

CHEMICAL KINETICS

Introduction Chemical kinetics is concerned with the dynamics of chemical reactions such as the way reactions take place and the rate (speed) of the process.

Collision theory

- particles must **COLLIDE** before a reaction can take place
- not all collisions lead to a reaction
- reactants must possess at least a minimum amount of energy - **ACTIVATION ENERGY**
- + • particles must approach each other in a certain relative orientation - **STERIC EFFECT**

Rate increase

to increase the rate one needs, according to collision theory, to have ...

more frequent collisions - increase particle speed or
have more particles present

more successful collisions - give particles more energy or
lower the activation energy

- increase surface area
- increase temperature
- use a light source (certain reactions only)
- add a catalyst
- increase pressure (gaseous reactions only)
- increase concentration

SURFACE AREA

- increasing surface area leads to more chances of a collision
 - catalysts (e.g. in catalytic converters) are used in a finely divided form for this reason
- + *in many organic reactions you have two liquid layers, one aqueous and the other non-aqueous. Shaking the mixture improves the reaction rate as an emulsion is often formed and the area of boundary layers is increased and more collisions can take place.*

Q.1 *What is the surface area of a cube of side 1cm?*

If you cut the cube in half, what is the new surface area ?

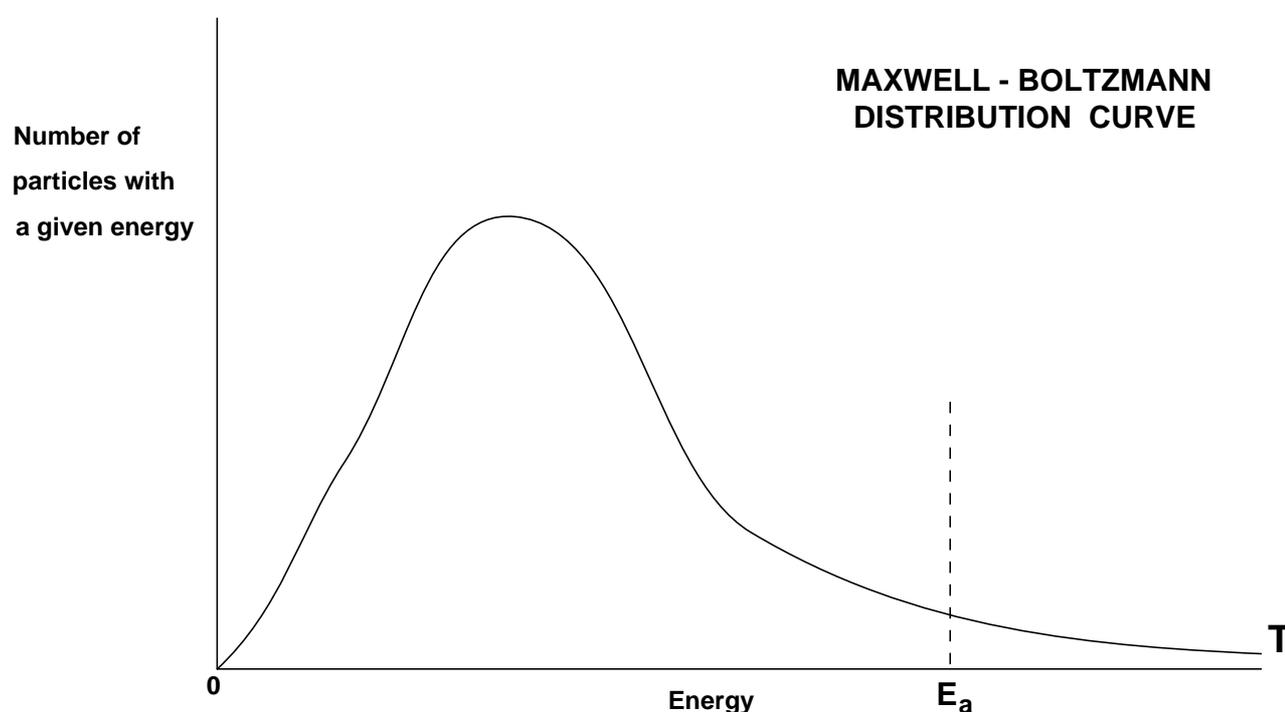
TEMPERATURE

- Effect*
- **increasing the temperature increases the rate** of a reaction
 - **particles get more energy** so they can overcome the energy barrier
 - **particle speeds increase** so collisions are more frequent

Distribution of molecular velocities and energies

Introduction Because of the many collisions taking place, there is a **spread of molecular velocities and energies**. This has been demonstrated by an experiment. It indicated that ...

