# 8 Reaction Kinetics

Collision theory

Reactions can only occur when collisions take place between particles having sufficient energy. The energy is usually needed to break the relevant bonds in one or either of the reactant molecules.
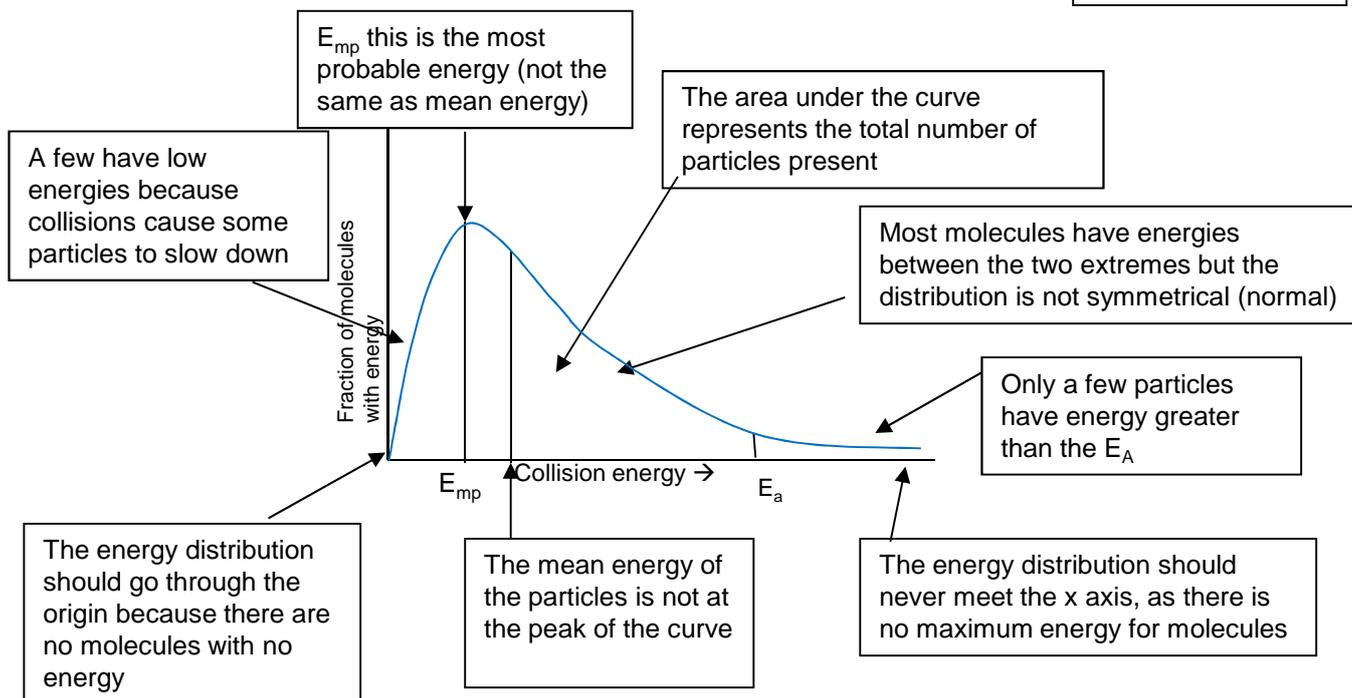
This minimum energy is called the Activation Energy

The **Activation Energy** is defined as the **minimum** energy which particles need to collide to start a reaction
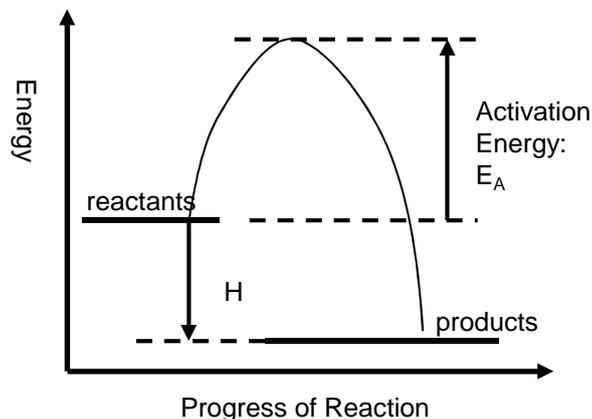
Maxwell Boltzmann Distribution

The Maxwell-Boltzmann energy distribution shows the spread of energies that molecules of a gas or liquid have at a particular temperature

Learn this curve carefully

E_{mp} this is the most probable energy (not the same as mean energy)

A few have low energies because collisions cause some particles to slow down

The area under the curve represents the total number of particles present

Most molecules have energies between the two extremes but the distribution is not symmetrical (normal)

Only a few particles have energy greater than the E_A

The energy distribution should go through the origin because there are no molecules with no energy

The mean energy of the particles is not at the peak of the curve

The energy distribution should never meet the x axis, as there is no maximum energy for molecules

Q. How can a reaction go to completion if few particles have energy greater than Ea?

A. Particles can gain energy through collisions

Measuring Reaction Rates

The rate of reaction is defined as the **change in concentration** of a substance **in unit time**

Its usual unit is mol dm^{-3}s^{-1}

When a graph of concentration of reactant is plotted vs time, the **gradient** of the curve is the rate of reaction.

The **initial rate** is the rate at the start of the reaction where it is fastest

Reaction rates can be calculated from graphs of concentration of reactants **or** products
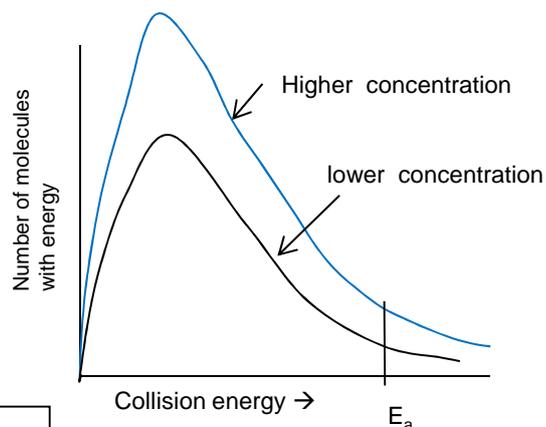
Initial rate = gradient of tangent
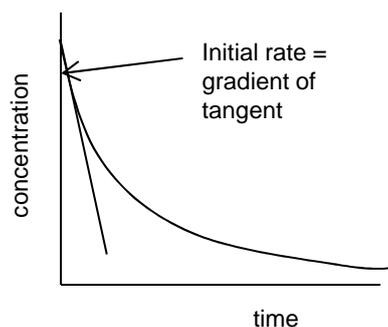
Effect of Increasing Concentration and Increasing Pressure

At higher concentrations(and pressures) there are **more particles per unit volume** and so **the particles collide with a greater frequency** and there will be a **higher frequency of effective collisions**.

