First order Reaction :-

Reaction in which, the rate of reaction is directly proportional to initial Concentration of reactant.

$$A \longrightarrow B$$

$t=0$	a_{mol}	$-$
$t=t$	$(a-x)$	x

$$r.o.r. = -\frac{d}{dt}[A]$$

$$r.o.r = -\frac{d}{dt}[(a-x)-a]$$

$$r.o.r = \frac{dx}{dt} \quad -(1)$$

Apply rate law.

$$r = k[A]^1 \quad -(2) \quad \{r \propto [A]\}$$

from. eq. (1) & (2)

$$\boxed{\frac{dx}{dt} = k[A]} \text{ or. } \boxed{-\frac{d}{dt}[A] = k[A]}$$

Differential rate eq.

Integrate rate eq.

From Diffⁿ eq.

$$-\frac{d[A]}{dt} = k[A]$$

$$-\frac{d[A]}{[A]} = k \cdot dt$$

Take $\int$ Both Side.

$$-\int \frac{d[A]}{[A]} = k\int 1 \cdot dt.$$

$$\boxed{-\ln[A]_t = kt + c}$$

at $t=0$, $[A] = [A]_0 = a$

put data in above eq.

$$-\ln[A]_0 = k \cdot 0 + c$$

$$\boxed{c = -\ln[A]_0}$$

Put Value of c in above eq.

$$-\ln[A]_t = kt - \ln[A]_0$$

$$\ln[A]_0 - \ln[A]_t = kt$$

$$\boxed{kt = \ln\left(\frac{[A]_0}{[A]_t}\right)}$$

$$\boxed{k = \frac{2.303}{t}\log\left(\frac{[A]_0}{[A]_t}\right)}$$ **

$$\# \ [A]_0 = a, \ [A]_t = a - x$$

$$\boxed{k = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right)} \ * \quad \text{--- (3)}$$

Here ÷ $a \Rightarrow$ initial Conc.

$x \rightarrow$ dissociated conc. at time t

$(a-x) \Rightarrow$ Conc. at time t.

Half life ÷ $t \longrightarrow t_{1/2}$

$$x = a/2$$

$$(a-x) = a - a/2 = a/2.$$

Put data in eq. no. (3)

$$k = \frac{2.303}{t_{1/2}} \log\left(\frac{\cancel{a}}{\cancel{a}/2}\right)$$

$$\boxed{t_{1/2} = \frac{2.303}{k} \log 2}$$

$$\left(\begin{array}{l} 2.303 \cdot \log 2. \\ = 0.693 \end{array} \right)$$

$$\boxed{t_{1/2} = \frac{0.693}{k}} \ **$$

$$\boxed{t_{1/2} \propto a^0}$$

\# Half life of I^{st} order Reaction is independent of initial Conc.

Wilhelmy equation :-

$$kt = \ln_e\left(\frac{a}{a-x}\right)$$

Antilog.

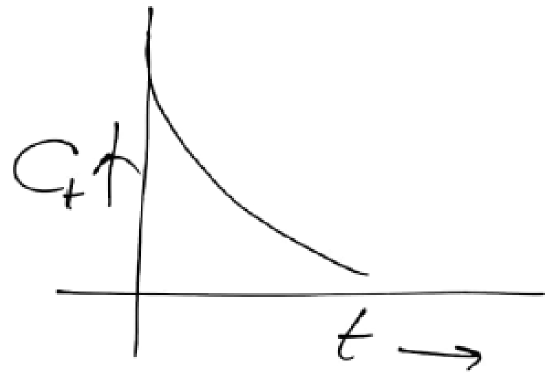
$$e^{kt} = \frac{a}{a-x}$$

Here $a \rightarrow C_0$

$a-x \rightarrow C_t$

$$e^{kt} = \frac{C_0}{C_t} \Rightarrow c^{t} = \frac{C_0}{e^{kt}}$$

Wilhelmy equation $\rightarrow$ $\boxed{C_t = C_0 \cdot e^{-kt}}$

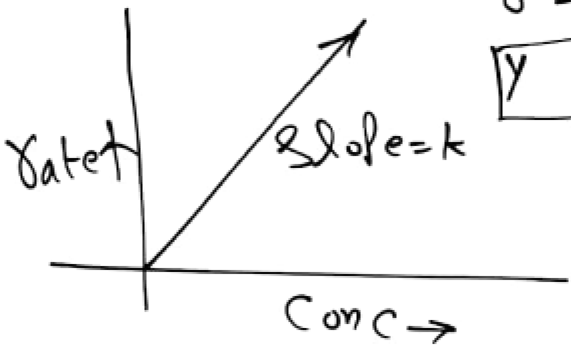


exponential graph.

