The Rates of
# Chemical Reactions

- **KEYWORDS:** Activation energy ... Catalysts ... Concentration effect ... Graphs-gas collection ... Graphs in general ... How reactions happen ... Interpreting results ... Light (catalyst) effect ... Measuring rate ... ... Pressure effect ... Rate of reaction ... Reaction profiles ... Stirring effect ... Surface area effect ... Temperature effect

What do we mean by Rate and how is it measured?

- The phrase 'rate of reaction' means 'how fast is the reaction'. It can be measured as the 'rate of formation of product' or the 'rate of disappearance of reactant'.
    - Rusting is a 'slow' reaction, you hardly see any change looking at it!,
    - weathering of rocks is a very slow reaction,
    - fermentation of sugar to alcohol is quite slow but you can see the carbon dioxide bubbles forming in the 'froth'!
    - a 'fast' reaction would be magnesium dissolving in hydrochloric acid,
    - and an explosion and burning/combustion reactions would be described as 'very fast'!
- The importance of "Rates of Reaction knowledge":
    - Time is money in industry, the faster the reaction can be done, the more economic it is.
        - Hence the great importance of catalysts eg transition metals or enzymes.
    - Health and Safety Issues:
        - Mixtures of flammable gases in air present an explosion hazard (gas reactions like this are amongst the fastest reactions known).
            - eg Methane gas in mines, petrol vapour etc. so knowledge of 'explosion/ignition threshold concentrations', ignition temperatures and activation energies are all important knowledge to help design systems of operation to minimise risks.
        - Flammable fine dust powders can be easily ignited eg coal dust in mines, flour in mills.
            - Fine powders have a large surface area which greatly increases the reaction rate causing an explosion. Any spark from friction is enough to initiate the reaction!
- A reaction will continue until one of the reactants is used up.
- To measure the 'speed' or 'rate' of a reaction depends on what the reaction is, and can what is formed be measured as the reaction proceeds? Two examples are outlined below.
- When a gas is formed from a solid reacting with a solution, it can be collected in a gas syringe (see diagram below and the graph).
    - The initial gradient of the graph eg in cm^3/min gives an accurate measure of how fast the gaseous product is being formed.
    - If the reaction is allowed to go on, you can measure the final maximum volume of gas and the time at which the reaction stops.
- **Reactions involving:**
    - **(i) metals dissolving in acid**
        - eg magnesium + sulphuric acid ==> magnesium sulphate + hydrogen

- $Mg_{(s)} + H_2SO_{4(aq)} ==> MgSO_{4(aq)} + H_{2(aq)}$
  - (ii) carbonates dissolving in acids
    - calcium carbonate + hydrochloric acid ==> calcium chloride + water + carbon dioxide
      - $CaCO_{3(s)} + 2HCl_{(aq)} ==> CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$
  - and (iii) the manganese(IV) oxide catalysed decomposition of hydrogen peroxide
    - hydrogen peroxide ==> water + oxygen,
    - $2H_2O_{2(aq)} ==> 2H_2O_{(l)} + O_{2(g)}$
  - **can all be followed with this method.**
  - **You can investigate the effects of**
    - **(a) the solution concentration,**
    - **(b) the temperature of the reactants,**
    - **(c) the size of the solid particles (surface area effect),**
    - **(d) the effectiveness of different catalysts on hydrogen peroxide decomposition.**
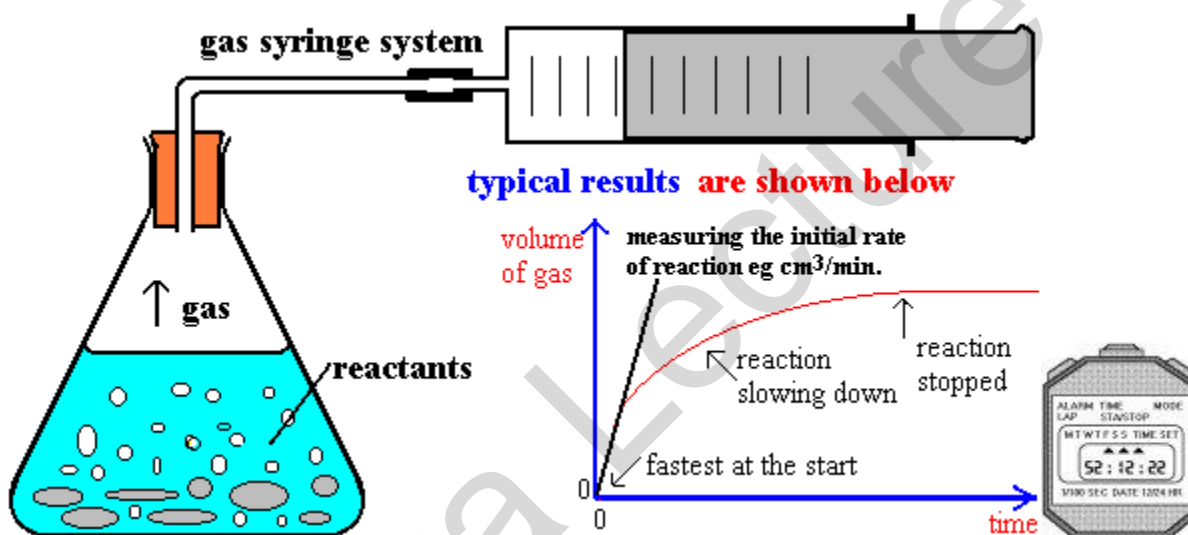

