# 4. Reaction Kinetics

From GCSE you should be aware that reactions can occur at different rates. Explosions and combustion reactions being good examples of fast reactions. Rusting and fermentation are examples of slower reactions. You should also remember changing temperature, concentration and surface area of the reactants can change the rate of reaction. Rates of reaction are determined by doing experiments

> 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 vs time by drawing a tangent to the curve and calculating the gradient of the tangent. This can be done at several different points on the graph


Initial rate = gradient of tangent
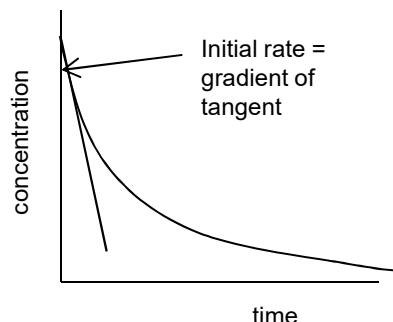
Continuous vs initial rate data

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.
Sometimes when doing multiple rate experiments varying something like concentration and temperature we just focus on the initial rate for each different experiment. We may still have to draw concentration vs time graphs to be able to calculate the initial rate but in some cases there are short cuts. We will meet some examples of these later.
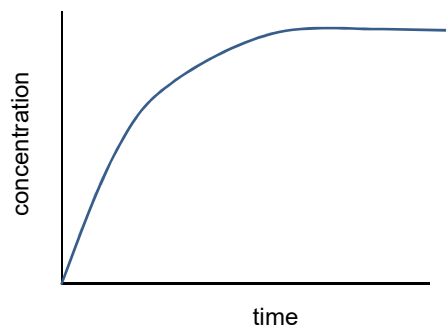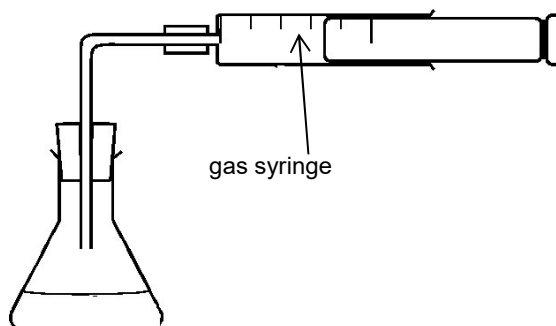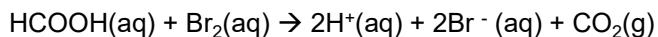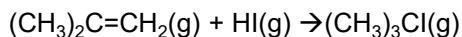

Techniques to investigate rates of reaction

There are several different methods for measuring reactions rates. We have to look at the properties of the reactants or products to find one that is easy to measure. 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. 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.

$(CH_3)_2C=CH_2(g) + HI(g) \rightarrow (CH_3)_3CI(g)$

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

gas syringe

Measurement of change of mass

Alternatively if a reaction gives off a gaseous product then the mass of the whole reaction mixture could be monitored over time if the gas produced is allowed to escape. This method works better with heavy gases such as CO_2 rather than light gases like hydrogen.

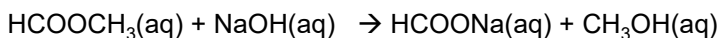$HCOOH(aq) + Br_2(aq) \rightarrow 2H^+(aq) + 2Br^- (aq) + CO_2(g)$
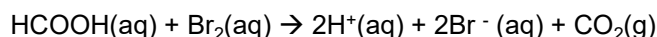
Titrating samples of reaction mixture with acid, alkali, sodium thiosulfate etc
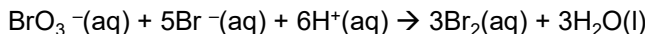
For some substances the only way of measuring their concentration is by titrating them with another substance that reacts with it. Often this is used if a reactant or product has acid/base properties. A large volume of the reactants will be reacted and then at regular time intervals small samples are removed from the reaction mixture, quenched (which stops the reaction) and then titrated with a suitable reagent. The method can be quite time consuming and involves disrupting the reaction mixture during the reaction which is not ideal.
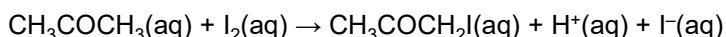
Quenching (which stops the reaction)- can be done by
- by dilution with water
- by cooling
- by adding a reagent that reacts with one of the reactants

$HCOOCH_3(aq) + NaOH(aq) \rightarrow HCOONa(aq) + CH_3OH(aq)$ 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

$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$ The I_2 could be titrated with sodium thiosulfate

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. Colorimeters can measure the intensity of a colour in a solution. This method has the advantage that it does not disrupt the reaction mixture and it leads to a much quicker determination of concentration.

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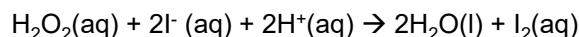
The I_2 produced is a brown solution

Measuring change in electrical conductivity

Measuring the conductivity of reaction mixture can be used if there is a change in the number of ions in the reaction mixture. The reaction on the right would increase in conductivity over time as the ionic products are produced.

