

## Chemical Kinetics :- (What it is?)

The direction of a chemical reaction  $\rightarrow$  the extent to which the reaction will proceed can be known from the study of thermodynamics  $\rightarrow$  chemical equilibrium. However, thermodynamics does not tell us anything about the time parameter, i.e. how fast the reaction occurs. To have knowledge of the rate of a reaction and the influence of different factors on the reaction rate, there is a branch in physical chemistry called chemical kinetics.

This chemical kinetics is also enables us to study (to elucidate) the mechanism by which a reaction occurs.



## Molecularity of a reaction :-

The molecularity of a reaction is defined as the number of molecules or atoms which take part in the process of a chemical change.

The reactions are said to be unimolecular, bimolecular or trimolecular, as one, two or three molecules are involved in the act leading to a chemical change.

## Order of a reaction :-

Order of a reaction is the quantitative dependence of its rate on the conc. of reacting substance can be indicated. The order is the number of conc. terms on which reaction rate depends. Thus,

if the rate of a reaction depends on the first power of the conc. of reactant, i.e.,

$$\text{Rate} = kC, \text{ the reaction is first order}$$

When the rate is proportional to the product of two reactant conc. or square of the conc. of a reactant, the reaction is 2nd order.

$$\text{Rate} = kC^2$$

The order of a reaction is an experimental quantity.



## Rate of a reaction :-

The rate of a reaction, i.e. the velocity of a reaction is the amount of chemical change occurring per unit time. The rate is generally expressed as the decrease in conc. of a reactant or as the increase in conc. of a product per unit time.

If  $c$  is the conc. of reactant at any time  $t$  the rate is  $-\frac{dc}{dt}$ , similarly if  $x$  is the conc. of product at any time  $t$  the rate is  $\frac{dx}{dt}$ .

## Rate law :- (Differential rate equation)

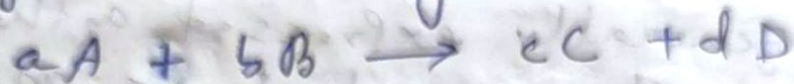
At constant temperature, the rate of reaction is a function of the conc. of the reactants. The functional relation between the rate of reaction and the conc. of the reactants is called the rate law.

The rate law is determined experimentally and is not possible to predict the expression for rate law of a reaction from the stoichiometry of the overall reaction.

The mathematical expression describing the functional relation between the rate of reaction and the conc. of reactants is referred to as differential rate law.



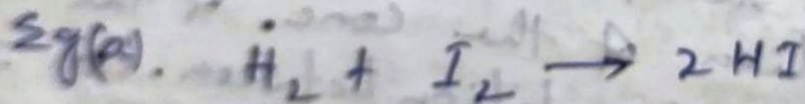
From law of mass action, the rate of a reaction is proportional to the product of a certain power of the molar conc. of the reacting species. Eg.



$$\text{Rate} \propto [A]^{\alpha} [B]^{\beta}$$
$$\Rightarrow \text{Rate} = k [A]^{\alpha} [B]^{\beta}$$

Where  $\alpha, \beta$  are may or may not equal to  $a, b$ . These  $(\alpha, \beta)$  dimensionless exponents are known as the order of the reaction.

$(\alpha + \beta)$  is the overall order of the reaction.



$$-\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = \frac{1}{2} \frac{d[HI]}{dt} = k [H_2][I_2]$$

$\therefore$  order of reaction  $1+1 = 2$  i.e. 2nd order reaction



$$-\frac{1}{2} \frac{d[N_2O_5]}{dt} = \frac{1}{4} \frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt} = k [N_2O_5]$$

$\therefore$  order of reaction = 1 i.e. 1st order react.



Rate law :- (Integrated rate equation):

1st order Reaction

The first order reaction is one in which the rate is directly proportional to the conc. of the one reactant.

In general, a first order react<sup>n</sup> is,



The diff. rate law is,  $-\frac{d[A]}{dt} = k[A]$

To know the quantitative relation between the conc. and time, it is necessary to integrate the diff. rate law.

Let, initial conc. of A = a mole/lit  $\rightarrow$   
time = t, let x mole  
of B is formed.

$\therefore$  Conc. of A at time t, = (a-x) mole/lit

Thus,

$$-\frac{d(a-x)}{dt} = k(a-x)$$

$$\Rightarrow \frac{dx}{dt} = k(a-x)$$

$$\Rightarrow \frac{dx}{a-x} = k dt$$

To find the value of k, and to obtain the conc. as a function of time it is necessary to integrate the eqn. Thus,



$$\int \frac{dx}{a-x} = \int k dt$$

$$\Rightarrow -\ln(a-x) = kt + I$$

Where,  $I$  is integrating constant,

When,  $t=0$ ,  $x=0 \Rightarrow I = -\ln a$

$$\therefore -\ln(a-x) = kt - \ln a$$

$$\Rightarrow k = \frac{1}{t} \ln \frac{a}{a-x}$$

$$\Rightarrow k = \frac{2.303}{t} \log \frac{a}{a-x}$$

This is the integrated rate equation of a first order reaction.

$$\frac{d(a-x)}{dt} = k(a-x)$$

$$\frac{d(a-x)}{a-x} = k dt$$

$$\ln(a-x) = kt + I$$