- **The shape of the graph is quite characteristic (see below).**
  - **The reaction is fastest at the start when the reactants are at a maximum (steepest gradient in cm^3/min).**
  - **The gradient becomes progressively less as reactants are used up and the reaction slows down.**
  - **Finally the graph levels out when one of the reactants is used up and the reaction stops.**
  - **The amount of product depends on the amount of reactants used.**
  - **The initial rate of reaction is obtained by measuring the gradient at the start of the reaction. A tangent line is drawn through the first part of the graph, which is usually reasonably linear from the x,y origin 0,0.**
    - **and so gives you an initial rate of reaction in cm^3 gas/minute.**

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Graph of volume of gas formed versus time
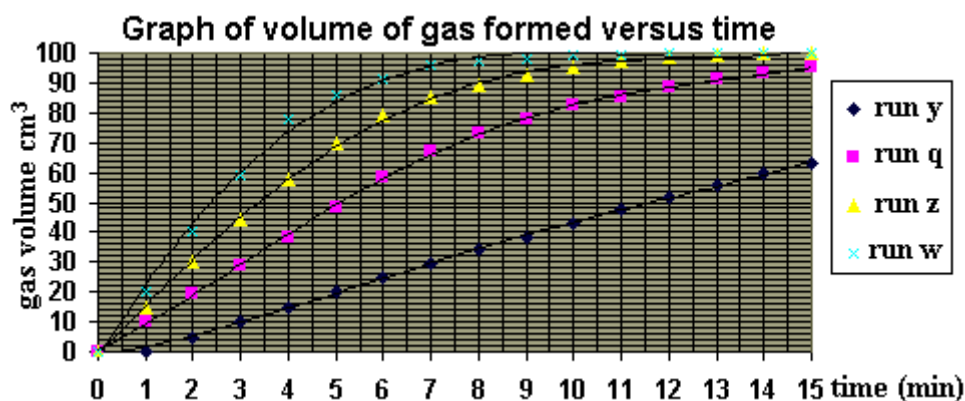
- **The rate of a reaction that produces a gas can also be measured by following the mass loss as the gas is formed and escapes from the reaction flask.**
  - o **The method is ok for reactions producing carbon dioxide or oxygen,**
  - o **but not very accurate for reactions giving hydrogen (low mass loss).**
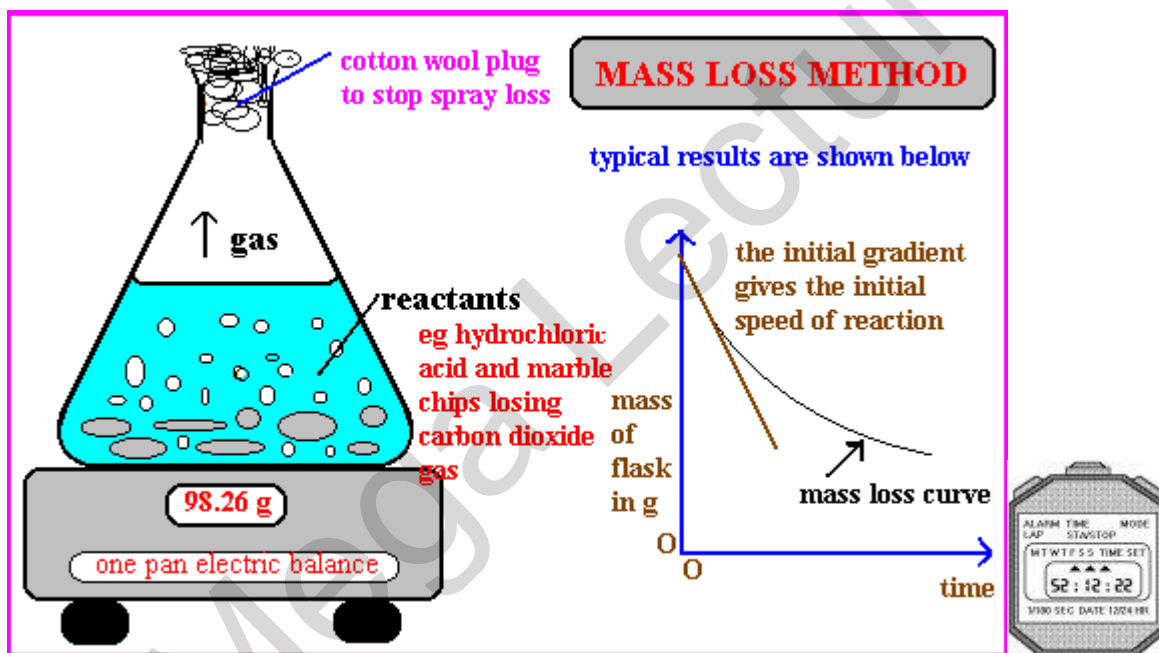
- **When sodium thiosulphate reacts with an acid, a yellow precipitate of sulphur is formed.**
  - o **To follow this reaction you can measure how long it takes for a certain amount of sulphur to form.**
  - o **You do this by observing the reaction down through a conical flask, viewing a black cross on white paper (see diagram below).**
  - o **The X is eventually obscured by the sulphur precipitate and the time noted.**
  - o **sodium thiosulphate + hydrochloric acid ==> sodium chloride + sulfur dioxide + water + sulphur**
  - o **$Na_2S_2O_{3(aq)} + 2HCl_{(aq)} ==> 2NaCl_{(aq)} + SO_{2(aq)} + H_2O_{(l)} + S_{(s)}$**