$HCOOH(aq) + Br_2(aq) \rightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(g)$
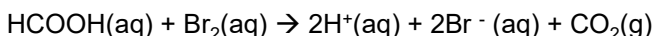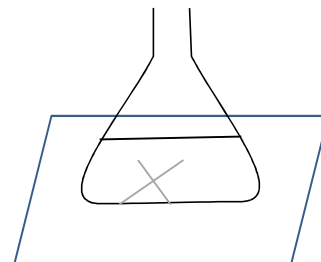
Measurement of optical activity.

If there is a change in the optical activity through the reaction this could be followed in a polarimeter. See chapter 6.1.5. isomerism for more on optical activity and polarimeters

$CH_3CHBrCH_3(l) + OH^-(aq) \rightarrow CH_3CH(OH)CH_3(l) + Br^-(aq)$
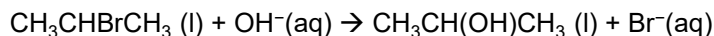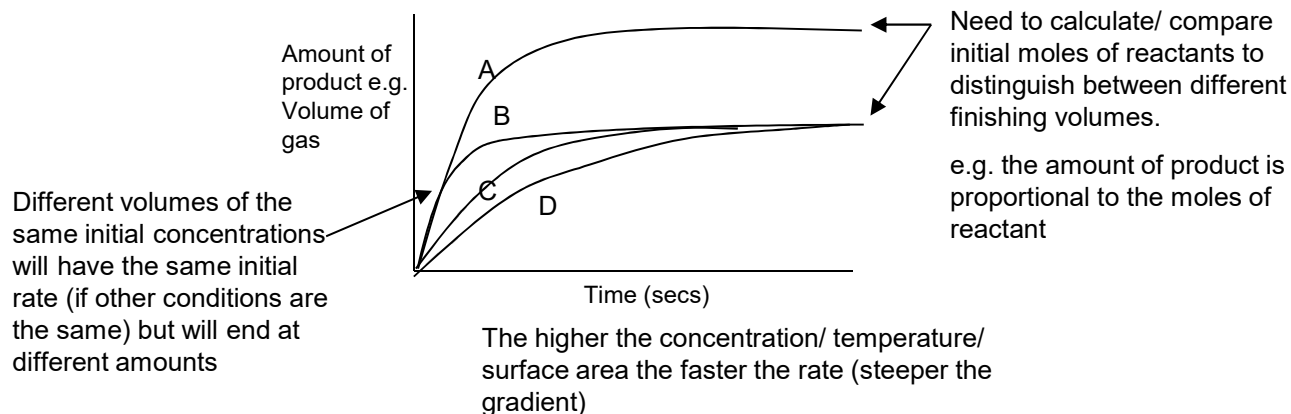
Classic experiment: sodium thiosulfate and hydrochloric acid

In the experiment between sodium thiosulfate 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 sulfur . $Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + S + H_2O$
This is an approximation for initial rate of reaction as it does not include the change in concentration term. We can use this because we can assume the amount of sulfur produced to block out the cross in each experiment is the same and constant so each time we do the experiment the same amount of sulfur is produced. The change in concentration of sulfur is therefore the same for each experiment so only the time taken to reach this concentration is relevant.

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)

Measuring Reaction Rates

Magnesium reacts with sulfuric acid with the following reaction

$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$
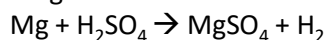
The reaction rate can be following by measuring the volume of hydrogen gas given off over time.

1. a) Draw a diagram of the apparatus used in this experiment (include reaction vessel and apparatus used to measure volume of gas.)

b) Why would measuring the loss of mass in this reaction not be an appropriate method?

2. a) If a student wanted to investigate the effect of changing concentration on the reaction rate, list all the relevant variables that should be controlled.

 b) How could temperature best be controlled on this reaction?

3. It is best to clean the magnesium ribbon used in this reaction to remove MgO coated on the surface of the magnesium. Why is this done?

The following data were collected for the reaction between 50 cm³ of 1M H_2SO_4 and a 2cm length of magnesium (0.09g)

Time /seconds	Volume H₂ Produced / cm³
10	30
20	50
30	65
40	76
50	84
60	90
70	90

4. Plot a graph of volume against time and draw a line of best fit.

5. a) Draw a tangent to the curve at time =30 and measure the gradient at this point and hence the reaction rate.

b) At what time has the reaction stopped?

6. a) In this reaction would there be any magnesium left at the end of the reaction?

b) How would the final volume of hydrogen and reaction rate at the start of this experiment vary if 50cm³ of 2M H_2SO_4 were used?

c) Explain in terms of the collision theory why the reaction rate will change if the concentration is increased.

7. The uncertainty in using a 50 cm³ measuring cylinder is ± 1.0 cm³. Calculate the maximum percentage uncertainty in using this apparatus when measuring 50 cm³ of solution.

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 which is defined as the minimum energy which particles need to collide to start a reaction.

