OCR A Chemistry A-level

Module 3.2: Physical Chemistry

Detailed Notes

3.2.1 Enthalpy Changes

Enthalpy Change

Enthalpy change is heat energy change and is represented by the symbol $\Delta H^{\ominus}$. Enthalpy is measured under standard conditions of **100 kPa pressure** and a specified temperature, generally **298 K**. Standard states are the physical states of reactants under standard conditions.

In a reaction, bonds are broken and then bonds are made. For bonds to be **broken**, energy is **taken in** from the surroundings and when bonds are **formed**, energy is **given out**. The overall energy change of the reaction depends on how much energy is transferred in these processes.

When energy is taken in from the surroundings, the **enthalpy change is positive**. This is an **endothermic** reaction. When energy is released to the surroundings, the **enthalpy change is negative**. This is an **exothermic** reaction.

Overall enthalpy change (ΔH) can be calculated as follows:

ΔH = energy to break bonds (+ve) + energy released by making bonds (-ve)

Activation Energy
Activation energy is the **minimum energy** required for a reaction to take place between two colliding reactant particles.

Enthalpy changes are shown on an **enthalpy profile diagram**. **Activation energy** is the difference between the reactants and the top of the hump on an enthalpy profile diagram and is represented by the symbol E_a.

Example:

Exothermic Reaction

Endothermic Reaction
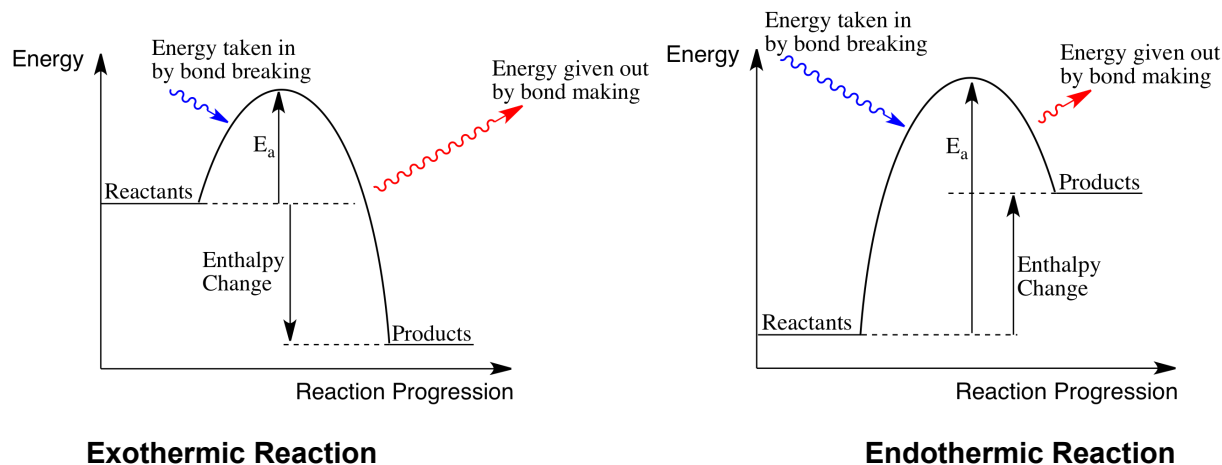
In **endothermic** reactions, more energy is needed to break bonds than to make new ones. Therefore, the overall **ΔH is positive** and **heat is taken in** from the surroundings.

In **exothermic** reactions, the opposite is true, with more energy being needed to make new bonds than break existing ones. Therefore, **heat is given out** and **ΔH is negative.**

Enthalpy Change of Reaction ($\Delta_r H^{\ominus}$)
This is defined as:

> **The enthalpy change associated with a stated reaction. Quantities of substances in standard states react completely under standard conditions.**

Enthalpy Change of Formation ($\Delta_f H^{\ominus}$)
This is defined as:

> **The enthalpy change when one mole of a substance is produced from its elements in their standard states under standard conditions.**

Enthalpy Change of Combustion ($\Delta_c H^{\ominus}$)
This is defined as:

> **The enthalpy change when one mole of a substance is burned completely in oxygen under standard conditions.**

Enthalpy Change of Neutralisation ($\Delta_n H^{\ominus}$)
This is defined as:

> **The enthalpy change when solutions of acid and alkali react together under standard conditions to produce one mole of water.**
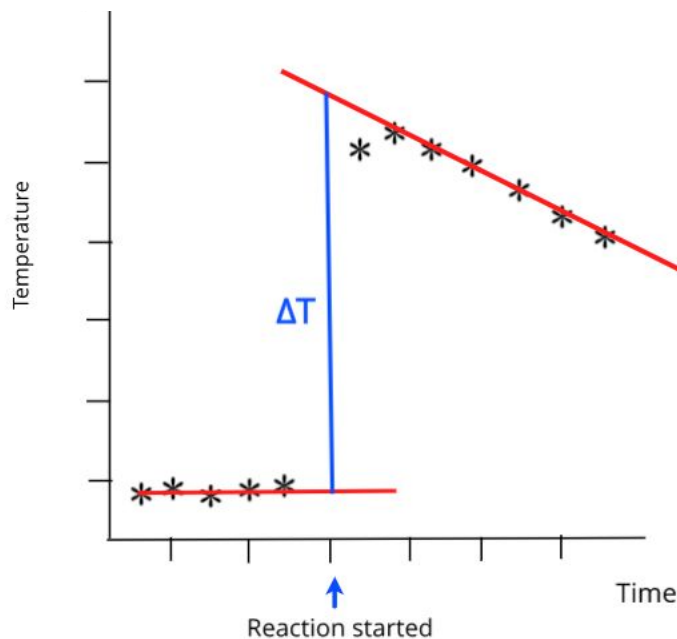
Calorimetry
Calorimetry is an **experimental method** for finding enthalpy change, which works by measuring **temperature change over time**. When recorded and plotted on a graph, data can be **extrapolated** to the exact point at which the reaction starts, giving a more accurate value for the change in temperature.

Example: Graph showing the extrapolated line of best fit

This measured change in temperature, ΔT, is **proportional** to the energy change:

$$q = mc\Delta T$$

where q = energy change (J), m = mass (g), c = specific heat capacity ($J\ g^{-1}K^{-1}$),
ΔT = temperature change (K).

This equation allows the energy change of a substance of known mass to be calculated. It depends on its **specific heat capacity**, defined as:

**The energy required to raise 1 g of substance by
1 K without a change of state.**

Using this energy value (q), **enthalpy change per mole** (kJ mol^{-1}) of substance can be calculated. **ΔH** represents the enthalpy change per mole of substance.

$$\Delta H = \frac{q \times 10^{-3}}{moles}$$

Sources of Error

ΔH values found using calorimetry are **never completely accurate,** since energy is easily lost from the system. Heat loss can occur due to **conduction**, **convection** or inaccuracies in measuring temperatures. The heat loss to the surroundings can be reduced by putting a **lid** on the calorimeter and **insulating** the outsides of the calorimeter, using an insulator like polystyrene.

Also, the **specific heat capacity** of the solution is generally taken to be 4.18 J g⁻¹ K⁻¹, which is the value for water and so might not be accurate for the **actual solution** being used. The **specific heat capacity** of the **calorimeter** is not taken into account so this leads to inaccuracies in the calculation.

Bond Enthalpies

Bond enthalpy data is an **averaged** value representing:

**The energy required to break one mole of the stated bond
in a gaseous state, under standard conditions.**

Different covalent bonds require different amounts of energy to be broken. Values can be found experimentally using **calorimetry** methods. The bond enthalpy values calculated in this way often differ from the **databook values** as they are **not exact** and they **vary in each situation**. This means the databook values are **averaged values**.

Mean bond enthalpy values tell you how much energy is required to break a particular bond, averaged out across the range of compounds containing that bond. These values relate to how **strong** a bond is, so they can be used to infer which bonds might **break first** in a chemical reaction. Bonds with **lower** bond enthalpy values would be expected to break first.

If a reaction requires the breaking of many strong bonds or the reaction is endothermic overall, then it is likely that the reaction will occur **slowly** at **room temperature.**

Bond Enthalpy Calculations

Mean bond enthalpy values can be used to calculate the **overall enthalpy change** for a reaction.

$$\Delta_r H = \Sigma\Delta H(bond\ breaking) - \Sigma\Delta H(bond\ making)$$

This means that the enthalpy change for a reaction is equal to the **sum** of the bond enthalpies for the bonds **broken** in the reaction (reactants), minus the **sum** of the bond enthalpies for the bonds **made** in the reaction (products).

Mean bond enthalpy values are often **tabulated.** You need to identify the bonds broken and formed during the reaction in order to calculate the overall enthalpy change.

Example:

Calculate the enthalpy change when methane undergoes complete combustion in oxygen using the bond enthalpies given.

Bond	Bond enthalpy (kJ mol^{-1})
C-H	413
O=O	498
O-H	464
C=O	799

Chemical equation: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Bonds formed
C=O x 2 = 799 x 2 = 1598
H-O x 4 = 464 x 4 = 1856

Bonds broken
C-H x 4 = 413 x 4 = 1652
O=O x 2 = 498 x 2 = 996

Enthalpy change = (1652+996) - (1856+1598)
= 2648 - 3454
= -806 kJ mol^{-1}

This is a negative value. This means that the reaction is **exothermic**.

