

## 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 ?*

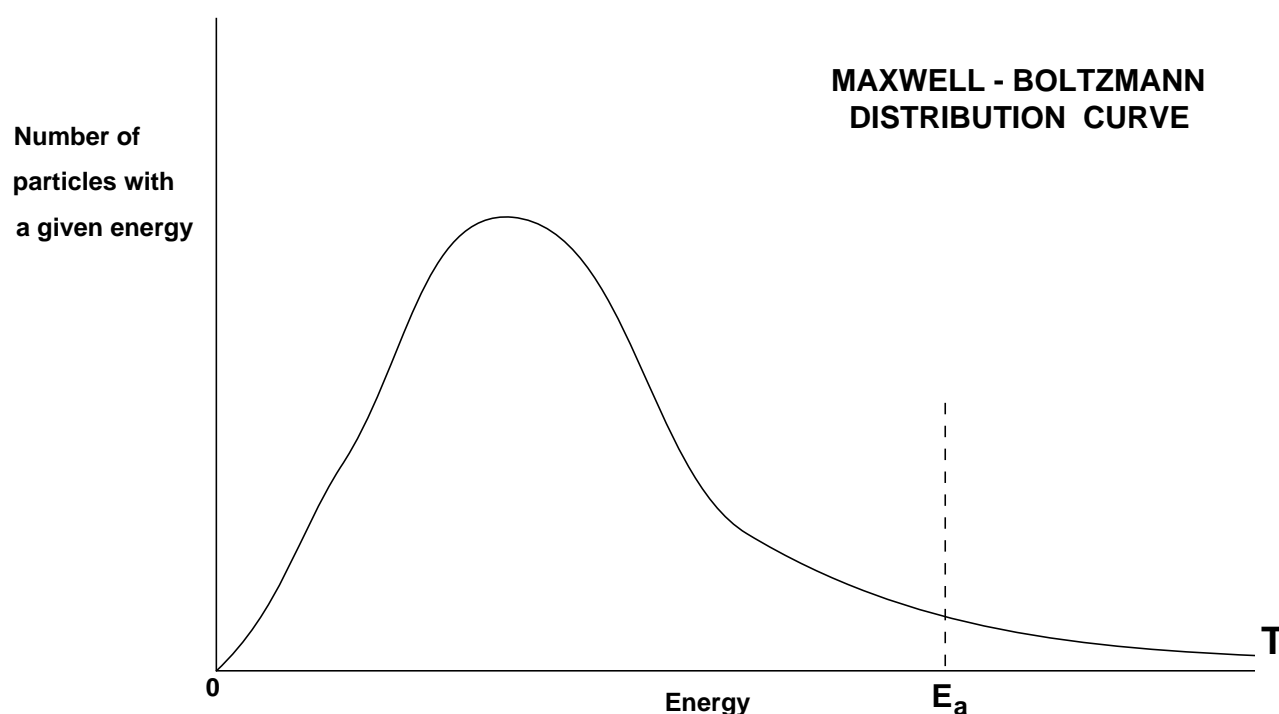
## TEMPERATURE

- 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.

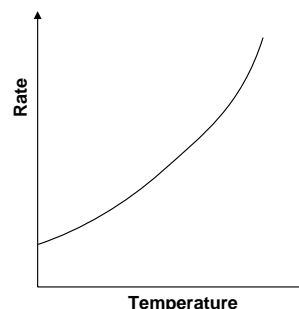
*Significance*  $E_a$  corresponds to the **Activation Energy**. The area under the curve beyond this value is proportional to the number of particles with energy greater than this limiting value.