When thinking about particles colliding we need to consider:

• The frequency of the collisions between the particles
• The energy of the collisions
• The orientation of the molecules in the collision
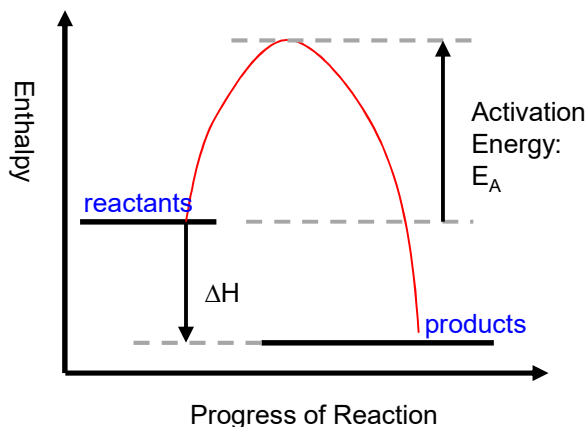
Temperature of gases

Increasing the temperature of a gas will make the gas particles have more energy. They will therefore travel faster and will collide more frequently. The particles will also collide with more energy which has a significant effect on the rate of reaction. The energy gaseous particles have at a certain temperature is not a simple matter. At any one fixed temperature the particles in a gas will have a wide range of energies. This range of energies can be illustrated by a distribution called the Maxwell-Boltzmann energy distribution.

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. It is not a symmetrical distribution. The particles have such a range of energies because in a sample of gas with many millions of particles there are constant collisions between particles. Often when there is a collision between two particles which bounce off each other, one particle may gain energy and speed up and the other particle must therefore lose this energy and slow down. This process results in there being a range of energies.
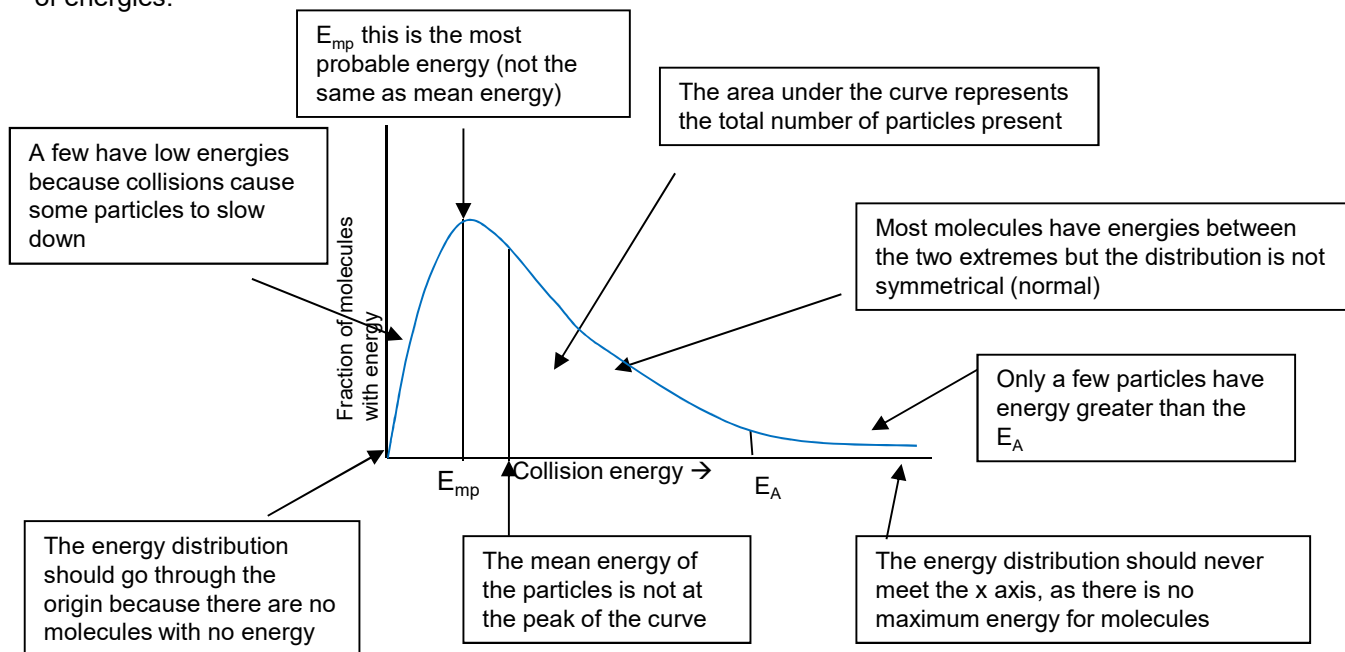

The particles that collide with energy greater than the activation energy will react successfully. The ones that collide with energy less than the activation energy will just bounce off each other.

You might ponder how a reaction go to completion if few particles have energy greater than the activation energy. The particles can through collisions gain energy so eventually a lower energy could potentially gain energy greater than activation energy. The size of the activation energy is an important limiting factor here though. Chemical reactions with high activation energies will be slow reactions.

