

## CHEMICAL KINETICS (RATES OF REACTION)

*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 a minimum amount of energy - **ACTIVATION ENERGY**
- + • particles must approach each other in a certain relative way - **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 (in catalytic converters) are used in a finely divided form for this reason
- + *in many organic reactions you have two liquid layers, one aqueous, the other non-aqueous. Shaking the mixture improves the 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 ?

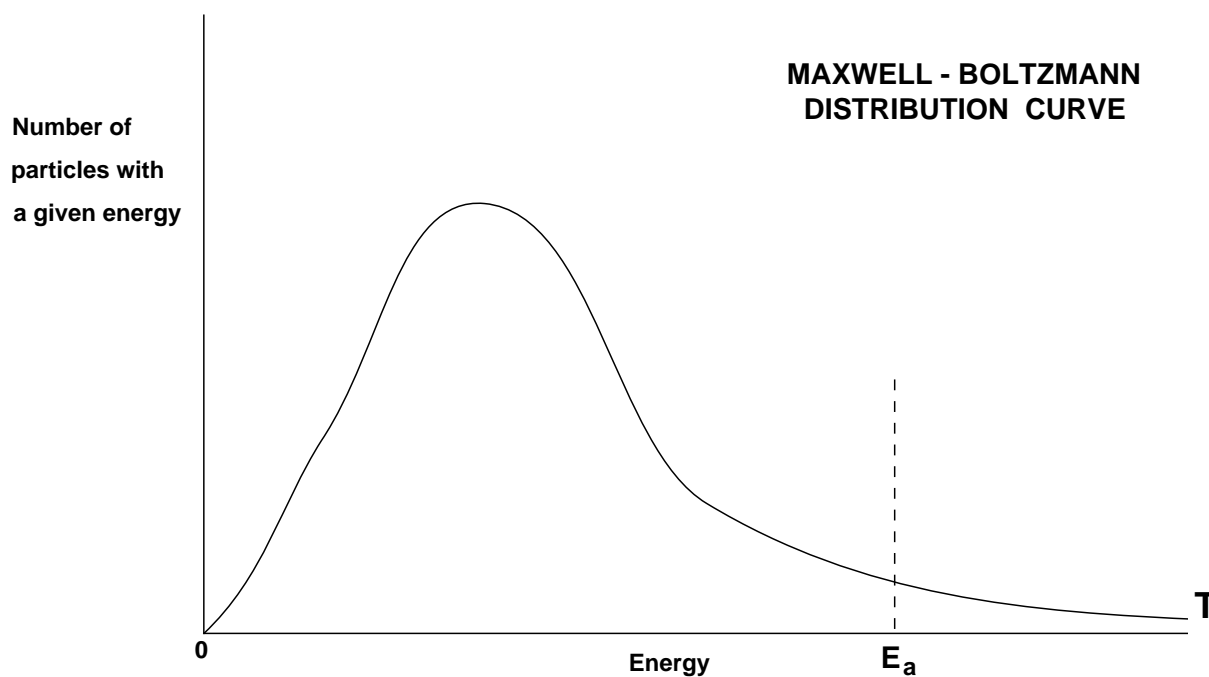
## TEMPERATURE

- 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.

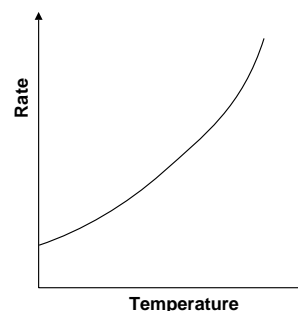
*Significance*  $E_a$  corresponds to the **Activation Energy**. The area under the curve beyond this value is proportional to the number of particles with energy greater than this limiting value.