- no particles have zero velocity
- some have very low and some have very high velocities
- most have intermediate velocities.



Q.2 Superimpose the curves you get at a higher (T_2) and a lower (T_1) temperature.

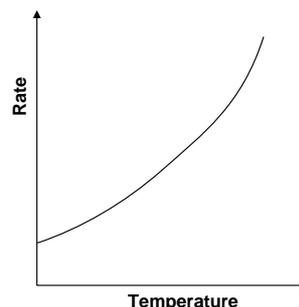
Significance E_a corresponds to the **Activation Energy**. The area under the curve beyond this value is proportional to the number of particles with energy greater than this limiting value.

Increasing the temperature alters the distribution;

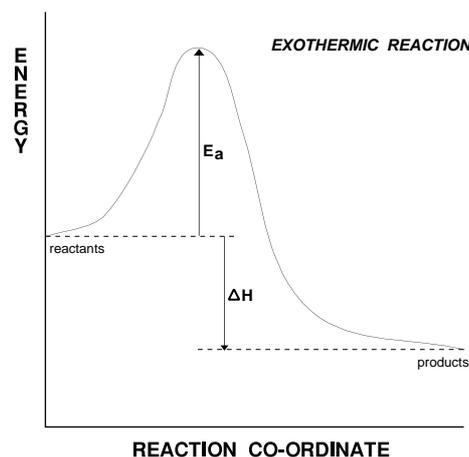
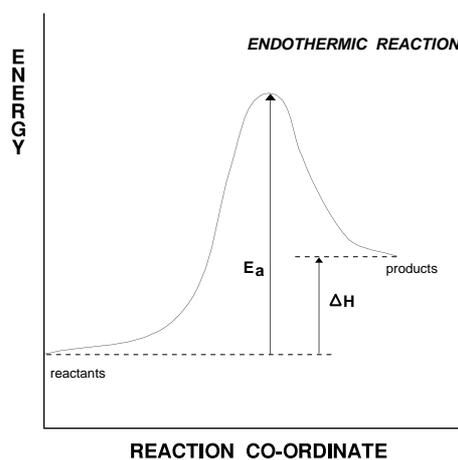
- get a **shift to higher energies/velocities**
- **curve gets broader and flatter** due to the greater spread of values
- **area under the curve stays constant** as it corresponds to the total number of particles

- Explanation**
- increasing the temperature gives more particles with energy greater than E_a
 - more reactants are able to overcome the energy barrier associated and form products
 - a small rise in temperature can lead to a large increase in rate

The Effect of Temperature on the Rate of a Reaction



- as a reaction takes place the energy of the system rises to a maximum, then falls
- if energy falls to below the original value = overall release of energy = **exothermic**
- if energy falls to above the original value = overall absorption of energy = **endothermic**



LIGHT

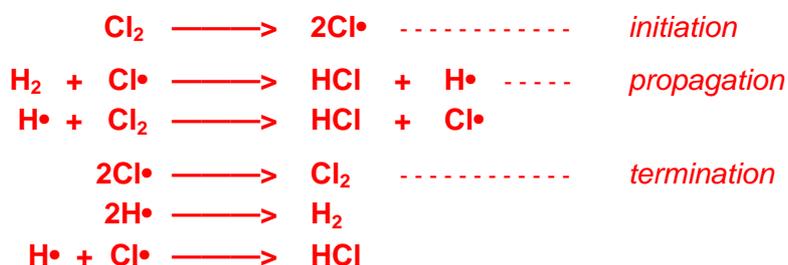
- shining a suitable light source onto some reactants increases the rate of reaction
- the light - often U.V. - provides energy to break bonds and initiate a reaction
- the greater the intensity of the light, the greater the effect

Examples

- the reaction between methane and chlorine - see *organic notes on alkanes*
- the reaction between hydrogen and chlorine

