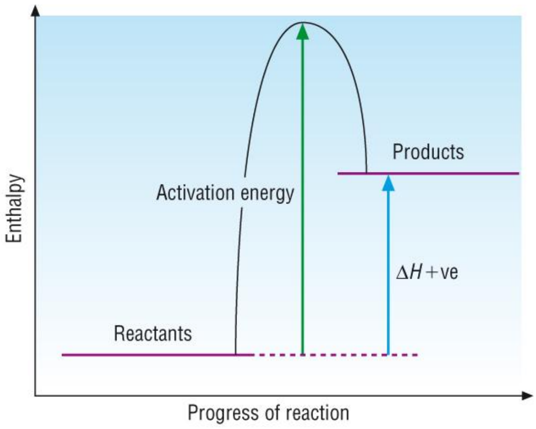
- The simple energy profile diagrams assumes that as soon as the reactants come in contact with each other a reaction takes place.
- Most reactions do not occur **'spontaneously'** but need a little bit of energy to get them going, a spark is needed to set gas alight.
- This **'bit of energy'** is called the **activation energy**. It is the energy required to **break the bonds in the reactants**.

Exothermic reactions:



- Even though the products are lower in energy than the reactants, a small amount of energy is needed to break the reactant bonds, the **activation energy**.
- We say the reaction has to overcome the energy barrier.
- After that, the exothermic nature of the reaction is enough to break more reactant bonds.
- A way of thinking of this is like a cyclist riding a bike up a small hill to gain a large amount of 'free wheeling' or energy.

Endothermic reactions:



- The products are higher in energy than the reactants, a small amount of energy is still needed to break the reactant bonds, the **activation energy**.
- The reaction has to overcome the energy barrier.
- This time there is no excess energy to break more reactant bonds, a sustained amount of energy needs to be continually supplied to keep the reaction going.
- This time the cyclist rides a bike up a large hill to gain a small amount of 'free wheeling' or energy.

Questions 1-2 P189

Standard enthalpy changes

Standards:

- Enthalpy changes for reactions will vary slightly depending upon the conditions under which the reaction is carried out.
- All data books have to have the same value for enthalpy changes.
- Chemists use **standard conditions** to ensure that all reactions and corresponding enthalpy changes are carried out under the same conditions.
- They are as close to normal lab conditions as possible.

Standard conditions:

Pressure at 100 kPa (which is 1 atmosphere) **Temperature at 298K (25°C)**

1 Mole or 1 Molar solutions

Normal physical states at standard temperature and pressure (above conditions)

A standard enthalpy change is shown by - ΔH^{θ}

H - Enthalpy

Δ - Change in

θ symbol represents **standard conditions**

Standard states:

- Standard enthalpy changes must have substances in their **standard states** under these standard conditions:

Substance	**Chemical symbol and state**	**Explanation**
Magnesium	$Mg_{(s)}$	Magnesium is a solid under standard conditions, **(s)**
Hydrogen	$H_{2(g)}$	Hydrogen is a gas under standard conditions, **(g)**
Water	$H_2O_{(l)}$	Water is a liquid under standard conditions, **(l)**

Standard enthalpy changes:

- There are 3 standard enthalpy changes that you need to know:

1) Standard enthalpy change of reaction, ΔH_r^θ

- For this enthalpy change we need a reaction to refer to.
- A value for the enthalpy change which is true for the molar quantities stated in the reaction:

$$H_{2(g)} + 1/2\ O_{2(g)} \rightarrow H_2O_{(l)} \quad \Delta H_r^\theta = -286\ KJMol^{-1}$$

For the reaction:

$$Fe_2O_{3(s)} + 2Al_{(s)} \rightarrow 2Fe_{(s)} + Al_2O_{3(s)}\ \Delta H^\theta_r = -851.50\ KJ\ Mol^{-1}$$

- For the same reaction with different stoichiometry:

$$1/2Fe_2O_{3(s)} + Al_{(s)} \rightarrow Fe_{(s)} + 1/2Al_2O_{3(s)}\ \Delta H^\theta_r = -425.75\ KJ\ Mol^{-1}$$

- Note that the reaction must be written in order for the information to be correct. ΔH^θ_r is half the value if the reaction is balanced using halves.