**Increasing the temperature alters the distribution;**

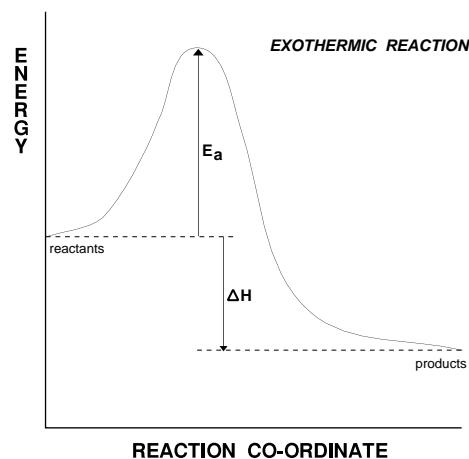
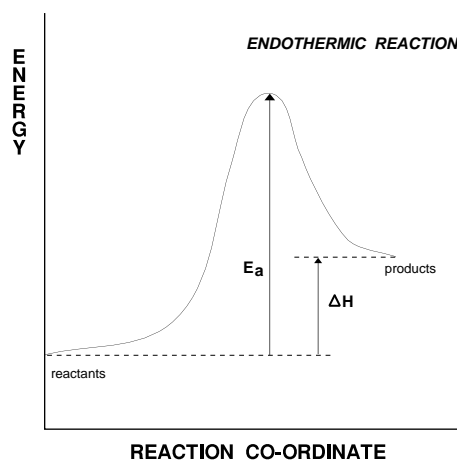
- get a **shift to higher energies/velocities**
- **curve gets broader and flatter** due to the greater spread of values
- **area under the curve stays constant**- corresponds to the total no. of particles

- Explanation**
- increasing the temperature gives more particles with energy greater than  $E_a$
  - more reactants can 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*



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

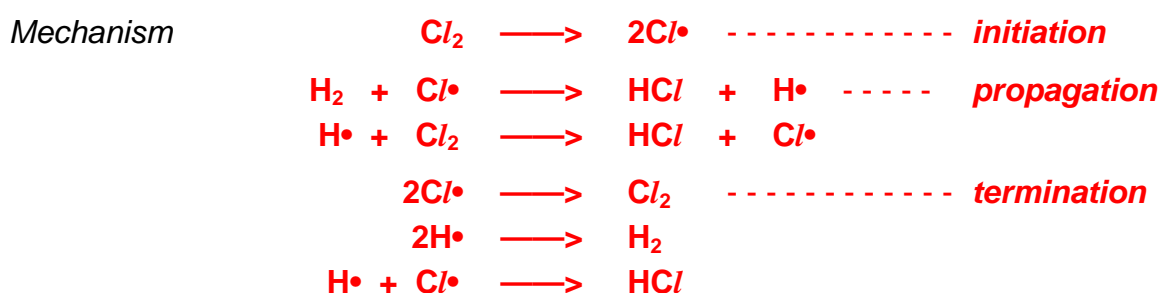
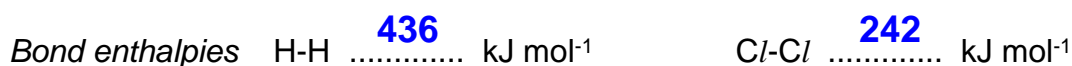