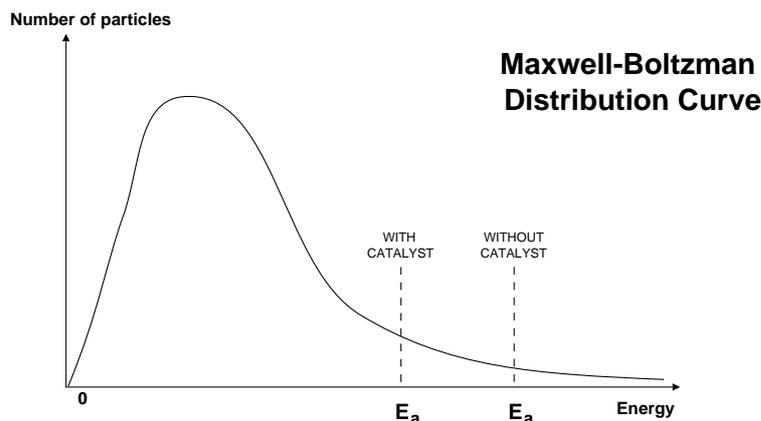


Mechanism



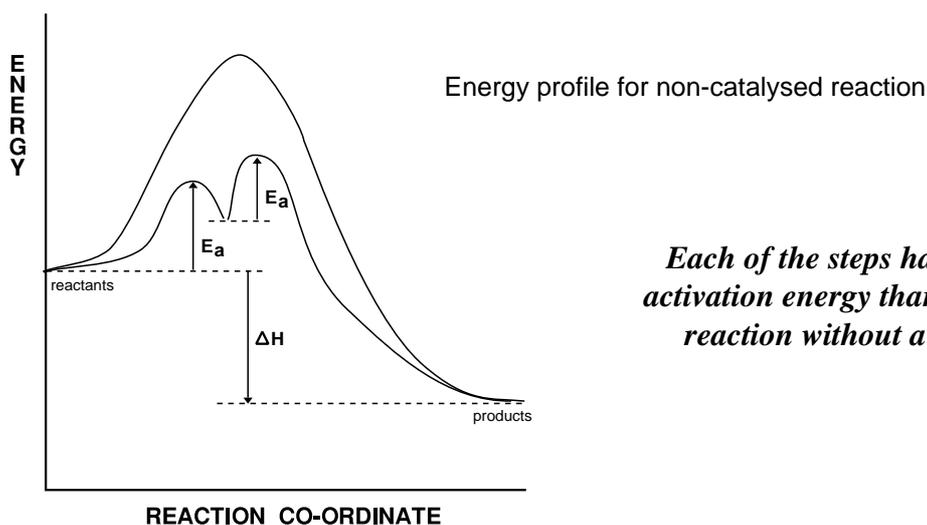
CATALYSTS

Operation • work by providing an **alternative reaction pathway with a lower Activation Energy**



Lowering E_a results in there being a greater area under the curve showing that more molecules have energies in excess of the Activation Energy

- decreasing the Activation Energy means that more particles will have sufficient energy to overcome the energy barrier and react
- using catalysts avoids the need to supply extra heat - safer and cheaper
- catalysts **remain chemically unchanged at the end** of the reaction.



Each of the steps has a lower activation energy than the single reaction without a catalyst

Types

Homogeneous Catalysts
same phase as reactants

Heterogeneous Catalysts
different phase to reactants

Uses

- widely used in industry especially where an increase in temperature would result in a lower yield due to a shift in equilibrium (e.g. Haber and Contact Processes)
- **CATALYSTS DO NOT AFFECT THE POSITION OF ANY EQUILIBRIUM** but they do affect the rate at which equilibrium is attained.
- a lot is spent on research into more effective catalysts as the savings can be dramatic
- catalysts need to be changed regularly as they get 'poisoned' by other chemicals
- catalysts are used in a finely divided state to increase the surface area

HETEROGENEOUS CATALYSIS

Catalyst is in a **different phase to the reactants**

e.g. *a solid catalyst in a gaseous reaction*

Action

- takes place at **active sites** on the **surface** of a solid
- gases are **adsorbed onto the surface**
- form weak bonds between gas and metal atoms

*Catalysis is thought to work in **three stages** as follows ...*

- Adsorption** • formation of bonds with surface weakens bonds in gas molecules makes a subsequent reaction easier
- Reaction** • adsorbed gases may be held on the surface increases chances of favourable collisions
- Desorption** • the products are then released from the active sites

HARD Hetero = **A**dsorption + **R**eaction + **D**esorption

The **strength of adsorption is critical** ...

- Too weak little adsorption - molecules will not bond to surface
- Too strong molecules are held tightly and remain on the surface thus blocking reactive sites and preventing further reaction
- Just right reactants are attracted yet products can leave to open up the active sites

Rate

Catalysis of gaseous reactions can lead to an increase in rate in several ways ...

- one species is adsorbed onto the surface and is more likely to undergo a collision
- one species is held in a favourable position for reaction to occur
- adsorption onto the surface allows bonds to break and fragments react quicker
- two reactants are adsorbed alongside each other give a greater concentration

Format

- used in a **finely divided** form increases the surface area provides more collision sites.
- mounted in a **support** medium maximises surface area and reduces costs.

