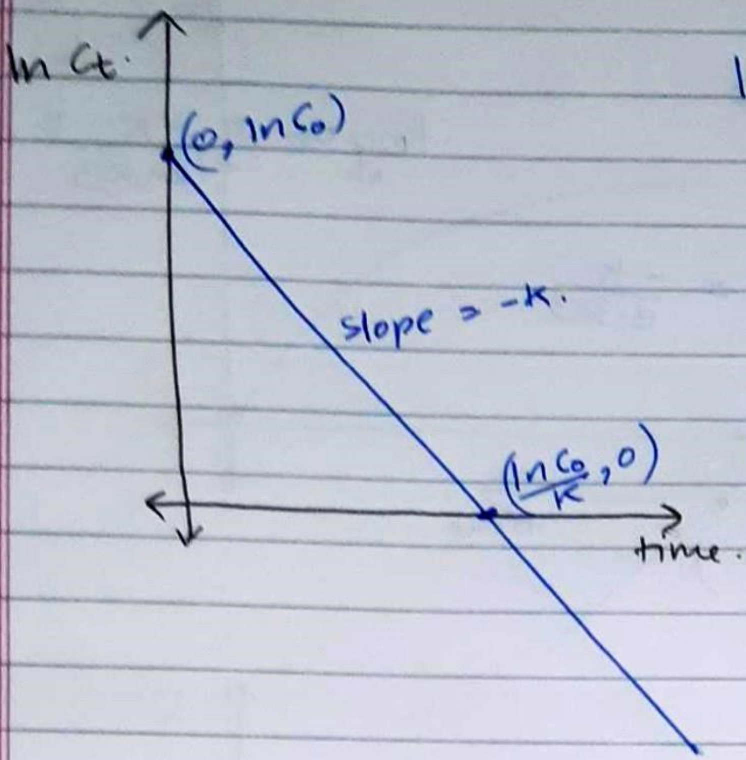
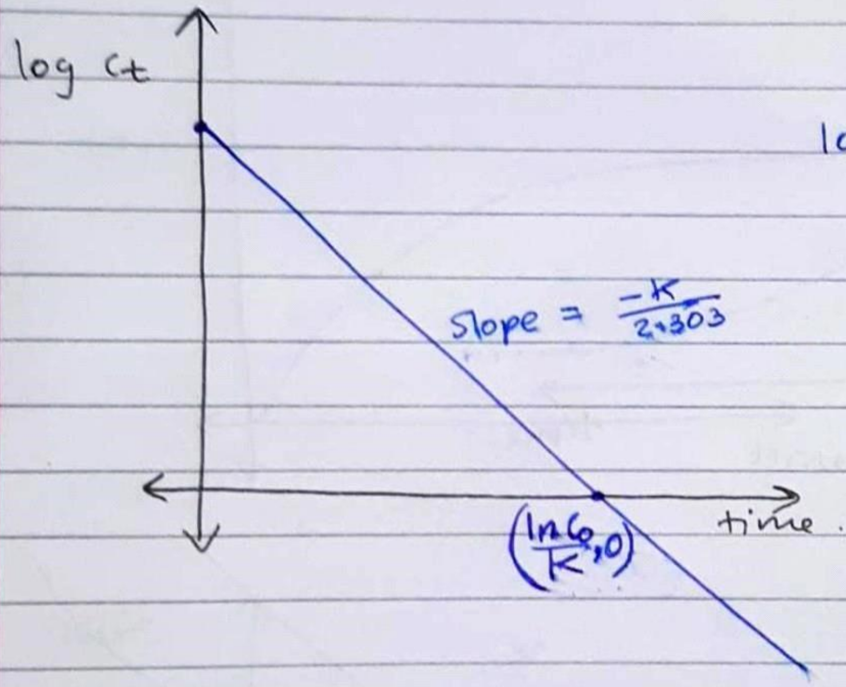
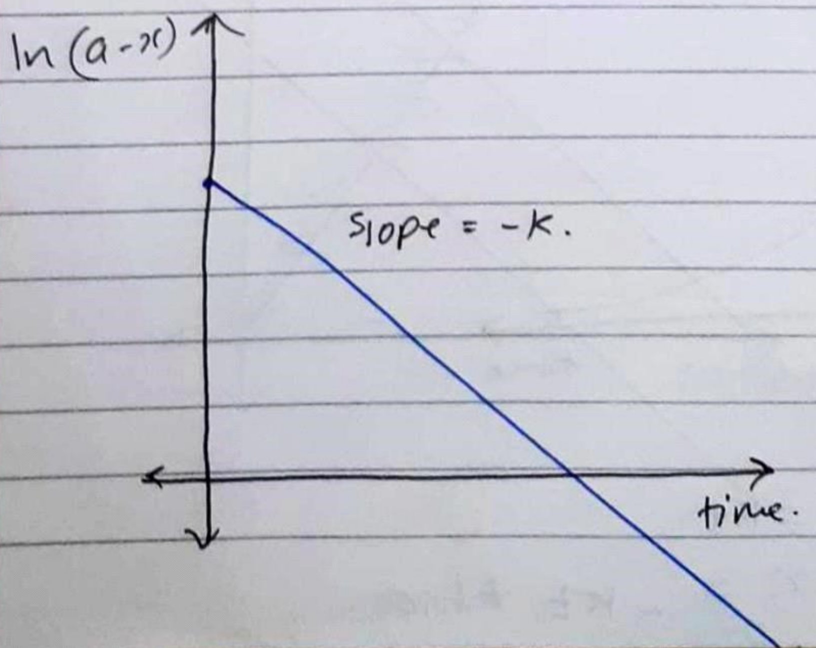