Mix➔   **➔ Ongoing**   **➔ Watch stopped**
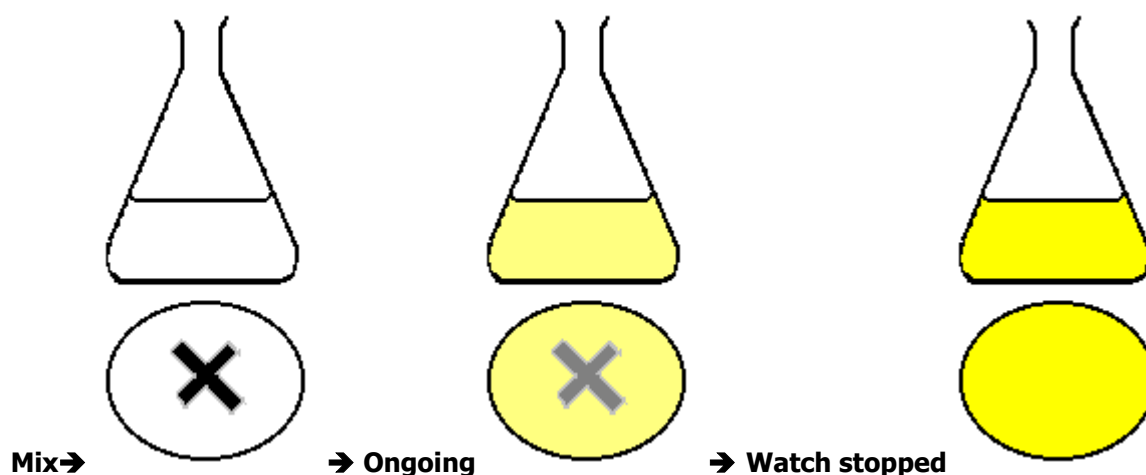
- **By using the same flask and paper X you can obtain a relative measure of the speed of the reaction in forming the same amount of sulphur.**
- **The speed or rate of reaction can expressed as 'x amount of sulphur'/time, so the rate is proportional to 1/time for a given set**
  - o **You can investigate the effects of**
    - ▪ **(a) the hydrochloric acid or sodium thiosulphate concentration**
   - ▪ **(b) the temperature of the reactants.**