Examples of catalysts

- Metals Ni, Pt hydrogenation reactions
 Fe Haber Process
- Oxides Al₂O₃ dehydration reactions
 V₂O₅ Contact Process

POLLUTANT GASES FROM INTERNAL COMBUSTION ENGINES

Carbon monoxide CO

Origin • incomplete combustion of hydrocarbons in petrol because not enough oxygen was present

Effect • poisonous
• combines with haemoglobin in blood
• prevents oxygen being carried

Oxides of nitrogen NO_x - NO, N₂O and NO₂

Origin • combination of atmospheric nitrogen and oxygen under high temperature conditions

Effect • aids formation of **photochemical smog** which is irritating to eyes, nose and throat

• aids formation of **low level ozone** which affects plant growth and is irritating to eyes, nose and throat

i) sunlight breaks down NO₂ NO₂ —> NO + O

ii) ozone is produced O + O₂ —> O₃

Hydrocarbons C_xH_y

Origin • hydrocarbons that have not undergone combustion

Effect • toxic and carcinogenic (cause cancer)

EQUATIONS FOR POLLUTION FORMATION

Nitrogen combines with oxygen N₂(g) + O₂(g) —> 2NO(g)

Nitrogen monoxide is oxidised 2NO(g) + O₂(g) —> 2NO₂(g)

Incomplete hydrocarbon combustion C₈H₁₈(g) + 8½O₂(g) —> 8CO(g) + 9H₂O(l)

EQUATIONS FOR POLLUTION REMOVAL

Oxidation of carbon monoxide 2CO(g) + O₂(g) —> 2CO₂(g)

Removal of NO and CO 2CO(g) + 2NO(g) —> N₂(g) + 2CO₂(g)

Aiding complete H/C combustion C₈H₁₈(g) + 12½O₂(g) —> 8CO₂(g) + 9H₂O(l)

HOMOGENEOUS CATALYSIS

Catalyst and reactants are in the **same phase**

- reaction proceeds through an **intermediate** species with **lower energy**
- there is usually more than one reaction step
- transition metal ions are often involved - **oxidation state changes** during the reaction

Examples

Acids e.g. hydrolysis of esters

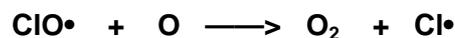
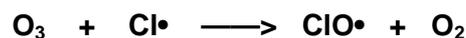
Gases **OZONE** in the atmosphere breaks down naturally as follows ...



However it breaks down more easily in the presence of chlorofluorocarbons (CFC's).

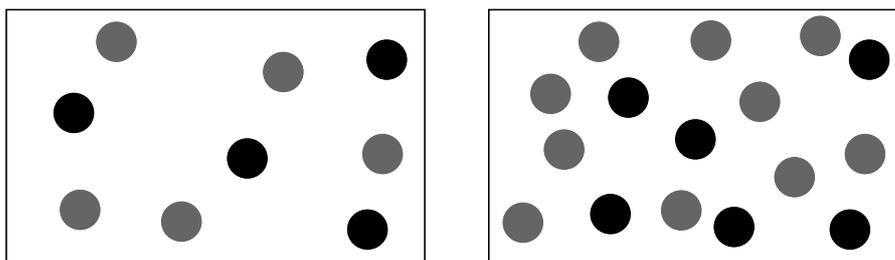
There is a series of complex reactions but the basic process is :-

- CFC's break down in the presence of UV light to form chlorine radicals
- chlorine radicals then react with ozone
- chlorine radicals are regenerated



Overall, chlorine radicals are not used up so a small amount of CFC's can destroy thousands of ozone molecules before they take part in a termination stage.

- PRESSURE**
- increasing the pressure makes gas particles get closer together
 - this increases the frequency of collisions so the reaction rate increases
 - many industrial processes occur at high pressure to increase the rate but it also can affect the position of equilibrium - see *Chemical Equilibrium*



The greater the pressure, the more frequent the collisions

CONCENTRATION

Introduction **Increasing concentration = more frequent collisions = increased rate of reaction**

However: *increasing the concentration of some reactants can have a greater effect than increasing others.*

Rate Reactions start off at their fastest and get slower as the concentration of reactants drops.