Hess's Law and Enthalpy Cycles

Energy in a reaction system must be **conserved**, as energy cannot be created or destroyed. Therefore, the **overall enthalpy change** for a reaction is **the same**, regardless of the **route taken**.

This idea is **Hess's Law** and it is used to determine the enthalpy changes for reactions where the enthalpy change **cannot be found directly** using an experimental method.

To do this, a **triangular cycle method** is used with an intermediate product. The direction of the arrows indicates whether the values should be added or taken away. They can be treated like vectors:
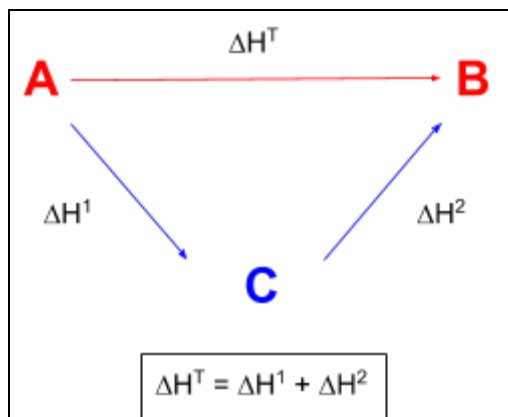
Enthalpies of Formation
Hess's law can be used to calculate an enthalpy change using given enthalpies of formation. When setting up the triangular diagram, the **arrows point out from the central elements at C** as both A and B are formed from these elements.

Example:
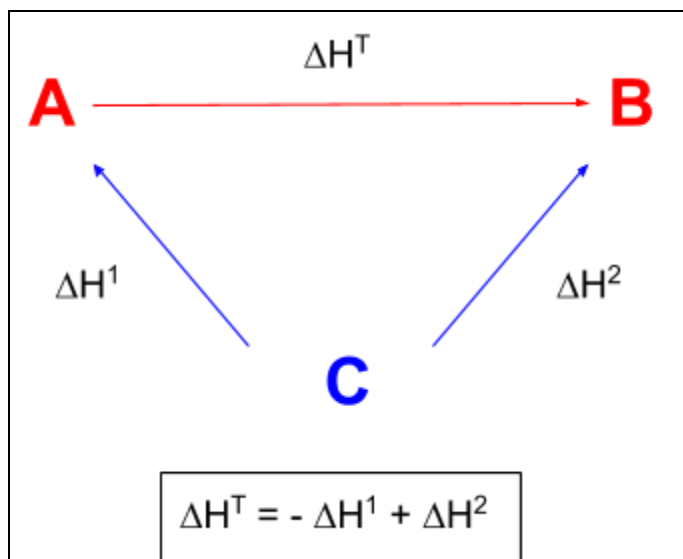
Note: ΔH^1 is subtracted as the reaction goes in the opposite direction to the arrow.
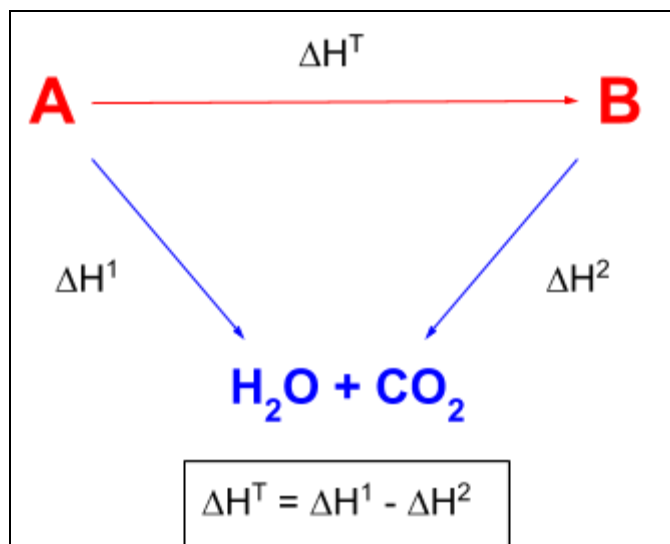
Enthalpies of Combustion

Hess's law can also be used to calculate an enthalpy change using given enthalpies of combustion. When setting up the triangular diagram, the **arrows point towards the central products (which always include H_2O and CO_2)** as both A and B burn (combust) to form the products at C.

Example:

Note: ΔH^2 is subtracted as the reaction goes in the opposite direction to the arrow.

The same principles can be **applied** to any given enthalpy values to then calculate the enthalpy change of a reaction. Just create an **alternate path of known enthalpies** to calculate the unknown value.

