5.1 - Exothermic and Endothermic Reactions

5.1.1 - Define the terms *exothermic reaction*, *endothermic reaction* and *standard enthalpy change of reaction*

Exothermic Reaction - A reaction that causes the temperature of the surroundings to increase.

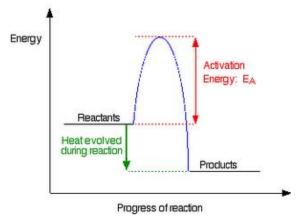
Energy is lost, or released, in the reaction, as the enthalpy of the products is less than the enthalpy of the reactants.

Endothermic Reaction - A reaction that causes the temperature of the surroundings to decrease.

Energy is used up in the reaction, as the enthalpy of the products is greater than the enthalpy of the reactants. Most endothermic reactions are not spontaneous

Standard Enthalpy Change of Reaction - The difference between the products and the enthalpy of the reactants under standard conditions.

This is affected by temperature, pressure, concentration of solutions and physical state. Therefore, we have to make sure that these are specified, otherwise results are not comparable. The **standard conditions** of heat energy transfer are pressure **101.3kPa** and temperature **298K**. Only the change in H can be measured for a given for a reaction, not H for the initial or final state of the species.





5.1.2 - State that combustion and neutralisation are exothermic reactions

Combustion is an exothermic reaction as heat energy is released into the surroundings

 $CH_4 + O_2 \rightarrow CO_2 + H_2O$

Neutralisation reactions are exothermic

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$

These are the reactions between acids and bases to form salt and water

5.1.3 - Apply the relationship between temperature change, enthalpy change and the classification of reactions as endothermic or exothermic

When the enthalpy of the products is greater than the reactants, energy is absorbed from the surroundings: an endothermic reaction. The temperature of the surroundings decreases

• This kind of reaction is used for ice packs in sports injuries

This is represented mathematically as the enthalpy of the products minus that of the reactants to find the change

$\Delta H = H_P - H_R$

When the change is **negative**, energy is lost to the surroundings, making the reaction **exothermic**

When the change is **positive**, energy is used from the surroundings, making the reaction **endothermic**

A **thermochemical equation** is when the equation is written with an associated change in enthalpy

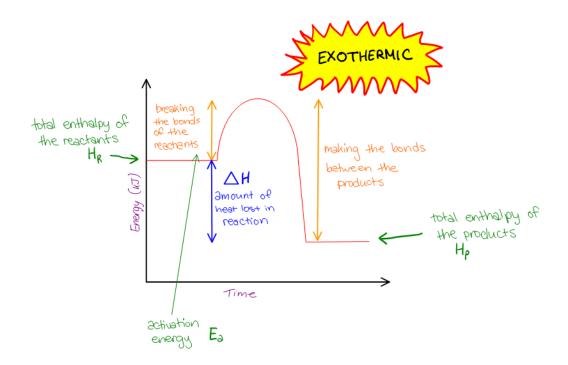
$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta H = -890 kJ \ mol^{-1}$$

$$NH_4NO_{3(s)} + aq \rightarrow NH_4^+_{(aq)} + NO_3^-_{(aq)} \qquad \Delta H = +25 \, kJ \, mol^{-1}$$



5.1.4 - Deduce, from an enthalpy level diagram, the relative stabilities of reactants and products, and the sign of the enthalpy change for the reaction

Enthalpy level diagrams, or energy profile diagrams, allow us to visualise what happens to the enthalpy of a reaction as it proceeds



The total enthalpy of the reactant species is labelled H_{R} , the products H_{P}

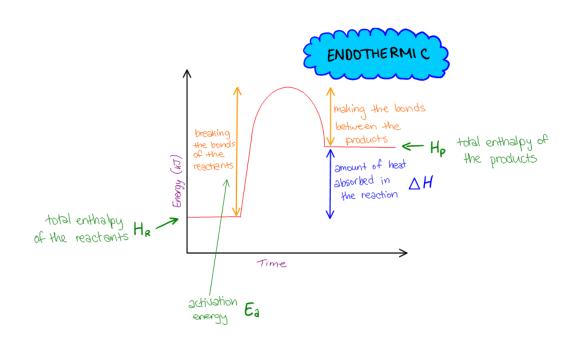
The <u>bonds between the reactants must first be broken</u> before they can be converted into products. They must collide with sufficient energy for this to happen. Some of this kinetic energy is converted into vibrational <u>energy</u>, <u>which overcomes the bonds</u> when it reaches a certain magnitude. Only then can the reaction be initiated

