CHAPTER 9: Rate of Reaction

<u>*Learning outcomes:*</u>

(a) explain and use the terms: rate of reaction, activation energy and catalysis.
(b) explain qualitatively, in terms of collisions, the effect of concentration changes on the rate of a reaction.
(c) show understanding, including reference to the Boltzmann distribution, of what is meant by the term activation energy.
(d) explain qualitatively, in terms both of the Boltzmann distribution and of collision frequency, the effect of temperature change on the rate of a reaction
(e) (i) explain that, in the presence of a catalyst, a reaction has a different mechanism, i.e. one of lower activation energy.
(ii) interpret this catalytic effect in terms of the Boltzmann distribution.
(f) describe enzymes as biological catalysts (proteins) which may have specific activity.

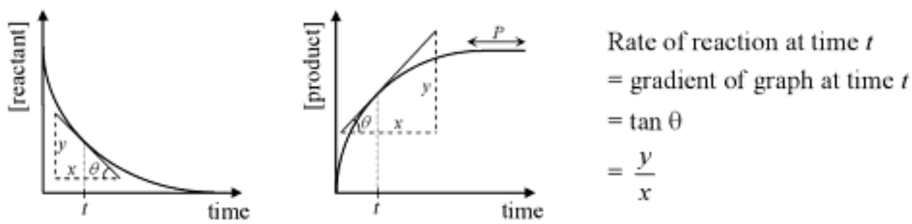
9.1 Rate of Reaction

What is the rate of reaction?

1) *Rate of reaction* is the change in concentration of reactants or products per unit time. It refers to the rate of product formed or the rate of reactant used up.

2) A balanced chemical equation gives no information about the rate of reaction. It has to be measured experimentally.

3) The rate of reaction can also be obtained by calculating the **gradient** of a concentration-time graph.



4) The higher the gradient(the steeper the graph), the higher the rate of reaction.

5) The gradient of the graph decreases with time, this shows that the **rate of reaction is inversely proportional to time**. Which means, the rate of reaction decreases as the reaction proceeds.

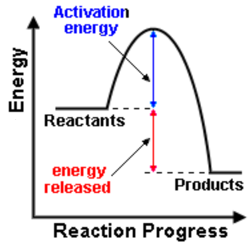
Collision theory

1) The *collision theory* states that, for the particles to react with each other, they must **collide** in the **correct orientation** with **energy greater than or equal to the activation energy**.

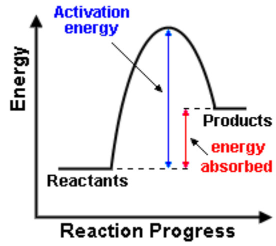
2) The *activation energy* is the minimum energy that that the reacting particles must possess for a successful collision to take place.

3) Every reaction has a specific activation energy.

4) If the collision results in the reactants changing into products, it is said to be an effective(or successful) collision.



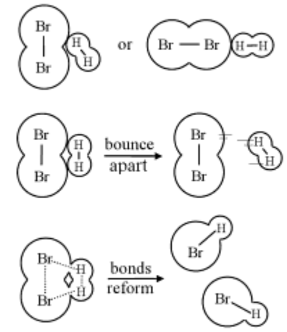
Exothermic reaction



Endothermic reaction

e.g. $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$

- If the molecules of H_2 and Br_2 collide with *incorrect orientation*, there is *no* reaction.
- If the molecules of H_2 and Br_2 collide with *insufficient energy*, there is *no* reaction.
- If the molecules of H_2 and Br_2 collide with *sufficient energy* and *correct orientation*, the bonds between H–H and Br–Br are broken and new H–Br bonds are formed. Hence, reaction takes place.



9.2 Factors Affecting the Rate of Reaction

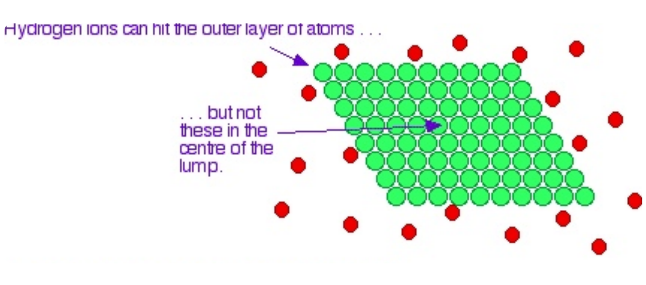
How to increase the rate of reaction?

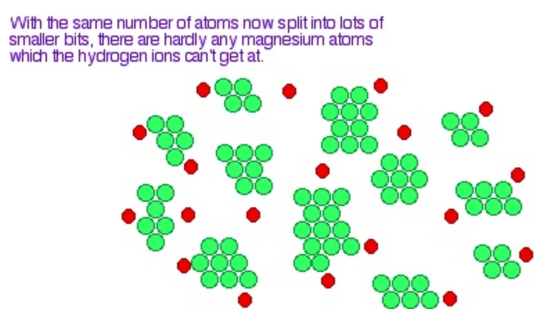
1) According to the collision theory, the rate of reaction will increase if:
   i. the frequency of collision and effective collision increases.
   ii. the proportion of particles with energy greater than activation energy increases.

Effect of surface area

1) The **larger** the surface area of the reactant particles, the **higher** the rate of reaction.

2) This is because the surface area exposed for collision is larger, **frequency of collision** between the reactant particles **increases** and hence the **frequency of effective collision also increases**. More products are formed per unit time and hence the rate of reaction increases.

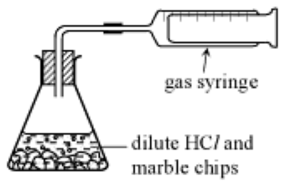


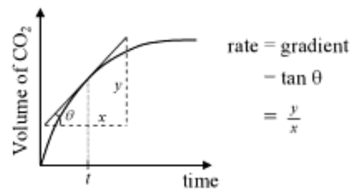


3) For example, the reaction between hydrochloric acid and marble chips(calcium carbonate) is as follow:

$$HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

The rate of reaction can be found by measuring the volume of CO_2 gas given out per unit time. The volume of CO_2 is determined at regular intervals. The set up of apparatus is as follow:





It is found that powdered marble chips react faster than big lumps of marble chips

4) This is because powdered marble chips are smaller in size and hence have a larger total surface area.

<u>Effect of concentration</u>

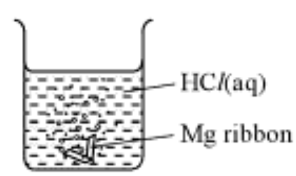
1) The **higher** the concentration of the reactant particles, the **higher** the rate of reaction.

2) This is because in a more concentrated solution, there are **more reactant particles per unit volume**. The **frequency of collision** between the reactant particles **increases** and hence the **frequency of effective collision also increases**. More products are formed per unit time and hence the rate of reaction is higher.

3) For example, the reaction between magnesium ribbon and hydrochloric acid is as follow:

$$Zn(s) + HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

The rate of reaction can be found by measuring the time taken for the magnesium ribbon to disappear from sight.



It is found that when HCl has a higher concentration, the time taken for the magnesium ribbon to disappear is shorter.

4) Since rate of reaction is inversely proportional to time, the shorter the time, the higher the rate of reaction.

5) There are also times where increasing the concentration does not help in increasing the rate of reaction:
   i. **Reactions involving only a single reactant particle splitting**
      - The rate of reaction is not governed by the rate of collision between them.
      - The rate is governed by the **amount of energy** possessed by the reactant particles.
      - If a large proportion of the particles have energy **greater than activation energy**, more particles will split up per unit time and hence the rate of reaction is higher.
   ii. **Where a catalyst is working as fast as it can**
      - If a high enough concentration of reactant particles is mixed with a small amount of catalyst, the reaction proceeds.
      - The rate of reaction will not increase if the concentration of the reactant particles is increased because the **catalyst is saturated**.
      - The rate of reaction can be increased by adding more catalysts.

<u>Effect of pressure</u>

1) The **higher** the pressure of the system, the **higher** the rate of reaction.

2) The explanation is the same as the one in the effect of concentration. However, increasing the pressure will only increase the rate of a reaction **involving gases**. Changing the pressure of a reaction which involves only solid or liquid has no effect on it.

<u>Effect of temperature</u>

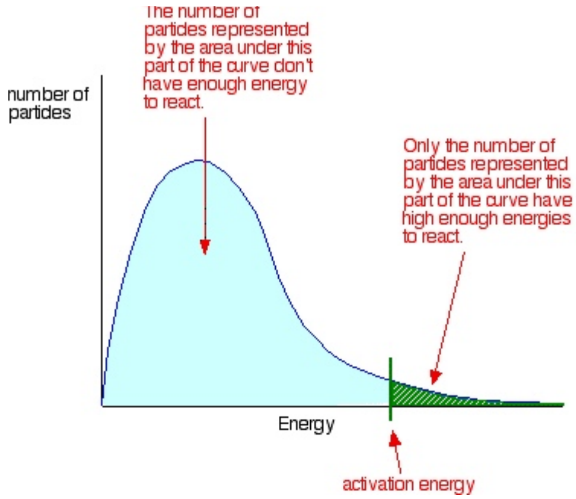
1) The **higher** the temperature of the reacting system, the **higher** the rate of reaction.

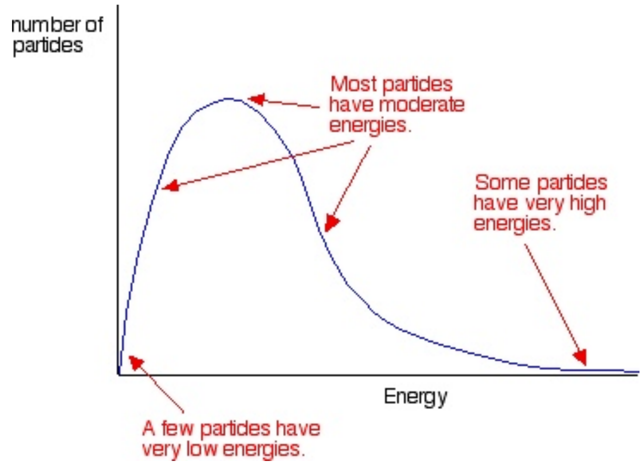
2) This is because at higher temperature, the **average kinetic energy of the particles increases**, so:
   i. more reacting particles have energy equal to or greater than the activation energy. (This is the major reason)
   ii. the reacting particles travel at higher speed, the frequency of collision between the reacting particles increases. (This is the minor reason)

   This causes the frequency of effective collision to increase. More products are formed per unit time and hence, the rate of reaction is higher.

3) In fact, the rate of reaction doubles for every increase in 10 °C.

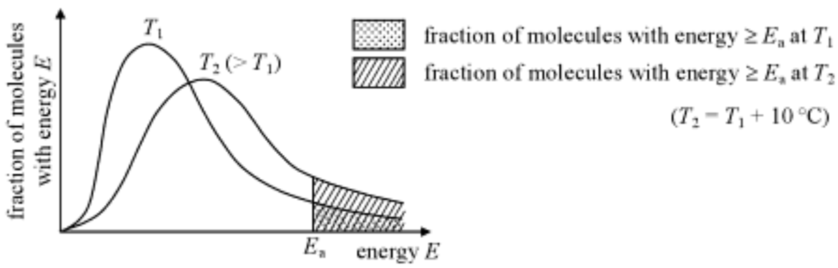
4) The effect of temperature on rate of reaction can be shown in a Maxwell-Boltzmann distribution curve. A typical curve looks like this:





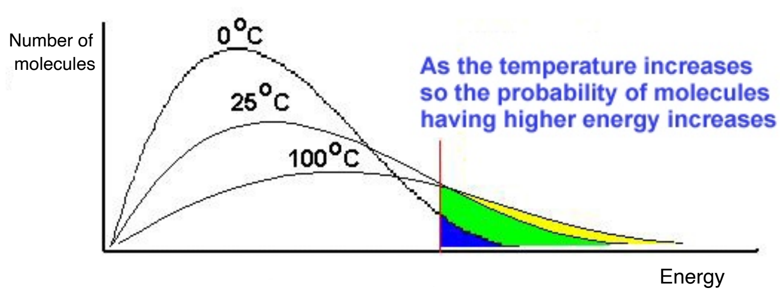
5) The area under the curve represents the **total number of molecules**, it is constant if no additional molecules are added.

6) An increase in temperature increases the number of particles with higher energy, the curve shifts to the right. So that there are more particles with energy greater than the activation energy, as illustrated below:



There are more particles with energy greater than the activation energy at T2

7) When drawing the curve at a higher temperature, the height of the curve should reduce so that the area under the curve remains constant.



9.3 Catalysis

What is a catalyst?

1) A *catalyst* is a substance that increases the rate of reaction but is chemically unchanged at the end of the reaction.

2) *Catalysis* is the increase in the rate of chemical reaction by a catalyst.

3) Characteristics of catalysts:
   i. Catalysts are needed in small amounts only. This is because a catalyst is not used up at the end of a reaction, the same catalyst can be used to catalyse a large number of reactions.
   ii. Catalysts do not initiate the reaction, they accelerate it.
   iii. Catalysts do not alter the enthalpy change of a reaction.
   iv. Catalysts can be poisoned by impurities, thus losing its catalytic abilities.
   v. Most catalysts are transition metals or compounds of them.
   vi. Catalysts are usually specific, a reaction can only be catalysed by a specific catalyst.

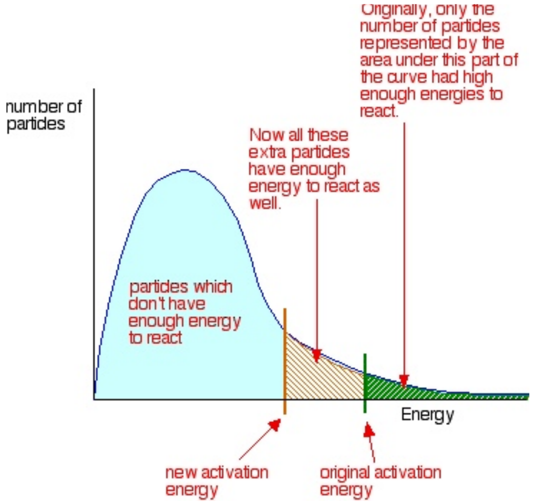
4) Examples of catalysts used in industries:

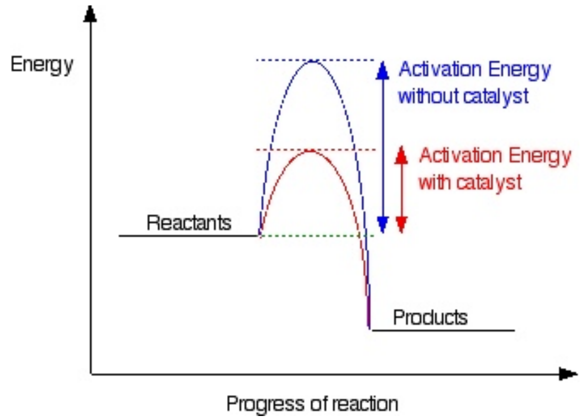
Reaction	Catalyst used
The conversion of SO_2 to SO_3 in the Contact process	Vanadium(V) oxide, V_2O_5
The manufacture of ammonia in the Haber process	Iron, Fe
The manufacture of nitric acid in the Ostwald process	Platinum, Pt
The manufacture of margarine by hydrogenation	Nickel, Ni
Catalytic cracking of long hydrocarbon molecules	Zeolite

The role of catalyst

1) A catalyst works by **providing an alternative route** for the reaction to occur. This alternative route has a **lower activation energy**. This increases the proportion of reacting particles with energy greater than the activation energy. As a result, the frequency of effective collision increases. More products are formed on per unit time and the rate of reaction is higher.

2) A catalyst neither alters the energies of reacting particles nor lower the original activation energy. It provides an **alternative route with lower activation energy**.





3) An example is the decomposition of hydrogen peroxide into water and oxygen.

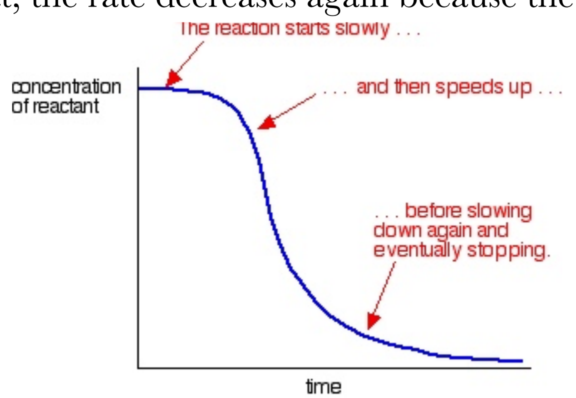
$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

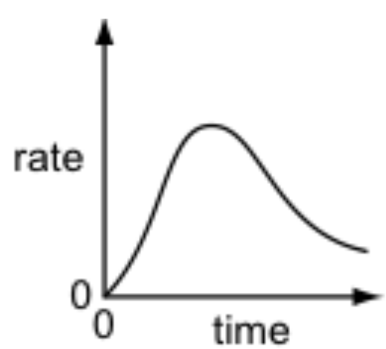
The reaction proceeds very slowly at room temperature and there are no observable changes. However, when a little manganese(VI) oxide, MnO_2 is added, effervescence is seen immediately. This suggests that oxygen gas is released.

Autocatalysis

1) For most reactions, the rate of reaction decreases with time because the concentration of reactants decreases.

2) However in some reactions, one of the **products can act as a catalyst** for that reaction. In these reactions, the rate is low at the beginning because there is no catalyst but increases as soon as the product(catalyst) is being formed. After that, the rate decreases again because the concentration of reactant decreases.



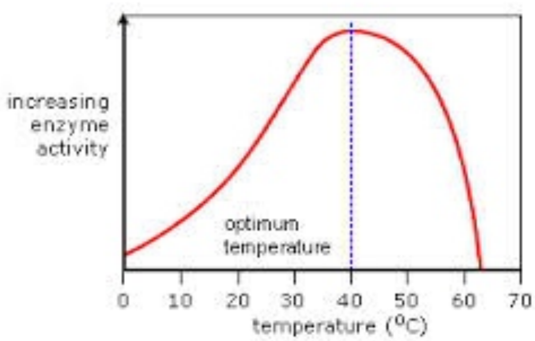


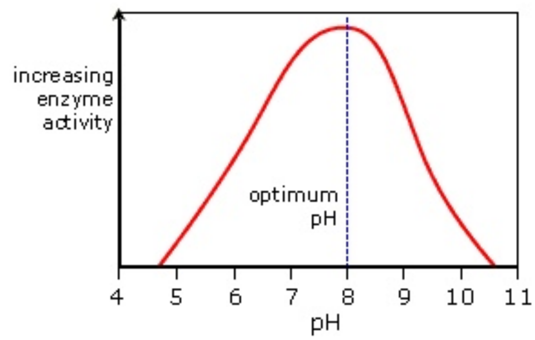
Enzymes as catalysts

1) *Enzymes* are proteins which have catalytic function and can act as biological catalysts that catalyses biological reactions in living organisms.

2) i. Enzymes are **highly specific**, catalysing only one type of reaction.

ii. Enzymes are also very sensitive to changes in pH and temperature. Most enzymes can only function in a small range of temperature(usually 37 °C, the body temperature) and pH.





iii. Enzymes are super-efficient catalysts, they are much more efficient compared to inorganic catalysts.

3) Enzymes function via the **lock-and-key mechanism**. According to this model, the substrate(reactant) molecule and the active site of the enzyme have complementary shapes so that the substrate fits in precisely.

4) The substrate binds to the active site of the enzyme just like a key binds to a lock. Bond-breaking and bond-forming processes then take place, transforming the substrate into products.