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Deg - I (H) Physical Chemistry (Paper-II)
Chapter - Chemical Kinetics
Topics - Characteristics of Second order Reaction

Characteristics of Second-order Rxns

(1) Units of Rate-Constant (K):-

From rate-Constant-expression,

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

$$= \frac{1}{\text{time}} \cdot \frac{\text{moles/lit}}{\text{moles/lit} \times \text{moles/lit}}$$

$$= \text{time}^{-1} \cdot \text{lit mole}^{-1}$$

Thus unit of rate-Constant is Conc^{-1} time^{-1}.

(2) Half Life-Period ($t_{1/2}$):-

The time-taken for half of the Conc^{n} of reactant to Complete (or react) Can be determined as:

when $t = t_{1/2}$, then $x = a/2$

Putting the value in rate expression

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

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

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

$$\text{or, } t_{1/2} = \frac{1}{a \cdot K}$$

Thus $t_{1/2}$ is inversely proportional to its initial Concentration.

(3) Second-order Reaction Confirms first order when one of the reactant present in large excess

Let the Concentration of $a >>> b$

In rate-expression.

$$K = \frac{2.303}{t(a-b)} \cdot \log \frac{b(a-x)}{a(b-x)}$$

Thus $a - x \simeq a$ & $(a-b) \simeq a$

The rate expression takes the form

$$k = \frac{2.303}{a \cdot t} \log \frac{b \times a}{a(b-x)}$$

Let $ka = k'$

Now, $$\boxed{k' = \frac{2.303}{t} \cdot \log \frac{b}{(b-x)}}$$

Since a is very large, may be treated as constant after the change.

The above Rate-expression follows first-order kinetics with respect to the Reactant taken relatively in small amount.

(4) Evaluation of Rate-Constant:

By graphical-method, the slope of line will directly give the value of k.

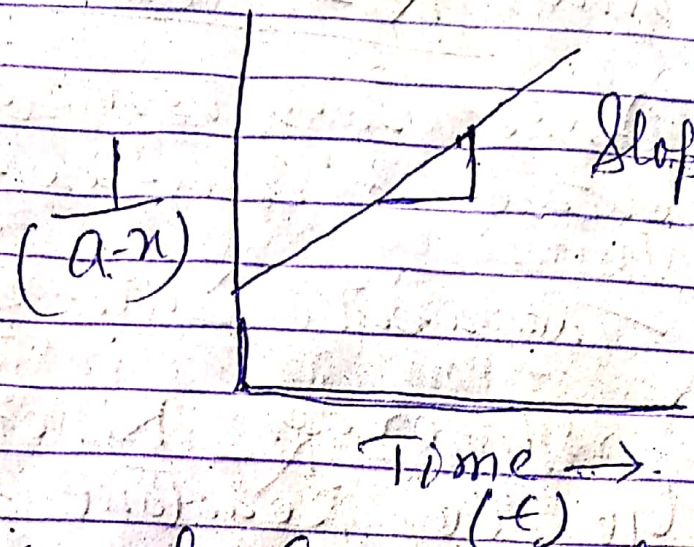
By rate expression for same-concentration

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

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

This eqn. like, $y = mx + c$, the

equation of straight-line. Thus a plot of $\frac{1}{(a-x)}$ Vs t should be a straight-line. It the reaction is of the second-order.



(5) Examples of Second-order-Rxns.

(1) Hydrolysis of ester by an alkali (Saponification)

$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

(2) Conversion of Ammonium Cyanate into Urea.

$NH_4CNO \longrightarrow (NH_2)_2CO$

(3) Conversion of ozone into O_2.

$2O_{3(g)} \longrightarrow 3O_{2(g)}$

(4) Thermal decomposition of Cl_2O.

$2Cl_2O \xrightarrow{200°C} 2Cl_2 + O_2$