Note: If a question mentions a **doubling** of concentration/rate then make sure you mention **double** the number of particles per unit volume and **double** the frequency of effective collisions.
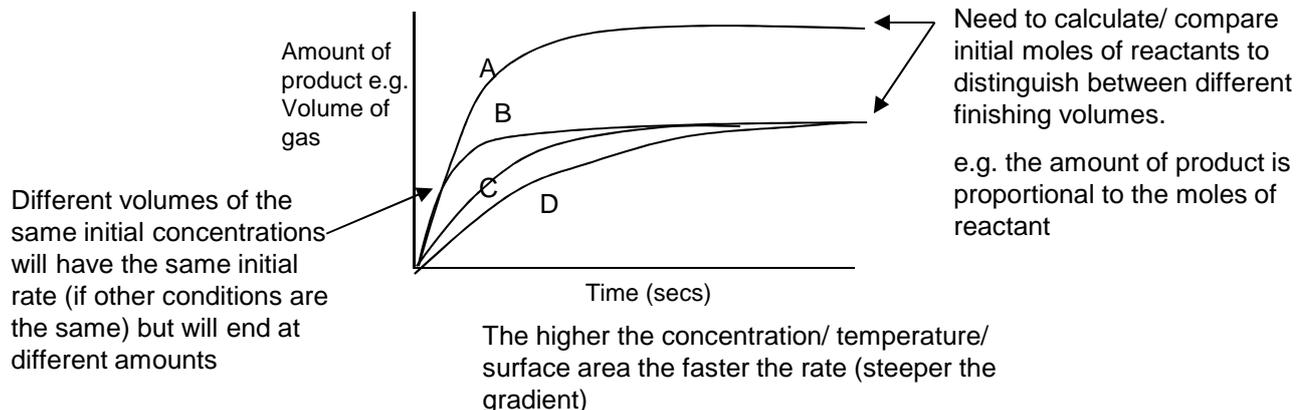
If concentration increases, the shape of the energy distribution curves do not change (i.e. the peak is at the same energy) so the E_{mp} and mean energy do not change

They curves will be higher, and the area under the curves will be greater because there are **more** particles

More molecules have energy > E_A (although not a greater proportion)

Number of molecules with energy

Higher concentration

lower concentration

Collision energy → E_a

Comparing rate curves

Amount of product e.g. Volume of gas

A
B
C
D

Time (secs)

Need to calculate/ compare initial moles of reactants to distinguish between different finishing volumes.

e.g. the amount of product is proportional to the moles of reactant

Different volumes of the same initial concentrations will have the same initial rate (if other conditions are the same) but will end at different amounts

The higher the concentration/ temperature/ surface area the faster the rate (steeper the gradient)

Rate Equations

The rate equation relates mathematically the rate of reaction to the concentration of the reactants.

For the following reaction,   aA + bB → products, the generalised rate equation is:

$$r = k[A]^m[B]^n$$

r is used as symbol for rate

The unit of r is usually **mol dm^{-3} s^{-1}**

m, n are called **reaction orders**

Orders are usually integers 0,1,2

0 means the reaction is zero order with respect to that reactant
1 means first order
2 means second order

NOTE: the orders have *nothing* to do with the stoichiometric coefficients in the balanced equation. They are worked out experimentally

The square brackets **[A]** means the concentration of A
(unit **mol dm^{-3}**)

k is called the **rate constant**

The **total order** for a reaction is worked out by adding all the individual orders together (m+n)

Calculating orders from initial rate data
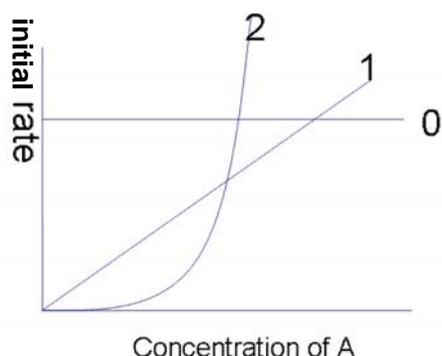
For zero order: the concentration of A has no effect on the rate of reaction   **r = k[A]^0 = k**

For first order: the rate of reaction is directly proportional to the concentration of A   r = k[A]^1

For second order: the rate of reaction is proportional to the concentration of A squared   **r = k[A]^2**

Graphs of initial rate against concentration show the different orders. The initial rate may have been calculated from taking gradients from concentration /time graphs

For a rate concentration graph to show the order of a particular reactant the concentration of that reactant must be varied whilst the concentrations of the other reactants should be kept constant.
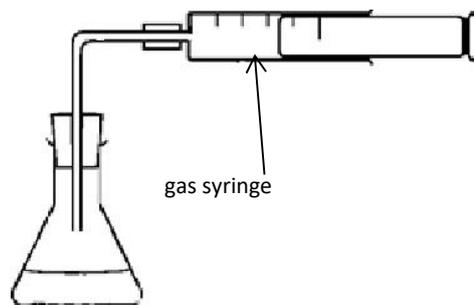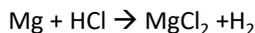
Continuous Monitoring

When we follow one experiment over time recording the change in concentration we call it a continuous rate method.

The gradient represents the rate of reaction. The reaction is fastest at the start where the gradient is steepest. The rate drops as the reactants start to get used up and their concentration drops. The graph will eventual become horizontal and the gradient becomes zero which represents the reaction having stopped.
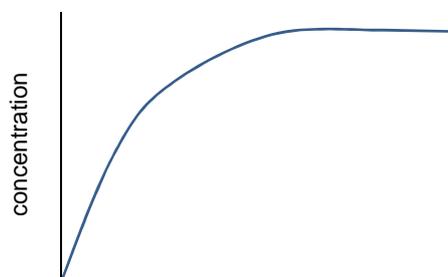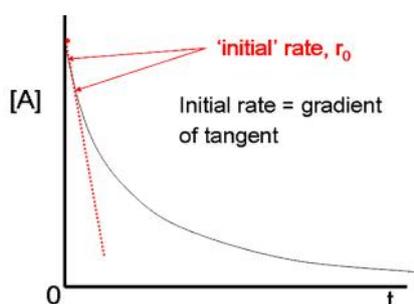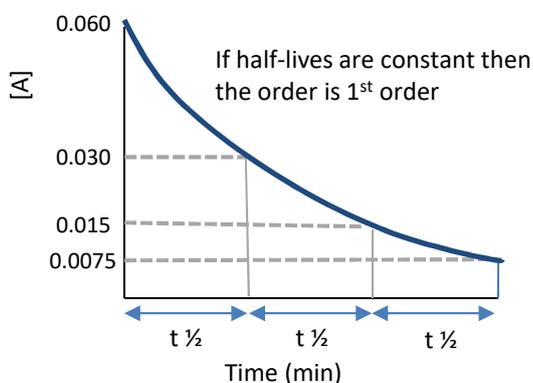
Measurement of the change in volume of a gas

This works if there is a change in the number of moles of gas in the reaction. Using a gas syringe is a common way of following this. It works quite well for measuring continuous rate but a typical gas syringe only measures 100ml of gas so you don't want at reaction to produce more than this volume. Quantities of reactants need to be calculated carefully.

$$Mg + HCl \rightarrow MgCl_2 + H_2$$

gas syringe

Typical Method
- Measure 50 cm³ of the 1.0 mol dm⁻³ hydrochloric acid and add to conical flask.
- Set up the gas syringe in the stand
- Weigh 0.20 g of magnesium.
- Add the magnesium ribbon to the conical flask, place the bung firmly into the top of the flask and start the timer.
- Record the volume of hydrogen gas collected every 15 seconds for 3 minutes.