Increasing temperature

As the temperature increases the distribution shifts towards having more molecules with higher energies
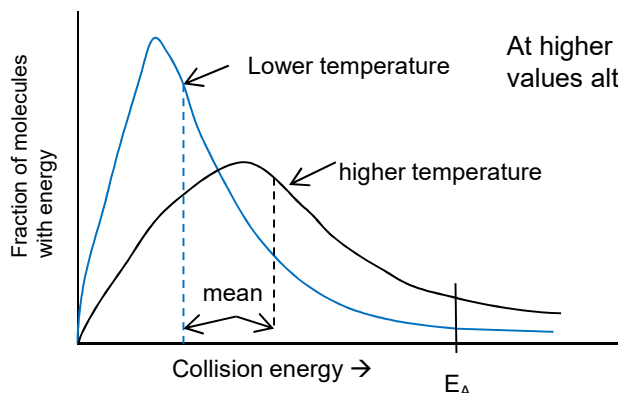
At higher temps both the E_{mp} and mean energy shift to high energy values although the number of molecules with those energies decrease
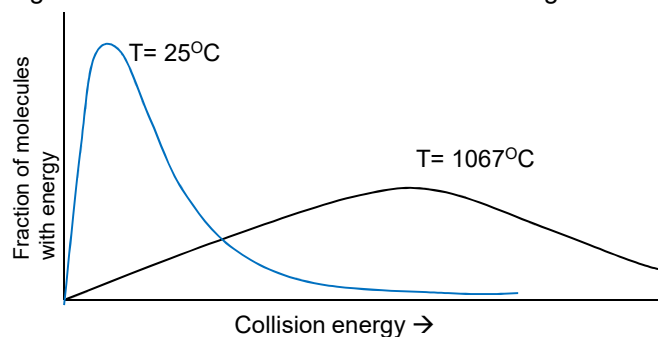
The total area under the curve should remain constant because the total number of particles is constant

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

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 will be successful and result in a reaction.

As the temperature increases, the Maxwell Boltzmann distribution 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 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
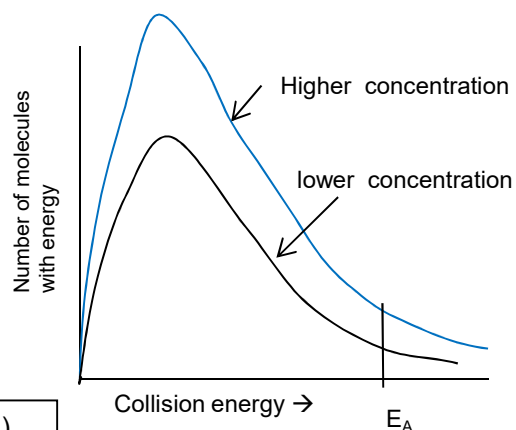
More molecules have energy > E_A (although not a greater proportion)

Effect of increasing surface area

Increasing the surface area of a solid reactant will significantly increase the reaction rate. This is why potatoes cook quicker when boiling if you cut them into smaller pieces. Powders have very high surface areas.

Increasing surface area will cause collisions to occur more frequently between the reactant particles leading to a higher frequency of effective collisions and this increases the rate of the reaction.

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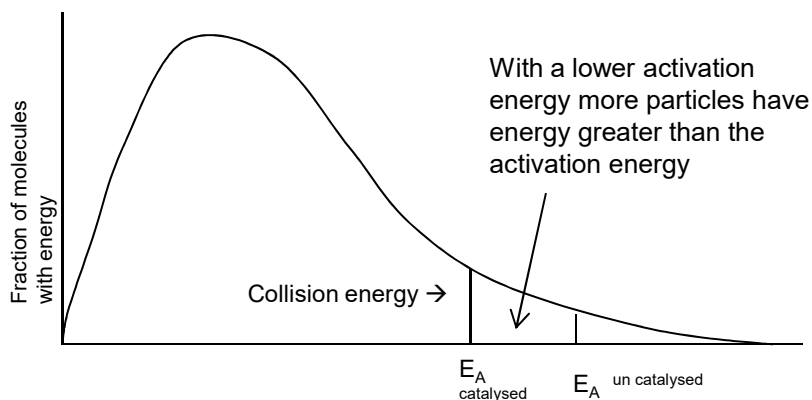
A **heterogeneous catalyst** is in a different phase from the reactants

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

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

Activation energy: uncatalysed

reactants

E_A catalysed

ΔH

products

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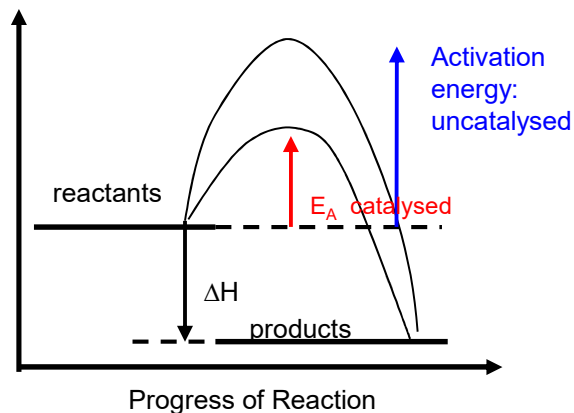
If the activation energy is lower, **more particles will have energy > E_A,** so there will be a higher frequency of effective collisions. The reaction will be faster.