The theory of how reactions happen

- **Reactions can only happen when the reactant particles collide, but most collisions are not successful in forming product molecules.**
- **The minority high kinetic energy collisions between particles which do produce a chemical change are called 'fruitful collisions'**
- **The reactant molecules must collide with enough energy to break the original bonds so those new bonds in the product molecules can be formed.**
- **All the rate-controlling factors are to do with the frequency and energy of reactant particle collision.**
- **In the case of temperature, the energy of the collision is even more important than the frequency effect.**
- **The particle theory of gases and liquids and the diagrams below will help you understand what is going on.**

The Factors affecting the Rate of Chemical Reactions

The effect of Concentration (see also graphs)

- **If the concentration of any reactant in a solution is increased, the rate of reaction is increased**
  - o **Increasing the concentration, increases the probability of a collision between reactant particles because there are more of them in the same volume.**
  - o **Examples .....**

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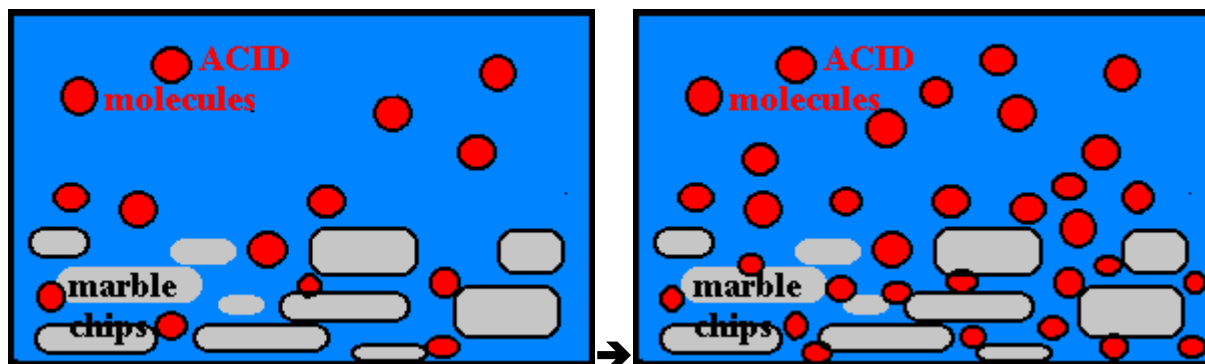
- **Increasing the concentration of acid molecules increases the frequency or chance at which they hit the surface of marble chips to dissolve them (slower ➔ faster).**
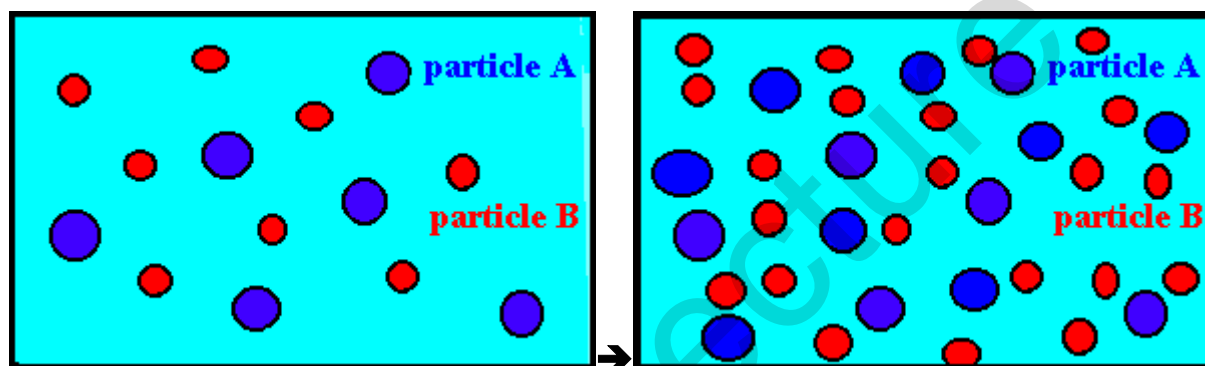