The initial rate is the rate at the start of the reaction, where it is fastest. It is obtained by taking the gradient of a continuous monitoring conc vs time graph at time = zero. A measure of initial rate is preferable as we know the concentrations at the start of the reaction

Large Excess of reactants
In reactions where there are several reactants, if the concentration of one of the reactant is kept in a large excess then that reactant will appear not to affect rate and will be pseudo-zero order . This is because its concentration stays virtually constant and does not affect rate.

[A]   'initial' rate, r_0

Initial rate = gradient of tangent

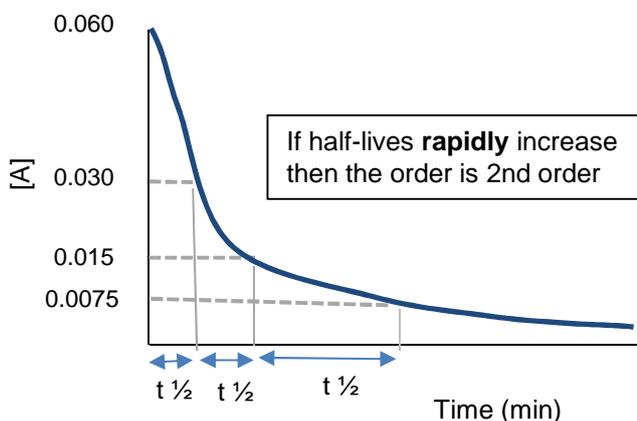**Continuous rate experiments**

Continuous rate data

This is data from one experiment where the concentration of one substance is followed throughout the experiment.

For this method to work the concentrations of the reactants not being followed must be in large excess in the experiment so their concentrations stay virtually constant and do not affect rate.

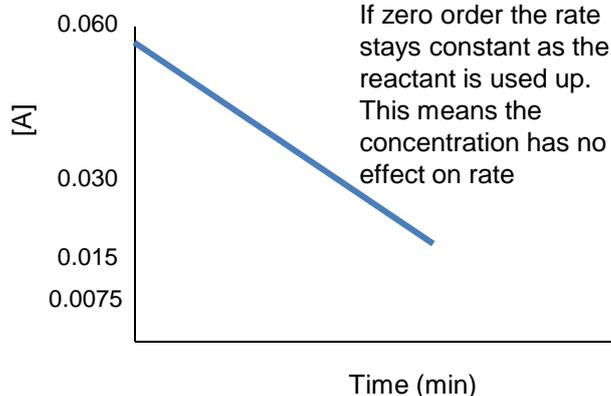If half-lives are constant then the order is 1st order

This data is processed by plotting the data and calculating successive half-lives.

The half-life of a first-order reaction is independent of the concentration and is constant

Second order

If half-lives **rapidly** increase then the order is 2nd order

zero order

If zero order the rate stays constant as the reactant is used up. This means the concentration has no effect on rate

The rate constant (k)

1. The units of k depend on the overall order of reaction. It must be worked out from the rate equation
2. The value of k is independent of concentration and time. It is constant at a fixed temperature.
3. The value of k refers to a specific temperature and it **increases** if we **increase temperature**

For a 1st order overall reaction the unit of k is **s^{-1}**

For a 2nd order overall reaction the unit of k is **$mol^{-1}dm^3s^{-1}$**

For a 3rd order overall reaction the unit of k is **$mol^{-2}dm^6s^{-1}$**

Example (first order overall)

Rate = $k[A][B]^0$ m = 1 and n = 0
- reaction is first order in A and zero order in B
- overall order = 1 + 0 = 1
- usually written: Rate = k[A]

Remember: the values of the reaction orders must be determined from experiment; they cannot be found by looking at the balanced reaction equation

Calculating units of k

1. Rearrange rate equation to give k as subject

$$k = \frac{Rate}{[A]}$$

2. Insert units and cancel

$$k = \frac{\cancel{mol\ dm}^{-3}s^{-1}}{\cancel{mol\ dm}^{-3}}$$

Unit of k = s^{-1}

Example: Write rate equation for reaction between A and B where A is 1st order and B is 2nd order.

r = $k[A][B]^2$ overall order is 3

Calculate the unit of k

1. Rearrange rate equation to give k as subject

$$k = \frac{Rate}{[A][B]^2}$$

2. Insert units and cancel

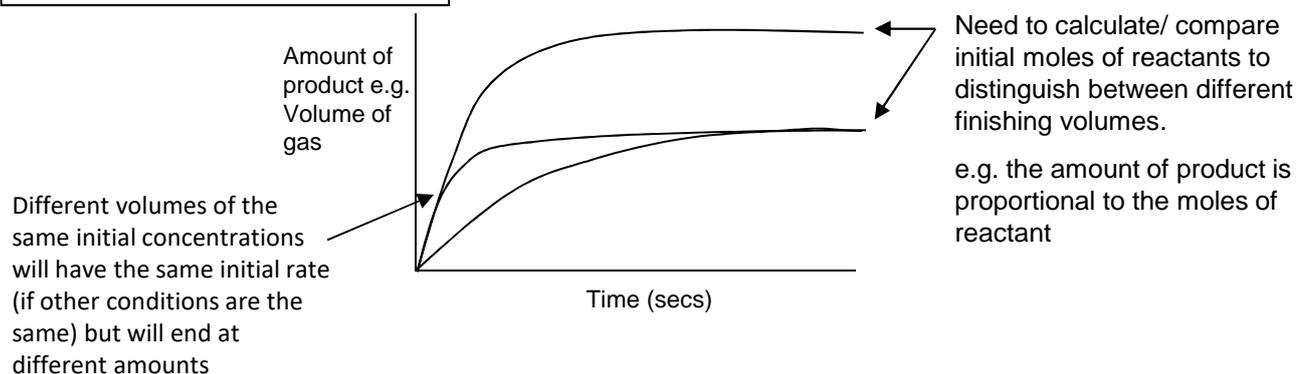$$k = \frac{\cancel{mol\ dm}^{-3}s^{-1}}{\cancel{mol\ dm}^{-3}.(mol\,dm^{-3})^2}$$

3. Simplify fraction

$$k = \frac{s^{-1}}{mol^2dm^{-6}}$$

Unit of k = $mol^{-2}dm^6s^{-1}$

Comparing continuous rate curves

The higher the concentration/ temperature/ surface area the faster the rate (steeper the gradient)

If the acid is in excess of the magnesium or marble chips then the final volume of gas produced will be proportional to the amount of moles of acid
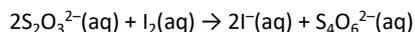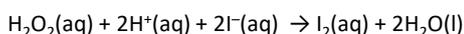
Amount of product e.g. Volume of gas

Need to calculate/ compare initial moles of reactants to distinguish between different finishing volumes.

e.g. the amount of product is proportional to the moles of reactant

Different volumes of the same initial concentrations will have the same initial rate (if other conditions are the same) but will end at different amounts

Time (secs)

Initial rate method

The initial rate can be calculated from taking the gradient of a continuous monitoring conc vs time graph at time = zero

Initial rate can also be calculated from clock reactions where the time taken to reach a fixed concentration is measured.