2) Standard enthalpy of combustion – ΔH^θ_c

- Combustion reactions are so common that they have a standard enthalpy change of their own:

Definition: The enthalpy change that occurs when 1 mole of a substance reacts completely with oxygen under standard conditions. All reactants and products are in their standard states.

ΔH^θ_c for ethane:

$$C_2H_{6(g)} + 3.5\ O_{2(g)} \rightarrow 3H_2O_{(l)} + 2CO_{2(g)} \quad \Delta H_c^\theta = -1560\ KJMol^{-1}$$

- ΔH^θ_c refers to the complete combustion of **1 mole** of ethane.
- This conforms with the definition -' **when 1 mole of a substance reacts completely with oxygen'**

3) Standard enthalpy change of formation, ΔH^{θ}_{f}

- Formation reactions are also so common that they have a standard enthalpy change of their own:

  Is the enthalpy change that takes place when 1 mole of a compound is formed from its constituent elements in their standard states under the standard conditions.

ΔH^{θ}_{f} for water:

$H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(l)}$ $\Delta H^{\theta}_{f} = -286$ KJ Mol^{-1}

- This refers to the **Standard enthalpy change of formation** of **1 mole of** water.
- This conforms with the definition -' **when 1 mole of a compound is formed from its elements'**

A problem:

- If we are forming an element H_2, there is no chemical change.
- We say that elements in their standard states under standard conditions have a standard enthalpy of 0 KJ Mol^{-1}

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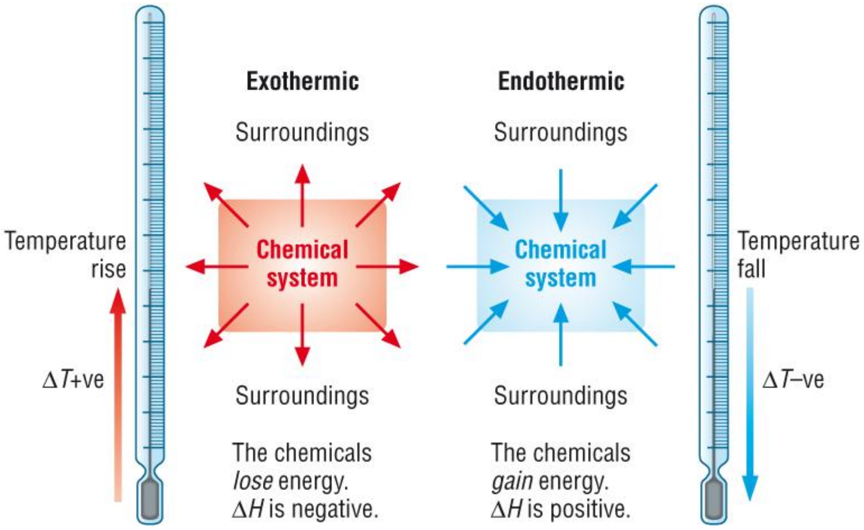
Determination of enthalpy changes

- Enthalpy content of reactants and products cannot be measured directly.
- You can measure the enthalpy change between the reactants and products - enthalpy change for a reaction, **ΔH_r**

Remember:

Heat loss in a chemical system = **Heat gain to the surroundings** **Temperature increases**

Heat gain in a chemical system = **Heat loss to the surroundings** **Temperature decreases**



- The enthalpy change for any reaction, **ΔH_r** is measured in **KJ Mol^{-1}**, which is **energy** per **mole**

- This means we need to know 2 things

  i) The energy change - for which we use temperature change

  ii) The amounts in moles of the limiting reagent that reacts

i) The energy change:

- To determine the energy change we use the formula:

  $$Q = \frac{mc\Delta T}{1000}$$

  Q – quantity of energy exchanged J, the 1000 converts J to kJ
  m – mass of the water g (ie cm^3 as the density if water is 1 gcm^{-3})
  c – specific heat capacity j g^{-1} K^{-1}
  ΔT – rise in temperature K, ($T_{initial}$ - T_{final})
- **Convert the energy calculated into KJ (divide by 1000).**

ii) Calculate the number of moles used:

$$\text{No Moles} = \frac{\text{Mass}}{\text{Mr}} \text{ or } c \times V$$

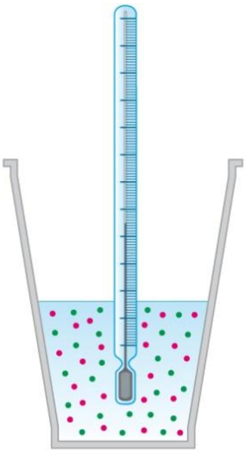
iii) Calculate the amount of energy exchanged per mole , this is the enthalpy:

$$\text{Enthalpy} = \frac{\text{Energy}}{\text{Moles}}$$

- **Check you have the sign correct:**

(-)ve for exothermic reactions **(+)ve for endothermic reactions**

Direct determination of enthalpy changes:



The particles are dissolved in the solution. The heat is exchanged from the particles into the solution. The heat exchange is measured using the thermometer.

- Most reactions involve adding one reactant to another and measuring the temperature rise.
- This is called direct determination and is carried out in a calorimeter.
- A calorimeter is an insulated reaction vessel which minimises heat exchange to the air as the surroundings we measure is the water / solvent.
- The simplest calorimeter is a polystyrene cup but they can get quite complex.

Example:

Excess Mg is added to 100cm^3 of 2.00 Mol dm^{-3} $CuSO_4$, the temperature rose from 20.0^{o}C to 65^{o}C.

i) The energy change:

Q = (m x c x ΔT) / 1000
Q = (100 x 4.18 x 45) / 1000
Q = 18.810 kJ
Temp rises, it is exothermic therefore is negative
Q = - 18.81 kJ

ii) Calculate the number of moles used:

No Moles = c x V
No Moles = 2 x 0.100
No Moles = 0.2

iii) Calculate the amount of energy exchanged per mole , this is the enthalpy:

Enthalpy = $\frac{\text{Energy}}{\text{Moles}}$

Enthalpy = $\frac{-18.81}{0.2}$

Enthalpy = - 94.05 Kj Mol^{-1}

Finally write the equation with the enthalpy change:

$$Mg_{(s)} + CuSO_{4(aq)} \rightarrow MgSO_{4(aq)} + Cu_{(s)} \quad \Delta H_r^\theta = -94.05\ KjMol^{-1}$$

Questions 1 - 2 P193

Enthalpy change of combustion

- This is any reaction involving oxygen forming oxides:

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(l)} \quad \Delta H_c^\theta = -890\ KjMol^{-1}$$

$$H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(g)} \quad \Delta H_c^\theta = -286\ KjMol^{-1}$$

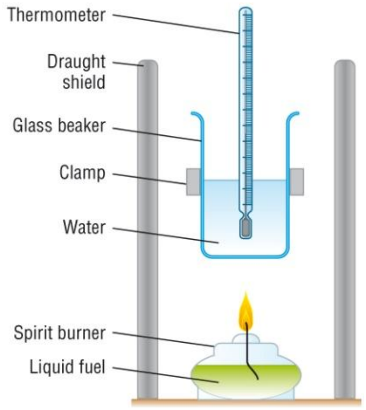
$$Al_{(s)} + 3/4O_{2(g)} \rightarrow 1/2\ Al_2O_{3(s)} \quad \Delta H_c^\theta = -1676\ KjMol^{-1}$$

Experimental determination of ΔH_c

- The enthalpy change of combustion, **ΔH_c** is also measured in **KJ Mol^{-1}**, which is **energy** per **mole**
- This means we need to know 2 things

i) The energy change - for which we use temperature change when heating water

ii) The amounts in moles of fuel used



- To calculate **ΔH_c**, measure a known mass (volume) of water - for **$Q = (mC\Delta T) / 1000$**.
- Take the initial temperature of the water.
- Weigh the burner before heating.
- Heat to raise the temperature by about 10°C.
- Take a final temperature.
- Reweigh the burner to get a mass of fuel used.

