

## 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 ?

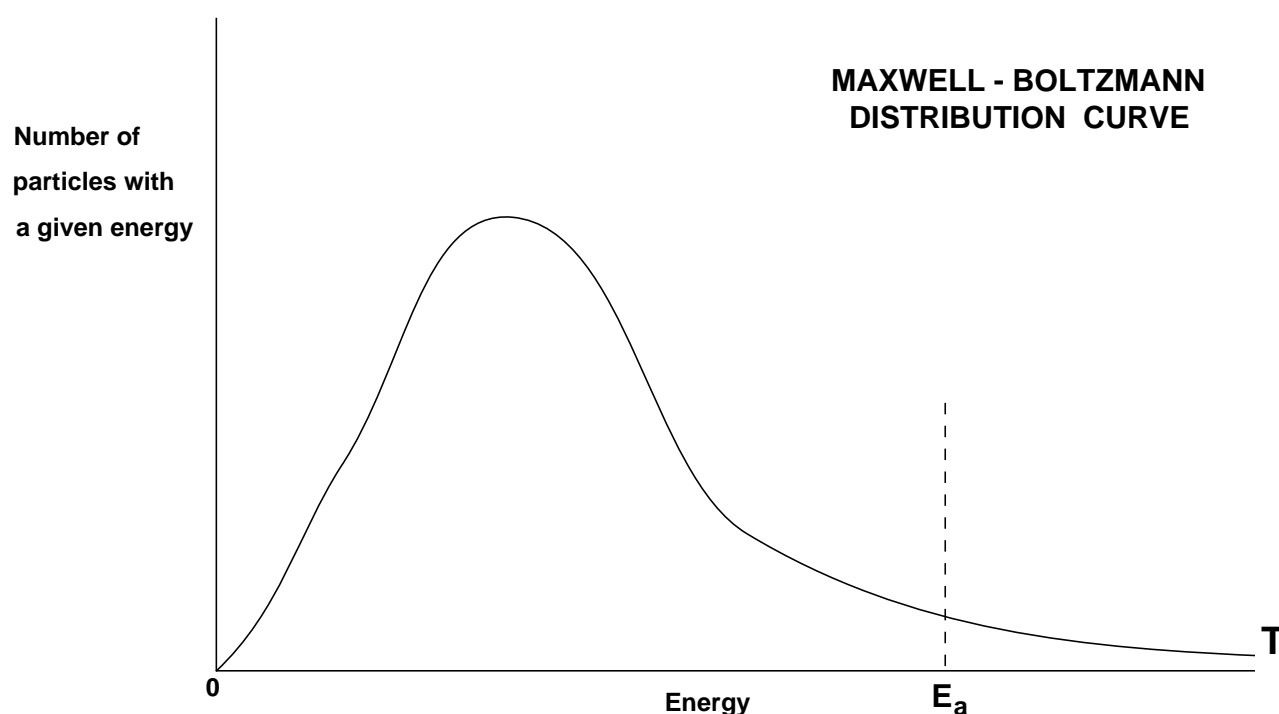
## TEMPERATURE

- 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.

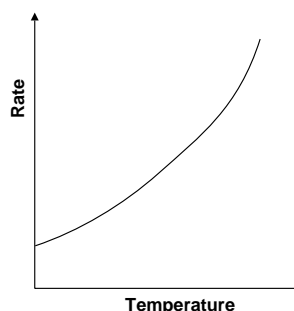
*Significance*  $E_a$  corresponds to the **Activation Energy**. The area under the curve beyond this value is proportional to the number of particles with energy greater than this limiting value.

**Increasing the temperature alters the distribution;**

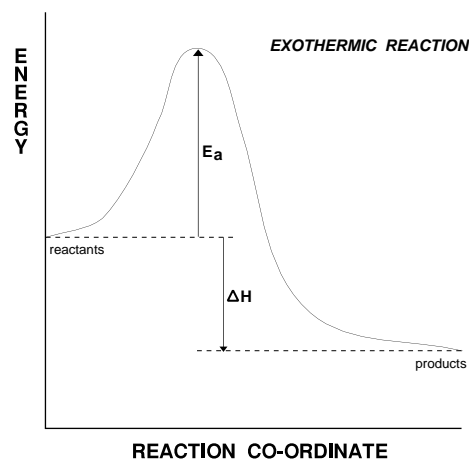
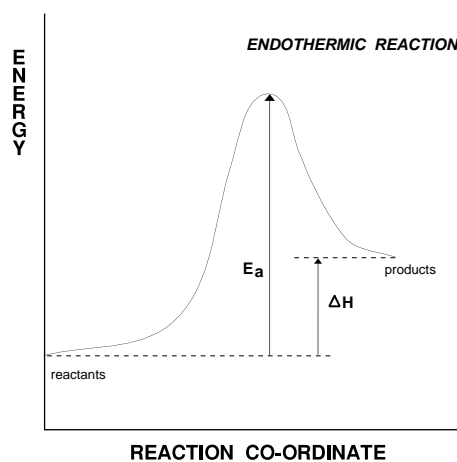
- get a **shift to higher energies/velocities**
- **curve gets broader and flatter** due to the greater spread of values
- **area under the curve stays constant** as it corresponds to the total number of particles