A Common Clock Reaction (no need to learn details)

Hydrogen peroxide reacts with iodide ions to form iodine. The thiosulfate ion then immediately reacts with iodine formed in the second reaction as shown below.

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

When the I_2 produced has reacted with all of the limited amount of thiosulfate ions present, excess I_2 remains in solution. Reaction with the starch then suddenly forms a dark blue-black colour.

A series of experiments is carried out, in which the concentration of iodide ions is varied, while keeping the concentrations of all of the other reagents the same. In each experiment the time taken (t) for the reaction mixture to turn blue is measured.

In clock reactions there are often two successive reactions and an end point is achieved when one limited reactant runs out, resulting in a sudden colour change

By repeating the experiment several times, varying the concentration of a reactant e.g. I^-, (keeping the other reactants at constant concentration)you can determine the order of reaction with respect to that reactant

The initial rate of the reaction can be represented as (1/t)

Experiment	Sulfuric acid (H$^+$)	Starch	Water	Potassium iodide(I$^-$)	Sodium Thiosulfate $S_2O_3^{2-}$
1	25	1	20	5	5
2	25	1	15	10	5
3	25	1	10	15	5
4	25	1	5	20	5
5	25	1	0	25	5

Working out orders from experimental initial rate data

Normally to work out the rate equation we do a series of experiments where the initial concentrations of reactants are changed (one at a time) and measure the initial rate each time.

Working out rate order graphically

In an experiment where the concentration of one of the reagents is changed and the reaction rate measured it is possible to calculate the order graphically
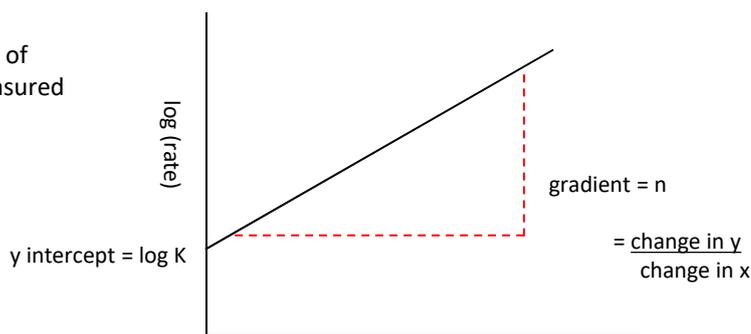
Taking rate equation

$$Rate = k\,[Y]^n$$

Log both sides of equation
Log rate = log k + n log [Y]

$$Y = c + mx$$

A graph of log rate vs log [Y] will yield a straight line where the gradient is equal to the order n

log (rate)

gradient = n

$= \dfrac{\text{change in y}}{\text{change in x}}$

y intercept = log K

In this experiment high concentrations with quick times will have the biggest percentage errors.

This initial rate data can also be presented in a table.

Example: work out the rate equation for the following reaction, **A+ B+ 2C → D + 2E,** using the initial rate data in the table

Experiment	[A] mol dm^{-3}	[B] mol dm^{-3}	[C] mol dm^{-3}	Rate mol dm^{-3} s^{-1}
1	0.1	0.5	0.25	0.1
2	0.2	0.5	0.25	0.2
3	0.1	1.0	0.25	0.4
4	0.1	0.5	0.5	0.1

In order to calculate the order for a particular reactant it is easiest to compare two experiments where **only that reactant** is being changed

If conc is doubled and rate stays the same: order= 0

If conc is doubled and rate doubles: order= 1

If conc is doubled and rate quadruples : order= 2

For reactant A compare between experiments **1 and 2**

For reactant A as the concentration **doubles** (B and C staying constant) so does the rate. Therefore the order with respect to reactant **A is first order**

For reactant B compare between experiments **1 and 3** :

As the concentration of B **doubles** (A and C staying constant) the rate **quadruples**.

Therefore the order with respect to **B is 2nd order**

For reactant C compare between experiments **1 and 4** :

As the concentration of C **doubles** (A and B staying constant) the rate **stays the same**.

Therefore the order with respect to C is zero order

The overall rate equation is r = k [A] [B]²

The reaction is 3rd order overall and the unit of the rate constant =mol^{-2}dm^{6}s^{-1}

Working out orders when two reactant concentrations are changed simultaneously

In most questions it is possible to compare between two experiments where only one reactant has its initial concentration changed. If, however, both reactants are changed then the effect of both individual changes on concentration are multiplied together to give the effect on rate.

In a reaction where the rate equation is $r = k [A] [B]^2$

If the [A] is x2 that rate would **x2**

If the [B] is x3 that rate would $x3^2$= **x9**

If these changes happened at the same time then the rate would x2x9= **x 18**

Example work out the rate equation for the reaction, between X and Y, using the initial rate data in the table

Experiment	Initial concentration of X/ mol dm^{-3}	Initial concentration of Y/ mol dm^{-3}	Initial rate/ mol dm^{-3} s^{-1}
1	0.05	0.1	0.15 x 10^{-6}
2	0.10	0.1	0.30 x 10^{-6}
3	0.20	0.2	2.40 x 10^{-6}

For reactant X compare between experiments **1 and 2**

For reactant X as the concentration **doubles** (Y staying constant) so does the rate. Therefore the order with respect to reactant **X is first order**

Comparing between experiments 2 and 3 :

Both **X and Y double** and the **rate goes up by 8**

We know X is first order so that will have doubled rate

The effect of Y, therefore, on rate is to have quadrupled it.

Y must be second order

The overall rate equation is r = k [X] [Y]^2

The reaction is 3rd order overall and the unit of the rate constant =mol^{-2}dm^{6}s^{-1}

Calculating a value for k using initial rate data

Using the above example, choose any one of the experiments and put the values into the rate equation that has been rearranged to give k. Using experiment 3:

$$r = k [X] [Y]^2 \longrightarrow k = \frac{r}{[X] [Y]^2} \qquad k = \frac{2.40 \times 10^{-6}}{0.2 \times 0.2^2} \qquad \textbf{k = 3.0 x 10}^{-4}\textbf{ mol}^{-2}\textbf{dm}^6\textbf{s}^{-1}$$

**Remember k is the same for all experiments done at the same temperature.**

Increasing the temperature increases the value of the rate constant k

zero order: Calculating k from Concentration-time graphs

For zero order reactants, the rate stays constant as the reactant is used up. This means the concentration of that reactant has no effect on rate.
Rate = k [A]^0 so rate = k
As the rate is the gradient of the graph on the right, the gradient is also the value of the rate constant.