**Increasing the temperature alters the distribution;**

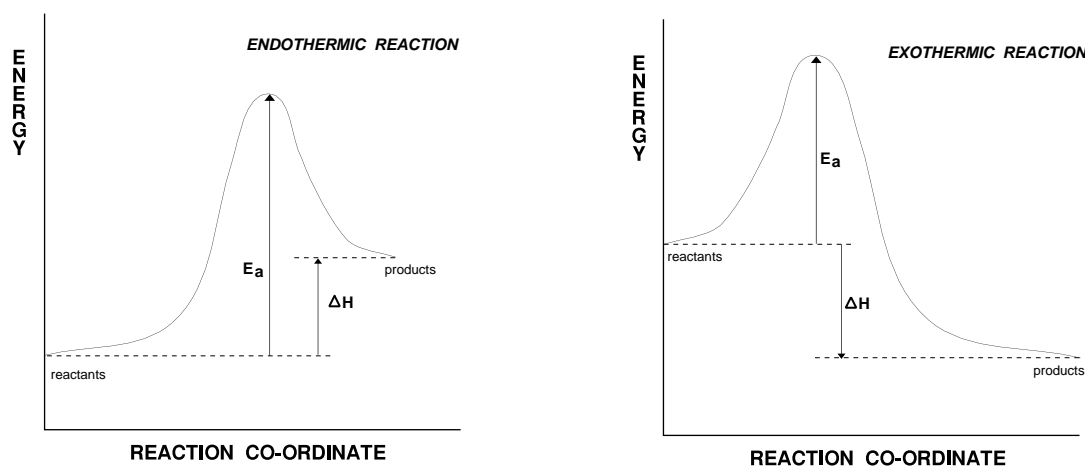
- get a **shift to higher energies/velocities**
- **curve gets broader and flatter** due to the greater spread of values
- **area under the curve stays constant** as it corresponds to the total number of particles

- 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**

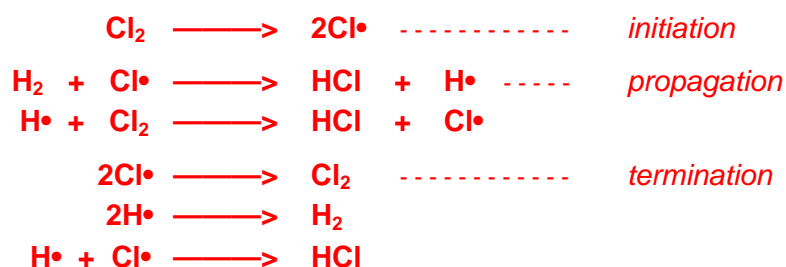
- shining a suitable light source onto some reactants increases the rate of reaction
- the light - often U.V. - provides energy to break bonds and initiate a reaction
- the greater the intensity of the light, the greater the effect

**Examples**

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

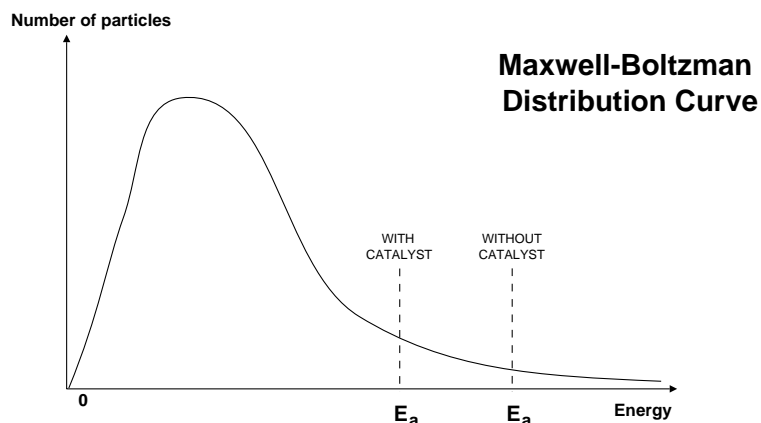


**Mechanism**



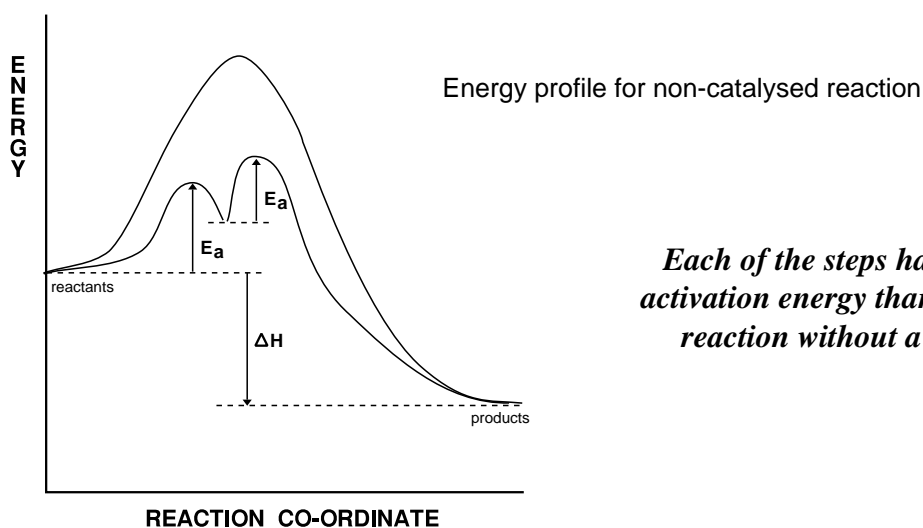
## CATALYSTS

*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      Al<sub>2</sub>O<sub>3</sub>      dehydration reactions  
                 V<sub>2</sub>O<sub>5</sub>      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<sub>x</sub> - NO, N<sub>2</sub>O and NO<sub>2</sub>