Example:

1.5g of propan-1-ol heated 250cm^3 of water by 45°C.

i) The energy change:

$Q = (m \times c \times \Delta T) / 1000$

$Q = (250 \times 4.18 \times 45) / 1000$

$Q = 47.025$ kJ **Temp rises, it is exothermic therefore is negative**

$Q = -47.025$ kJ

ii) Calculate the number of moles used:

No Moles = $\frac{\text{Mass}}{\text{Mr}}$

No Moles = $\frac{1.5}{60}$

No Moles = 0.025

iii) Calculate the amount of energy exchanged per mole , this is the enthalpy:

Enthalpy = $\frac{\text{Energy}}{\text{Moles}}$

Enthalpy = $\frac{-47.025}{0.025}$

Enthalpy = - 1881 Kj Mol^{-1}

Comparison of experimental value with standard enthalpy change:

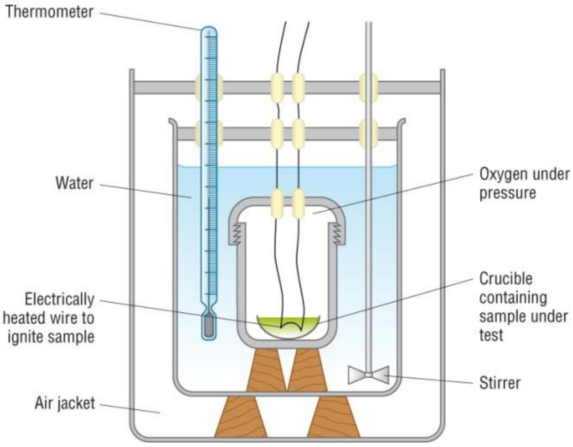
Standard enthalpy change of combustion of C_3H_7OH, ΔH_c^{θ} - 2021 Kj Mol^{-1}

Experimental enthalpy change of combustion of C_3H_7OH, ΔH_c - 1881 Kj Mol^{-1}

Errors:

- **Incomplete combustion of the fuel - less heat energy given out**
- **Heat loss to the surroundings - less heat energy measured**

Improvements:



- Use a **Bomb calorimeter** (left).
- This apparatus reduces heat loss s the water is insulated from the surroundings.
- It is burnt in oxygen to ensure complete combustion.

Questions 1-2 P195

<u>Bond enthalpies</u>

Bond enthalpy:

Is the enthalpy change that takes place when breaking by homolytic fission1 mole of a given bond in the molecules of a gaseous species

- To summarise - it is the energy required to break 1 mole of bonds in the gaseous state.

Breaking bonds	=	**Energy is put in to break bonds**	**Endothermic process**
Forming bonds	=	**Energy is released when bonds are formed**	**Exothermic process**

- Some examples:

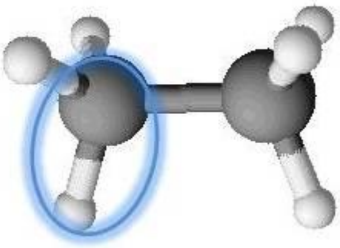
$$H - H_{(g)} \rightarrow 2H_{(g)} \qquad \Delta H = +436\ KjMol^{-1}$$

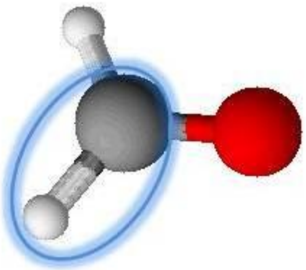
$$H - Cl_{(g)} \rightarrow H_{(g)} + Cl_{(g)} \qquad \Delta H = +432\ KjMol^{-1}$$

- These bonds enthalpies can only exist in these examples but some bonds can exist in very different molecules.
- In cases like this we use the **Average bond enthaply**

Average bond enthalpy:

- Bonds like C - H exist in all hydrocarbons but their bond enthalpies will vary depending on their environment:

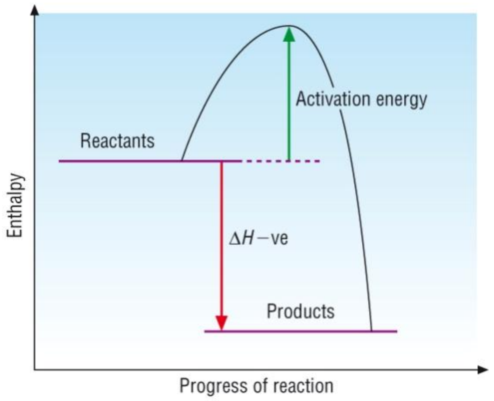


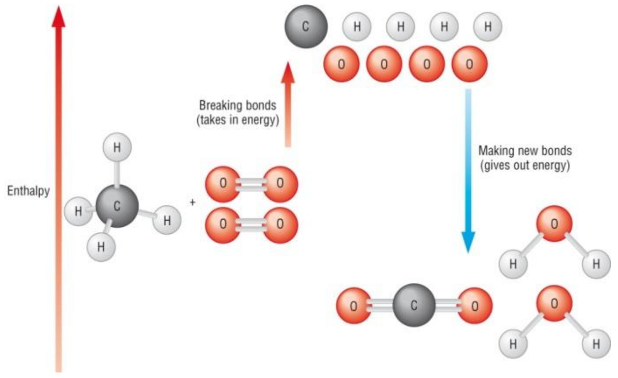


- The C - H bond enthalpy will be different in an alkane than the C - H bond enthalpy in an aldehyde where the C atom is adjacent to an oxygen atom.
- For bond enthalpies that are common, we use **average bond enthalpies:**

Bond	**Average bond enthalpy / KJ Mol^{-1}**
C - H	**+413**
O = O	**+497**
O - H	**+463**
C = C	**+612**
H - H	**+436**

Breaking and making bonds:





- In this and any reaction, reactant bonds will be broken and new product bonds will be formed.
- When **bonds are broken** energy is required making it an **endothermic** process, **the activation energy**.
- When new **bonds are formed** energy is release making it an **exothermic** process.
- If the **energy released** when new bonds form making the products **is greater** than the **energy needed** to break the bonds of the reactants, the reaction is **exothermic**.
- If the **energy released** when new bonds form making the products **is less** than the **energy needed** to break the bonds of the reactants, the reaction is **endothermic**.
- Strong bonds require lots of energy to break but they also release lots of energy when they form:

Breaking strong bonds → Forming weak bonds Endothermic process
Breaking weak bonds → Forming strong bonds Exothermic process

Using bond enthalpies to determine enthalpy changes:

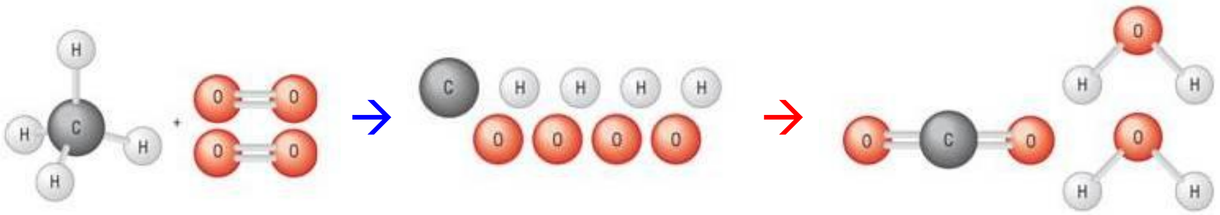
- The symbol Σ is used for 'sum of' or adding together

Energy required to break bonds = Σ (Bond enthalpies of bonds broken)
Breaking weak bonds = Σ (Bond enthalpies of bonds formed)

Formula:

$$\Delta H = \Sigma\text{ (Bond enthalpies of bonds broken)} - \Sigma\text{ (Bond enthalpies of bonds formed)}$$

Worked example:



Σ (Bond enthalpies of bonds broken) **Σ (Bond enthalpies of bonds formed)**

Reactants				Products			
Bond	Number	Bond energy	Total	Bond	Number	Bond energy	Total
C - H	4	413	1652	C = O	2	805	1610
O = O	2	497	994	O - H	4	463	1852
Σ (Bond enthalpies of bonds broken) =			2646	Σ (Bond enthalpies of bonds formed) =			3462

$$\Delta H = \Sigma\text{ (Bond enthalpies of bonds broken)} - \Sigma\text{ (Bond enthalpies of bonds formed)}$$

$$\Delta H = 2646 - 3462$$

$$\Delta H = -816\text{ Kj Mol}^{-1}$$

Questions 1-2 P197

Enthalpy changes from ΔH_c^θ - Hess's law

Measuring enthalpy changes indirectly:

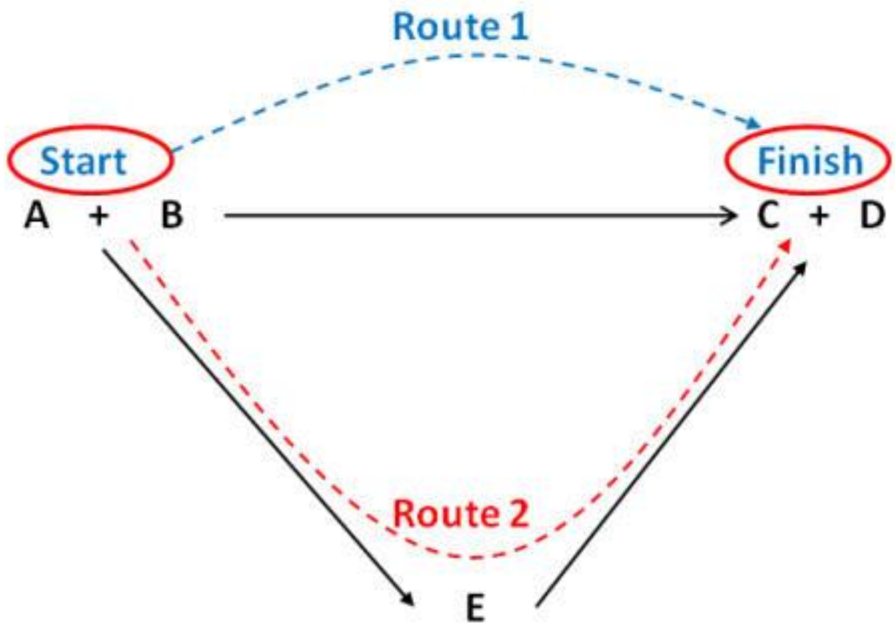
- Sometimes it is not possible to measure an enthalpy change directly.
- This may be due to:

High activation energy
Slow rate of reaction
More than one reaction occurring at the same time

- Hess's law allows us to work out enthalpy changes that are not possible to measure:

Definition: Hess's Law

> **The total enthalpy change accompanying a chemical change is independent of the route by which the chemical change takes place provided the initial and final conditions are the same.**



- If this was not true, it could be possible to gain energy via route A instead of going via route B. This would break the **1st law of thermodynamics**.
- It is found that reactants can be converted into the same products by more than 1 route.
- The total energy for each route is the same: These are called **Enthalpy cycles**.

Using Hess's law: Enthalpy cycles

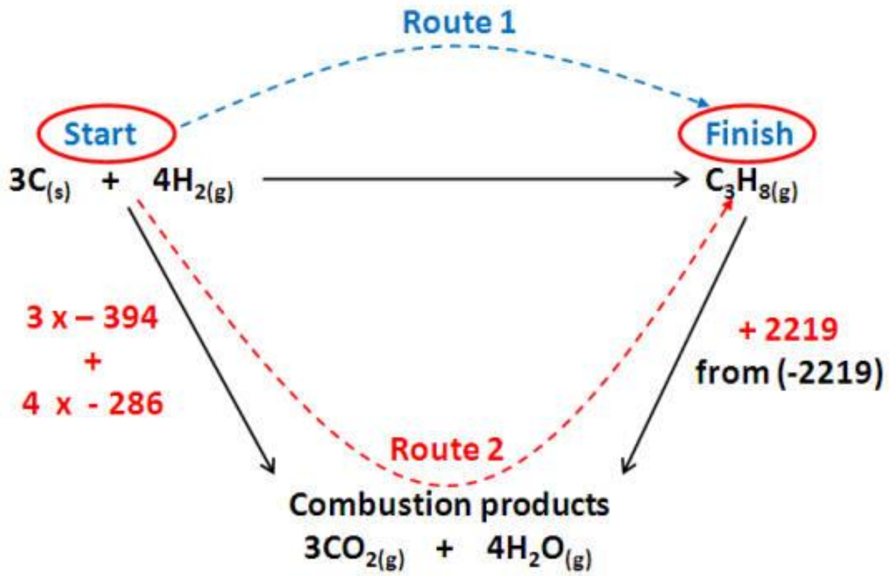
- Enthalpy cycles are used to determine enthalpy changes for reactions that are not easily measured directly.
- This can be done in 2 ways:
    1. **Enthalpy changes of combustion**
    2. **Enthalpy changes of formation**