- 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**

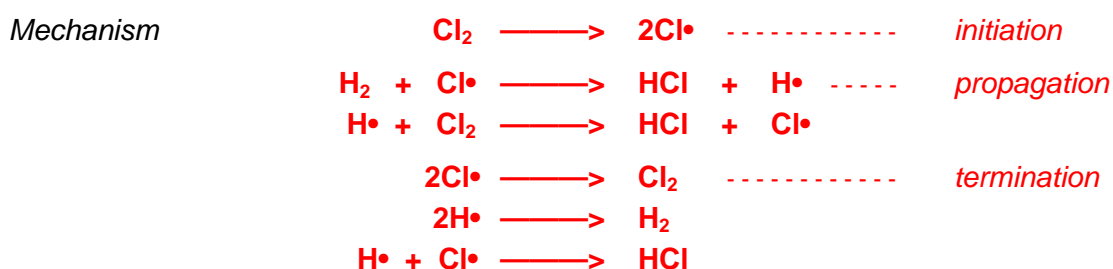


**LIGHT**

- 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

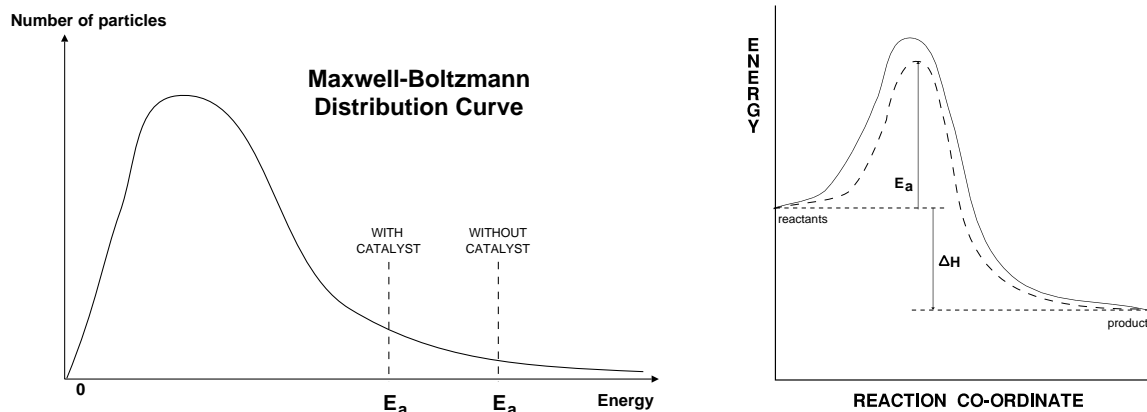
*Examples*

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



## 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.

*Types*

**Homogeneous Catalysts**  
same phase as reactants

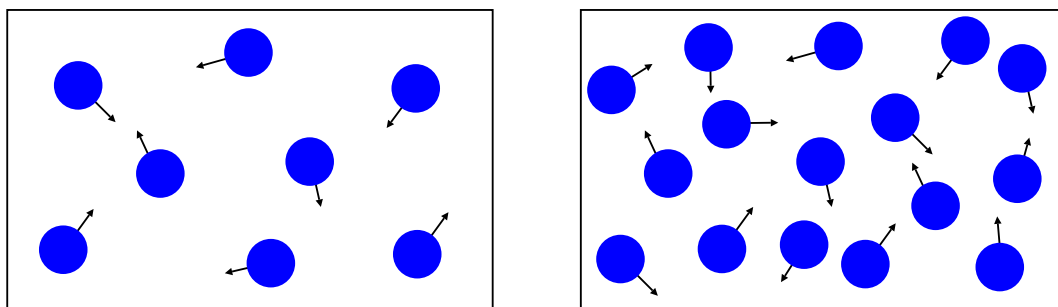
**Heterogeneous Catalysts**  
different phase to reactants