$$\ln C_0 - \ln C_t = kt.$$
$$\ln C_t = -kt + \ln C_0.$$

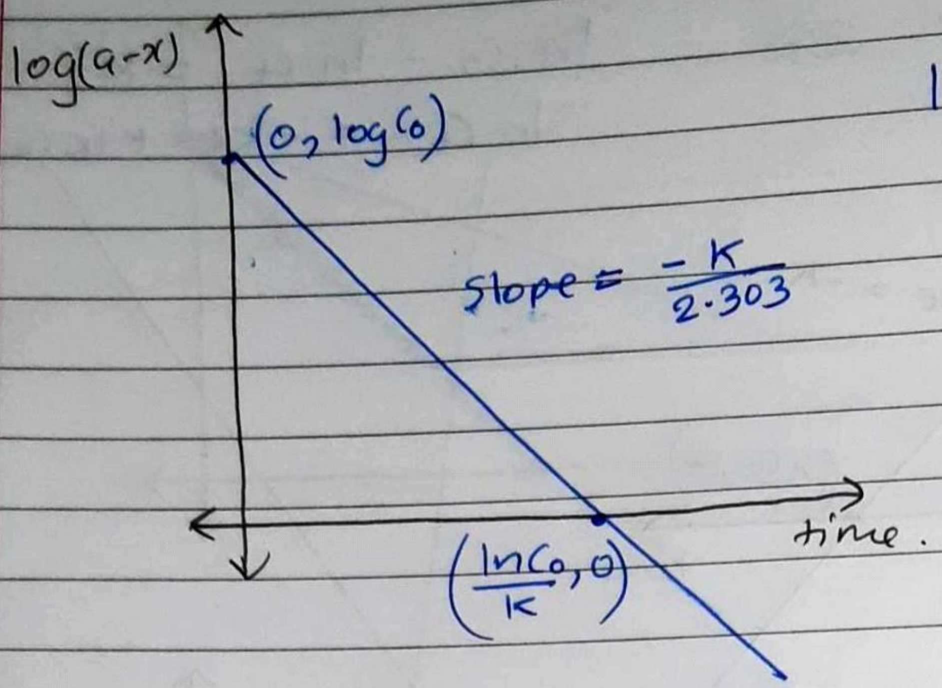


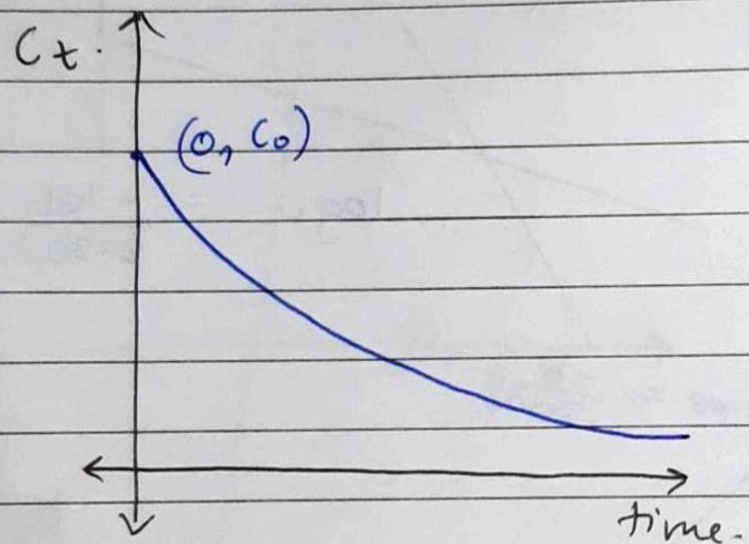
$$\log C_t = \frac{-kt}{2.303} + \log C_0.$$

