*. Expression of rate Constant for 1st Order Reaction :-

Let us consider a first order reaction -

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

Let the initial Concentration of A be 'a' mole/litre and after 't' sec. the remaining Concentration is $(a-x)$ mole/litre i.e. 'x' mole/litre of A dissociate after 't' sec.

Then the rate of reaction -

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

i.e. $$\frac{dx}{dt} = K(a-x)$$

where, K = rate constant

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

taking integration on both sides -

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

or $$-\ln(a-x) = Kt + I \qquad \text{——— (1)}$$

where, I = Integration Constant.

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

from Eqⁿ - (1)

$$-\ln a = I$$

putting the value of I in Eqⁿ - (1)

$$-\ln(a-x) = Kt - \ln a \qquad \text{——— (2)}$$

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$$\text{or} \quad Kt = \ln a - \ln(a-x)$$

$$\text{or} \quad Kt = \ln \frac{a}{(a-x)}$$

$$\text{or} \quad \boxed{K = \frac{2.303}{t} \log \frac{a}{(a-x)}} \quad \text{—(3)} \quad \left(\ln = 2.303 \log\right)$$

It is the expression for the rate constant of 1st order reaction.

*. characterstics of 1st order reaction —

(1) Graph :-

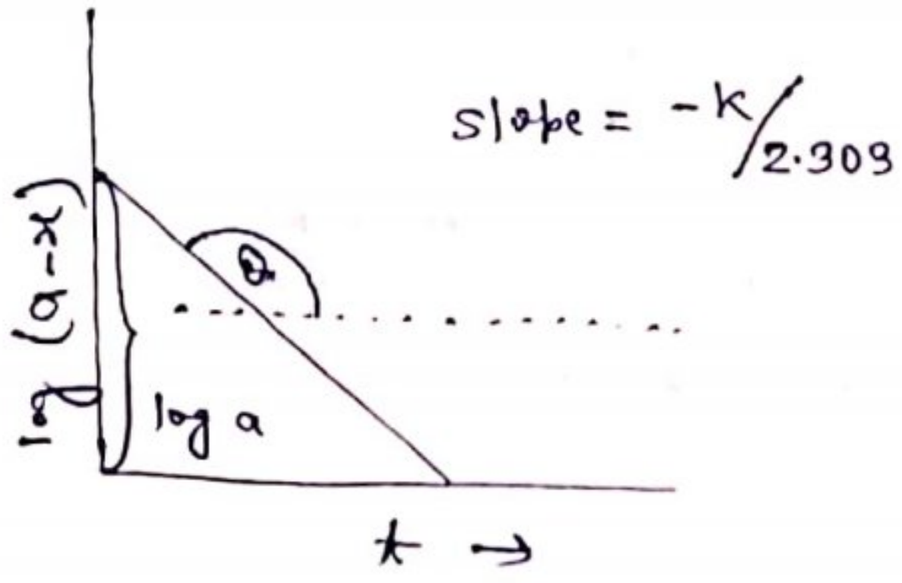
from Eq^{n} — (2)

$$-\ln(a-x) = Kt - \ln a$$

$$\text{or} \quad \ln(a-x) = -Kt + \ln a$$

$$2.303 \log(a-x) = -Kt + 2.303 \log a$$

A plot of $\log(a-x)$ Vs t gives a straight line, the slop of which is $\frac{-K}{2.303}$ where, $\log a$ is the intercept.



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characterstics of 1st Order reaction :-

(2) Half life time (Period) ($t_{1/2}$)

The time (Period) during which half of the initial Concentration of reactants is dissociated into Product, is called half life time.

From first Order reaction

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

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

Then we have-

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

$$\text{or} \quad t_{1/2} = \frac{2.303}{K} \log \frac{a}{a/2}$$

$$\text{or} \quad t_{1/2} = \frac{2.303}{K} \log 2.$$

$$\text{or} \quad t_{1/2} = \frac{2.303}{K} \times 0.301 \quad (\log 2 = 0.301)$$

$$\text{or} \quad \boxed{t_{1/2} = \frac{0.693}{K}}$$

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(3) Examples of 1st Order reaction :-

(1) Decomposition of N_2O_5

$$2N_2O_5 \longrightarrow 2N_2O_4 + O_2$$

Nitrogen pentoxide — Nitrogen tetraoxide

(2) Decomposition of H_2O_2

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Hydrogen peroxide — Water

(3) Radioactive disintigration

$$^{238}_{92}U \xrightarrow{\alpha\text{-particle}} ^{234}_{90}Th + ^{4}_{2}He$$

(4) Hydrolysis of Methyl acetate

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

Methyl acetate — Acetic acid — Methanol

(5) Inversion of Cane Sugar —

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

Cane Sugar — Glucose — fructose.

*. Pseudo unimolecular reaction :-

Those reaction which are Bimolecular, termolecular etc but whose order of reaction is unity, are called Pseudo-unimolecular reaction.

for example—

(1) Inversion of Cane Sugar

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow \overset{C_6H_{12}O_6}{\text{Glucose}} + \overset{C_6H_{12}O_6}{\text{Fructose}}$$

Here,

Rate $r = K [C_{12}H_{22}O_{11}]^1 [H_2O]^0$

Molecularity (m) = 1+1 = 2 Bimolecular

Order (n) = 1+0 = 1

first order reaction.

(2) Hydrolysis of methyl acetate —

$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$

Here, Rate $r = K [CH_3COOCH_3]^1 [H_2O]^0$

Molecularity (m) = 1+1 = 2 Bimolecular

Order (n) = 1+0 = 1

first order reaction.

(3) Hydrolysis of ethyl acetate in acid medium —

$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

Ethyl acetate Acetic acid Ethanol

Here, Rate, $r = K [CH_3COOC_2H_5]^1 [H_2O]^0$

Molecularity (m) = 1+1 = 2 Bimolecular

Order (n) = 1+0 = 1

first order reaction.

—x—

from.
Dr. A. K. Gupta
Chemistry (L.S. College)

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