3.2.2 Reaction Rates

Simple Collision Theory

Chemical reactions occur when reactant particles **collide**. For a reaction to occur successfully, these collisions must have energy greater than or equal to the **activation energy** of the reaction, and the **particle orientation** must be correct. The activation energy is the minimum amount of energy required for two particles to react.

Reaction Conditions

The conditions of a reaction impact the collisions of the particles and can be altered to give the particles **more energy**. Therefore, the conditions can be changed to increase the likelihood of a collision occurring with **sufficient energy** to react. This will lead to a greater **rate of reaction**.
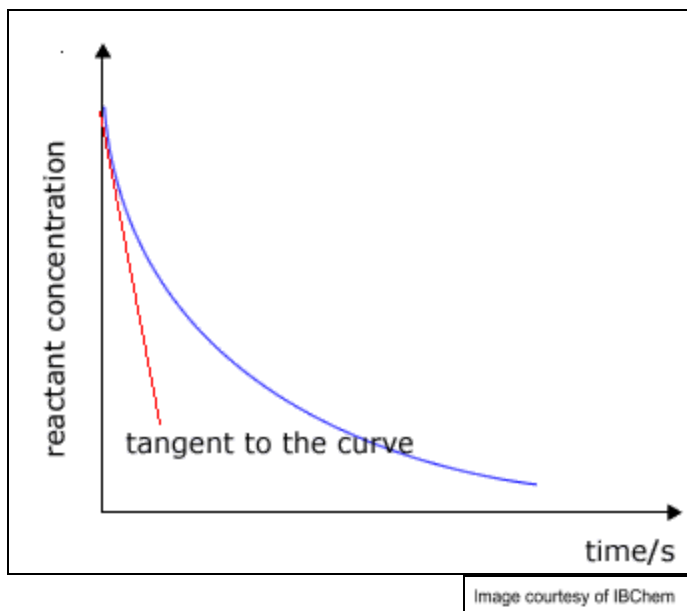
Rate of Reaction

Rate of reaction considers how fast **reactants** are being **used up** or **products** are being **formed**. It can be calculated from empirical data that has been plotted on graphs.

On a **concentration-time graph**, the rate of reaction is equal to the gradient of the curve at a given point. Therefore, the graph can be used to find the **rate** at a certain time by drawing a **tangent** to the curve at this given time and calculating the **gradient** of the tangent.

Gradient = (change in y) ÷ (change in x)

Drawing a **tangent** to the curve when **time = 0** finds the **initial rate** of reaction. The tangent at any other position finds the rate of reaction at that moment in time. The units of rate calculated in this way are generally **mol dm⁻³s⁻¹**.

Example:

Image courtesy of IBChem

Suitable **physical quantities** to **monitor** which affect the rate of reaction include concentration, gas volume, and mass.

Effect of Temperature

When a substance is heated, **thermal energy** is transferred to it. This energy is converted to **kinetic energy** and the molecules of the substance move **faster and further**. Increased movement of the molecules means **collisions occur more often** and with **greater energy**. As a result, more collisions have energy greater than the activation energy and result in a reaction.

Therefore, **increasing the reaction temperature will increase the rate of reaction** as there are more frequent successful collisions.

Effect of Concentration and Pressure

When the concentration of a sample is increased, there are more molecules of substance in the same volume, meaning they are **packed closer together**. Therefore, collisions between molecules become **more likely** and the probability of a collision occurring with energy greater than or equal to the activation energy increases. As a result, the rate of reaction increases.

Increasing the **pressure** of a gas has a similar effect as molecules are **packed closer together** into a smaller volume.

Effect of Surface Area

Increasing the surface area of a reactant, for example by crushing it into a powder, increases the **number of exposed reactant particles**. This means there are more frequent, successful collisions, so the rate of reaction **increases**.
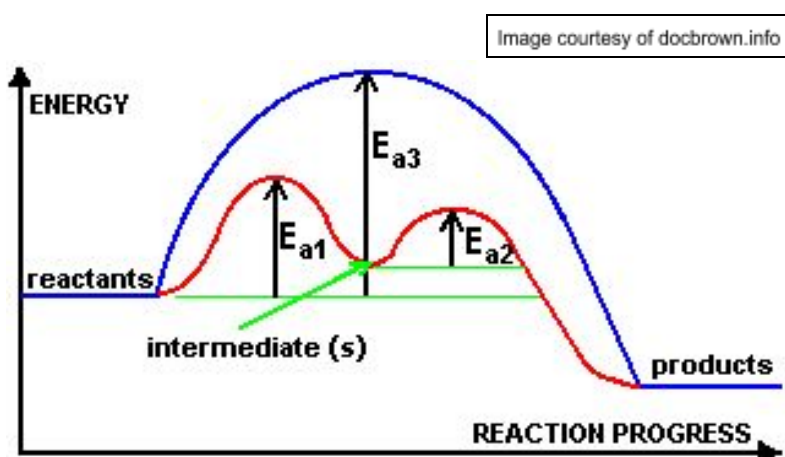
Catalysts

A catalyst is a substance that **increases the rate of reaction without being used up** in the reaction. It works by providing an **alternative reaction path** with a **lower activation energy.**

Catalysts are used in industry because they **lower the energy costs** of the reaction process. They allow lower temperatures and pressures to be used, whilst still achieving the same rate of reaction. They can also give a **higher atom economy**. Hence, they are economically important.