This amount of energy is known as the **activation energy**, E_a , seen as a hump on the diagram

The <u>distance between H_R and the top of the hump</u> is the total amount of activation energy required. This is always a positive value

When bonds are made to form the products, this always releases energy, causing the diagram to drop at H_P



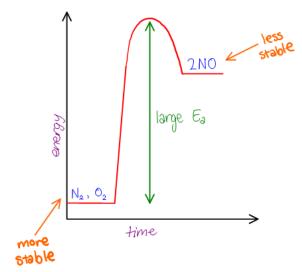


We can also deduce the relative stabilities of the reactants and products

The higher the enthalpy, the less stable the substance

In exothermic reactions, the products have a lower enthalpy than the reactants, and so are more stable, and vice versa for endothermic reactions. Large activation energies indicate strong bonds in the reactants, i.e.

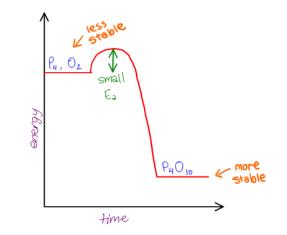
$$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(G)} \qquad \Delta H = +180.6 \ kJ \ mol^{-1}$$





Other reactions have small activation energies. The reaction with white phosphorus below is exothermic. White phosphorus is highly reactive and dangerous, so the less reactive red phosphorus is used in safety matches

 $P_{4(s)} + 5O_{2(q)} \rightarrow P_4O_{10(s)} \qquad \Delta H = -3008 \, kJ \, mol^{-1}$



The instability of the reactants makes it easier for their bonds to be broken, which is why the activation energy is so low.

Here are a few more reactions you need to be aware of:

Ionisation – Endothermic

$$Na_{(g)} \rightarrow Na^+_{(g)} + e^- + \Delta H$$

Change of State: Melting, Evaporation and Sublimation - Endothermic

$$H_2 \mathbf{0}_{(s)} \rightarrow H_2 \mathbf{0}_{(l)} + \Delta H$$
$$H_2 \mathbf{0}_{(l)} \rightarrow H_2 \mathbf{0}_{(g)} + \Delta H$$
$$I_{2(s)} \rightarrow I_{2(g)} + \Delta H$$



Change of State: Vaporisation and Condensation – Exothermic

$$H_2 O_{(g)} \rightarrow H_2 O_{(l)} - \Delta H$$
$$H_2 O_{(l)} \rightarrow H_2 O_{(s)} - \Delta H$$
$$I_{2(g)} \rightarrow I_{2(s)} - \Delta H$$

Remember that **bond breaking is endothermic** and **bond making is exothermic**

Summary

Type of Thermochemical Reaction	Exothermic	Endothermic
Enthalpy change	Products < Reactants	Products > Reactants
ΔН	negative	positive
Change in surrounding temperature	increases	decreases
Enthalpy level diagram	(D) 160mg	(c) Klong



5.2 – Calculation of Enthalpy Changes

5.2.1 - Calculate the heat energy change when the temperature of a pure substance is changed

Specific Heat Capacity – Symbol c – The amount of heat energy required to raise the temperature of 1.00g of the substance by 1.00°C or 1.00K

Substance	Specific Heat Capacity (J °C ⁻¹ g ⁻¹)
Water	4.18
Aluminium	0.889
Ammonia	2.06
Copper	0.386
Ethanol	2.46
Gold	0.128
Iron	0.448

The specific heat capacity for some common substances is shown below

The equation to calculate the heat energy change is

$$q = m \times c \times \Delta T$$

q = heat energy change – J

m = mass of the substance - g

c = specific heat capacity of the substance – J °C⁻¹ g⁻¹ or J K⁻¹ g⁻¹

 ΔT = change in temperature - °C or K

For the equation to work, all these figures must relate to the one substance



5.2.2 - Design suitable experimental procedures for measuring the heat energy changes of reactions

Here, you need to know two types of experiments. One involves a **reaction in aqueous solution** and the other involves **combustion reactions**.