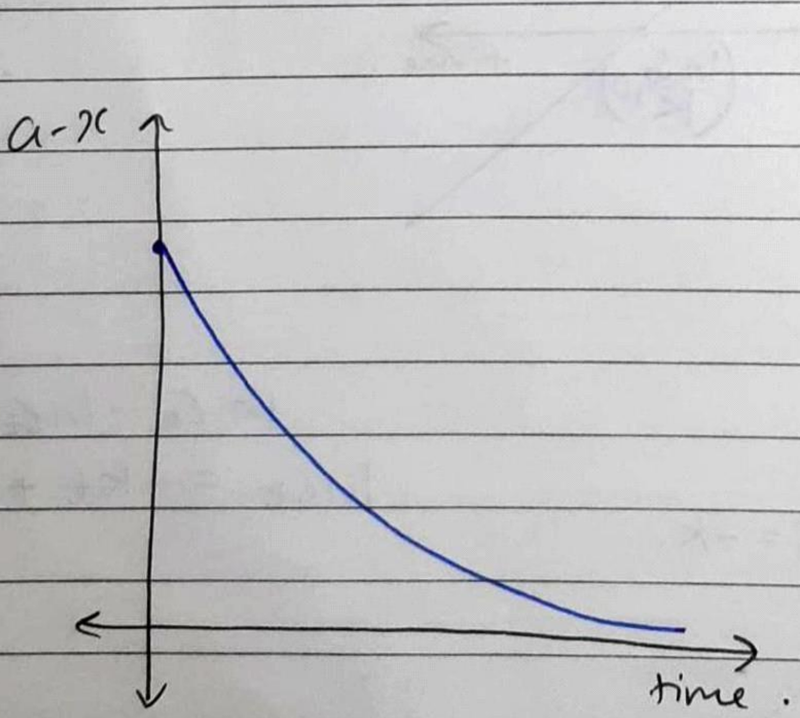


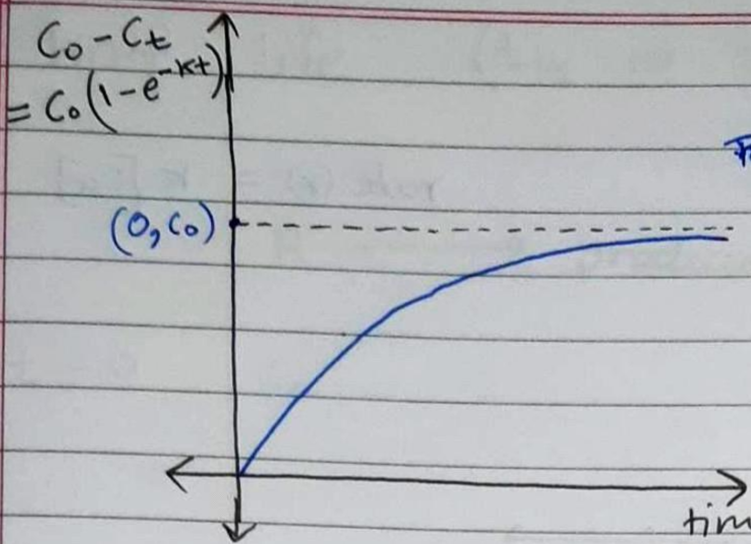
$$\ln C_0 - \ln C_t = kt.$$
$$\ln C_t = -kt + \ln C_0.$$

$$\log C_t = \frac{-k}{2.303}t + \log C_0$$









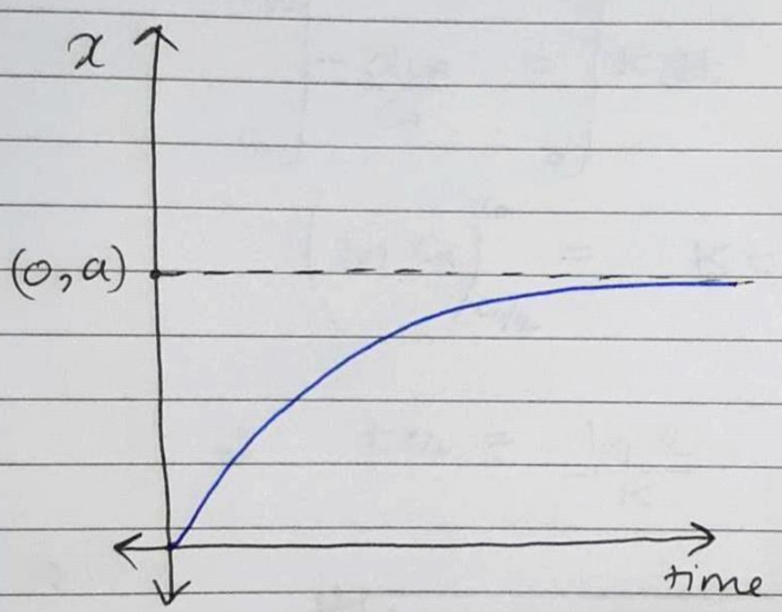
~~$C_t = C_0 e^{-kt}$~~.