With a lower activation energy more particles have energy greater than the activation energy

Fraction of molecules with energy

Collision energy →

E_A catalysed E_A un catalysed

Rate Equations

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

For the following reaction, $aA + bB \rightarrow$ 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

<u>NOTE</u>: 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
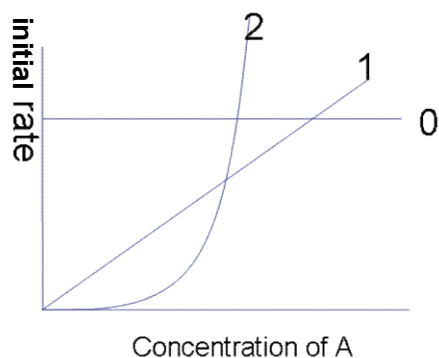
For zero order: the concentration of A has no effect on the rate of reaction $r = k[A]^0 = k$

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 rate experiments

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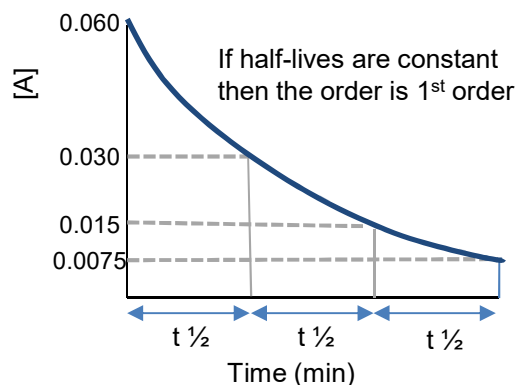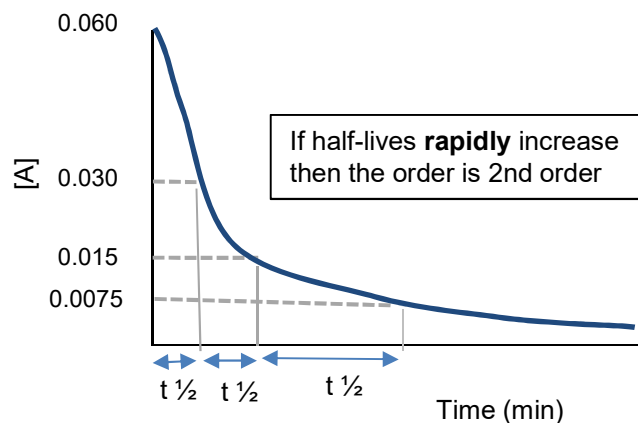
Continuous rate data

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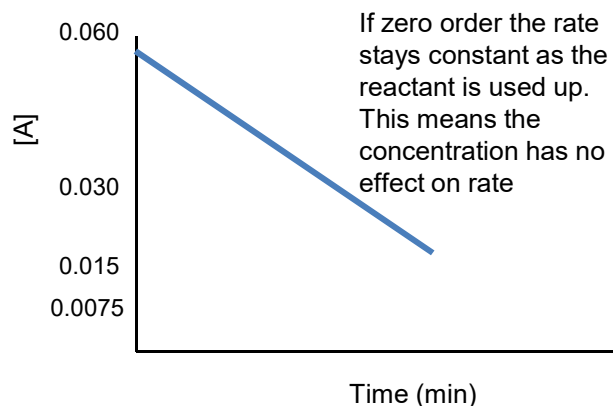
This data is processed by plotting the data and calculating successive half-lives.

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

Second order

0.060

[A] 0.030

0.015

0.0075

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

t ½ t ½   t ½

Time (min)

zero order

0.060

[A]

0.030

0.015

0.0075

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

Time (min)

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

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

3. Simplify fraction

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

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

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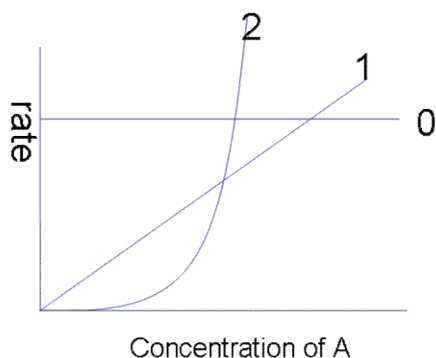0 means the reaction is zero order with respect to that reactant
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The square brackets **[A]** means the concentration of A
 (unit **mol dm^{-3}**)

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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^{3}s^{-1}**

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

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- reaction is first order in A and zero order in B
- overall order = 1 + 0 = 1
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Calculating units of k

1. Rearrange rate equation to give k as subject

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

2. Insert units and cancel

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

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

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

3. Simplify fraction

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

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

Working out orders from experimental initial rate data

The initial rate is the rate at the start of the reaction, where it is fastest. It is often obtained by taking the gradient of the conc vs time graph.

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. This data is normally presented in a table.

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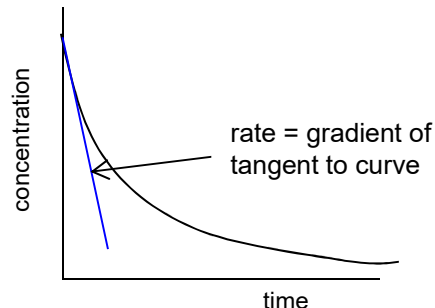
Example: work out the rate equation for the following reaction, **A+ B+ 2C → D + 2E,** using the initial rate data in the table

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 B 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 =$\text{mol}^{-2}\text{dm}^6\text{s}^{-1}$

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 $\longrightarrow$ $k = \dfrac{r}{[X]\,[Y]^2}$ $\qquad k = \dfrac{2.40 \times 10^{-6}}{0.2 \times 0.2^2}$ $\qquad$ **k = 3.0 x 10^{-4} mol^{-2}dm^{6}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**

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 $k = Ae^{-E_A/RT}$ where A is the Arrhenius constant, R is the gas constant, and E_A is activation energy.
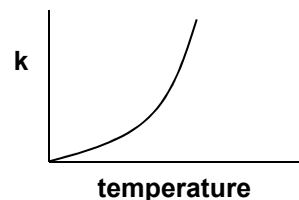
k / temperature

Using the Arrhenius equation (equations will be given in the exam)

$$k = Ae^{-E_A/RT}$$

The Arrhenius equation is usually rearranged to (You don't need to know how)

$\ln k = \ln A - E_A/(RT)$

You should be able to do rearrangements and substitute values into both these equations.