In a reaction such as $A + 2B \longrightarrow C$ the concentrations **might** change as shown

- the steeper the curve the faster the rate of the reaction
- reactions start off quickly because of the greater likelihood of collisions
- reactions slow down with time because there are fewer reactants to collide

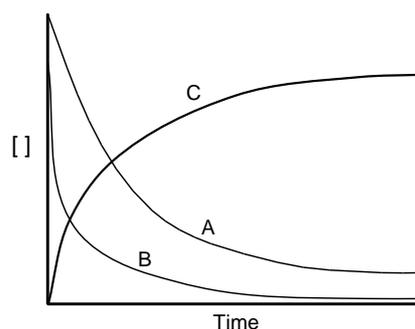
Reactants (A and B)

Concentration decreases with time

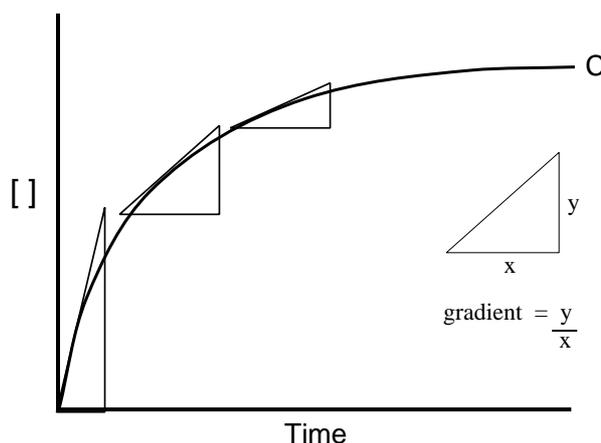
Products (C)

Concentration increases with time

[] refers to the concentration in mol dm^{-3}



- the **rate of change** of concentration is found from the **slope** or **gradient** of the curve
- the slope at the start of the reaction will give the **INITIAL RATE**
- the slope gets less (showing the rate is slowing down) as the reaction proceeds



Experimental Investigation

- the variation in concentration of a reactant or product is followed with time
- the method depends on the reaction type and the properties of the reactants/products

- e.g.
- *Extracting a sample from the reaction mixture and analysing it by titration.*
 - *Using a colorimeter or UV / visible spectrophotometer.*
 - *Measuring the volume of gas evolved.*
 - *Measuring the change in conductivity.*

More details of these and other methods can be found in suitable text-books.

THE RATE EQUATION

- Format*
- is an equation that links the rate of reaction to the concentration of reactants
 - can only be found by doing actual experiments
 - cannot be found by just looking at the equation

the equation...



might have a rate equation like this $r = k [A] [B]^2$

where	r	rate of reaction	units	conc. / time	usually mol dm ⁻³ s ⁻¹
	k	rate constant	units	depend on the rate equation	
	[]	concentration	units	mol dm ⁻³	

Interpretation The above rate equation tells you that the rate of reaction is...

- proportional to the concentration of reactant A doubling [A] - will double rate
- proportional to the square of the concentration of B doubling [B] - will quadruple rate

Order of reaction

Individual order **The power to which a concentration is raised in the rate equation**
Overall order **The sum of all the individual orders in the rate equation.**

e.g. in the rate equation $r = k [A] [B]^2$

- | | | |
|-----|------------------------------------|-----------|
| | • the order with respect to A is 1 | 1st Order |
| | • the order with respect to B is 2 | 2nd Order |
| and | • the overall order is 3 | 3rd Order |

Value(s)

- orders **need not be whole numbers**
- orders **can be zero** if the rate is unaffected by how much of a substance is present

Remember The rate equation is derived from experimental evidence not by looking at an equation.

- species appearing in the stoichiometric equation sometimes aren't in the rate equation
- similarly substances not in the stoichiometric equation can appear in the rate equation

Q.3 State the overall order, and the individual orders, for the following ?

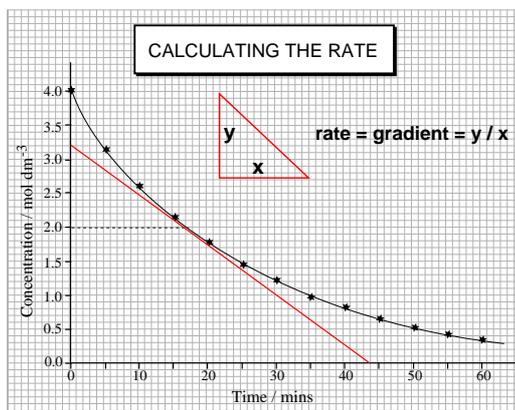
a) $rate = k[C]^3[D]$

b) $rate = k [A] [B]^{1/2}$

Q.4 What substances appear in the rate, but not in the stoichiometric, equation ?