## LIGHT

- 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

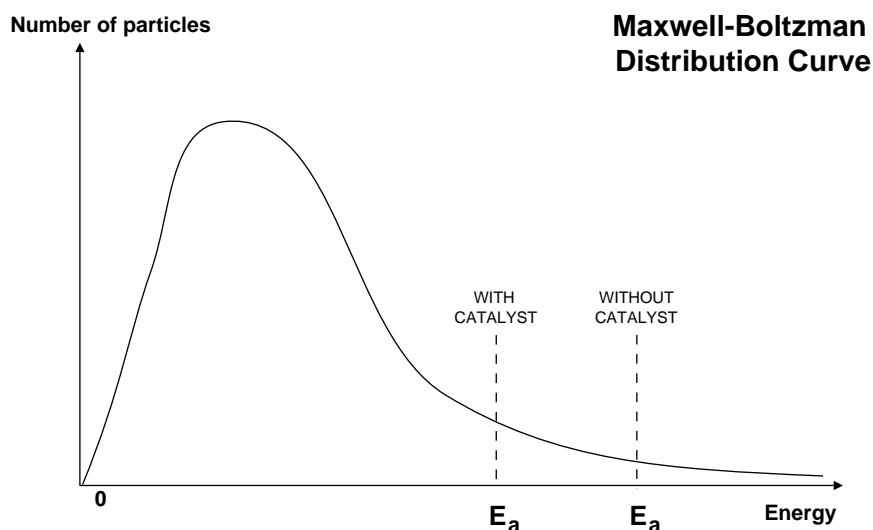
## Examples

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



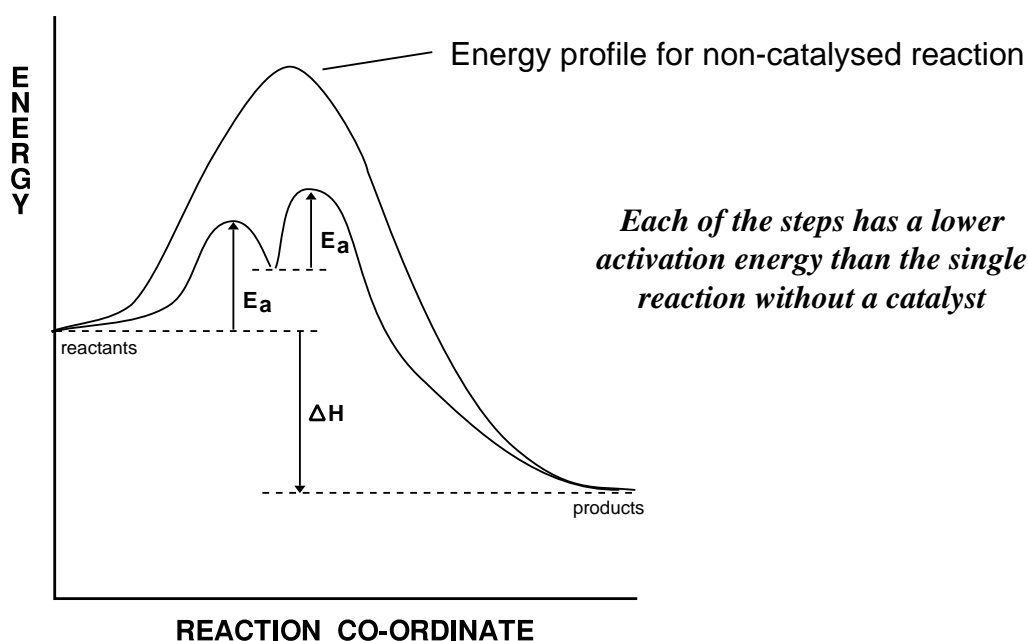
## CATALYSTS

*Operation* • provide 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 are **not used up by the overall reaction - the same amount remains**
- catalysts **remain chemically unchanged at the end** of the reaction.



*Types*

**Homogeneous Catalysts**  
**same** phase as reactants

**Heterogeneous Catalysts**  
**different** phase to reactants

*Uses*

- widely used in industry 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 - 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

**Catalysts...**

- allow reactions to take place at lower temperatures      SAVE ENERGY  
REDUCE CO<sub>2</sub> OUTPUT
- enable different reactions to be used      BETTER ATOM ECONOMY  
REDUCE WASTE
- are often enzymes      GENERATE SPECIFIC PRODUCTS  
OPERATE EFFECTIVELY AT ROOM TEMPERATURES
- have great economic importance in industry in the manufacture of...  
POLY(ETHENE)  
SULPHURIC ACID  
AMMONIA  
ETHANOL
- can reduce pollution      CATALYTIC CONVERTERS IN CARS

*Pros/cons*

- The benefits to the environment of  
must be outweighed against
- improved sustainability
  - the toxicity of some catalysts.