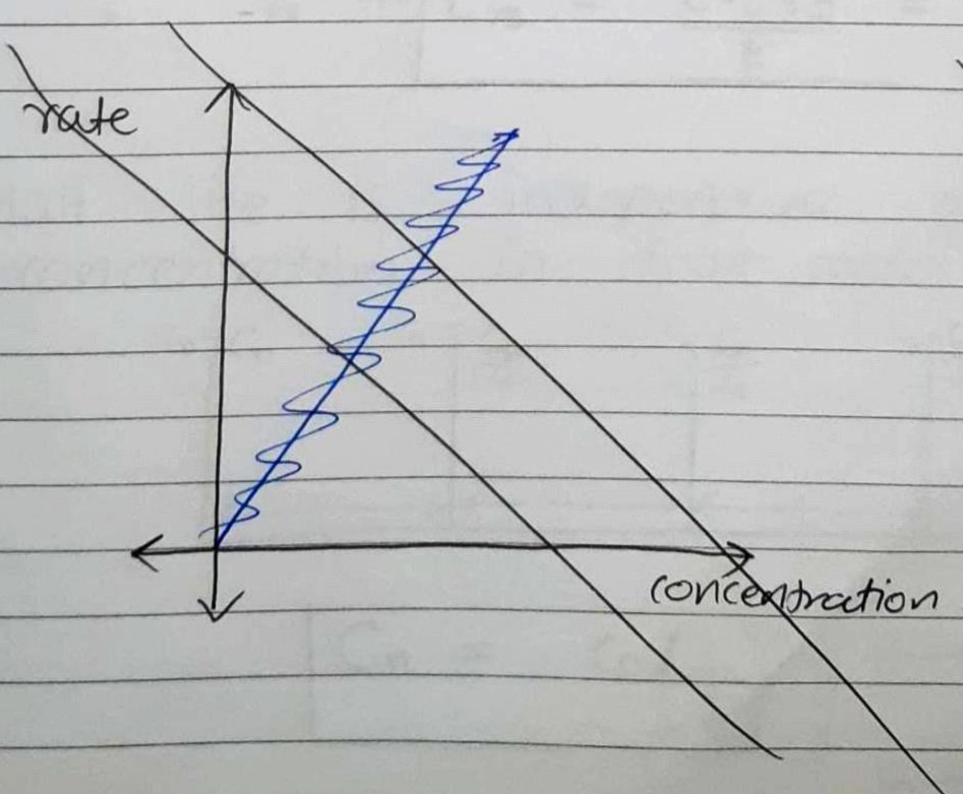
use Transformation.

$$\left\{ e^{-t} \longrightarrow e^{-kt} \longrightarrow -e^{-kt} \right.$$

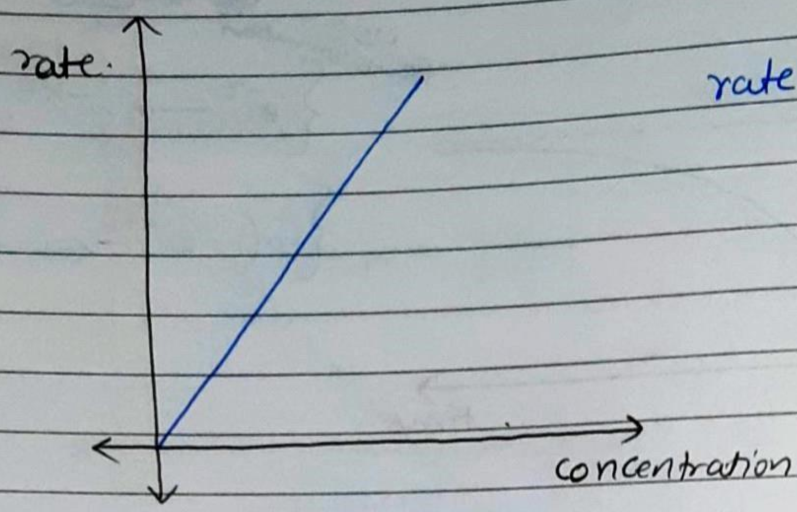
$$\downarrow$$

$$\left\{ C_0(1-e^{-kt}) \longleftarrow 1-e^{-kt} \right.$$





~~$r = k[C_A]$~~



rate $(r) = K[C_A]$

☆ Half life ($t_{1/2}$ or $t_{50\%}$ or $t_{0.5}$)

$$A \longrightarrow \text{product.}$$

rate $= K(C_A)$.