Units
Temperature uses the unit **K**
$R = 8.31$ J mol^{-1}K^{-1}
Activation energy will need to be in **J mol^{-1}** to match the units of R
The unit of the Arrhenius constant A will be the same as the unit of the rate constant k

---

Example
A reaction carried out at 30°C has a value of $k = 4.26 \times 10^{-8}$ s^{-1}
The activation energy $Ea = 95.8$ kJ mol^{-1}
The gas constant $R = 8.31$ J K^{-1} mol^{-1}
Calculate a value for the Arrhenius constant, A, for the reaction.

Using Equation $k = Ae^{-E_A/RT}$

Rearrange to A = $\dfrac{k}{e^{-E_A/RT}}$ = $\dfrac{4.26 \times 10^{-8}}{e^{-95800/(8.31 \times 308)}}$ = $\dfrac{4.26 \times 10^{-8}}{e^{-37.4}}$ = $\dfrac{4.26 \times 10^{-8}}{5.55 \times 10^{-17}}$

= 7.67×10^{8} s^{-1}

Example
A reaction carried out at 25°C has a value of $k = 3.3 \times 10^{-3}$ mol^{-1} dm^3 s^{-1}
$\ln A = 17.1$
The gas constant $R = 8.31$ J K^{-1} mol^{-1}
Calculate a value for the activation energy in kJ mol^{-1}

Using Equation $\ln k = \ln A - E_A/(RT)$

Rearrange to $E_A = (\ln A - \ln k) \times RT$ = $(17.1 - -5.71) \times 8.31 \times 298$

= 56486 J mol^{-1}

= 56.5 kJ mol^{-1}

Calculating the activation energy graphically from experimental data

Using the rearranged version

$$\ln k = \ln A - E_A/(RT)$$

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.

1/T

ln (Rate)

Gradient = - E_A/ R

E_A = - gradient x R
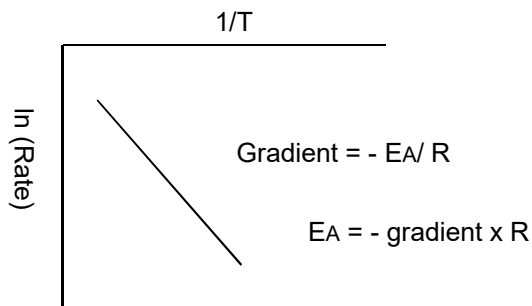
Example

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

gradient = $\dfrac{y_2 - y_1}{x_2 - x_1}$

The gradient should always be -ve

In above example gradient =-5680

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

The unit of E_A using this equation will be J mol^{-1}.
Convert into kJ mol^{-1} by dividing 1000
 E_A = +47.2 kJ mol^{-1}

1/T

| 0.0029 | 0.003 | 0.0031 | 0.0032 | 0.0033 | 0.0034 |

ln (Rate)

x_1, y_1

x_2, y_2
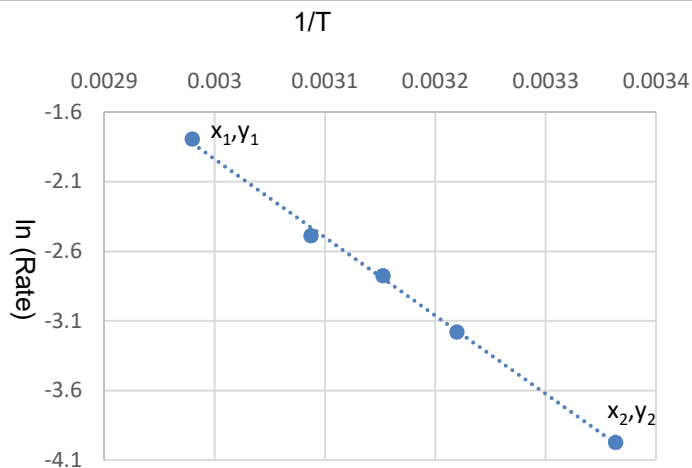
- use a line of best fit
- the plotted points should fill all graph paper (generally don't start at the origin)
- choose points far apart on the graph to calculate the gradient

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 $\rightarrow$ X + D slow**
Step 2 $X + C \rightarrow Y$ fast
Step 3 $Y + B \rightarrow E$ fast
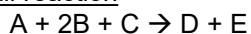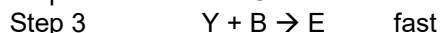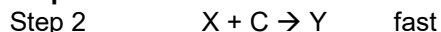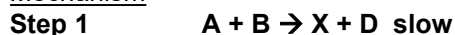
$$r = k\,[A]^1[B]^1[C]^0$$

