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Deg-I (H): Physical-Chemistry
(Paper-II)
Chapter — Chemical-Kinetics
Topics — Kinetics of first-order Reaction

First-order Reaction:—

A reaction is said to be first-order if its rate is determined by the change of one concentration term only.
OR,
A reaction whose rate depend upon single-power of the concentration term only.

Consider the following general Rxn

$$A \longrightarrow \text{Product}$$

Rate Expression / Kinetics of first-order Reaction.

Let us supposed a hypothetical first-order Reaction

$$A \longrightarrow \text{Product}$$

If the initial Concentration of A is a mole/lit and after time 't' the Concentration of A becomes (a-x) mole/lit. x mole/lit has been changed into product

The Rate of reaction after time t is expressed as

$$\frac{dx}{dt} = k \cdot (a-x)$$ k = rate Const.

After Rearranging

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

Upon integration of the above equation,

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

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

Where C is called Integration Constant

When $t=0$, $x=0$

Than $c = -\ln a$

Putting the value of c

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

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

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

or $k = \frac{2.303}{t} \log \frac{a}{(a-x)}$

Characteristics of first order R.N.

(1) Units of K.

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

$$= \frac{1}{\text{time}} \cdot \frac{\text{mole/Lit}}{\text{mole/Lit}}$$

$$= \frac{1}{\text{Sec}} = \text{Sec}^{-1}$$

(2) Half-life Period ($t_{1/2}$) of first order Reaction:

When $t = t_{1/2}$, its Concentration, $x = a/2$

Putting the value in rate expression

$$k = \frac{2.303}{t_{1/2}} \cdot \log \frac{a}{a - a/2}$$

$$= \frac{2.303}{t_{1/2}} \cdot \log 2 \qquad | \log 2 = 0.3010$$

$K = \frac{0.693}{t_{1/2}}$. Thus $\boxed{t_{1/2} = \frac{0.693}{K}}$

It means that $t_{1/2}$ of first order Reaction is independent of its initial concentration.

(3) Evaluation of Rate-Constant —

From integrated rate equation, we evaluate the value of K (rate-const) by graphical Method.

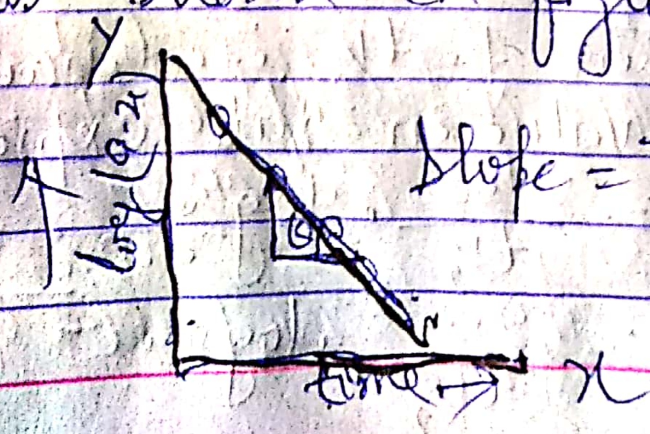
$$K = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

or, $\log(a-x) = -\frac{Kt}{2.303} + \log a$

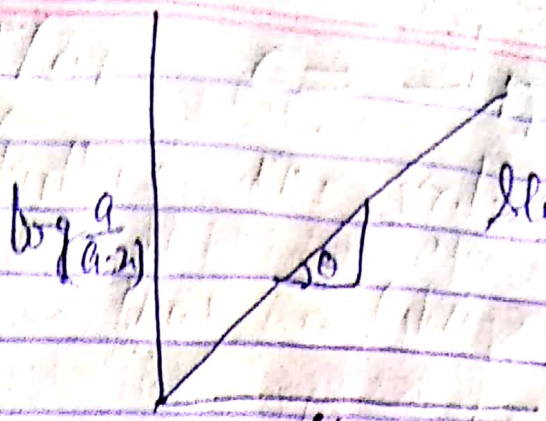
$y = mx + c$

The above equation is comparable to straight line equation, $y = mx + c$

upon plotting a graph b/w $\log(a-x)$ & time 't' we get a straight line as shown in figure.



$$\text{Slope} = \frac{-K}{2.303}$$



$\text{Slope} = \frac{K}{2.303}$

Slope = gradient = $\tan\theta$

By knowing the value of slope K can be determined.

(v) Examples of first-order Rxn.

(i) Decomposition of H_2O_2 in aqueous solution

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2}O_2$$

(ii) Hydrolysis of ethyl Acetate.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{Acid} CH_3COOH + C_2H_5OH$$

(iii) Decomposition of NH_4NO_2 in aqueous solution.

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

(iv) All Radioactive decay follow first order kinetics.