They also increase **sustainability** of a reaction by lowering temperatures and reducing energy demand from combustion of fossil fuels. This results in a **reduction of CO_2 emissions**. These benefits to the environment of improved sustainability must be weighed against the negative effect of the toxicity of some catalysts.

The Reaction Profile of a Catalysed Reaction

The red line shows the pathway for a catalysed reaction, while the blue line shows the pathway for when the reaction occurs without a catalyst.

Image courtesy of docbrown.info

There is a **dip** in the **energy profile** for the catalysed reaction. This represents the **intermediate** formed during the reaction. The intermediate is **less stable** (and therefore higher in energy) than the reactants and products.

Homogeneous Catalysts
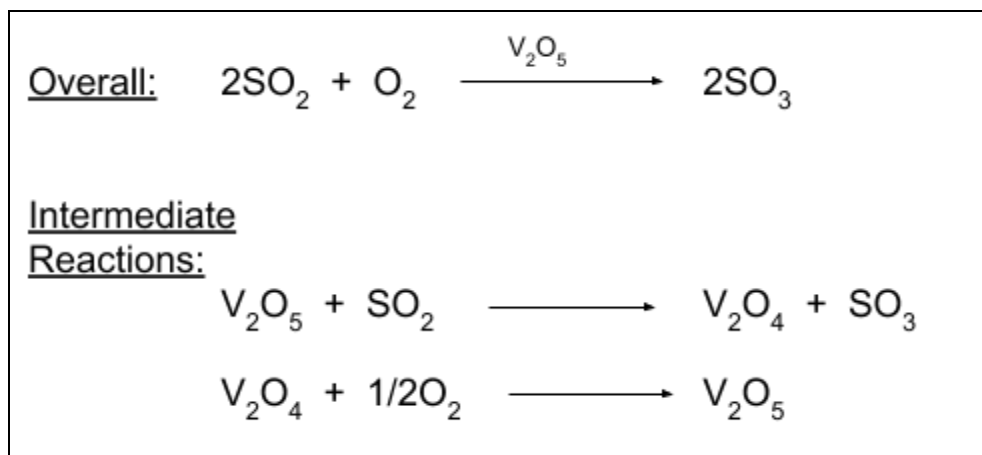Homogeneous catalysts are catalysts that are in the **same phase** as the reactants.

Heterogeneous Catalysts
Heterogeneous catalysts are catalysts that are in a **different phase** to the species in the reaction. An example of this is in the Haber Process, where a **solid iron catalyst** is used to speed up the reaction between hydrogen and nitrogen **gases**.

Transition Metal Catalysts
Transition metals make good catalysts as they have variable oxidation states. **Electrons are transferred** to produce a **reactive intermediate** and speed up the reaction rate. An example of this is the **contact process** which uses a vanadium oxide catalyst to speed up the conversion of sulfur dioxide to sulfur trioxide.

Example:

Overall: $2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$

Intermediate Reactions:

$V_2O_5 + SO_2 \longrightarrow V_2O_4 + SO_3$

$V_2O_4 + 1/2O_2 \longrightarrow V_2O_5$

Vanadium is **reduced** from an oxidation state of +5 to +4. It is then **oxidised** back to its original oxidation state, showing it has acted as a catalyst for the reaction.
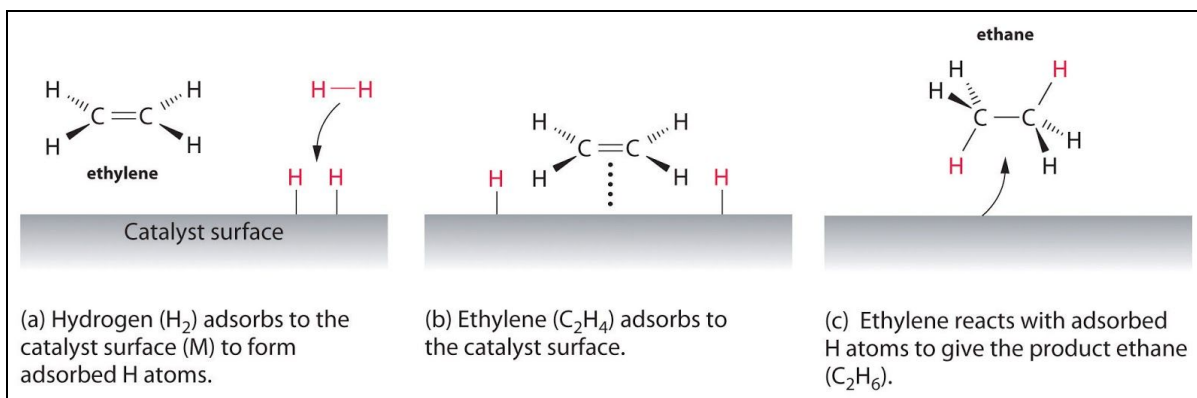
Adsorption
A solid catalyst works by **adsorbing** molecules onto an **active site** on the surface of the catalyst. These active sites **increase the proximity** of molecules and **weaken the covalent bonds** in the molecules so that reactions occur more easily and the rate is increased. These catalysts are used in **industry** to give a **surface** for the reaction to occur on.

Example: Adsorption

(a) Hydrogen (H_2) adsorbs to the catalyst surface (M) to form adsorbed H atoms.

(b) Ethylene (C_2H_4) adsorbs to the catalyst surface.

(c) Ethylene reacts with adsorbed H atoms to give the product ethane (C_2H_6).

The Boltzmann Distribution

Not all molecules in a substance have the same amount of energy. Their energies are **distributed** in a pattern called the **Maxwell-Boltzmann distribution**. This is a plot of the number of molecules against kinetic energy.

The **peak** is the **most probable energy** of a molecule. The **mean** energy is just to the right of this and divides the area below the graph into two equal halves. The curve is **asymptotic** - it doesn't quite reach the x axis. This is because there can be no maximum value for the kinetic energy of a molecule.
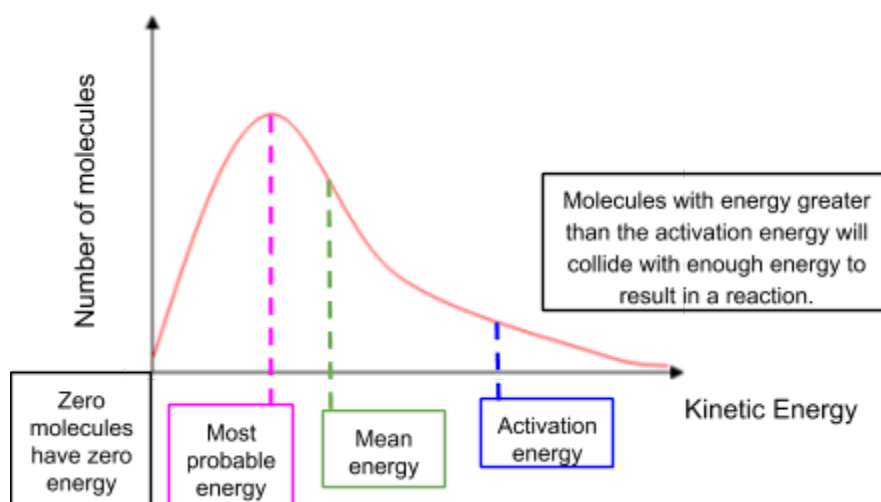
Changing the reaction conditions will **alter the shape of the curve,** so that the number of particles with energy greater than the activation energy is different. The total **area under the curve** represents the **total number of molecules** in the sample, and so this area **must remain constant**.
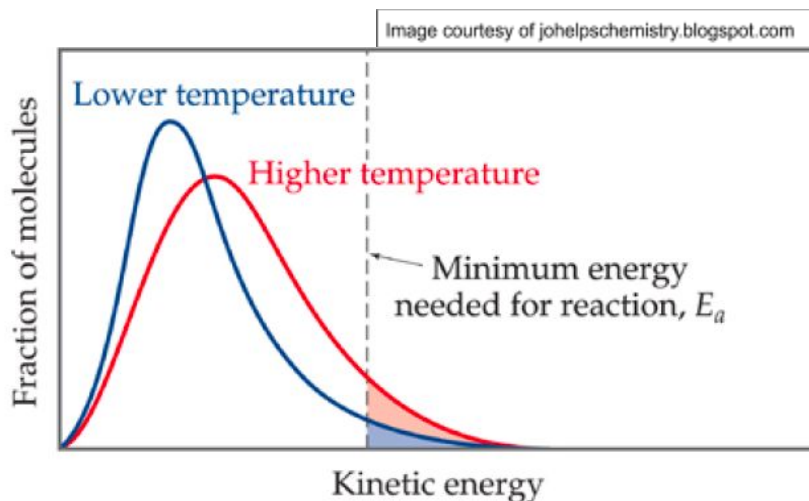
Effect of Temperature

The Maxwell-Boltzmann distribution at an increased temperature **shifts to the right** because a **greater proportion** of molecules have greater kinetic energy. As a result, a greater proportion of molecules will have energy greater than or equal to the activation energy.

Example:

Image courtesy of johelpschemistry.blogspot.com

Effect of Concentration, Pressure and Surface Area

Increasing the **concentration**, **pressure** or **surface area** of reactants make successful collisions occur more frequently, however, they don't change the **energy** of the **individual particles**. Therefore, the shape of the Maxwell-Boltzmann distribution **does not change**.

Effect of Catalysts

On the addition of a catalyst, the Maxwell-Boltzmann distribution curve is **unchanged in shape** but the **position of the activation energy is shifted to the left** so that a greater proportion of molecules have sufficient energy to react.

Example:

Image courtesy of slideshare.net
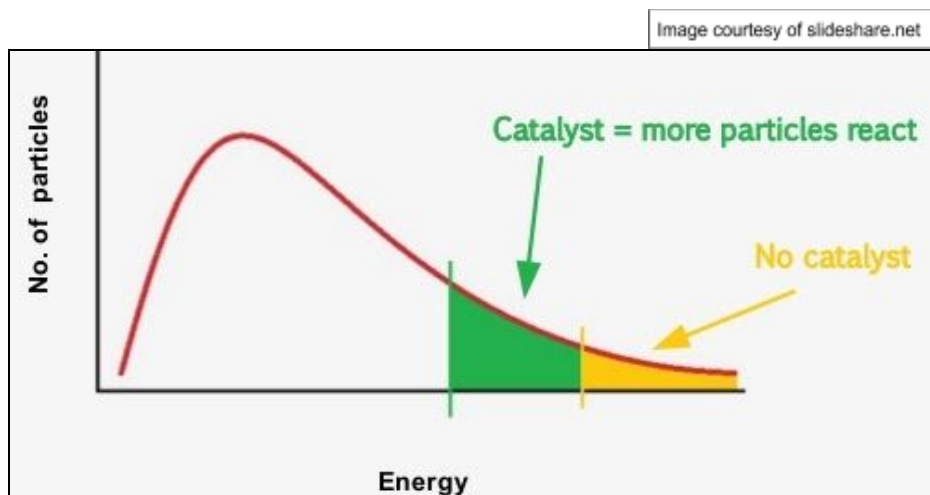
3.2.3 Chemical Equilibrium

Dynamic Equilibrium and Le Chatelier's Principle

Dynamic Equilibrium

Reversible reactions are reactions in which the products of a reaction can react together to reform the original reactants. They are represented using a **double arrow**. In each reaction system, one reaction direction will be **endothermic** and the opposite reaction direction will be **exothermic**.

Example:

$$N_2 + 3H_2 \rightleftharpoons NH_3$$
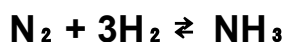
Reversible reactions will eventually reach a state of **dynamic equilibrium**. Dynamic equilibrium exists in a closed system when the **rate** of the forward reaction is **equal** to the rate of the reverse reaction. At this point, the **concentrations** of the reactants and products remain **constant.**

Dynamic equilibrium can only occur in **closed systems** where no substances can get in or out.

Le Chatelier's Principle

Le Chatelier's principle is used to predict how an equilibrium mixture will change if the **reaction conditions are altered**. It states:

> **When a system is subject to a change in conditions, the position of equilibrium will shift to lessen the effect of that change.**

It is a useful principle to consider in industry, since the reaction conditions can be altered to **maximise the yield** of a desired product.

Changing Temperature

If you **increase** the temperature, the position of equilibrium will shift to favour the **endothermic reaction** (+ve ∆H) as the excess heat needs to be removed from the system to lessen the effect of the initial increase. It will increase the yield of the endothermic products.

Likewise, if you **decrease** the temperature, the position of equilibrium will shift to favour the **exothermic reaction** (-ve ∆H) as heat needs to be gained and the yield of the exothermic products will be increased.

In exam questions, the **∆H of the forward reaction will be given** so it is clear which direction is endothermic and which is exothermic.

Changing Pressure
Increasing pressure favours the side of the reaction with **fewer moles** of gas, as this helps to release the buildup in pressure. It will increase the yield of the products on the side of the reaction with the fewest moles of gas.

Likewise, **decreasing** pressure favours the side of the reaction with **more moles,** as pressure has been lost. The yield of the products on this side of the reaction will be increased.