$t = 0 \qquad C_0.$

$$-\frac{dC_A}{dt} = KC_A$$

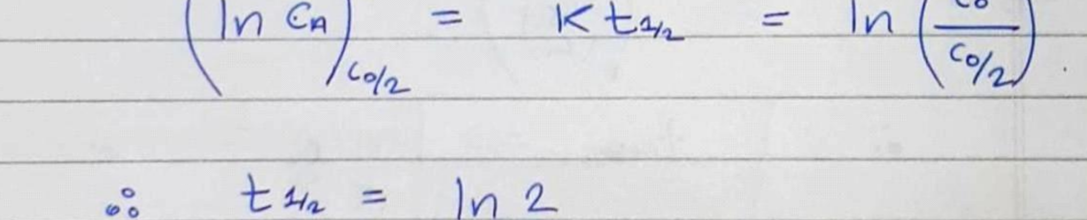
$$\int_{C_0}^{C_0/2} -\frac{dC_A}{C_A} = \int_{0}^{t_{1/2}} K\,dt$$

$$\left(\ln C_A\right)_{C_0/2}^{C_0} = Kt_{1/2} = \ln\left(\frac{C_0}{C_0/2}\right).$$

$$\therefore \quad t_{1/2} = \frac{\ln 2}{K}.$$

$$\therefore \# \boxed{t_{1/2} = \frac{0.693}{K} = \frac{\ln 2}{K}}$$

Half life is independent of initial concentration in first order reaction.



$$\boxed{C_n = C_0\left(\frac{1}{2}\right)^n}$$

$n \rightarrow$ no. of half life.

$C_n \rightarrow$ concentration at n^{th} half life.

Q: For first order kinetics calculate

1) $\frac{t_{75\%}}{t_{50\%}}$ 2) $\frac{t_{99\%}}{t_{50\%}}$.

iii) $\frac{t_{99.9\%}}{t_{50\%}}$ iv) $\frac{t_{7/8}}{t_{1/2}}$.

Soln

i) $$\ln\left(\frac{C_0}{C_t}\right) = kt.$$

$$\therefore \ln\left(\frac{C_0}{\left(\frac{C_0}{4}\right)}\right) = k t_{75}$$

$$\therefore t_{75\%} = \frac{\ln 4}{k}.$$

$$t_{50\%} = \frac{\ln 2}{k}$$

$$\therefore \frac{t_{75\%}}{t_{50\%}} = \frac{\ln 4}{\ln 2} = \frac{\log 4}{\log 2} = \underline{\underline{2}}$$

ii) $$\ln\left(\frac{C_0}{C_t}\right) = kt.$$

$$t_{99\%} \longrightarrow \left(\frac{100-99}{100}\right) C_0.$$

$$= \frac{C_0}{100}.$$

$$\therefore t_{99\%} = \frac{\ln\left(\frac{c_0}{\frac{c_0}{100}}\right)}{k} = \frac{\ln 100}{k}.$$

$$\therefore t_{50\%} = \frac{\ln 2}{k}.$$

$$\therefore \frac{t_{99\%}}{t_{50\%}} = \frac{\ln 100}{\ln 2} = \frac{\log 100}{\log 2}$$

$$= \frac{2}{0.3}$$

$$= \frac{20}{3} = 6.67$$

iii) $t_{99.9\%} = \frac{1}{k} \ln\left[\frac{c_0}{\left(\frac{100-99.9}{100}\right)c_0}\right]$

$$= \frac{\ln(1000)}{k}$$

$$t_{50\%} = \frac{\ln 2}{k}$$

$$\therefore \frac{t_{99.9\%}}{t_{50\%}} = \frac{\ln 1000}{\ln 2} = \frac{\log 1000}{\log 2} = \frac{30}{3}$$

$$= \underline{\underline{10}}$$

iv) $\frac{t_{7/8}}{t_{1/2}} = \frac{\log\left[\frac{c_0}{(1-\frac{7}{8})c_0}\right]}{\log\left[\frac{c_0}{(1-\frac{1}{2})c_0}\right]} = \frac{\log 8}{\log 2} = \underline{\underline{3}}$

Note: ⇒ after 10 half life reaction will be practically completed.

Q: For first order kinetics. what will be time required for getting concentration 0.1 mole/Litre to 0.025 mole/Litre if rate constant for the reaction is ~~$K = 6.93\ min^{-1}$~~

$K = 0.0693\ min^{-1}$

$$Kt = \ln\left(\frac{C_0}{C_t}\right)$$

$$0.0693\, t = \ln\left(\frac{0.1}{0.025}\right)$$

$$0.0693 \times t = \ln 4$$

$$t = \frac{2 \times 0.693}{0.0693}$$

$$\boxed{t = 20\ min.}$$

$$t_{1/2} = \frac{0.693}{0.0693} = 10\ min.$$

∴ two half life is there from 0.1M to 0.025 M

Q: $2A \longrightarrow$ product.

