Paper : Physical Chemistry
Topic : Chemical Kinetics

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.... continued from page (33)

Chain Reactions :-

There are certain reactions whose rate is much greater than predicted from collision theory. Such reactions do not proceed through simple mechanism and the steps which produces products do not involve only the reactant molecules. These reactions proceed by a long series of self-repeating and thus millions of molecules react together. Such reactions are called chain reactions.

Hence, a chain reaction is defined as "series of successive elementary reactions in which highly reactive (transient, i.e; short-lived) species (atoms or free radicals) are produced as intermediates which carry out the reaction at a rapid rate due to a long series of self-repeating steps."

These reactions were first studied by Frank O. Rice and Karl F. Herzfeld (in 1934) and are also known as Rice - Herzfeld chain reactions. 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 called "chain carriers" which may be atoms, free radicals or energised molecules of one of the products formed during the course of reaction. The chain initiation may take place thermally or photochemically.

(ii) Chain Propagation :— The active intermediate species formed in the chain initiation step, now react with the molecules of other reactants (or reactant) resulting in the formation of the product and regeneration of active intermediate species; thus, restarting the reaction leading to the formation of 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 are generated. These steps are called chain transfer steps. In chain transfer steps, initial chain carrier 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 reactions. Such steps are known as chain inhibiting steps. The chain inhibition may complete when the concentration of product becomes significant.

(v) Chain Termination or Chain Breaking :— In this step the active intermediate species are removed or destroyed and are no longer available for chain initiation and propagation. The chain 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.

(a) Characteristic Features of Chain Reactions :—

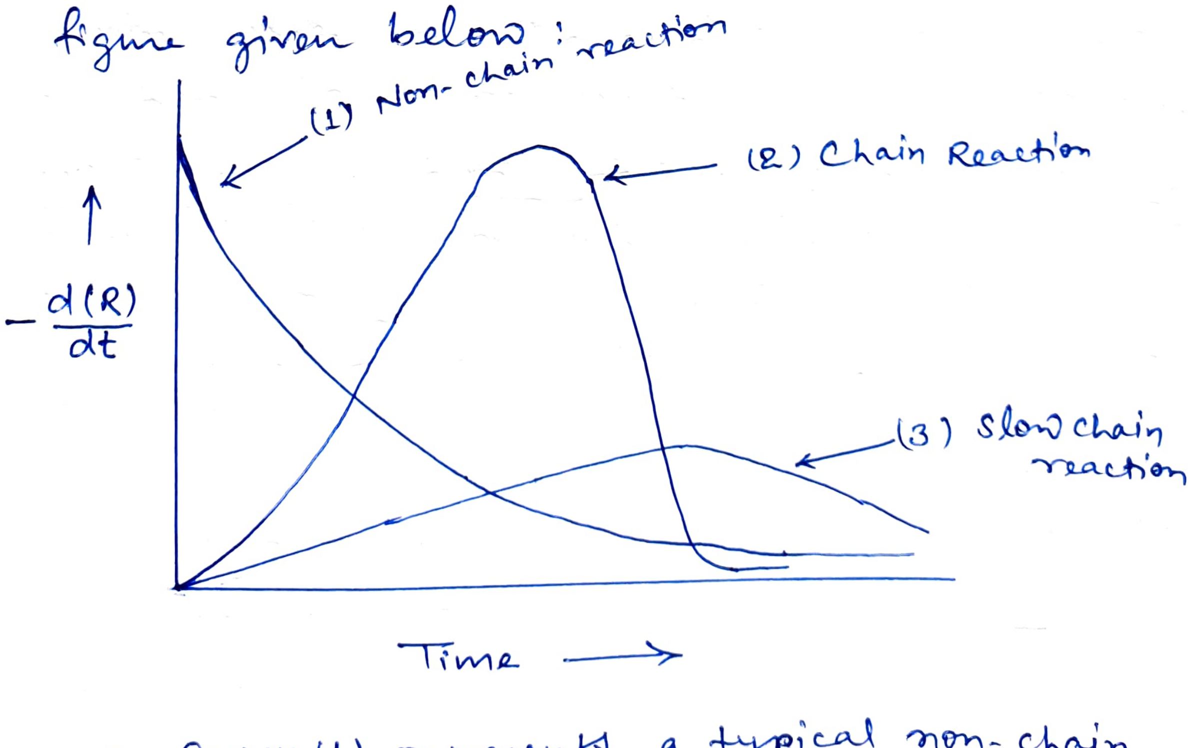
The following are the distinguishing features of chain reaction :

(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 reactions, the rate is highest in the begining and falls off with time, whereas in chain reactions, the rate is zero in the begining, then rises to maximum and finally decreases with time. This can be shown in the figure given below :



a. Curve (1) represents a typical non-chain reaction. In all non-chain reactions, the highest rate is observed at the begining and the rate of reaction falls off with time.

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.

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

(7.) They are sensitive to foreign substances: the speed may be accelerated or retarded.

(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 begining, it requires enough time so that the rate could be experimentally detected. This time-lag is called "induction period".

(b.) Steady-State Hypothesis :-

The assumptions involved in the steady-state hypothesis is that concentration of reactive intermediates can be assumed to be constant. If "C_i" is the reactive intermediate, then

$$[C_i] = \text{constant}$$

$$\therefore \quad \frac{d[C_i]}{dt} = 0$$

Note that the steady state approximation can only be applied to short-lived (or very reactive species). The following steps are used to calculate the rate law in terms of stable species:

(i) The differential rate laws are written down for each species.

(ii) The differential rate laws of reactive intermediates are put equal to zero and concentration of reactive intermediates are calculated in terms of stable species.

(iii) Steady-state concentrations of intermediate species calculated in step (ii) are substituted in the expression so that the rate laws can be written only in terms of stable species (reactants and products).

(C.) Chain reactions include gas-phase pyrolysis (i.e. high temperature decomposition) of hydrocarbons, aldehydes, several other carbonyl compounds, polymerizations and reactions of hydrogen with halogens and oxygen.

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