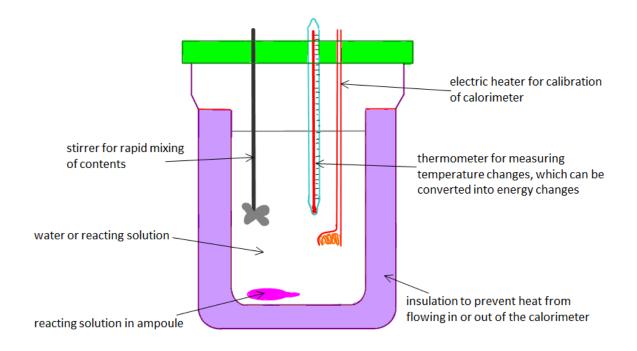
A simple <u>Calorimetry</u> is the most appropriate method here. In this type of procedure, the heat energy released is measured

The heat transfers to the can of water holding the reactants; however this is an **incomplete transfer**. The calculations of enthalpy change are based on the temperature change of the water and the mass of the fuel.

Reactions in Aqueous Solutions

These reactions can be done in a simple calorimeter, such as a **Styrofoam cup**. The volume of water must be accurately known for accurate calculations.

There will always be error in this measurement as <u>heat is lost to the surroundings</u>, as well as the can





Combustion Reactions

For these reactions, we measure the amount of heat produced by the combustion of **one mole of the fuel**. Note that this is not necessarily the same as the <u>enthalpy of combustion</u>. The <u>heat of combustion</u> for the reaction below is actually 5464 kJ mol⁻¹, however the enthalpy is twice this because there are two moles of octane involved.

 $2C_8H_{18(g)} + 25O_2 \rightarrow 16CO_{2(g)} + 18H_2O_{(l)} \qquad \Delta H = -10928 \, kJ \, mol^{-1}$

When the fuels are used in the form of complex mixtures, the heat of combustion is expressed as $kJ g^{-1}$ or $MJ dm^{-3}$

Hydrocarbon	Heat of Combustion		
	kJ mol⁻¹	kJ g⁻¹	
Methane	889	55.6	
Ethane	1557	51.9	
Propane	2217	50.4	
Butane	2874	49.6	
Octane	5464	47.9	

Some examples of the heat of combustion for certain compounds are given below

Common Fuels	Heat of Combustion	
	kJ g ⁻¹	MJ dm ⁻³
Liquid Hydrogen	142	286
Ethanol	29.7	19.6
Petrol	47.3	29.0
Diesel	44.8	32.2
LPG	51	22.2
Wood	15	n/a
Brown, dried coal	25	n/a
Black, dried coal	32	n/a



5.2.3 - Calculate the enthalpy change for a reaction using experimental data on temperature changes, quantities of reactants and mass of water

In thermochemical equations, the value for ΔH is always given for the equation exactly as it is written. Therefore, if you double the equation, then ΔH is also doubled. Also, if the reaction is reversed [swapping the products and the reactants], then the **sign changes**. Compare the equations below

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta H = -890 \ kJ \ mol^{-1}$$

$$2CH_{4(g)} + 4O_{2(g)} \rightarrow 2CO_{2(g)} + 4H_2O_{(l)} \qquad \Delta H = -1780 \ kJ \ mol^{-1}$$

$$CO_{2(g)} + 2H_2O_{(l)} \rightarrow CH_{4(g)} + 2O_{2(g)} \qquad \Delta H = +890 \ kJ \ mol^{-1}$$

For example:

Calculate the amount of energy released when 500cm3 of methane gas at STP reacts with excess air according to the equation

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta H = -890 \, kJ \, mol^{-1}$$

$$n(CH_{4}) = \frac{V}{V_{m}} = \frac{0.500}{22.4} = 0.0223 \text{ mol}$$

The equation tells us that 1 mol CHy releases 890 k) energy

$$\frac{\$90}{1} = \frac{x}{0.0223}$$

 $x = 890 \times 0.0223 = 19.9 \text{ k}$

Therefore, the energy released in this combustion reaction is 19.9 kJ



5.2.4 - Evaluate the results of experiments to determine enthalpy changes

Basically what you need to do here is take the results from an experiment, put them into the equation, and do the appropriate calculations.