Changing Concentration
Increasing the concentration of the reactants will favour the **forward** reaction that **produces the products** as more molecules are available to react. It will increase the yield of the products on the right hand side of the reaction.

Likewise, **decreasing** the concentration of reactants will favour the **backwards** reaction that **reforms the reactants**.

Catalysts
Catalysts do not affect the equilibrium position as they **increase the rate of the forward and backward reactions equally**. This means they allow equilibrium to be reached **faster** but have no effect on the position of equilibrium.

Compromise between Rate of Reaction and Product Yield
Changing the conditions of reaction can shift the position of the equilibrium to favour the production of either the products or the reactants, as described above. However, a condition change which produces a **higher proportion of the product** may also **reduce the rate of the reaction**. The rate of reaction is increased by increases in temperature, pressure or concentration.

For example, **decreasing the temperature** of a reaction with a **forward endothermic reaction** would **increase** the product **yield**, but **decrease** the **rate** of reaction.

In the industry, when a factor increases the product yield but decreases the rate of a reaction, a **compromise** must be made. If the product yield was the only thing taken into account, the rate of reaction would occur **so slowly** that the product is not actually made at a useful rate. Therefore, reaction conditions are selected to give both a **relatively good product yield** and a **relatively fast rate of reaction**. You must also consider safety and economics when determining the conditions used in industrial reactions.
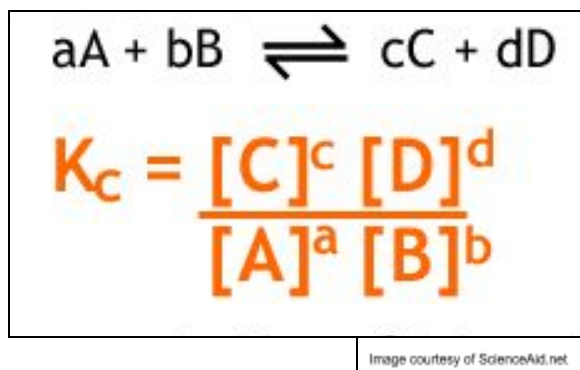
The Equilibrium Constant, (Kc)

For reversible reactions, there is an equilibrium constant, **Kc**, that indicates the **position of equilibrium** for a reaction at a certain temperature. Kc for a reaction always has the **same value** unless the reaction conditions are changed, which in turn changes the position of equilibrium and hence Kc.

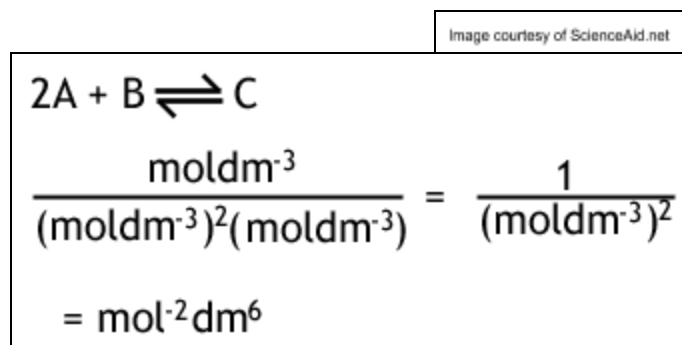In order to find the value of Kc, the **concentrations** of the reactants and products at equilibrium must be known. Kc is equal to the **concentration of the products divided by the concentration of the reactants**. Any variation in the number of moles **raises the concentration of that substance to a power** with the same value as the number of moles.

Example:

$$aA + bB \rightleftharpoons cC + dD$$

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Image courtesy of ScienceAid.net

The equilibrium constant has **varying units** depending on the chemical reaction. The units can be found by **subbing the concentration units into the Kc expression**. Some of these then cancel to give the overall units of Kc for that reaction.

Example:

Image courtesy of ScienceAid.net

$$2A + B \rightleftharpoons C$$

$$\frac{mol\,dm^{-3}}{(mol\,dm^{-3})^2(mol\,dm^{-3})} = \frac{1}{(mol\,dm^{-3})^2}$$

$$= mol^{-2}dm^6$$

The value of Kc is **not affected by concentration change or use of a catalyst**, however it is affected by changing the reaction **temperature,** as the equilibrium position change results in different concentrations of reactants and products.

Concentration changes and the addition of a **catalyst** affect the **rate** of the reaction (the kinetics) but not the **position** of the equilibrium. They only affect how fast the system reaches equilibrium, hence they have **no impact** on the equilibrium constant.

The **position of equilibrium** can be estimated by the **magnitude** of the value of **Kc**. A large value for Kc indicates that product formation is favourable and the position of equilibrium will be far to the right. A small value for Kc indicates the opposite.