- **Increasing the concentration of reactant A or B will increase the chance or frequency of collision between them and increase the speed of product formation (slower ➔ faster).**

The effect of Pressure

- **If one or more of the reactants is a gas then increasing pressure will effectively increase the concentration of the reactant molecules and speed up the reaction.**
    - **because the increased chance of a 'fruitful' collision produces the increase in reaction.**

The effect of Stirring

- **In doing rate experiments with a solid reactant (eg marble chips-acid solution) or a solid catalyst (manganese(IV) oxide-hydrogen peroxide solution) it is sometimes forgotten that stirring the mixture is an important rate factor.**
- **If the reacting mixture is not stirred 'evenly' then the reactant concentration in solution becomes much less near the solid, which tends to settle out.**
- **At the bottom of the flask the reaction prematurely slows down distorting the overall rate measurement and making the results uneven and therefore inaccurate.**

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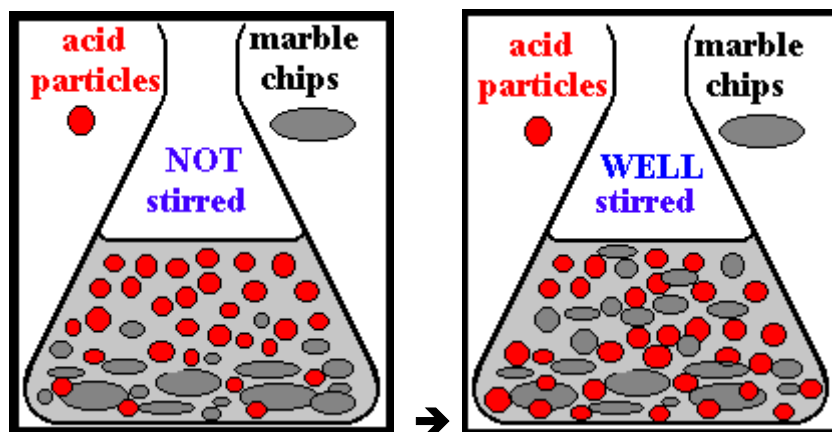
The effect of Surface Area - solid particle size

- If a solid reactant or a solid catalyst is broken down into smaller pieces the rate of reaction increases.
- The speed increase happens because smaller pieces of the same mass of solid have a greater surface area compared to larger pieces of the solid.
- Therefore, there is more chance that a reactant particle will hit the solid surface and react.
- The diagrams below illustrate the acid–marble chip reaction, but they could also represent a solid catalyst in a solution of reactants.
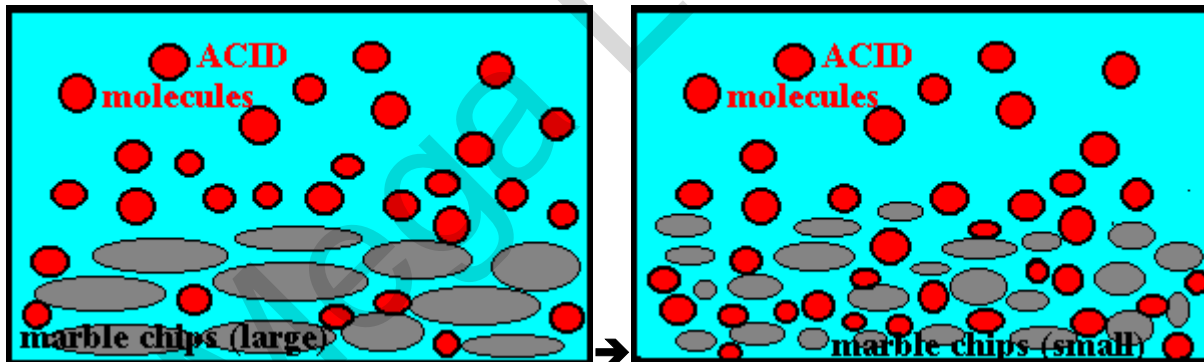

The effect of Temperature (see also graphs)

- When gases or liquids are heated the particles gain kinetic energy and move faster (see diagrams below).
- The increased speed increases the chance of collision between reactant molecules and the rate increases.
- However this is not the main reason for the increased reaction speed.