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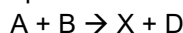Step 3 $Y + B \rightarrow E$ fast
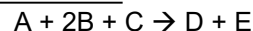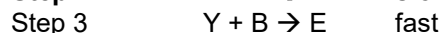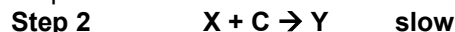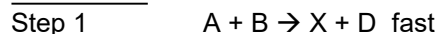
$r = k\,[X]^1[C]^1$
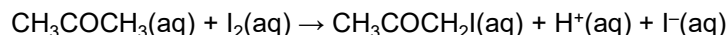The intermediate X is not one of the reactants so must be replaced with the substances that make up the intermediate in a previous step
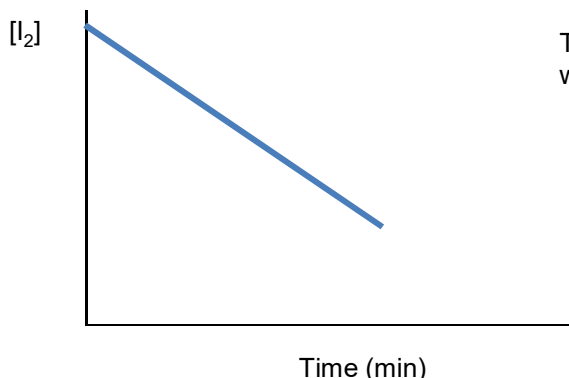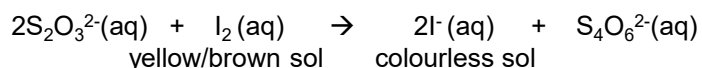$A + B \rightarrow X + D$
$$r = k[A]^1[B]^1[C]^1$$

Investigating the rate of reaction between iodine and propanone

Propanone reacts with iodine in acidic solution (the acid is a catalyst) as shown in the equation below.
$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$

This reaction can be followed by removing small samples from the reaction mixture with a volumetric pipette. The sample is then quenched by adding excess sodium hydrogencarbonate to neutralize acid catalyst which stops the reaction. Then the sample can be titrated with sodium thiosulfate using a starch catalyst.

$$2S_2O_3{}^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6{}^{2-}(aq)$$
           yellow/brown sol   colourless sol

[I_2] vs Time (min) — a decreasing straight line graph

This reaction is zero order with respect to I_2 but 1st order with respect to the propanone and acid catalyst

The rate equation for the reaction is
Rate = $k[CH_3COCH_3(aq)][H^+(aq)]$

If there is a zero order reactant there must be at least two steps in the mechanism because the rate determining step will not involve the zero order reactant

The rate determining step of this reaction must therefore contain one propanone molecule and one H^+ ion forming an intermediate. The iodine will be involved in a subsequent faster step.

Example 3: S_N1 or S_N2?

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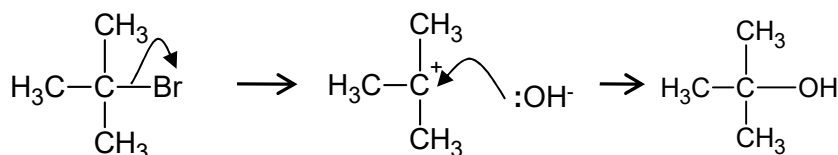
This is a one step mechanism

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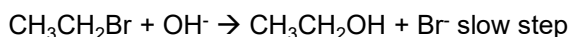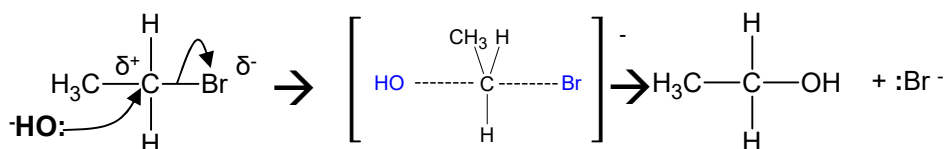
The rate equation is

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

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

Primary halogenalkanes tend to react via the SN2 mechanism
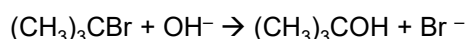

SN₁ nucleophilic substitution mechanism for tertiary halogenoalkanes

The Br first breaks away from the halogenoalkane to form a carbocation intermediate
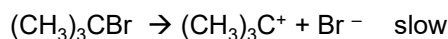
The hydroxide nucleophile then attacks the positive carbon

Tertiary halogenoalkanes undergo this mechanism as the tertiary carbocation is stabilised by the electron releasing methyl groups around it. (see alkenes topic for another example of this). Also the bulky methyl groups prevent the hydroxide ion from attacking the halogenoalkane in the same way as the mechanism above

Overall Reaction

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

Mechanism:

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

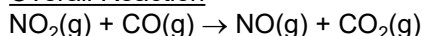$(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$ fast
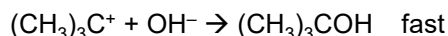
The rate equation is

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

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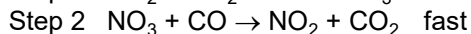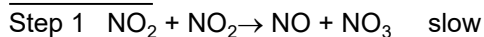**1** molecule in rate determining step

Primary halogenoalkanes do not do the SN_1 mechanism because they would only form an unstable primary carbocation.