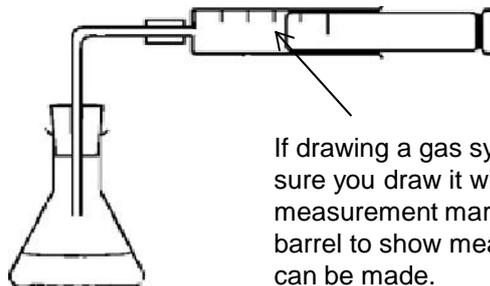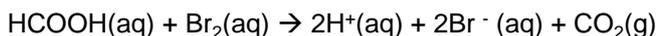
The gradient of this graph is equal to the rate constant
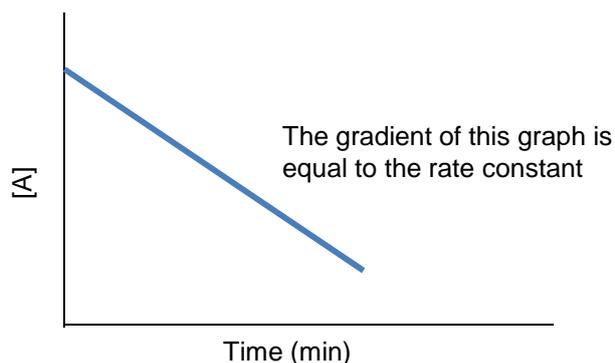
Techniques to investigate rates of reaction

There are several different methods for measuring reactions rates. Some reactions can be measured in several ways

Measurement of the change in volume of a gas

This works if there is a change in the number of moles of gas in the reaction. Using a gas syringe is a common way of following this.
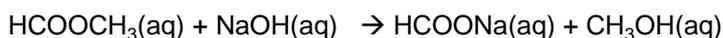
$(CH_3)_2C=CH_2(g) + HI(g) \rightarrow (CH_3)_3CI(g)$

$HCOOH(aq) + Br_2(aq) \rightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(g)$

If drawing a gas syringe make sure you draw it with some measurement markings on the barrel to show measurements can be made.

Measurement of change of mass

This works if there is a gas produced which is allowed to escape. Works better with heavy gases such as CO_2

$HCOOH(aq) + Br_2(aq) \rightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(g)$
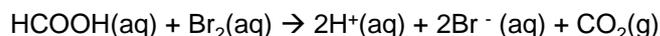
Titrating samples of reaction mixture with acid, alkali, sodium thiosulphate etc

Small samples are removed from the reaction mixture, quenched (which stops the reaction) and the titrated with a suitable reagent.

$HCOOCH_3(aq) + NaOH(aq) \rightarrow HCOONa(aq) + CH_3OH(aq)$ The NaOH could be titrated with an acid
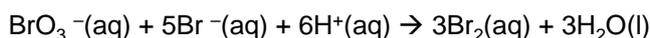
$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$ The H^+ could be titrated with an alkali
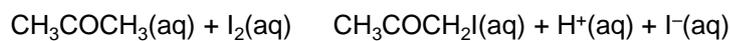
$CH_3COCH_3(aq) + I_2(aq) \quad CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$ The I_2 could be titrated with sodium thiosulphate

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Colorimetry.
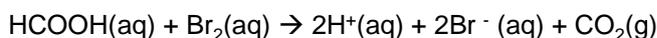
If one of the reactants or products is coloured then colorimetry can be used to measure the change in colour of the reacting mixtures

$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow 2H_2O(l) + I_2(aq)$
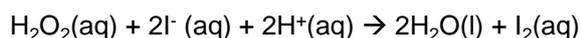
The I_2 produced is a brown solution
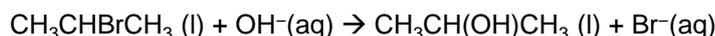
Measuring change in electrical conductivity

Can be used if there is a change in the number of ions in the reaction mixture

$HCOOH(aq) + Br_2(aq) \rightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(g)$

Measurement of optical activity.

If there is a change in the optical activity through the reaction this could be followed in a polarimeter

$CH_3CHBrCH_3 (l) + OH^-(aq) \rightarrow CH_3CH(OH)CH_3 (l) + Br^-(aq)$

In the experiment between sodium thiosulphate and hydrochloric acid we usually measure reaction rate as **1/time** where the time is the time taken for a cross placed underneath the reaction mixture to disappear due to the cloudiness of the Sulphur . $Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + S + H_2O$
This is an approximation for rate of reaction as it does not include concentration. We can use this because we can assume the amount of Sulphur produced is **fixed and constant**.

Rate Equations and Mechanisms

A mechanism is a series of steps through which the reaction progresses, often forming intermediate compounds. If all the steps are added together they will add up to the overall equation for the reaction

Each step can have a different rate of reaction. The slowest step will control the overall rate of reaction. **The slowest step is called the rate-determining step**.

The molecularity (number of moles of each substance) of the molecules in the slowest step will be the same as the order of reaction for each substance.
  e.g. 0 moles of A in slow step would mean A is zero order.
    1 mole of A in the slow step would mean A is first order

Example 1
overall reaction
    $A + 2B + C \rightarrow D + E$
Mechanism
Step 1   A + B → X + D slow
Step 2 $X + C \rightarrow Y$ fast
Step 3 $Y + B \rightarrow E$ fast
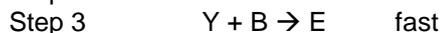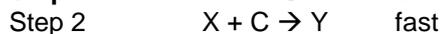
    $r = k\ [A]^1[B]^1[C]^0$

C is zero order as it appears in the mechanism in a fast step after the slow step

Example 2
overall reaction
    $A + 2B + C \rightarrow D + E$
Mechanism
Step 1 $A + B \rightarrow X + D$ fast
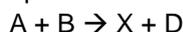**Step 2   X + C → Y   slow**
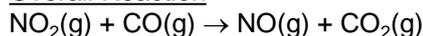Step 3 $Y + B \rightarrow E$ fast
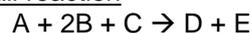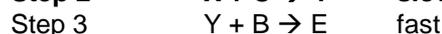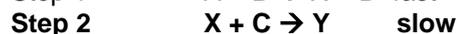
$r = k\ [X]^1[C]^1$
The intermediate X is not one of the reactants so must be replaced with the substances that make up the intermediate in a previous step
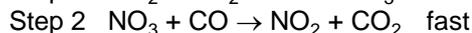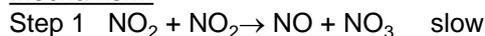$A + B \rightarrow X + D$
    $r = k[A]^1[B]^1[C]^1$

Example 3

Overall Reaction
$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

Mechanism:
Step 1 $NO_2 + NO_2 \rightarrow NO + NO_3$ slow
Step 2 $NO_3 + CO \rightarrow NO_2 + CO_2$ fast
• NO_3 is a reaction intermediate

NO_2 appears twice in the slow steps so it is second order. CO does not appear in the slow step so is zero order.

    $r = k\ [NO_2]^2$

Example 4

Using the rate equation rate = $k[NO]^2[H_2]$ and the overall equation $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$, the following three-step mechanism for the reaction was suggested. X and Y are intermediate species.
Step **1 NO + NO → X**
Step **2 X + H$_2$ → Y**
Step **3 Y + H$_2$ → N$_2$ + 2H$_2$O**
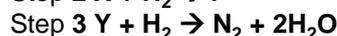
Which **one of the three steps is the rate-determining step?**

Step 2 – as H_2 appears in rate equation and combination of step 1 and 2 is the ratio that appears in the rate equation.