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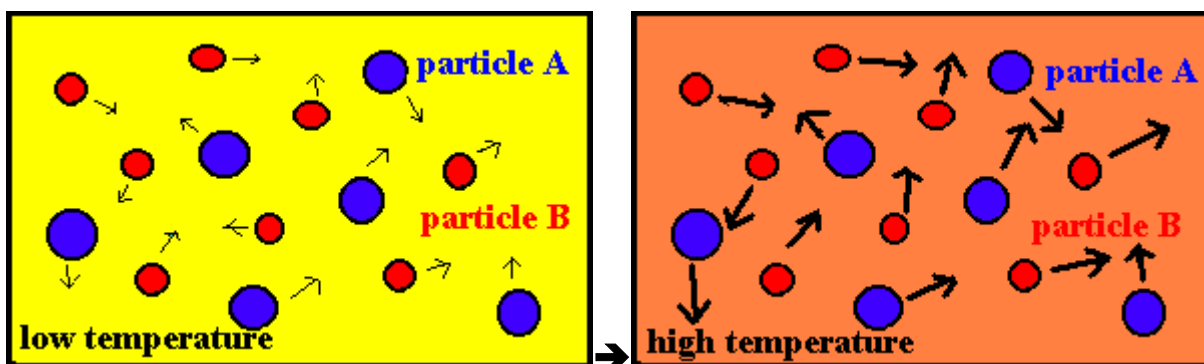
- **Most molecular collisions do not result in chemical change.**
- **Before any change takes place on collision, the colliding molecules must have a minimum kinetic energy called the Activation Energy shown on the energy level diagrams below.**
  - o **Going up and to top 'hump' represents bond breaking on reacting particle collision.**
    - ▪ **The arrow up represents this minimum energy needed to break bonds to initiate the reaction.**
  - o **Going down the other side represents the new bonds formed in the reaction products.**
- **It does not matter whether the reaction is an exothermic or an endothermic energy change.**
- **Now when heated molecules have a greater kinetic energy, a greater proportion of them have the required activation energy to react.**
- **The increased chance of 'fruitful' higher energy collisions greatly increases the speed of the reaction.**
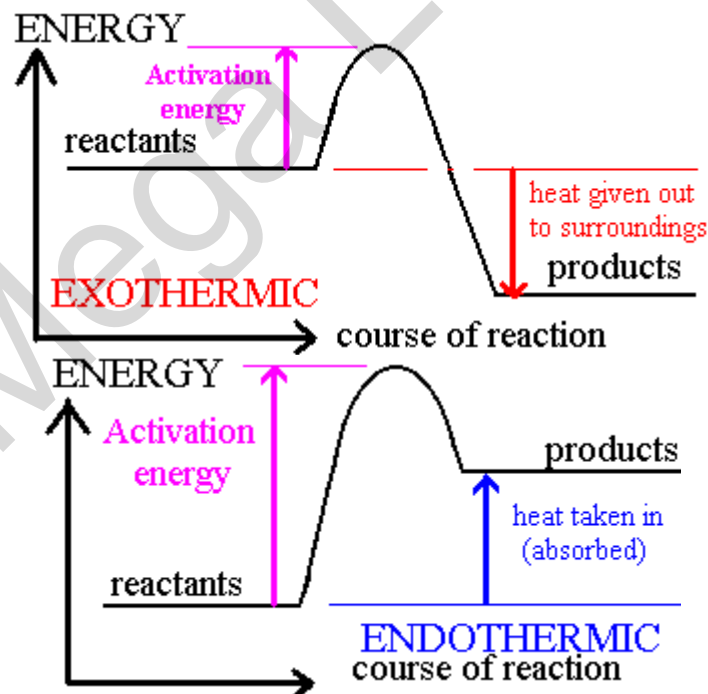
The effect of a Catalyst (see also light effect and graphs)

- I was once asked "what is the opposite of a catalyst?"
- There is no real opposite to a catalyst, other than the uncatalysed reaction!
- The word catalyst means changing the rate of a reaction with some other material 'added to' or in 'contact with' the reaction mixture.
- There are the two phrases you may come across:
    - a 'positive catalyst' meaning speeding up the reaction
    - OR a 'negative catalyst' slowing down a reaction
- Catalysts increase the rate of a reaction by helping break chemical bonds in reactant molecules.
- This effectively means the Activation Energy is reduced (see diagram below).
- Therefore at the same temperature, more reactant molecules have enough kinetic energy to react compared to the uncatalysed situation.
- Although a true catalyst does take part in the reaction, BUT does not get used up and can be reused with more reactants.
    - It is chemically the same at the end of the reaction but it may change a little physically if its a solid.
    - In the hydrogen peroxide solution decomposition by the solid black catalyst manganese dioxide, the solid can be filtered off when reaction stops 'fizzing'.
    - After washing with water, it can be collected and added to fresh colourless hydrogen peroxide solution and the oxygen production 'fizzing' is instantaneous!
        - Note: At the end of the experiment the solution is sometimes stained brown from minute manganese dioxide particles, the reaction is exothermic and the heat has probably caused some disintegration of the catalyst.
- A solid catalyst might change physically by becoming more finely divided, especially if the reaction is exothermic.
- Different reactions need different catalysts and they are extremely important in industry: examples ..
    - nickel catalyses the hydrogenation of unsaturated fats to margarine
    - iron catalyses the combination of unreactive nitrogen and hydrogen to form ammonia
    - enzymes in yeast convert sugar into alcohol
    - zeolites catalyse the cracking of big hydrocarbon molecules into smaller ones
    - most polymer making reactions require a catalyst surface or additive with the monomer molecules.
- Enzymes are biochemical catalysts
    - They have the advantage of bringing about reactions at normal temperatures and pressures which would otherwise need more expensive and energy-demanding equipment.
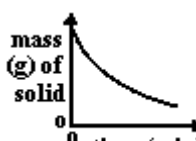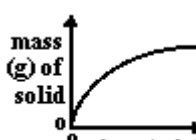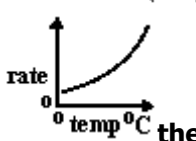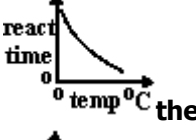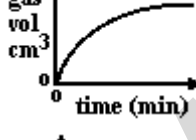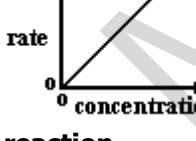

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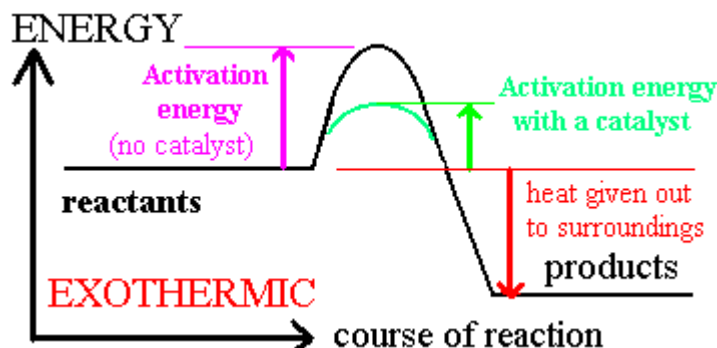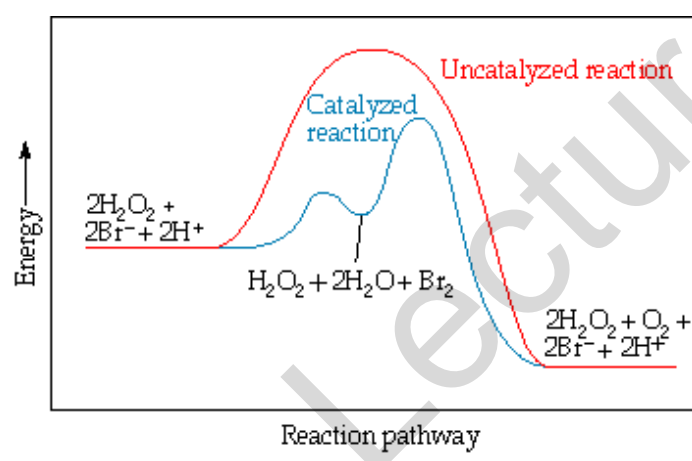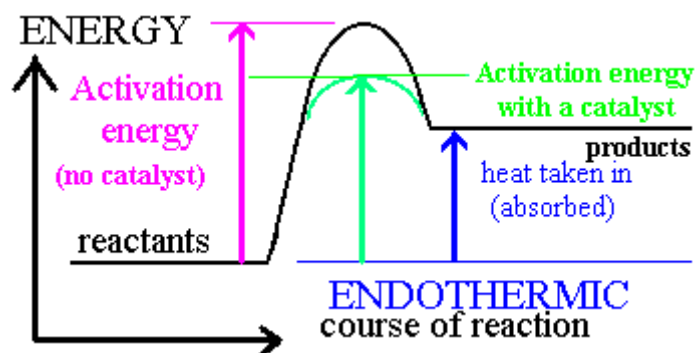
The Effect of Light