Experimental determination of order

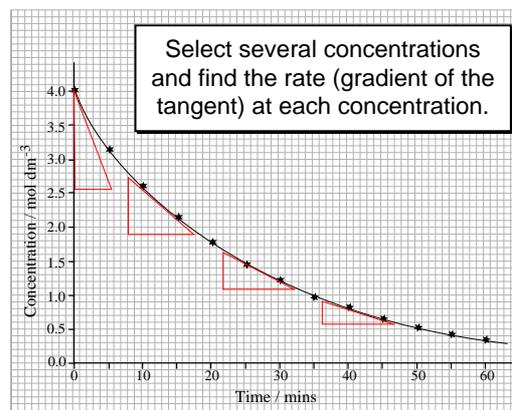
Method 1 1. Plot a concentration/time graph and calculate the rate (gradient) at points on the curve



When the concentration is 2.0 mol dm^{-3}
the gradient = $\frac{-3.2 \text{ mol dm}^{-3}}{44 \text{ minutes}}$

The gradient is negative because
the concentration is decreasing

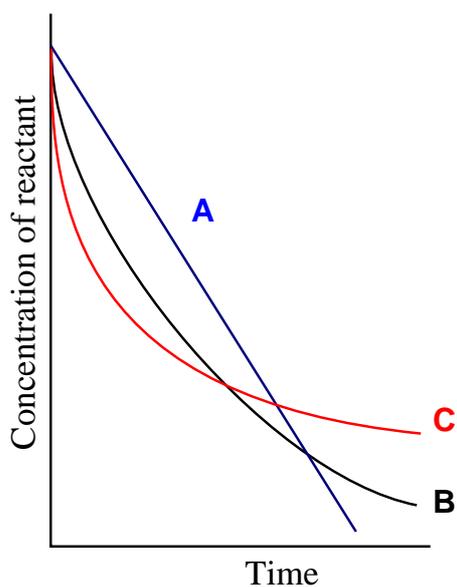
$$\text{rate} = -7.3 \times 10^{-2} \text{ mol dm}^{-3} \text{ min}^{-1}$$



Notice how the gradient gets less as
the reaction proceeds. This shows that
the rate of reaction is getting less.

CONCENTRATION v. TIME GRAPHS

WHAT TO LOOK FOR



A ZERO ORDER

a straight line with constant slope

B FIRST ORDER

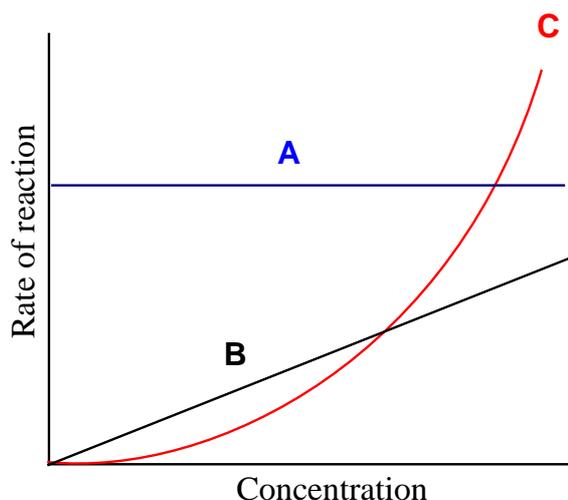
downwardly sloping curve
with a constant half life

C SECOND ORDER

steeper downwardly sloping curve
which levels out quicker

Method 1
(cont)

2. Plot another graph of rate (*y axis*) versus the concentration (*x axis*)



A ZERO ORDER

a straight line horizontal to the *x axis*
rate is independent of concentration

B FIRST ORDER

a straight line with a constant slope
rate is proportional to concentration

GRADIENT = RATE CONSTANT (k)