Example 5: S_N1 or S_N2? You don't need to remember the details here.

Remember the nucleophilic substitution reaction of haloalkanes and hydroxide ions.
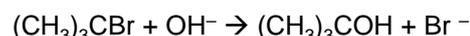
This is a one step mechanism

$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$ slow step
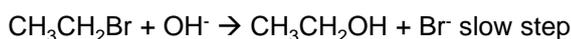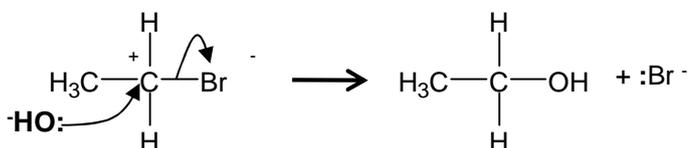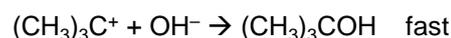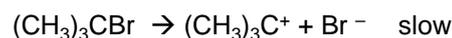
The rate equation is

$r = k\ [CH_3CH_2Br]\ [OH^-]$

This is called S_N2. **S**ubstitution, **N**ucleophilic, **2** molecules in rate determining step

The same reaction can also occur via a different mechanism

Overall Reaction

$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$

Mechanism:

$(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$ slow

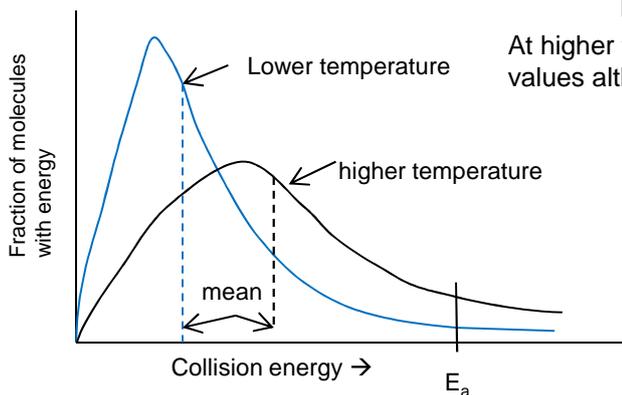$(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$ fast

The rate equation is

$r = k\ [(CH_3)_3CBr]$

This is called S_N1. **S**ubstitution, **N**ucleophilic, **1** molecule in rate determining step

Increasing Temperature

As the temperature increases the distribution shifts towards having more molecules with higher energies

At higher temps both the E_{mp} and mean energy shift to high energy values although the number of molecules with those energies decrease
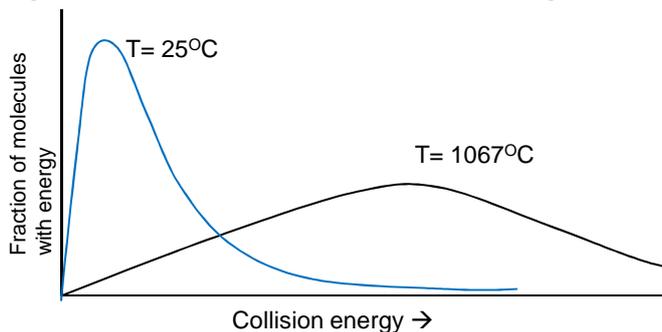

The total area under the curve should remain constant because the total number of particles is constant

At higher temperatures the molecules have a wider range of energies than at lower temperatures.

Effect of Increasing Temperature

At higher temperatures the energy of the particles increases. They collide more frequently and more often with energy greater than the activation energy. More collisions result in a reaction

As the temperature increases, the graph shows that a **significantly bigger** proportion of particles have **energy greater than the activation energy**, so the **frequency of successful collisions increases**
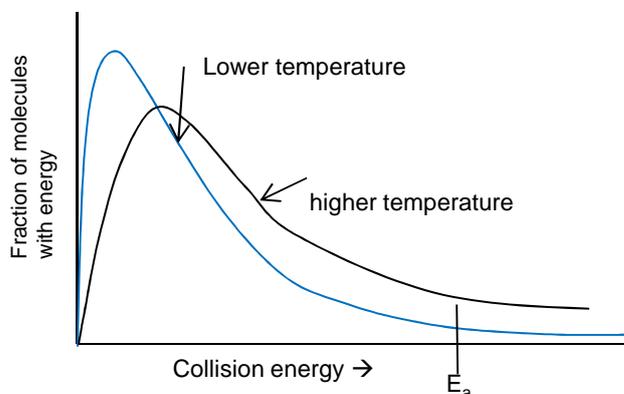

Effect of Increasing Surface area

Increasing surface area will cause successful **collisions to occur more frequently** between the reactant particles and this increases the rate of the reaction.

Effect of Temperature on Rate Constant: The Arrhenius Equation

Increasing the temperature increases the value of the rate constant k

Increasing temperature increases the rate constant k. The relationship is given by the Arrhenius equation $k = Ae^{-Ea/RT}$ where A is a constant R is gas constant and Ea is activation energy.
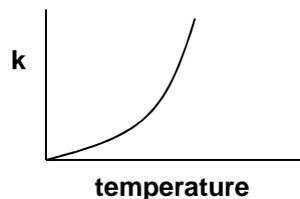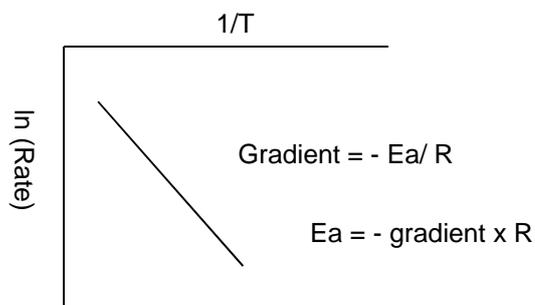

The Arrhenius equation can be rearranged

$$\ln k = \text{constant} - Ea/(RT)$$

k is proportional to the rate of reaction so ln k can be replaced by ln(rate)

From plotting a graph of ln(rate) or ln k against 1/T the activation energy can be calculated from measuring the gradient of the line