*e.g.*

*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

- 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

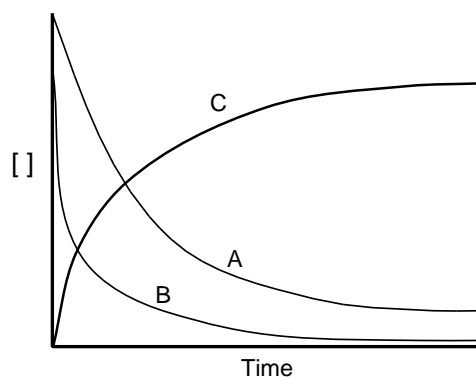
- the steeper the curve the faster the rate of the reaction
- reactions start off quickly because of the greater likelihood of collisions
- reactions slow down with time because there are fewer reactants to collide

### Reactants (A and B)

Concentration decreases with time

### Products (C)

Concentration increases with time



**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

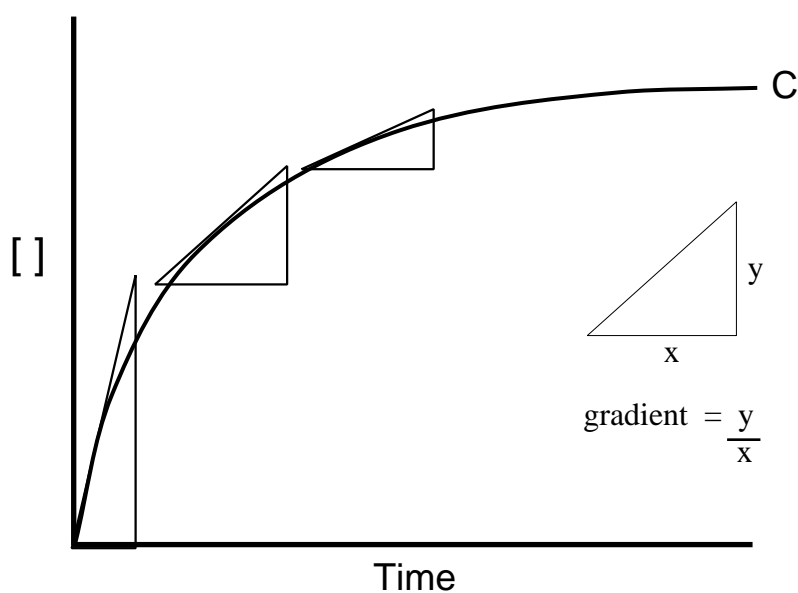
- e.g.
- Extracting a sample from the reaction mixture and analysing it by titration.
    - this is often used if an acid is one of the reactants or products
  - Using a colorimeter or UV / visible spectrophotometer.
  - Measuring the volume of gas evolved.
  - Measuring the change in conductivity.

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

**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 concentration of C will increase with time



[ ] refers to the concentration in  $\text{mol dm}^{-3}$  ( $\text{mol l}^{-1}$ )

- 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

## 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

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

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

b)  $\text{rate} = k [Z]$

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

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

## Experimental determination of order

**Method 1** Plot a concentration / time graph and calculate the rate (gradient) at points on the curve  
 Plot another graph of the rate found (*y axis*) versus the concentration at that point (*x axis*)  
 If this gives a straight line - rate is directly proportional to concentration i.e. 1st ORDER.  
 If the plot is a curve then it must have another order. Try plotting rate v. (conc.)<sup>2</sup>.  
 A straight line would mean 2nd ORDER. This method is based on trial and error.

**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 and calculate the initial rate (slope of curve at start) for each reaction. From the results calculate the relationship between concentration and rate and hence deduce the rate equation. To find order directly, logarithmic plots are required.

## Rate constant (k)

**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.5** 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.6** 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

### 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 Mn<sup>2+</sup><sub>(aq)</sub> on the decomposition of MnO<sub>4</sub><sup>-</sup><sub>(aq)</sub>. You will notice it in a titration of KMnO<sub>4</sub> with either hydrogen peroxide or ethanedioic (oxalic) acid.

### Molecularity

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

e.g.  $A + 2B \longrightarrow C + D$  molecularity is 3 - one A and two B's need to collide  
 $A \longrightarrow 2B$  however has a molecularity of 1 - only one A is involved

## 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

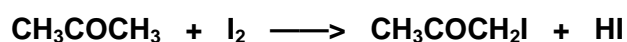


$$\text{rate} = k[\text{RX}]$$

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

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.