C SECOND ORDER

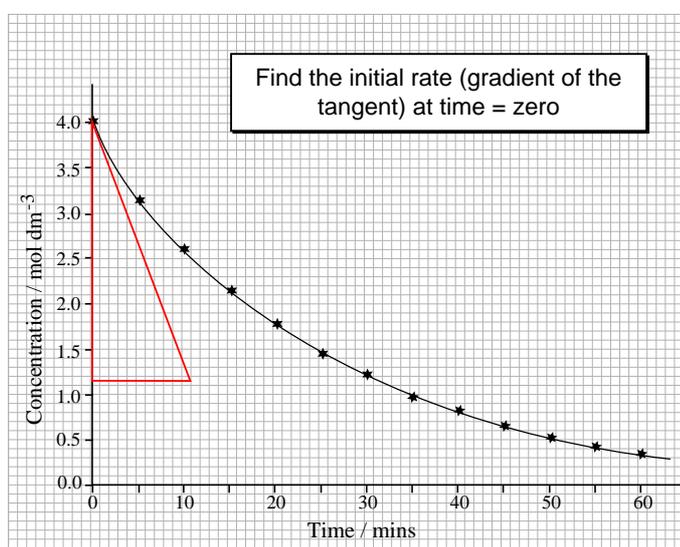
an upwardly sloping curve
plotting rate v. conc^2 gives a straight line

Method 2

The initial rates method.

Do a series of experiments (at the same temperature) at different concentrations of a reactant but keeping all others constant.

- Plot a series of concentration / time graphs
- Calculate the initial rate (slope of curve at start) for each reaction.
- Plot each initial rate (*y axis*) against the concentration used (*x axis*)
- From the graph, calculate the relationship between concentration and rate
- Hence deduce the rate equation - see *the graph at the top of the page*
- To find order directly, logarithmic plots are required.



Half-life ($t_{1/2}$) One of the characteristics of a **FIRST ORDER REACTION** is that it has a **constant half life** which is independent of the concentration. It is very similar to radioactive decay.

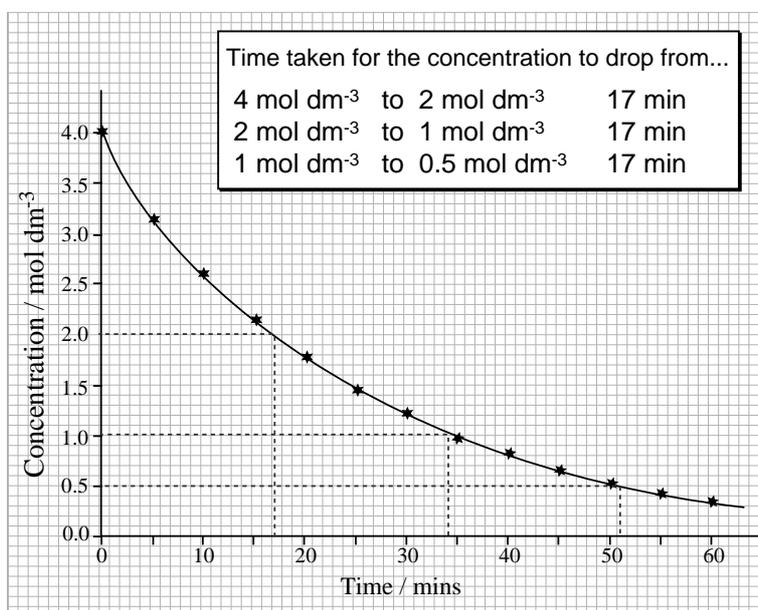
Definition The time taken for the concentration of a reactant to drop to half of its original value.

the time taken to drop...
 from 1 to $1/2$ = one half life
 $1/2$ to $1/4$ = one half life
 $1/4$ to $1/8$ = one half life

A useful relationship

$$k t_{1/2} = \log_e 2 = 0.693$$

$t_{1/2}$ = the half life



**TO CALCULATE THE RATE CONSTANT (k)
FOR A FIRST ORDER REACTION**

$$k = \frac{0.693}{t_{1/2}}$$

Q.5 In the reaction, $A + B \rightarrow X + Y$, the concentration of A was found to vary as shown in the table. It was later found that the order with respect to (wrt) B was 0.

- plot a graph of $[A]$ v. time
- calculate the time it takes for $[A]$ to go from...
 - 1.30 to 0.65
 - 1.00 to 0.50
 - 0.50 to 0.25 (all in units mol dm⁻³)
- deduce from the graph that the order wrt A is 1
- calculate the value of the rate constant, k

Time / s	$[A]$ / mol dm ⁻³
0	1.30
20	1.05
40	0.85
60	0.68
80	0.55
100	0.45
120	0.36
140	0.29
160	0.24
180	0.19
200	0.15

Rate constant (k)

- Value**
- The value of the rate constant is **affected by temperature**
 - **Increasing the temperature increases the value of the rate constant**
 - If k increases, so does the rate
 - An increase of 10°C **approximately** doubles the rate of a reaction

Units The units of k depend on the overall order of reaction.

e.g. if the rate equation is of the form **rate = k [A]²** the units of k will be **dm³ mol⁻¹ sec⁻¹**

Divide the rate (conc per time) by as many concentrations as appear in the rate equation.