Gradient = - Ea/ R

Ea = - gradient x R

Example

| Temperature T (K)	1/T	time t (s)	1/t	Ln (1/t)
297.3	0.003364	53	0.018868	-3.9703
310.6	0.00322	24	0.041667	-3.1781
317.2	0.003153	16	0.0625	-2.7726
323.9	0.003087	12	0.083333	-2.4849
335.6	0.00298	6	0.166667	-1.7918

$$\text{gradient} = \frac{y_2 - y_1}{x_2 - x_1}$$

The gradient should always be -ve

In above example gradient =-5680

Ea = - gradient x R (8.31)
 = - -5680 x8.31
 = 47200 J mol^{-1}

The unit of Ea using this equation will be J mol^{-1} .
Convert into kJ mol^{-1} by dividing 1000
 Ea = +47.2 kJ mol^{-1}
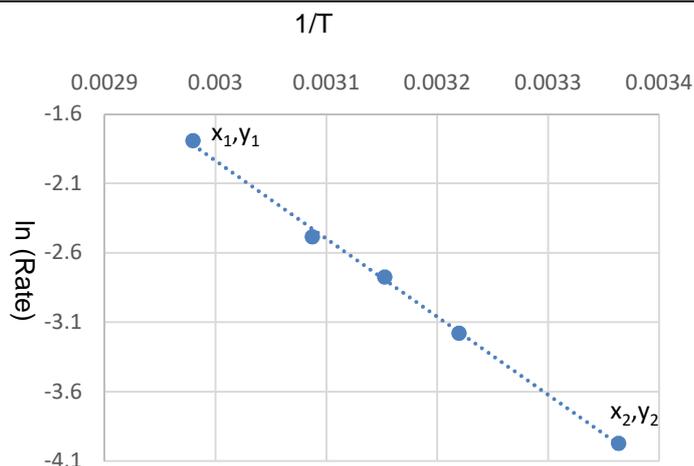
use a line of best fit
use all graph paper
choose points far apart on the graph to calculate the gradient

Effect of Catalysts

Definition: Catalysts increase reaction rates without getting used up.

Explanation: They do this by **providing an alternative route or mechanism** with a **lower activation energy**

Comparison of the activation energies for an uncatalysed reaction and for the same reaction with a catalyst present.

Progress of Reaction
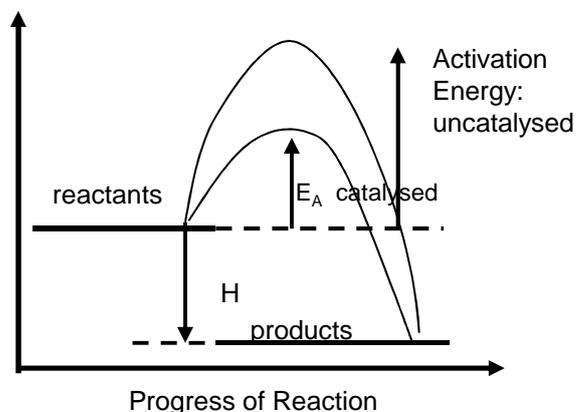
If the activation energy is lower, **more particles will have energy > E_A**, so there will be a higher frequency of effective collisions. The reaction will be faster

With a lower activation energy more particles have energy greater than the activation energy
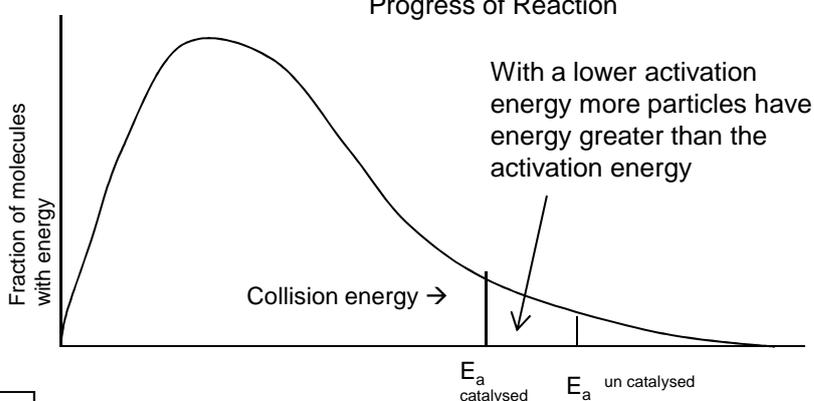
Transition metals and their compounds can act as heterogeneous and homogeneous catalysts.

A **heterogeneous catalyst** is in a different phase from the reactants

A **homogeneous catalyst** is in the same phase as the reactants

Heterogeneous catalysis

Heterogeneous catalysts are usually solids whereas the reactants are gaseous or in solution. The reaction occurs at the surface of the catalyst.

Adsorption of reactants at active sites on the surface may lead to catalytic action. The **active site** is the place where the **reactants adsorb** on to the **surface of the catalyst**. This can result in the bonds within the reactant molecules becoming weaker, or the molecules being held in a more reactive configuration. There will also be a higher concentration of reactants at the solid surface so leading to a higher collision frequency.

Strength of adsorption
The strength of adsorption helps to determine the effectiveness of the catalytic activity.
Some metals e.g. **W** have **too strong** adsorption and so the products cannot be released.
Some metals e.g. **Ag** have **too weak** adsorption, and the reactants do not adsorb in high enough concentration.
Ni and Pt have about the right strength and are most useful as catalysts.

Transition Metals can use the 3d and 4s e- of atoms on the metal surface to form weak bonds to the reactants.

Steps in Heterogeneous Catalysis

1. Reactants form bonds with atoms at **active sites** on the surface of the catalyst (adsorbed onto the surface)

2. As a result bonds in the reactants are weakened and break

3. New bonds form between the reactants held close together on catalyst surface.

4. This in turn weakens bonds between product and catalyst and product leaves (desorbs).

Surface area:
Increasing the surface area of a solid catalyst will improve its effectiveness. A support medium is often used to maximise the surface area and minimise the cost (e.g. Rh on a ceramic support in catalytic converters).

Examples of heterogeneous catalysts

Fe is used as a catalyst in the Haber Process
$N_2 + 3H_2 \rightarrow 2NH_3$
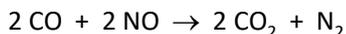
V_2O_5 is used as a catalyst in the Contact Process.
Overall equation : $2SO_2 + O_2 \rightarrow 2SO_3$
step 1 $SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$
step 2 $2V_2O_4 + O_2 \rightarrow 2V_2O_5$

Catalytic converters

These remove CO, NO_x and unburned hydrocarbons (e.g. octane, C_8H_{18}) from the exhaust gases, turning them into 'harmless' CO_2, N_2 and H_2O.

$2\ CO\ +\ 2\ NO\ \rightarrow\ 2\ CO_2\ +\ N_2$

$C_8H_{18}\ +\ 25\ NO\ \rightarrow\ 8\ CO_2\ +\ 12\frac{1}{2}\ N_2\ +\ 9\ H_2O$

Converters have a ceramic honeycomb coated with a thin layer of catalyst metals **Platinum, Palladium, Rhodium** – to give a large surface area.

Poisoning has a cost implication e.g. poisoning by sulphur in the Haber Process and by lead in catalytic converters in cars means that catalysts lose their efficiency and may need to be replaced.

Poisoning Catalysts
Catalysts can become poisoned by impurities and consequently have reduced efficiency.

Homogeneous catalysis

When catalysts and reactants are in the same phase, the reaction proceeds through an intermediate species.

The intermediate will often have a different oxidation state to the original transition metal. At the end of the reaction the original oxidation state will reoccur. This illustrates importance of variable oxidation states of transition metals in catalysis.