*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

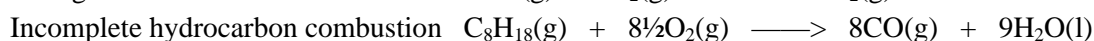
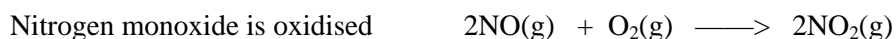


### Hydrocarbons C<sub>x</sub>H<sub>y</sub>

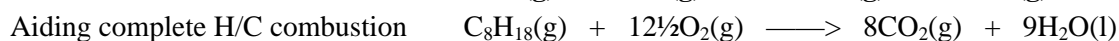
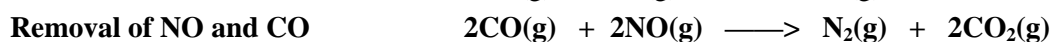
*Origin* • hydrocarbons that have not undergone combustion

*Effect* • toxic and carcinogenic (cause cancer)

### EQUATIONS FOR POLLUTION FORMATION



### EQUATIONS FOR POLLUTION REMOVAL



## 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

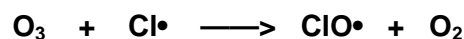
**Gases** **OZONE** in the atmosphere breaks down naturally as follows ...



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

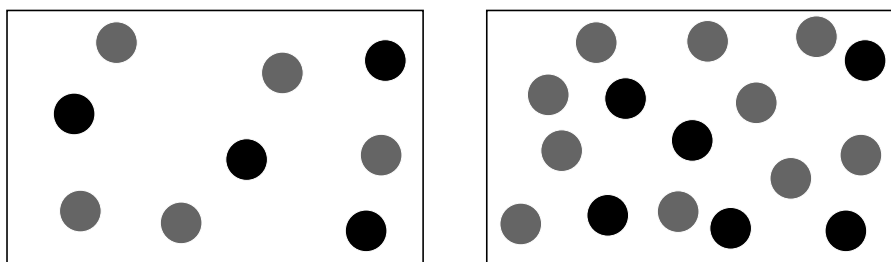
There is a series of complex reactions but the basic process is :-

- 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

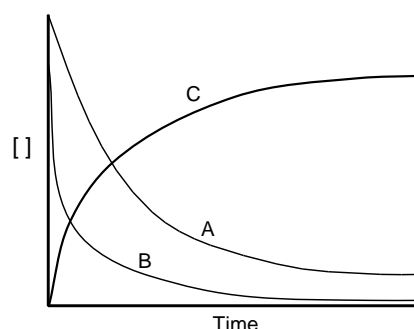
### Reactants (A and B)

Concentration decreases with time

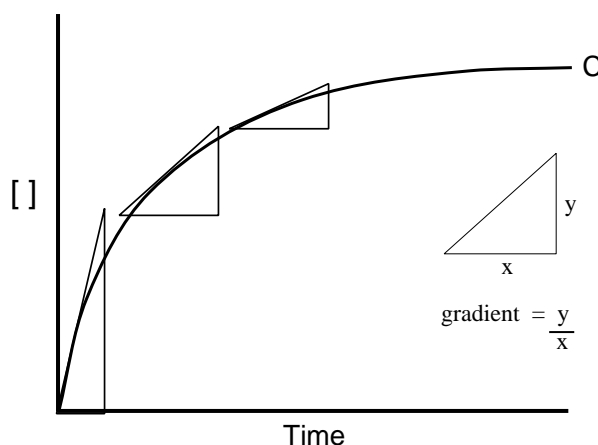
### Products (C)

Concentration increases with time

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



- 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 $\text{mol dm}^{-3} \text{s}^{-1}$
	k	rate constant	units	depend on the rate equation	
	[ ]	concentration	units	$\text{mol dm}^{-3}$	

*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 ?