$t=0 \quad C_0$

rate $= kC_A$.

half life = ?

$$-\int_{C_0}^{C_0/2} \frac{dC_A}{C_A} = \int_0^{t_{1/2}} 2K\, dt$$

$$\ln 2 = 2Kt_{1/2}.$$

$$\therefore \boxed{t_{1/2} = \frac{\ln 2}{2K}}$$

Q:- $2A \longrightarrow$ product.

$t=0$ $\quad C_0$. $\qquad r_A = K C_A$.

$$-\frac{dC_A}{dt} = K C_A$$

$$\int_{C_0}^{C_0/2} -\frac{dC_A}{C_A} = \int_0^{t_{1/2}} K\,dt$$

$$\boxed{t_{1/2} = \frac{\ln 2}{K}}$$

Q:- $2A + 3B \longrightarrow$ product.

$$\text{rate} = K C_A (C_B)^0.$$

$$-\frac{1}{2}\frac{dC_A}{dt} = -\frac{1}{3}\frac{dC_B}{dt} = K C_A (C_B)^0$$

$$\int_{a}^{C_{At}} -\frac{dC_A}{C_A} = \int_0^{t_{1/2}} 2K\,dt$$

$$\ln\left(\frac{a}{C_{At}}\right) \cancel{\ln\left(\frac{a}{\ }\right)} = 2K t_{1/2}$$

$$t_{1/2} = \cancel{\frac{\ln a}{C_{At}}} \cancel{\frac{\ln 2}{2K}} \frac{\ln\left(\frac{a}{C_{At}}\right)}{2K}.$$

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$$2A + 3B \longrightarrow \text{product}.$$

$t=0$	a	b	$-$
$t=t$	$a-2x$	$b-3x$.	

$$-\frac{1}{2}\frac{dC_A}{dt} = -\frac{1}{3}\frac{dC_B}{dt} = K\, C_A (C_B)^0$$

i) $$-\frac{d(a-2x)}{dt} = 2K(a-2x)$$

$$2\frac{dx}{dt} = 2K(a-2x)$$

$$\int_a^x \frac{dx}{a-2x} = \int_0^t K\,dt.$$

$$-\frac{1}{2}\ln(\underline{a-2x})\Big|_a^x = Kt.$$

$$\therefore \quad \ln\left(\frac{a-2x}{-a}\right) = -2Kt$$

$$\frac{a-2x}{-a} = e^{-2Kt}$$

$$\cancel{2x = a - e^{-2Kt}}$$

$$\cancel{\boxed{x = \frac{1}{2}\left(a - e^{-2Kt_{1/2}}\right)}}$$

$\therefore \cancel{C_{A \cdot t} = a - 2 \times \frac{1}{2}\left(a - e^{-2kt}\right)}$

$$\cancel{\boxed{C_{A \cdot t} = e^{-2kt}}}$$

$$\frac{2x - a}{a} = e^{-2kt}$$

$$\frac{2x}{a} = 1 + e^{-2kt}.$$

$$\boxed{x = \frac{a}{2}\left(1 + e^{-2kt}\right)}$$

$\therefore$ $C_{A \cdot t} = a - a\left(1 - e^{-2kt}\right)$

$$\boxed{C_{A \cdot t} = a e^{-2kt}.}$$

$\therefore$ $C_{B \cdot t} = b - \frac{3a}{2}\left(1 - e^{-2kt}\right)$

$$= b - \frac{3a}{2} + \frac{3a}{2} e^{-2kt}.$$

$$\boxed{C_{B \cdot t} = b - \frac{3a}{2}\left(1 - e^{-2kt}\right)}$$

$$\boxed{\frac{C_0}{C_t} = \frac{n_0}{n_t} = \frac{N_0}{N_t} = \frac{W_0}{W_t}}$$

