IV. Surface Reactions

The reactions which take place exclusively on the walls of containing vessel are surface reactions. The study of the kinetics of such reactions has led to the discovery ... addition to reactions of simple orders, there are other reactions which are of fractional order ... surface reactions have effects on the rate of reactions. The degree of such effects depends ... surface area, nature of adsorbent and adsorbate and method of preparing the surface. The ... such gaseous reactions depends on the pressure of gas. Examples are the decomposition ... PH_3 and AsH_3.

$$4PH_3 \longrightarrow P_4 + 6H_2$$

The above reaction is tetramolecular, but of first order. Barrer experimentally observed ... decomposition of phosphine on tungsten surface follows first order kinetics at low pressure ... phosphine and zero order kinetics at high pressure.

$$\therefore \quad \text{at low pressure :} \quad \frac{dx}{dt} = k\,[PH_3]$$

$$\text{and} \quad \text{at high pressure :} \quad \frac{dx}{dt} = k\,[PH_3]^0$$

The decomposition of ammonia on platinum surface takes place according to the following rate law :

$$\frac{dx}{dt} = k\,[NH_3]\,[H_2]^{-1}$$

3. CHAIN REACTIONS

There are certain reactions whose rate is much greater than predicted from collision ... Such reactions do not proceed through simple mechanism and the steps producing products ... involve only the reactant molecules. This group of reactions proceed by a long ... self-repeating and thus millions of molecules react together. Such reactions are called ... *reactions*. Hence *chain reaction is defined as series of successive elementary processes ... active intermediate species are consumed and regenerated before the products are obtained* ... chain reactions are special case of consecutive reactions.

The chain reactions consist of the following steps :

(*i*) *Chain initiation.* It consists of slow generation of active intermediate species ... *chain carriers* which may be atoms, free radicals or energised molecules of one of the ... formed during the course of reaction. The chain initiation may take place thermally ... photochemically.

(*ii*) *Chain propagation.* The active intermediate species formed in the chain ... step, now react with the molecules of other reactant or reactants, resulting in the formation ... product and regeneration of active intermediate species; thus, restarting the reaction leading ... formation of the final products. Such steps are called *chain propagation steps*. Chain propagation ... is much faster and most of the products are formed in these steps.

(*iii*) *Chain transfer.* In some of these chain propagating steps, *new chain carriers* ... generated. These steps are called *chain transfer steps*. In chain transfer steps, initial chain ... generates a new chain carrier by reaction with some existing molecular species.

(*iv*) *Chain inhibition.* This step consists of removal of the products with simultaneous ... regeneration of more active species with a net decreasing effect on the rate of overall ... Such steps are termed as chain inhibiting steps. The chain inhibition may complete ... concentration of product becomes significant.

(*v*) *Chain termination or breaking.* In this step the active intermediate species ... removed or destroyed and are no loner available for chain initiation and propagation ...

breaking stage comes when there are no more or not enough reactant molecules to be converted into products, and active intermediate species are converted into nonactive molecular species.

(i) **Characteristic features of Chain Reactions.** The following are the distinguishing features of chain reactions :

1. Every chain reaction involves initial slow step, generating active intermediate species, which are helpful in starting fast propagating steps.

2. Their rate is much higher than expected from collision theory.

3. Their mechanism is not simple.

4. In all non-chain reaction, the rate is highest in the beginning and falls off with time, whereas in chain reactions, the rate is zero in the beginning, then rises to maximum and finally decreases with time.

This is shown in the Fig. 4.7.

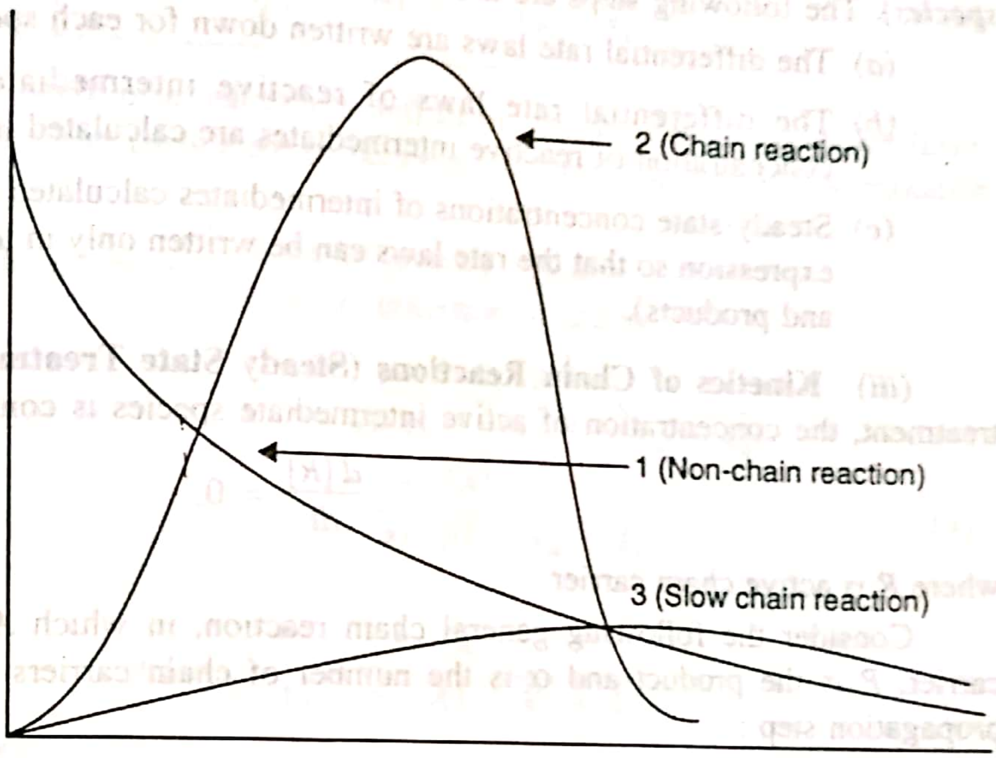

Fig. 4.7. Comparison of slow and fast chain reactions with non-chain reactions.

(a) Curve 1 represents a typical non-chain reaction.

(b) Curve 2 indicates a very rapid chain reaction, in which very high value of rate is momentarily attained and this corresponds to an ignition. Hence such reactions may momentarily reach very high temperature, be luminous, accompanied by an audible click and possibly cause explosion.

(c) Curve 3 represents much slower chain reaction. The maximum rate is not obtained until after a considerable interval of time. The maximum rate is maintained for an appreciable period before slowly falling off.

5. They are highly influenced by pressure or concentration of reactants.

6. In case of photochemical chain reactions, very high quantum yield is observed.

7. They are sensitive to foreign substances ; the speed may be accelerated or retarded.

8. Foreign gases, which are chemically unchanged, in a chain reacting gas mixture, often modify the reaction kinetics.

9. The chain reactions are rarely of simple orders *i.e.*, they generally show fractional orders. Their orders depend on the shape of vessel and other conditions.

10. Chain reactions have *induction period*. Since chain reaction has zero rate in the beginning, it requires enough time so that the rate could be experimentally detected. This time-lag is called *induction period*.

(ii) **Steady-State H**... involved in the steady-state hypothesis is