Graph (i) Rate V/s Conc.

$r = k[A]^1$

$\boxed{y = mx}$

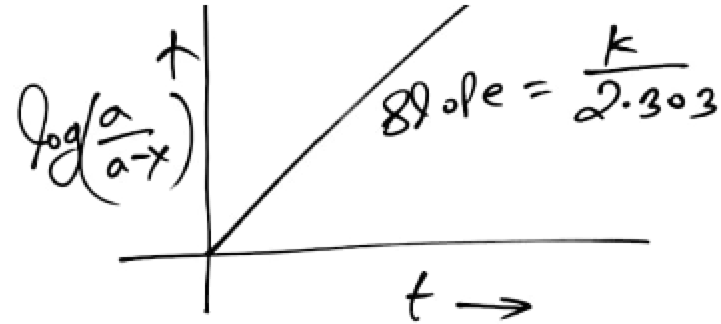


(2) $\log\left(\frac{a}{a-x}\right)$ V/s t

$$kt = 2.303 \log\left(\frac{a}{a-x}\right)$$

$$\boxed{\underbrace{\log\left(\frac{a}{a-x}\right)}_{y} = \underbrace{\frac{k}{2.303}}_{m} \cdot \underbrace{t}_{x}}$$

$\boxed{y = mx}$



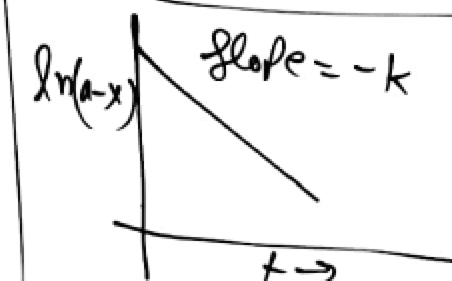
(3) $\ln(a-x)$ V/s t

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

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

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

$$\boxed{y = -mx + c}$$



Graph

$t_{1/2}$ V/s a (initial Conc.)

$$t_{1/2} = \frac{0.693}{k}$$

$$\boxed{t_{1/2} \propto a^0}$$

Ques. Cal $t_{3/4}$ of Ist order Reaction
or $t_{75\%}$
or
Cal. relation B/w $t_{3/4}$ & $t_{1/2}$

Sol.

$$A \longrightarrow B$$

$t=0$ a $-$

$t = t_{3/4}$ $a - \frac{3a}{4}$ $3a/4$

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

$$k = \frac{2.303}{t_{3/4}} \log\left(\frac{a}{a - 3a/4}\right)$$

$$t_{3/4} = \frac{2.303}{k} \log\left(\frac{a}{a/4}\right)$$

$$t_{3/4} = \frac{2.303}{k} \log(4)$$

$$t_{3/4} = \frac{2.303}{k} \log(2^2)$$

$$t_{3/4} = 2 \cdot \frac{2.303}{k} \cdot (\log 2.)$$

$$t_{3/4} = 2 \cdot \frac{0.693}{k} \Rightarrow \boxed{t_{3/4} = 2\, t_{1/2}} \; **$$

Ques. Cal. $t_{99.9}$ of I^{st} order Rexn OR

Cal. relation B/W $t_{99.9}$ & $t_{1/2}$

Sol. $t_{99.9} \rightarrow$ when 99.9% reaction Completed

$$A \longrightarrow B$$

$t=0$ 100   –

$t=t_{99.9}$ $100-\frac{99.9}{\cancel{100}}\times \cancel{100}$

$\Rightarrow 0.1$

$$K = \frac{2.303}{t_{99.9}}\log\left(\frac{100}{100-99.9}\right)$$

$$t_{99.9} = \frac{2.303}{k}\log\left(\frac{1000}{0.1}\right)$$

$$t_{99.9} = \frac{2.303}{k}\log(10)^3$$

$$t_{99.9} = 3\cdot\frac{2.303}{0.693}\cdot t_{1/2}\cdot\log_{10}$$

$$\left\{ t_{1/2} = \frac{0.693}{k} \quad k = \frac{0.693}{t_{1/2}} \right.$$

$$\boxed{t_{99.9} = 10\cdot t_{1/2}}$$