Overall Order	0	1	2	3
units of k	mol dm ⁻³ sec ⁻¹	sec ⁻¹	dm ³ mol ⁻¹ sec ⁻¹	dm ⁶ mol ⁻² sec ⁻¹
example	in the rate equation $r = k [A]$			k will have units of sec ⁻¹
	in the rate equation $r = k [A] [B]^2$			k will have units of dm ⁶ mol ² sec ⁻¹

Q.6 Derive suitable units for the rate constant k in the following rate equations.

$$r = k[C]^3[D]$$

$$r = k [Z]^2$$

$$r = k [A] [B]$$

$$r = k [A] [B]^{1/2}$$

Q.7 Using the data, construct the rate equation for the reaction between nitric oxide and oxygen. What is the value and the units of the rate constant (k) ?

Expt	Initial [NO] / mol dm ⁻³	Initial [O ₂] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	1	2	7
2	2	1	28
3	2	2	56
4	3	3	?

Hint Compare Expts. 2 and 3 to find the order with respect to O₂
Compare Expts. 1 and 3 to find the order with respect to NO

Rate determining step

- many reactions consist of a series of separate stages
- each of these stages has its own rate and hence its own rate constant
- the overall rate of a multi-step process is governed by the slowest step
- *rather like a production line where the output can be held up by a slow worker*
- the **slowest step is known as the rate determining step.**

Example - The hydrolysis of haloalkanes

Haloalkanes (RX) are hydrolysed
by aqueous hydroxide ion



There are **two possible mechanisms**

Mech 1

- one step reaction
- requires both species to collide
- rate is affected by both reactants
- **second order** overall

$$\text{rate} = k[\text{RX}][\text{OH}^-]$$

Mech 2

- two step reaction
- step (i) is **slower** as it **involves bonds breaking** and will thus be the **rate determining step**

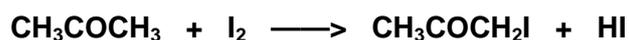


- rate depends only on [RX]
- **first order** overall

$$\text{rate} = k[\text{RX}]$$

Mechanism 2 is very common with tertiary (3°) haloalkanes whereas primary (1°) and secondary (2°) haloalkanes usually undergo hydrolysis via a second order process.

Example 1 Iodine reacts with propanone...



The rate equation for the reaction is

$$\text{rate} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$$

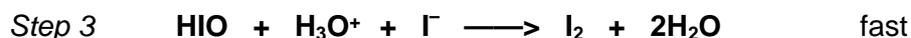
- Why is $[\text{H}^+]$ in the rate equation?
- Why is $[\text{I}_2]$ not in the rate equation?

the reaction is catalysed by acid
the reaction has more than one step and the slowest step doesn't involve iodine

The rate determining step must therefore involve propanone and acid.

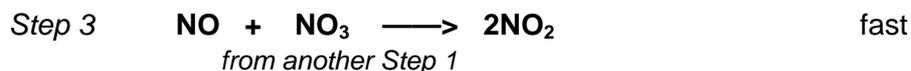
Investigation of the rate equation gives an idea of whether, or not, a reaction takes place in a series of steps.

Example 2 The reaction $\text{H}_2\text{O}_2 + 2\text{H}_3\text{O}^+ + 2\text{I}^- \longrightarrow \text{I}_2 + 4\text{H}_2\text{O}$ takes place in 3 steps



The rate determining step is STEP 1 as it is the slowest

Example 3 The reaction $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$ takes place in 3 steps



The rate determining step is STEP 1 as it is the slowest

The rate equation for the reaction is $\text{rate} = k [\text{N}_2\text{O}_5]$

Molecularity

The number of individual particles of the reacting species taking part in the rate determining step of a reaction

e.g. $\text{A} + 2\text{B} \longrightarrow \text{C} + \text{D}$ molecularity is 3 - one A and two B's need to collide

$\text{A} \longrightarrow 2\text{B}$ has a molecularity of 1 - only one A is involved

Autocatalysis

A small number of reactions appear to speed up, rather than slow down, for a time. This is because one of the products is acting as a catalyst and as more product is formed the reaction gets faster. One of the best known examples is the catalytic properties of $\text{Mn}^{2+}_{(\text{aq})}$ on the decomposition of $\text{MnO}_4^-_{(\text{aq})}$. You will notice it in a titration of KMnO_4 with either hydrogen peroxide or ethanedioic (oxalic) acid.