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For Deg I Chemistry Hons Paper II &
Deg I sub course

Kinetics for 1st order reaction: -
The reaction in which the rate depends on the concentration of single reactant only is called 1st order reaction.

Consider a general type of 1st order reaction



Initially a mole/l 0 mole/l

After time t $(a-x)$ mole/litre x mole/litre

$\therefore \frac{dx}{dt} \propto (a-x)$ According to Law of mass action

$$\text{or } \frac{dx}{dt} = k_1 (a-x) \quad \text{--- (1)}$$

k_1 is velocity coefficient or specific reaction rate. on rearranging eq (1)

$$\text{we get } \frac{dx}{(a-x)} = k_1 dt \quad \text{--- (2)}$$

On integration of eq (2) we get

$$\int \frac{dx}{(a-x)} = k_1 \int dt$$

$$\ln(a-x) \text{ or } -\log(a-x) = k_1 t + I_1 \quad \text{--- (3)}$$

Where I_1 is integration constant.

When $t=0$ $x=0$ Putting these values in eq (3) we get

$$-\log a = I_1$$

Putting the value of I_1 in eq. (3) we get

$$-\log(a-x) = k_1 t - \log a \quad \text{--- (4)}$$

$$\text{or } \log a - \log(a-x) = k_1 t$$

$$\text{or } k_1 t = \log \frac{a}{a-x}$$

$$\text{or } k_1 = \frac{2.303}{t} \log_{10} \frac{a}{a-x} \quad \text{--- (5)}$$

Equation (5) is known as kinetic equation for the 1st order reaction.

Half Life of 1st order reaction

The time during which half of the reactant consumed is called half life of the reaction. It is denoted by $t_{1/2}$.

When $t = t_{1/2}$ then $x = \frac{a}{2}$

Putting these values in the equation (5)

$$k_1 = \frac{2.303}{t_{1/2}} \log_{10} \frac{a}{a - \frac{a}{2}}$$

$$\text{or } t_{1/2} = \frac{2.303 \log_{10} 2}{k_1} = \frac{2.303 \times 0.30103}{k_1}$$

$$\text{or } t_{1/2} = \frac{0.693}{k_1} \quad \text{--- (6)}$$

Half life of 1st order reaction is independent of the initial concentration of reactant.

Unit of k_1 :-

From equation (5) we know that

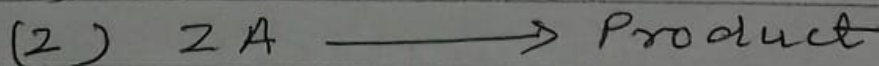
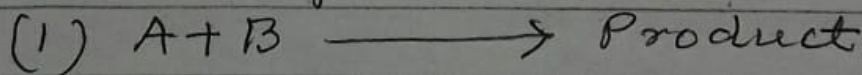
$$k_1 = \frac{2.303 \log \frac{\text{mole/litre}}{\text{mole/litre}}}{\text{time}^{-1}}$$

Unit of $k_1 = \text{time}^{-1} = \text{min}^{-1}$ ✓

Kinetics for 2nd order reaction

The reaction in which the rate depends on the concentration of two reactants or the square of the concentration of single reactant it is said to be of second order.

It can be represented in the general way as



Case - (1) $A + B \longrightarrow \text{Product}$

Initially a mole/l b mole/l 0 mole/l

~~After~~ After time t (a-x) mole/l (b-x) mole/l x mole/l

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

$$\frac{dx}{dt} = k_2 (a-x)(b-x) \quad \text{--- (1)}$$

On separating the variables we have

$$\frac{dx}{(a-x)(b-x)} = k_2 dt \quad \text{--- (2)}$$

On using Partial fraction eq (2) may be written as

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

On integration we get

$$\frac{1}{(a-b)} \left[\int \frac{dx}{(b-x)} - \int \frac{dx}{(a-x)} \right] = k_2 \int dt$$

$$\text{or } \frac{1}{(a-b)} \left[-\log(b-x) + \log(a-x) \right] = k_2 t + I_2 \quad \text{--- (3)}$$

Where I_2 is constant of integration when $t=0$ $x=0$ Putting these values in equation (3) we get

$$\frac{1}{(a-b)} \left[-\log b + \log a \right] = I_2$$

$$\text{or } \frac{1}{(a-b)} \log \frac{a}{b} = I_2$$

Substituting the value in eq (3)

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

$$\text{or } \frac{1}{(a-b)} \log \frac{(a-x)}{(b-x)} = k_2 t + \frac{1}{(a-b)} \log \frac{a}{b}$$

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

$$\text{or } k_2 = \frac{1}{(a-b)t} \cdot \log \frac{b(a-x)}{a(b-x)}$$

$$\text{or } k_2 = \frac{2.303}{(a-b)t} \log_{10} \frac{(a-x) \cdot b}{(b-x) \cdot a} \quad \text{--- (4)}$$

Equation (4) is known as kinetic equation of the second order reaction.

Case-II Consider the reaction
 $2A \rightarrow \text{Product}$

$$\text{Here } \frac{dx}{dt} = k_2 (a-x)^2 \quad \text{--- (1)}$$

on integration of equation (1)

$$\int \frac{dx}{(a-x)^2} = k_2 \int dt$$

$$\frac{1}{(a-x)} = k_2 t + I_2 \quad \text{--- (2)}$$

$$I_2 = \frac{1}{a}$$

$$\frac{1}{(a-x)} = k_2 t + \frac{1}{a}$$

$$k_2 t = \frac{x}{a(a-x)}$$

$$\text{or } k_2 = \frac{x}{a t (a-x)} \quad \text{--- (III)}$$

Eq. (III) is also the kinetic equation of 2nd order reaction.

✓ Unit of k_2 (Rate constant of 2nd order)

We know that $k_2 = \frac{x}{at(a-x)}$

$$k_2 = \frac{1}{\text{minute}^{-1}} \cdot \frac{\text{mole/l}}{(\text{mole/l})(\text{mole/l})}$$

$$= \text{litre} \cdot \text{mole}^{-1} \cdot \text{minute}^{-1}$$

Half Life of 2nd order reaction :-

We know that $k_2 = \frac{x}{at(a-x)}$

For Half life when $t = t_{1/2}$, $x = \frac{a}{2}$

Putting these values in the above equation

$$k_2 = \frac{1}{t_{1/2}} \cdot \frac{a/2}{a(a - \frac{a}{2})}$$

or $k_2 = \frac{1}{t_{1/2} \cdot a}$

or $t_{1/2} = \frac{1}{k_2 \cdot a}$

or $t_{1/2} \propto \frac{1}{a}$ ✓

Thus half life of a second order reaction is inversely proportional to the initial concentration (a) of the reactant.