Examples of homogeneous catalysts

Reaction between iodide and persulphate ions

The reaction between I^- and $S_2O_8^{2-}$ catalysed by **Fe^{2+}**
overall $S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$

Catalysed alternative route
stage 1 $S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$
stage2 $2I^- + 2Fe^{3+} \rightarrow 2Fe^{2+} + I_2$

The uncatalysed reaction is very slow because the reaction needs a collision between **two negative ions**. **Repulsion** between the ions is going to hinder this – meaning **high activation energy.**

Both of the individual stages in the catalysed mechanism involve collision between positive and negative ions and will have lower activation energies.

Fe^{3+} ions can also act as the catalyst because the two steps in the catalysed mechanism can occur in any order.
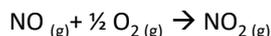
Catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide

Nitrogen dioxide catalyses the conversion of sulphur dioxide to sulphur trioxide.
The first step of the reaction is

$NO_{2\ (g)} + SO_{2\ (g)} \rightarrow SO_{3\ (g)} + NO_{(g)}$
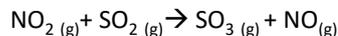
The second step of the reaction is

$NO_{(g)} + \frac{1}{2}\ O_{2\ (g)} \rightarrow NO_{2\ (g)}$

The nitrogen dioxide is regenerated at the end of the reaction so is classed as a catalyst.
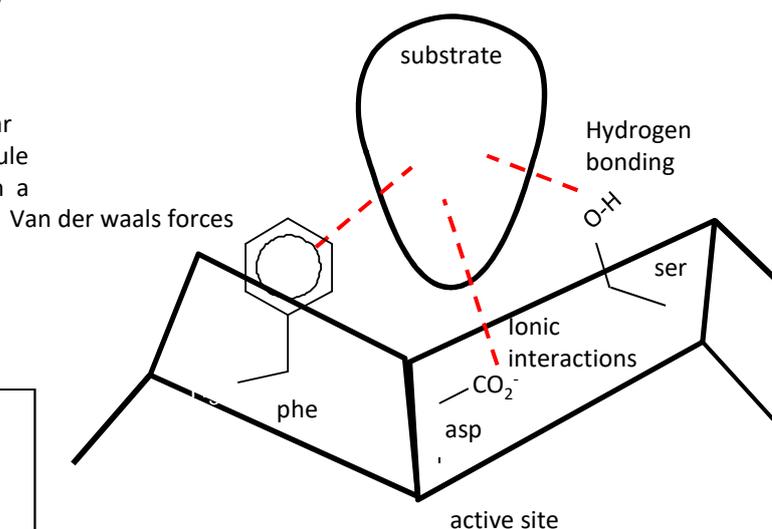
Enzymes

Enzymes are proteins. They are biological catalysts

The active site is usually a hollow in the globular protein structure into which a substrate molecule can bond to the amino acid side chains through a variety of interactions including
- Hydrogen bonding
- Van der waals forces
- Permanent dipole forces
- Ionic interactions

The interactions need to be strong enough to hold the substrate for long enough for the enzyme catalysed reaction to occur but weak enough for the product to be released

Only substrate molecules with the right shape and correct positions of functional groups will fit and bind to the active site- called the **lock and key hypothesis**


When the enzyme bonds to the active site it is called and enzyme-substrate complex

The enzyme has a specific shape that is complementary to active site . The substrate bonds to the active site. Other substrates do not fit into active site

pH and Temperature can affect the shape and bonds in an enzyme. High temperatures cause the enzymes to change shape – called denaturing

stereospecific active site

If the substrate is chiral then its likely that only one enantiomer will fit in the enzyme and so only one isomer will be catalysed

Strong binding

weak binding
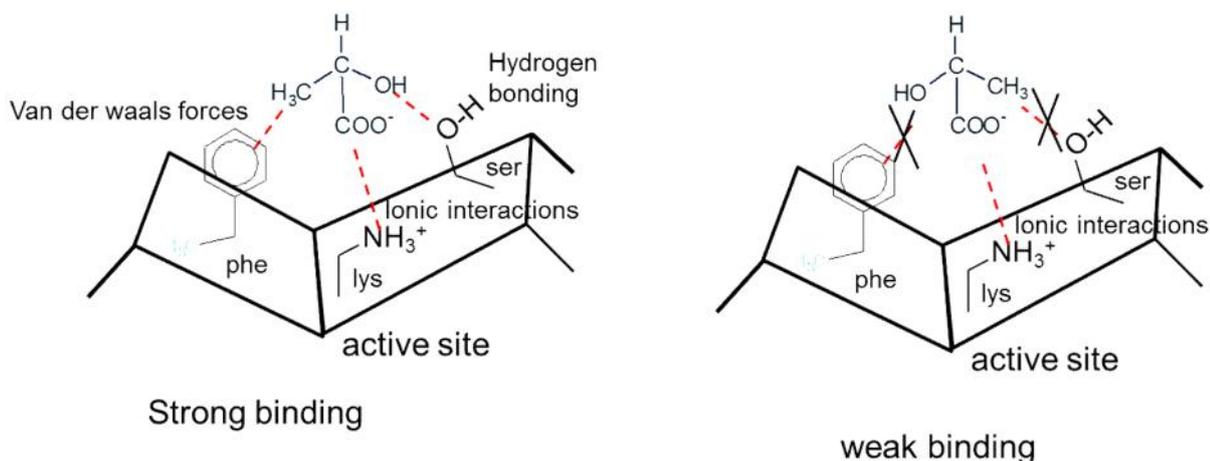
Drugs as Enzyme Inhibitors

Many drugs act as an enzyme inhibitor by blocking the active site.
The inhibitor will often bind to the active site strongly so stopping the substrate attaching to the enzyme.
(Some Inhibitors can also attach elsewhere on the enzyme but in doing so can change the shape of the active site which also stops its effectiveness)
Computers can be used to help design such drugs

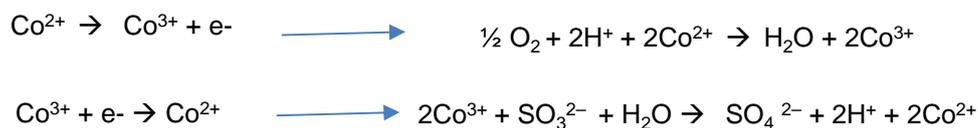## Constructing a catalysed mechanism for a reaction

Example

The following reaction is catalysed by Co^{2+} ions in an acidic solution. $SO_3^{2-} + ½ O_2 \rightarrow SO_4^{2-}$.
Write a mechanism for the catalysed reaction by writing two equations involving Co^{2+} and Co^{3+} ions.

Split the full equation into its two half equations

$$SO_3^{2-} + ½ O_2 \rightarrow SO_4^{2-}$$

$$½ O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$$

Add in cobalt to make two new redox equations. Making sure the oxidised cobalt equation is combined with the original reduced half equation and vice versa

$$Co^{2+} \rightarrow Co^{3+} + e^-$$

$$½ O_2 + 2H^+ + 2Co^{2+} \rightarrow H_2O + 2Co^{3+}$$

$$Co^{3+} + e^- \rightarrow Co^{2+}$$

$$2Co^{3+} + SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2Co^{2+}$$

Check your two mechanism equations add up to the original full non-catalysed equation.