$q = m \times c \times \Delta T$

Once you have done this, you also need to be able to **consider the problems or errors with the results**. These should include:

- In combustion reactions, <u>heat is lost</u> to the surroundings
- There is a great deal of error in this method
 - Does not allow for the heat energy absorbed by the can or polystyrene cup
- Therefore, the calculated heat energy change is inaccurate

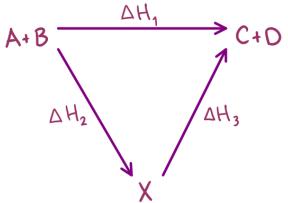


5.3 - Hess's Law

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

The energy difference between two states is independent of the route between them

 i.e. The heat evolved or absorbed in a chemical process is the same, whether the process takes place in one or several steps



Energy can be neither created nor destroyed, it can only change state. This law can be used to determine the enthalpy of a reaction by manipulating known equations that could be used as a <u>reaction pathway</u> to the desired reaction

i.e. To determine the enthalpy for $A + B \rightarrow C + D$, we can use

 $A + B \rightarrow X$ and $X \rightarrow C + D$

The reactions are added. They are all put into an enthalpy cycle to show the relationship between them.



$$\begin{split} & \mathsf{N}_{2(q)} + 2\mathsf{O}_{2(q)} \rightarrow 2\mathsf{NO}_{2(q)} \quad \Delta \mathsf{H} = \mathsf{x} \\ & \mathsf{Using}: \\ & \textcircled{O} \quad \mathsf{N}_{2(q)} + \mathsf{O}_{2(q)} \rightarrow 2\mathsf{NO}_{(q)} \quad \Delta \mathsf{H} = +180 \text{ kJ mol}^{-1} \\ & \textcircled{O} & 2\mathsf{NO}_{2(q)} \rightarrow 2\mathsf{NO}_{(q)} + \mathsf{O}_{2(q)} \quad \Delta \mathsf{H} = +112 \text{ kJ mol}^{-1} \\ & \texttt{Method:} \\ & \mathsf{Reverse the second reaction:} \\ & \mathsf{2\mathsf{NO}}_{(q)} + \mathsf{O}_{2(q)} \rightarrow 2\mathsf{NO}_{2(q)} \quad \Delta \mathsf{H} = -112 \text{ kJ mol}^{-1} \\ & \mathsf{Add the equations:} \\ & \mathsf{N}_{2(q)} + \mathsf{O}_{2(q)} + 2\mathsf{NO}_{2(q)} \rightarrow 2\mathsf{NO}_{2(q)} \rightarrow 2\mathsf{NO}_{2(q)} \rightarrow 2\mathsf{NO}_{2(q)} \\ & \mathsf{Cancel out any}^{\mathcal{O}} \qquad \Delta \mathsf{H} = (+18\mathsf{O} - 112) \text{ kJ mol}^{-1} \\ & \mathsf{Simplify:} \\ & \mathsf{N}_{2(q)} + 2\mathsf{O}_{2(q)} \rightarrow 2\mathsf{NO}_{2(q)} \quad \Delta \mathsf{H} = +68 \text{ kJ mol}^{-1} \\ \end{split}$$



5.4 - Bond Enthalpies

5.4.1 - Define the term average bond enthalpy

Average Bond Enthalpy - The amount of energy required to break one mole of bonds in the gaseous state averaged across a range of compounds containing that bond.

For example, in determining the bond enthalpy of C-H:

 $CH_{4(q)} \rightarrow C_{(q)} + 4H_{(q)} \qquad \Delta H = +1662 \, kJ \, mol^{-1}$

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

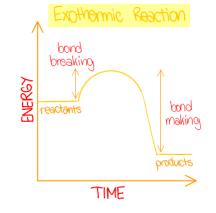
Bond breaking

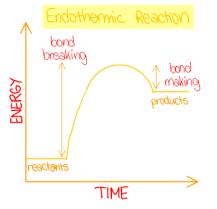
This is an endothermic process, as energy is absorbed to break the bonds between the atoms.

Bond making

This is an exothermic process, as energy is released when the bonds form between the atoms.

If more energy is released in the formation of bonds in the products that was required to break the bonds of the reactants, then the reaction is **exothermic.** If more energy is required to break the bonds of the reactants than is released in the formation of bonds in the products, then the reaction is **endothermic**







http://ibscrewed4chemistry.blogspot.com/

The bond enthalpies are used to calculate the enthalpies of the reaction. This is only approximate because only average bond enthalpies are used

Enthalpy of Reaction =
$$\sum D$$
 (bonds broken) - $\sum D$ (bonds formed

 $\pmb{\Sigma}$ is the sum of the terms

D is the bond enthalpy per mole of bonds

For example:

