CHEMICAL KINETICS

Topic-3

Collision theory and concepts, activation energy and its importance

VERY SHORT ANSWER QUESTIONS

1. What is law of mass action?

This law relates rate of reaction with active mass or molar concentration of reactants.

At a given temperature, the rate of a reaction at a particular instant raised to powers which are numerically equal to the numbers of their respective molecules in the stoichiometric equation describing the reaction."

Active mass = molar concentration of the substance

= (number of gram moles at the substance)/(volume in litres)

= (w/M)/V=n/V

where w = mass of substance and 'M' is the molecular mass in grams. 'n' is the number of g moles and V is volume in litres.

2. 4 g of hydrogen and 128 g of hydrogen iodide are present in a 2 litre flask. What are their active masses?

Solution: Mass of hydrogen = 4 g , Mol. mass of hydrogen = 2

Volume of the flask = 2 litres

Active mass of hydrogen = 4/2*2 = 1 mol L^{-1}

Mass of HI = 128 g

Mol. mass of HI = 128 g

Volume of the flask = 2 litre

Active mass of hydrogen iodide = 128/(128*2) = 0.5 mol L^{-1}

3. **What are very fast reactions?**

Very fast or instantaneous reactions:

These reactions are so fast that they occur as soon as the reactants are bought together. Generally, these reactions involve ionic species and thus known as ionic reactions. These reactions take about 10^{-14} to 10^{-16} seconds for completion. It is almost impossible to determine the rates of these reactions. Some such examples are:

(i) Precipitation of AgCl when solutions of silver nitrate and sodium chloride are mixed.

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$$

(ii) Precipitation of $BaSO_4$ when solutions of barium chloride and sulphuric acid and mixed.

$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$$

(iii) Neutralisation of an acid with a base when their aqueous solutions are mixed.

$$HCl + NaOH \rightarrow NaCl + H_2O$$

Acid Base Salt

4. **What are very slow reactions?**

Very slow reactions:

There are certain reactions which are extremely slow. They make take months together to show any measurable change at room temperature. It is also difficult to study the kinetics of such reactions.

Some examples are:

(i) **Reaction between hydrogen and oxygen at room temperature room temperature**

$$2H_2+O_2 \longrightarrow 2H_2O \text{ (very slow reaction)}$$

(ii) **Reaction of atmospheric H_2S on basic lead acetate**.

White basic lead acetate paint turns black very slowly (due to formation of PbS.)

(iii) Reaction between carbon and oxygen at room temperature

$C + O_2 \dashrightarrow CO_2$

5. **What are moderate reactions?**

Ans: Moderate reactions:

Between the above two extremes, there are a number of reactions which take place at moderate and measurable rates at room temperature and it is these reactions which are studied in chemical kinetics. Mostly these reactions are molecular in nature. Some common examples of such type are given below:

(i) Decomposition of hydrogen peroxide

$2H_2O_2 \rightarrow 2HO + O_2$

(ii) Decomposition of nitrogen pentoxide

$2N_2O_5 \rightarrow 2N_2O_4 + O_2$

SHORT ANSWER QUESTIONS

1. **What is the importance of Chemical kinetics?**

Ans: The chemical reactions can be slowed down or speeded up by changing conditions under which they occur. For example, very slow reaction. $CO + 2H_2 \rightarrow CH_3OH$, can be speeded up by maintaining temperature around 400^oC, pressure about 300 atmosphere and using a catalyst containing ZnO and Cr_2O_3. The decay of food articles can be slowed down by reserving them in refrigerators. There are two principal reasons for studying chemical kinetics.

(i) To predict the rate of a particular reaction under specified conditions:

The conditions can be adjusted to make the reactions to go at a desired rate, either rapidly or slowly or moderately. The field of chemical kinetics is useful in industry as the conditions for maximum yields of industrial products can be ascertained.

(ii) To predict the mechanism of the reaction:

The intelligent guess regarding various elementary processes responsible for the formation of products can be made which should be consistent with experimental data.

2. **What are the main postulates of collision theory?**

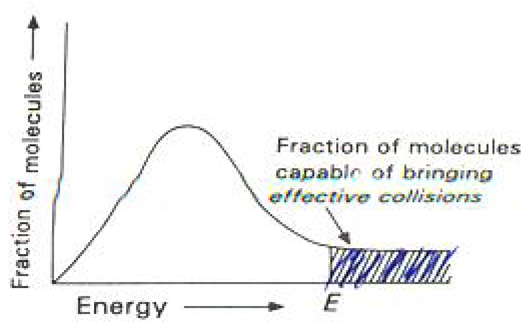
(1) A chemical reaction takes place due to collision among reactant molecules. The number of collisions taking place per second per unit volume of the reaction mixture is known as collision frequency (Z). The value of collision frequency is very high, of the order of 10^{25} to 10^{28} in case of binary collisions.

(2) Every collision does not bring a chemical change. The collisions that actually produce the products are effective collisions. The effective collisions which bring chemical change are few in comparison to the form a product are ineffective elastic collisions, i.e., molecules just collide and disperse in different directions with different velocities. For a collision to be effective, the following two barriers are to be cleared.

3. **What are energy barrier, threshold energy and activation energy?**

Ans: Energy barrier

The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur, is known as threshold energy.



In the graph 'E' corresponds to minimum or threshold energy for effective collision in a hypothetical reaction.

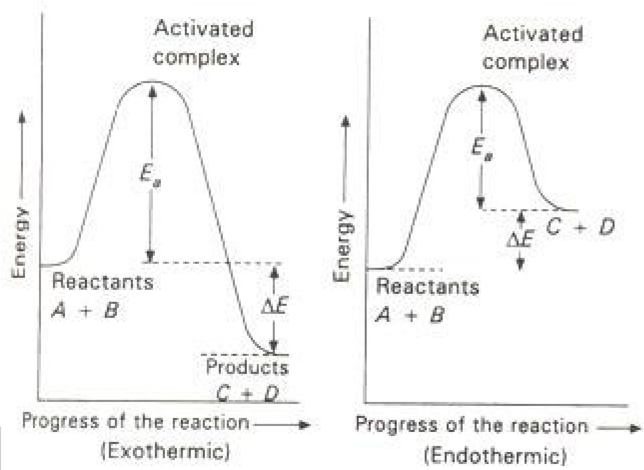
There is an energy barrier for each reaction. The reacting species must be provided with sufficient energy as to cross the energy barrier.

The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy.

Activation energy = threshold energy - average kinetic energy of reacting molecules

Threshold energy = initial potential energy of reactant molecules + activation energy.

A collision between high energy molecules overcomes the forces of repulsion and brings the formation of an unstable molecule cluster, called the activated complex. The life span of an activated complex is very small. Thus, the activated complex breaks either into reactants again or new substances, i.e., products. The activation energy (E_a) depends upon the nature of chemical bonds undergoing rupture and is independent of enthalpies of reactants and products. The energy changes during exothermic and endothermic reactions versus the progress of the reaction are shown in the figure below.



<u>LONG ANSER QUESTIONS\</u>

1. What are the main postulates of simple collision theory of reaction?

Ans: <u>COLLISION THEORY OF REACTION RATE (ARRHENIUS THEORY OF REACTION RATE)</u>

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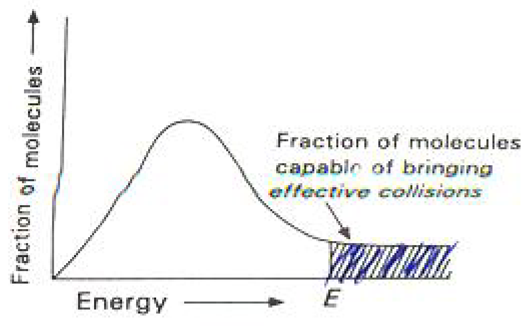

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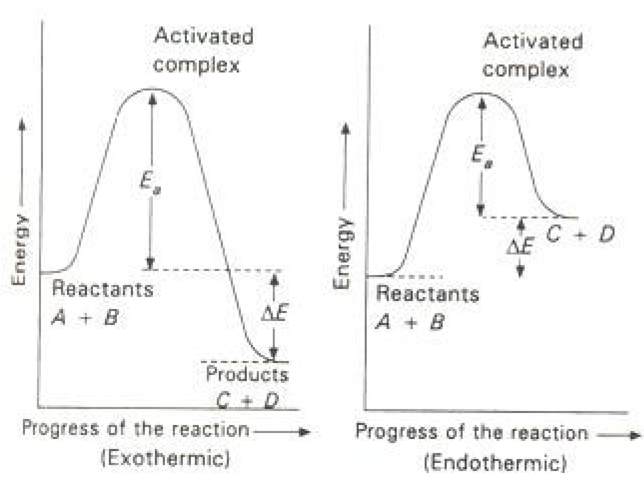

Thus, every chemical reaction whether exothermic or endothermic has an energy barrier which has to be overcome before reactants can be transformed into products. If the reactant molecules have sufficient energy, they can reach the peak of the energy barrier after collision and then they can go to the right side of the slope and consequently change into products. If the activation energy for a reaction is low, the fraction of effective collisions will be large and the reaction will be fast. On the other hand, if the activation energy is high, then fraction of effective collisions will be small and the reaction will be slow. When temperature is increased, the number of active molecules increases, i.e., the number of effective collisions will increase and the rate of reaction will increase.

Activation energy E_a - $E_{(activated\ complex)}$ - $E_{(ground\ state)}$

ΔH = activation energy of forward reaction - activation energy of background reactions

Orientation barrier

Energy alone does not determine the effectiveness of the collision. The reacting molecules must collide in proper manner if the reaction is to occur. This has been shown in Fig.8.5.

Rate of reaction is directly proportional to the number of effective collisions.

Rate = dx/dt = collision frequency × factor of effective collisions

= z × f