$\cancel{(t_{1/2})_A}$

$$C_{A.t} = a e^{-2kt}.$$

$$a - 2x = \frac{a}{2}.$$

$$2a - 4x = a.$$

$$a = 4x.$$

$$\left(x = \frac{a}{4}\right).$$

$$\frac{\cancel{a}}{2} = \cancel{a} e^{-2kt_{1/2}}.$$

$$\ln 2 = 2k\, t_{1/2}.$$

$$\boxed{(t_{1/2})_A = \frac{\ln 2}{2K.}}$$

☆ Second order Kinetics

$$A \longrightarrow \text{product}$$

$t = 0$ $\qquad C_0$

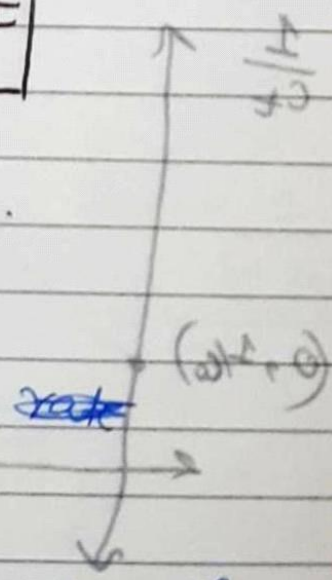
$t = t$ $\qquad C_t$

$$-\frac{dC_A}{dt} = K(C_A)^2$$

$$\int_{C_0}^{C_t} -\frac{dC_A}{(C_A)^2} = \int_0^t K\,dt$$

$$\boxed{\left(-\frac{1}{-C_A}\right)_{C_0}^{C_t} = Kt} \; \#$$

$$\# \; \boxed{\frac{1}{C_t} - \frac{1}{C_0} = Kt}$$



$$A \longrightarrow \text{product}$$

$t = 0$ $\qquad a$

$t = t$ $\qquad a - x$

$$-\frac{d(a-x)}{dt} = K(a-x)^2$$

$$\int_0^x \frac{dx}{(a-x)^2} = \int_0^t k\,dt$$

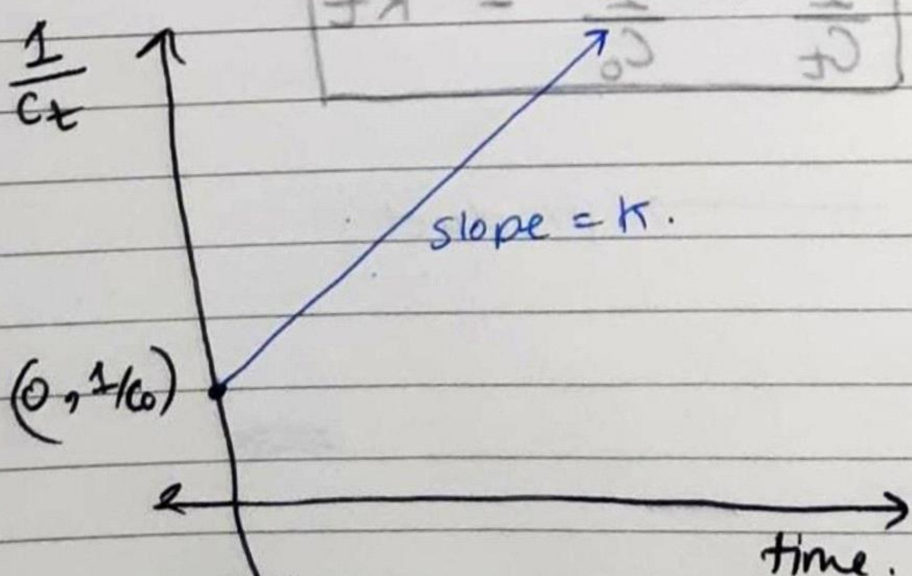
$$\left[\frac{1}{a-x}\right]_0^x = kt.$$