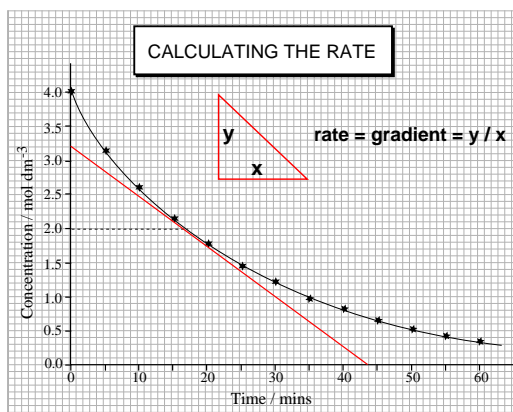
a)  $\text{rate} = k[C]^3[D]$

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

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

## Experimental determination of order

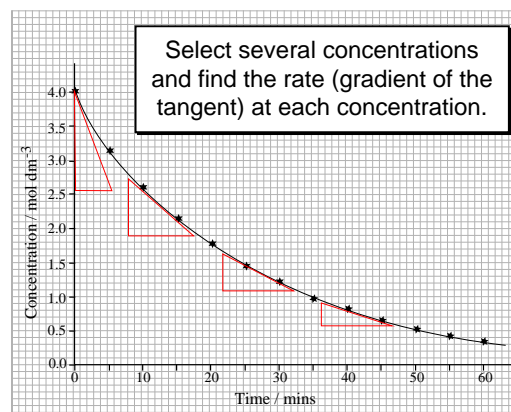
*Method 1* 1. Plot a concentration/time graph and calculate the rate (gradient) at points on the curve



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

The gradient is negative because  
the concentration is decreasing

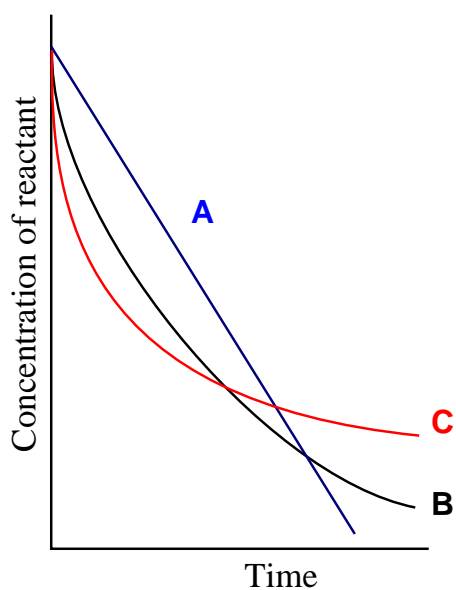
$$\text{rate} = -7.3 \times 10^{-2} \text{ mol dm}^{-3} \text{ min}^{-1}$$



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

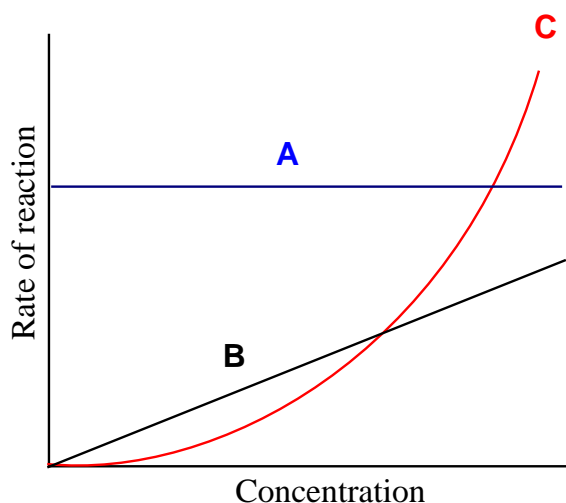
downwardly sloping curve  
with a constant half life

#### **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**

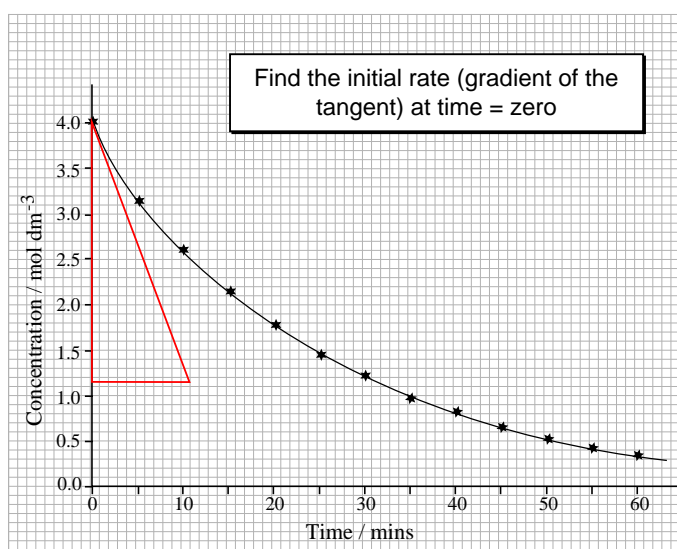
an upwardly sloping curve  
plotting rate v.  $\text{conc}^2$  gives a straight line