Example 4

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 5

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 + H₂ → Y**
Step **3 Y + H₂ → N₂ + 2H₂O**
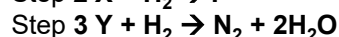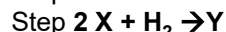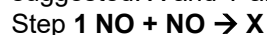
Which **one of the three steps is the rate-determining step?**

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.
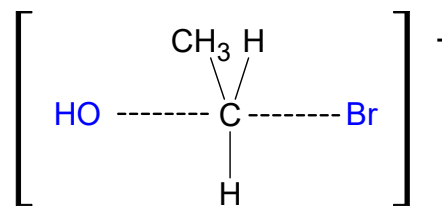
Transition States

During a chemical reaction, reactants do not suddenly convert to products.
 The formation of products is a continuous process of bonding breaking and forming.
 At some point, a transitional species is formed containing "partial" bonds.
 This species is called the transition state.

$$\left[\begin{array}{c} CH_3\ H \\ \backslash\ / \\ HO \text{-------} C \text{-------} Br \\ | \\ H \end{array} \right]^{-}$$

•At the top of the hump the reactants are at a stage where the old bonds are not quite broken and the new bonds are not quite made.
•This is the point of maximum potential energy and is called the transition state.
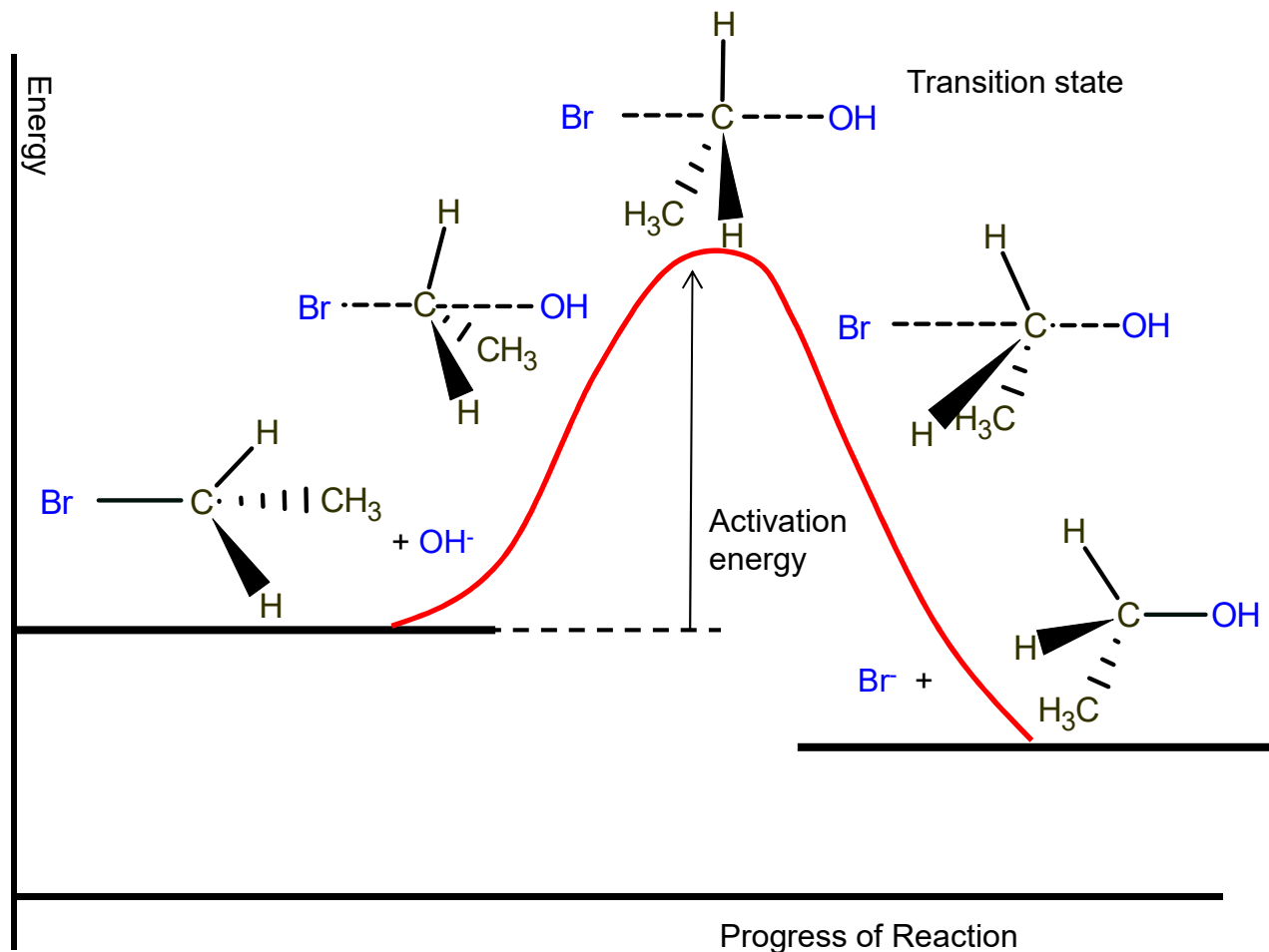
•The activation energy is therefore the energy needed to reach the transition state