1 Calculating ΔH^{θ} from enthalpy changes of combustion:

- Consider the enthalpy change below:

$$3C_{(s)} + 4H_{2(g)} \rightarrow C_3H_{8(g)}$$

- Combustion reactions can be used to find this enthalpy change as carbon hydrogen and propane all burn in oxygen.
- This means that their enthalpy changes of combustion can all be measured
- Constructing an enthalpy cycle:



- **we use the opposite sign for - 2219 as our route, Route 2 goes the opposite way to the enthalpy change**

Route 2 = (3 x - 394) + (4 x - 286) + 2219

Route 2 = - 107 Kj Mol^{-1}

Remember

Route 1 = Route 2

Route 1 = - 107 Kj Mol^{-1}

Using the formula:

$$\Delta H = \Sigma \Delta H_c^{\theta} \text{ (reactants)} - \Sigma \Delta H_c^{\theta} \text{ (products)}$$

$$\Delta H = (3 \times -394) + (4 \times -286) - -2219$$

$$\Delta H = -107 \text{ Kj Mol}^{-1}$$

Question 1 P199

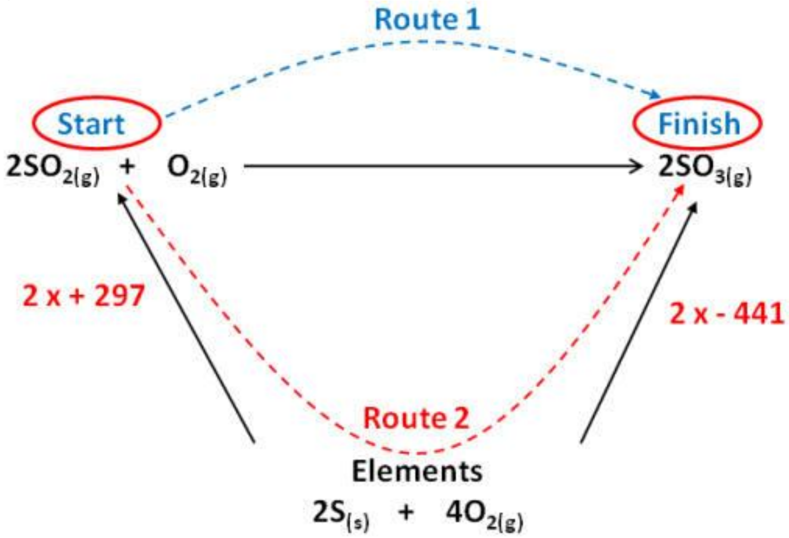
Enthalpy changes from ΔH^θ_f - Hess's law

Using enthalpy change of formation

- As with enthalpy changes of combustion, enthalpy changes of formation can be used in Hess's cycles to work out enthalpy changes.
- Consider the reaction:

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

- The enthalpy cycle would be:



- **we use the opposite sign for - 297 = + 297 as our route, Route 2 goes the opposite way to the enthalpy change**

Route 2 = (2 x + 297) + (2 x - 441)

Route 2 = - 288 Kj Mol^{-1}

Remember

Route 1 = Route 2

Route 1 = - 288 Kj Mol^{-1}

Using the formula:

$$\Delta H = \Sigma \Delta H_f^\theta \text{ (products)} - \Sigma \Delta H_f^\theta \text{ (reactants)}$$

$$\Delta H = (2 \times -441) - (2 \times -297)$$

$$\Delta H = -288 \text{ Kj Mol}^{-1}$$

Other enthalpy cycles:

- As long as there is a link between reactants and products, Hess's law can be applied and enthalpy cycles can be constructed.
- Follow the principles as outlined above and you won't go wrong.

Summary of enthalpy cycles:

Step 1:- Write a balanced chemical equation for the reaction.

Step 2:- Construct the Enthalpy cycle.

Step 3:- Decide on your routes and draw them on the cycle

Step 4:- Write in the ΔH^{θ} for each compound / element next to the arrows.

Step 5:- Look up the values of each ΔH^{θ} and write them in. Add them up for each route.

Step 6:- Write out Hess's law – Route 1 = Route 2

Step 7:- Put in your numbers.

Step 8:- Calculate ΔH^{θ}

Question 1-2 P201 / 1-7 P215 / 1,3-5 P217