Ph.D. Course Work

Paper: II

Advance Courses in Chemistry:-

Unit I

a) Study of kinetics of reactions including fast reactions:

Brief Introduction to kinetics of reactions:

a) Differential rate law:-

$$aA + bB \longrightarrow cC + dD$$

Therefore rate of reaction:-

$$r = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}.$$

The negative signs implies that reactant concentration decreases with time.

b) Integr Rate law equation:

$$xA + yB \longrightarrow C$$

Therefore rate of reaction

$$r = k[A]^x [B]^y$$

for [A] = E and y = 1 The rate of reaction

For [A] = 1 and [B] = 1 rate of reaction

$$r = k$$

where k is the rate constant of the reaction.

In general rate constant is defined as the rate of reaction when the concentration of reactants is unity.

Order of the reaction:

The sum of the powers by which concentration terms are raised to express the rate in rate law equation is called order of the reaction.

Integrated expression for rate of reaction:-

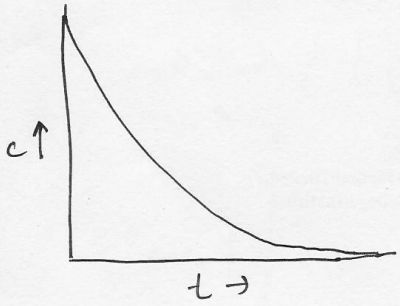
① First order:-

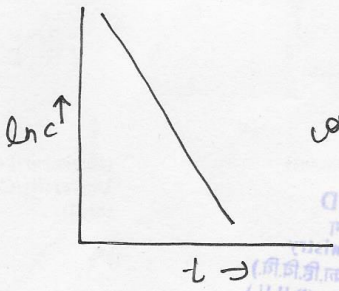
$$k_1 = \frac{1}{t} \ln \frac{a}{a-x}$$

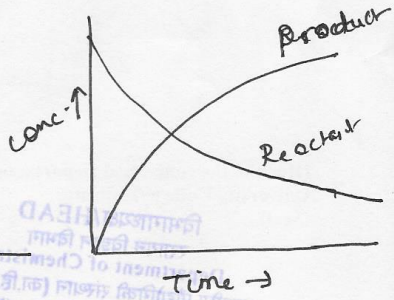
where k_1 = rate constant for first order reaction
t = time
a = initial concentration of reactant
x = moles that react in time t

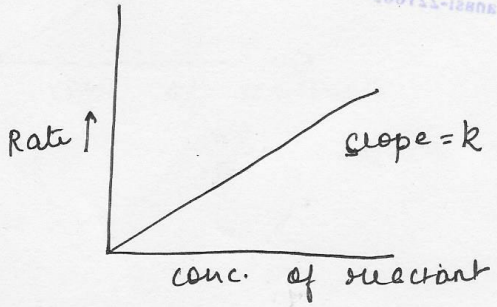
$$c = c_0 e^{-k_1 t}$$

where c = conc. at time t
c_0 = initial concentration









② Integration of Rate-Expression for second order reactions:-

① When the reactants are different:

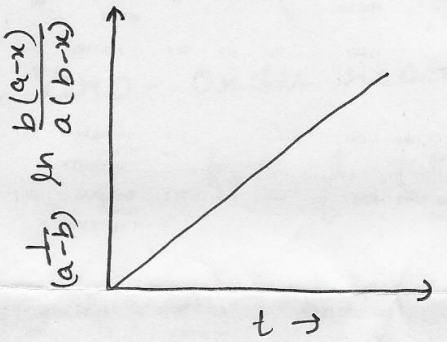
$$A + B \longrightarrow P$$

$$k_2 = \frac{1}{t}\left[\frac{1}{(a-b)} \ln \frac{b(a-x)}{a(b-x)}\right]$$

where a = initial concentration of A

b = " " " B

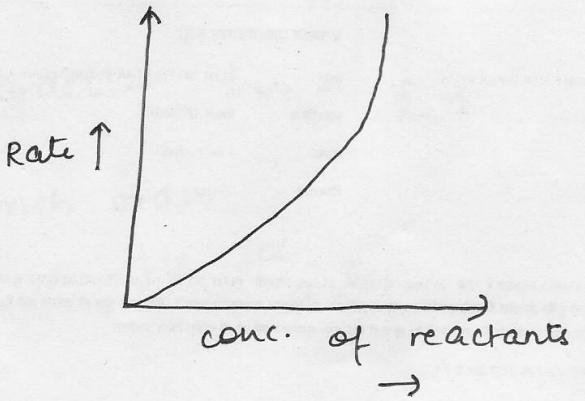
x = no. of moles of a and b that react to form product.



② When the reactants are same:-

$$2A \longrightarrow P$$

$$k_2 = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right] = \frac{1}{t}\left[\frac{x}{a(a-x)}\right]$$



(3) Integration of rate expression for third order reaction:-

$$3A \longrightarrow P$$

$$k_3 = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right] = \frac{1}{2t}\left[\frac{x(2a-x)}{a^2(a-x)^2}\right]$$

$$2A + B \longrightarrow P$$

$$k_3 = \frac{1}{t(2b-a)^2}\left[\ln\frac{b(a-2x)}{a(b-x)} + \frac{(2b-a)(2x)}{a(a-2x)}\right]$$

(4) Zero-Order reaction:-

$$k_0 = \frac{1}{t}\left([A]_0 - [A]\right)$$

Half life-time of reaction:-

Time required for half of the reaction to be completed.

(1) First order:- $k_1 = \frac{0.693}{t_{1/2}}$ or $t_{1/2} = \frac{0.693}{k_1}$

(2) Second order:- $t_{1/2} = \frac{1}{k_2 a}$

For nth order

$$t_{1/2} \propto \frac{1}{a_0^{n-1}}$$