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.

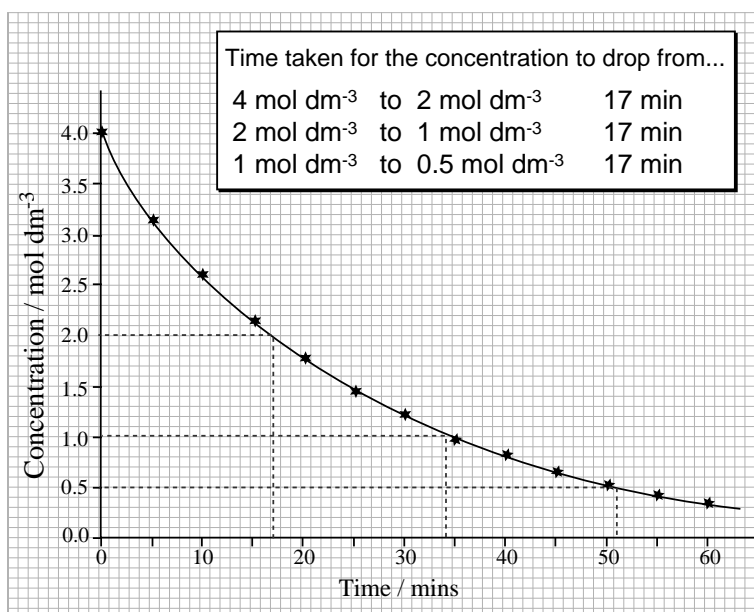
**Definition** The time taken for the concentration of a reactant to drop to half of its original value.

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<sup>-3</sup>)
- deduce from the graph that the order wrt A is 1
- calculate the value of the rate constant,  $k$

Time / s	$[A]$ / mol dm <sup>-3</sup>
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]<sup>2</sup>** the units of k will be **dm<sup>3</sup> mol<sup>-1</sup> sec<sup>-1</sup>**

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 <sup>-3</sup> sec <sup>-1</sup>	sec <sup>-1</sup>	dm <sup>3</sup> mol <sup>-1</sup> sec <sup>-1</sup>	dm <sup>6</sup> mol <sup>-2</sup> sec <sup>-1</sup>
example	in the rate equation $r = k [A]$			k will have units of sec <sup>-1</sup>
	in the rate equation $r = k [A] [B]^2$			k will have units of dm <sup>6</sup> mol <sup>2</sup> sec <sup>-1</sup>

**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 <sup>-3</sup>	Initial [O <sub>2</sub> ] / mol dm <sup>-3</sup>	Initial rate / mol dm <sup>-3</sup> s <sup>-1</sup>
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 O<sub>2</sub>  
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**

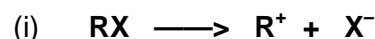
#### Mech 1

- 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**

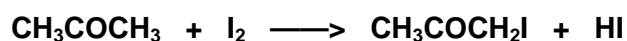


- rate depends only on [RX]
- **first order** overall

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

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

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

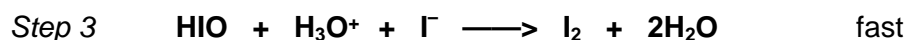
- Why is  $[\text{H}^+]$  in the rate equation?
- Why is  $[\text{I}_2]$  not in the rate equation?

*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.

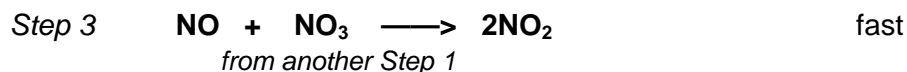
**Investigation of the rate equation gives an idea of whether, or not, a reaction takes place in a series of steps.**

**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  $\text{KMnO}_4$  with either hydrogen peroxide or ethanedioic (oxalic) acid.