7.5. Order and Molecularity of a reaction

Order of a reaction : The order of a reaction may be defined as the total number of molecules whose concentration determines the rate of reaction.

In other words it is also defined as

The sum of powers (exponents) to which the concentration or pressure terms are raised in the rate equation of a given chemical reaction is called **order of reaction.**

Thus, for a given general reaction

$$aA + bB + ... \longrightarrow \text{Products}$$

The rate equation can be written as follows :

$$r = \frac{dx}{dt} = k\,[A]^a\,[B]^b\,.....$$

Thus, the order of reaction $(n) = (a + b + ...)$

The value of order of reaction may be an integer, positive, negative or even fractional. A reaction may be zero, first, second or third order according to the value of $(a + b + ...)$ comes out to be zero, one, two or three respectively.

(*i*) For zero order reaction :

$$r = \frac{dx}{dt} = k\,[A]^0\,[B]^0\,.....$$

Hence order of reaction $(n) = 0$

i.e. the rate of the reaction is independent on

Molecularity of a reaction : The molecularily of a reaction may be defined as the number of reactant molecules involved in the formation of products is called **molecularity of the reaction.** Thus, the molecularily of reaction may be 1, 2 or 3 according as one, two or three reactant molecules are taking part in the reaction.

On the basis of molecularily, reactions may be of the following types :

(1) Unimolecular reactions : If only one molecule is involved, the reaction is said to be unimolecular. For example,

(*a*) Decomposition of PCl_5

$$PCl_5 \longrightarrow PCl_3 + Cl_2$$

7.6 Zero order reaction

The reaction in which the rate of reaction is independent of the concentration of any reactant is called **zero order reaction.** In such a reaction the sum of the exponents in the rate equation is zero.

⏭ Expression for rate constant :

Let us consider the following zero-order reaction,

$$\underset{a}{A} \longrightarrow \underset{0}{\text{Products}} \qquad \text{initially}$$

For a zero order reaction, the rate of reaction at any time '*t*' is given by

$$\frac{dx}{dt} = k \qquad (k = \text{velocity constant})$$

or

$$dx = k\,dt$$

Integrating it, we get

$$\int dx = \int k.dt$$

or

$$x = kt + I \qquad \text{... (7, 2)}$$

where I is the integration constant

when $t = 0, x = 0$

$\therefore \qquad I = 0$

Substituting the value of I is eq (7, 2), we have

$$x = kt \qquad \text{... (7, 3)}$$

This is the general equation for rate constant of zero-order reaction.

Characteristics of zero-order reaction :

(*i*) The concentration of the products increases linearly with time. If we plot a graph between '*x*' and time '*t*', a straight line passing through the origin is obtained.

(*ii*) The unit of zero-order rate constant (k) is conc. time^{-1} *e.g.* mol lit^{-1} s^{-1}, if the time is expressed in second.

(*iii*) Half life of zero-order reaction is proportional to initial concentration *i.e.* $t_{1/2} \propto a$.

Examples : A number of photochemical and enzymic reactions are zero orders *e.g.*

(*i*) Photochemical combination of hydrogen and chlorine

$$H_2\,(g) + Cl_2\,(g) \xrightarrow{h\nu} 2HCl\,(g)$$

(*ii*) Decomposition of NH_3 in presence of molybdenum or tungsten.

$$2NH_3 \xrightarrow{Mo} N_2 + 3H_2$$