## 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 active sites

### Rate

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

- one species is adsorbed onto the surface so 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 to reduce costs

### Examples

- |          |                                |                         |
|----------|--------------------------------|-------------------------|
| • 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         |

## 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 often involved - **oxidation state changes** during reaction

### Examples

**Acids** e.g. hydrolysis of esters

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



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*

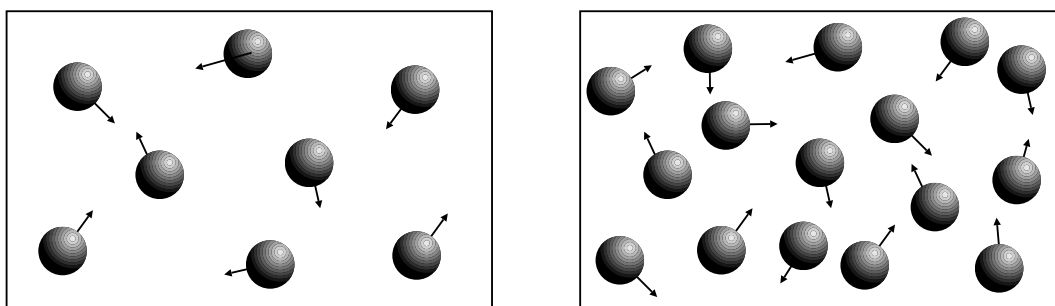
$$\text{CCl}_2\text{F}_2 \longrightarrow \text{Cl}\cdot + \cdot\text{CClF}_2$$
- *chlorine radicals then react with ozone*

$$\text{O}_3 + \text{Cl}\cdot \longrightarrow \text{ClO}\cdot + \text{O}_2$$
- *chlorine radicals are regenerated*

$$\text{ClO}\cdot + \text{O} \longrightarrow \text{O}_2 + \text{Cl}\cdot$$

Overall, chlorine radicals are not used up so a small amount of CFC's can destroy thousands of ozone molecules before the 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**

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

*Rate*    Reactions start off at their fastest then slow as the reactant concentration drops.

eg In the reaction  $A + 2B \rightarrow C$  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

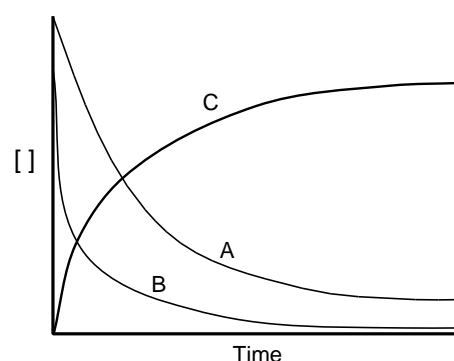
### Reactants (A and B)

Concentration decreases with time

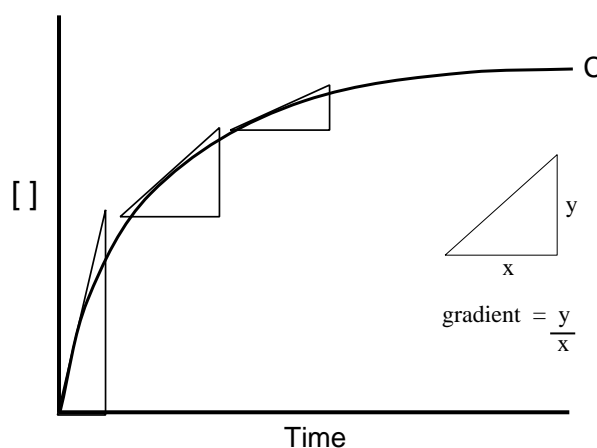
### Products (C)

Concentration increases with time

[ ] *refers to the concentration in mol dm<sup>-3</sup>*



- the **rate of change** of concentration is found from the **slope** or **gradient**
- 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
- method depends on the reaction type and the properties of 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.*