B.Sc. Part-2 Chemistry (Subs)

1st Paper

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CHEMICAL KINETICS

❖ SECOND ORDER REACTION :

'A second order reaction is one in which the velocity of reaction is proportional to the product of concentration of two reactants or the second power of the concentration of a single reactant'.

$2A \rightarrow X$

$\frac{dx}{dt} \propto [A]^2$

eg, $2O_3 \triangleq 3O_2$

$A + B \rightarrow X$

$\frac{dx}{dt} \propto [A]\,[B]$

eg, Saponification of Esters:

$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

❖ DERIVATION OF EXPRESSION FOR VELOCITY CONSTANT OF SECOND ORDER REACTION :

(a) When rate of reaction depends on two mole of only one reactant :

Let us consider a second order reaction expressed by-

$A + A \rightarrow X$

Let a moles/litre of the initial concentration of reactant 'A' after time t, x moles/ litre of A decomposed into product.

$\frac{dx}{dt} \propto (a-x)\,(a-x)$

$$\frac{dx}{dt} = k\,(a-x)^2$$

$$\frac{dx}{(a-x)2} = k\,dt$$

Integrating both sides

we get ,

$$\int \frac{dx}{(a-x)2} = \int k\,dt$$

$$\frac{1}{(a-x)} = kt + C \text{ ———————— (i)}$$

where C is integration constant.

When t=0, x=0,

then from equation (i);

$$\frac{1}{a} = C$$

Putting the value of C in equation (i),

we get,

$$\frac{1}{(a-x)} = kt + \frac{1}{a}$$

Or, $kt = [\frac{1}{(a-x)} - \frac{1}{a}]$

Or, $k = \frac{1}{t} . [\frac{1}{(a-x)} - \frac{1}{a}]$

Or, $k = \frac{1}{t} . \frac{x}{a(a-x)}$ ———————— (ii)

Equation (ii) is known as expression for velocity constant of second order Reaction.

(b) **<u>When the concentration of both the reactants are different :</u>**

Let us consider a second order reaction given by,

$$A + B \rightarrow X$$

Let a and b be the initial concentration of reactants A and B respectively.
After time t, x of each reactants reacts to form products X.
The concentration of A after time t = (a-x)
The concentration of B after time t = (b-x)
Now the velocity of the reaction will be given by:

$$\frac{dx}{dt}\ \alpha\ (a-x)\,(b-x)$$

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

Or, $\frac{dx}{(a-x)\,(b-x)} = k\,dt$

Or, $\frac{1}{(a-b)} [\frac{1}{(b-x)} - \frac{1}{(a-x)}] dx = k\,dt$

On integrating, we will get

$$\frac{1}{(a-b)} \int [\frac{1}{(b-x)} - \frac{1}{(a-x)}] dx = \int k\,dt$$

$$\frac{1}{(a-b)} \int [\frac{dx}{(b-x)} - \frac{dx}{(a-x)}] = \int k\,dt$$

$$\frac{1}{(a-b)} [-\log(b-x)+\log(a-x)] = kt + C \text{ ———(iii)}$$

where C is integration constant.

When t=0, x=0,

then from equation (iii);

$$\frac{1}{(a-b)} [-\log b + \log a] = C$$

$$C = \frac{1}{(a-b)} \log \frac{a}{b}$$

Putting the value of C in equation (iii),

we get,

$$\frac{1}{(a-b)} \log \frac{(a-x)}{(b-x)} = kt + \frac{1}{(a-b)} \log \frac{a}{b}$$

Or, $kt = \frac{1}{(a-b)} \log \frac{(a-x)}{(b-x)} - \frac{1}{(a-b)} \log \frac{a}{b}$

Or, $kt = \frac{1}{(a-b)} \log \frac{b(a-x)}{a(b-x)}$

Or, $k = \frac{1}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$ ————(iv)

Equation (iv) is known as expression for velocity constant of second Order reaction.

❖ CHARACTERISTICS OF SECOND ORDER REACTION :

1. Unit of k :

We know that,

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

$$k = \frac{1}{sec} \frac{moles/litre}{(moles/litre)(moles/litre)} = \frac{1}{sec} \frac{1}{moles/litre}$$

So, unit of k is a second order rate expression will be given by $(\text{time})^{-1}$ $(\text{concentration})^{-1}$ or $(\text{mole/litre})^{-1}$ sec^{-1}, if time is expressed in second.

2. The time required to complete a certain fraction of the reaction is inversely proportional to the concentration of the reactants.
   Let $t_{1/2}$ be the time required for the completion of half the reaction. Its value can be calculated by substituting x=a/2 in equation (iv), therefore, we have

$$k = \frac{1}{t_{1/2}} \cdot \frac{\frac{a}{2}}{a(a-\frac{a}{2})}$$

$$k = \frac{1}{t_{1/2}} \cdot \frac{\frac{a}{2}}{a \cdot \frac{a}{2}}$$

$$\text{Or,} \quad \frac{1}{t_{1/2}} = k \cdot \frac{1}{a}$$

$$\text{Or,} \quad \frac{1}{t_{1/2}} \;\alpha\; k \cdot \frac{1}{a}$$

The time required to complete three-forth of a reaction will be given by putting $x = \frac{3}{4}$ a. Hence equation (ii) reduces to :

$$k = \frac{1}{t_{3/4}} \cdot \frac{\frac{3}{4}a}{a(a-\frac{3}{4}a)}$$

$$\frac{1}{t_{3/4}} = \frac{1}{k} \cdot \frac{\frac{3}{4}a}{a \cdot \frac{a}{4}} = \frac{1}{ak}$$

$$\frac{1}{t_{3/4}} \;\alpha\; \frac{1}{k}$$

3. When concentration of one reactant is too large, the second order rate expression becomes a first order rate expression.
   From equation (iv), we have

$$k = \frac{1}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

Suppose the value of a is much larger than b, then the values of b and x can be neglected in comparison to a, then we have

$$k = \frac{1}{t \cdot a} \log \frac{b \cdot a}{a(b-x)}$$

$$k \cdot a = \frac{1}{t} \log \frac{b}{b-x}$$

$$k' = \frac{1}{t} \log \frac{b}{b-x} \text{ ———— (v)}$$

eq^n (v) is same as for a first order rk^n