- **Light energy (uv or visible radiation) can initiate or catalyse particular chemical reactions.**
    - o **As well as acting as an electromagnetic wave, light can be considered as an energy 'bullets' called photons and they have sufficient 'impact' to break chemical bonds, that is, enough energy to overcome the activation energy.**
- **Examples:**
    - o **Silver salts are converted to silver in the chemistry of photographic exposure of the film.**
        - ▪ **Silver chloride (AgCl), silver bromide (AgBr) and silver iodide (AgI) are all sensitive to light ('photosensitive'), and all three are used in the production of various types of photographic film to detect visible light and beta and gamma radiation from radioactive materials.**
        - ▪ **Each silver halide salt has a different sensitivity to light.**
        - ▪ **When radiation hits the film the silver ions in the salt are reduced by electron gain to silver**
            - ▪ $Ag^+ + e^- ==> Ag$, **the halide ion is oxidised to the halogen molecule** $2X^- ==> X_2 + 2e^-$
        - ▪ **AgI is the most sensitive and used in X-ray radiography, AgCl is the most sensitive and used in 'fast' film for cameras.**
    - o **Photosynthesis in green plants:**
        - ▪ **The conversion of water + carbon dioxide ==> glucose + oxygen**
        - ▪ $6H_2O_{(l)} + 6CO_{2(g)} ==> C_6H_{12}O_{6(aq)} + O_{2(g)}$ **requires the input of sunlight**

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energy
▪ **The green chlorophyll molecules absorb the photon energy packets and initiate the chemical changes shown above.**
o **Photochemical Smog:**
▪ **This is very complex chemistry involving hydrocarbons, carbon monoxide, ozone, nitrogen oxides etc.**
▪ **Many of the reactions to produce harmful chemicals are catalysed by light energy.**

More examples of interpreting graphical results (see two other graphs and notes)

- **the decrease in the amount of a solid reactant with time**

- **the increase in the amount of a solid product with time**

- **the increase in speed of a reaction with increase in temperature**

- **the decrease in reaction time with increase in temperature**

- **the increase in the amount of a gas formed in a reaction with time**

- **typical graph showing the effect of concentration on the speed of a reaction**

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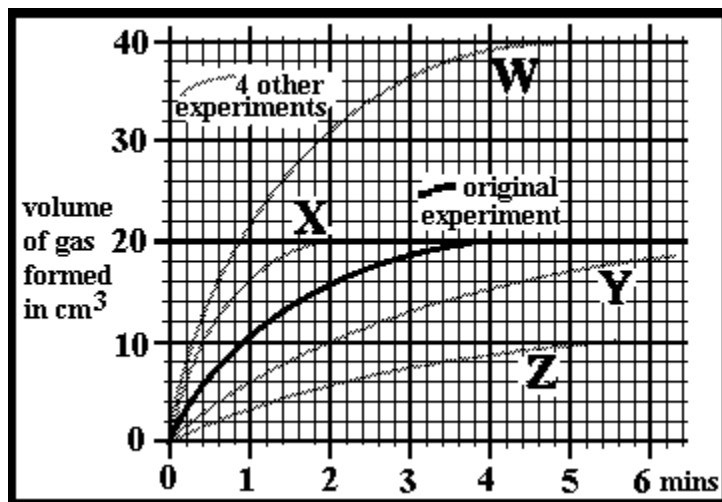
- **The graphs on the left is typical of where a gaseous product is being collected. The middle graph might represent the original experiment 'recipe' and temperature. Then the experiment repeated with variations eg**
- **X could be the same recipe but a catalyst added, forming the same amount of product, but faster.**
- **Initially, Y and Z might represent progressively lower concentrations.**
- **Z could represent taking half the amount of reactants or half a concentration. Its slower and only half as much of the original gas is formed.**

W might represent taking double the quantity of reactants to forming twice as much gas eg same volume of reactant solution but doubling the concentration, so producing twice as much gas with initially double the speed (gradient).

DONE