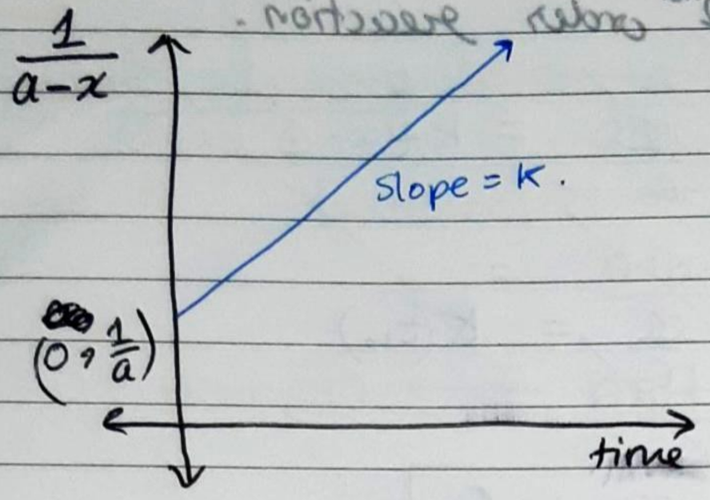
$$\frac{1}{a-x} - \frac{1}{a} = kt.$$

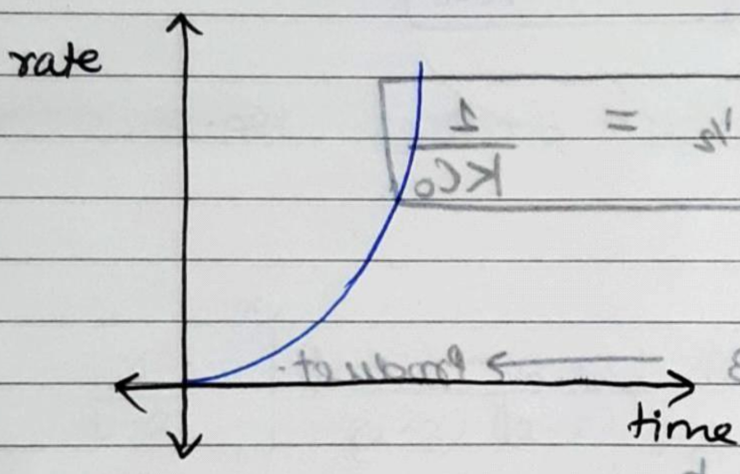
$$\therefore \quad x = a - \frac{a}{1+akt}$$

$$x = \frac{a^2kt}{1+akt}.$$

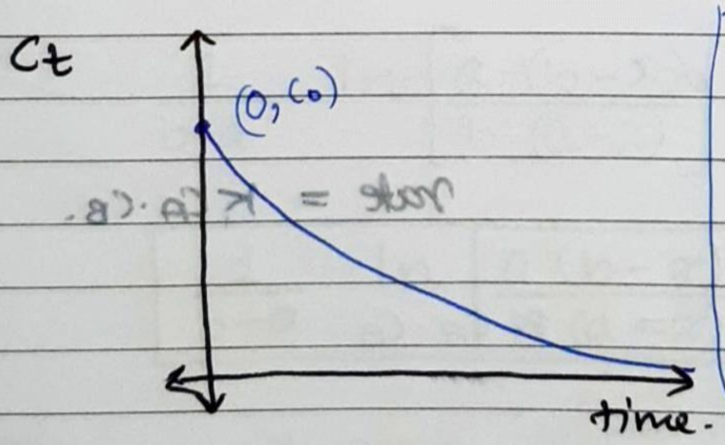
$$\# \quad \boxed{x = \frac{a^2kt}{1+akt}}$$







rate = $k(C_A)^2$.



$$\frac{1}{t} \longrightarrow \frac{t}{1+t}$$

$$\downarrow$$

$$\frac{C_0}{1+C_0kt} \longleftarrow \frac{1}{1+C_0kt}$$

★ half life. in 2^{nd} order reaction.

$$\frac{1}{C_t} - \frac{1}{C_0} = kt.$$

$$\frac{2}{C_0} - \frac{1}{C_0} = K(t_{1/2})$$

$$\therefore \boxed{t_{(1/2)} = \frac{1}{KC_0}}$$

$$\# \boxed{t_{1/2} = \frac{1}{KC_0}}$$

Q:: $A + B \longrightarrow$ Product.

$t=0.$ $\quad a \quad b.$

$t=t.$ $\quad a-x \quad b-x.$

$$\text{rate} = K C_A \cdot C_B.$$

$$-\frac{dC_A}{dt} = K C_A \cdot C_B.$$

$$-\frac{d(a-x)}{dt} = K(a-x)(b-x)$$

$$\int_0^x \frac{dx}{(a-x)(b-x)} = \int_0^t K\,dt.$$

$$\frac{1}{b-a}\int_0^x \frac{(b-x)-(a-x)}{(a-x)(b-x)}\,dx = \int_0^t k\,dt$$

$$= \frac{1}{b-a}\int_0^x \left(\frac{1}{a-x} - \frac{1}{b-x}\right)dx.$$

$$\frac{1}{b-a}\ln\left[\frac{a(b-x)}{b(a-x)}\right] = kt$$

$$\boxed{\frac{1}{b-a}\ln\left[\frac{a(b-x)}{b(a-x)}\right] = kt}$$

pseudo first order kinetics.

Case : $b >> a$. (~~the~~ pseudo first order kinetics w.r.t a)

$$\frac{1}{b}\ln\left(\frac{a}{a-x}\right) = (kb)t = k't.$$

$a >> b$. (pseudo first order kinetics w.r.t b).

$$\frac{-1}{a}\ln\left(\frac{\cancel{a}(b-x)}{\cancel{a}b}\right) = kt.$$

$$\Rightarrow \ln\left(\frac{b}{b-x}\right) = (ka)t = k''t.$$

eg:- Sucrose + $H_2O \longrightarrow$ glucose + fructose.

$$\text{rate} = k\,[\text{sucrose}].$$

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + CH_3CH_2OH.$$

$$\text{rate} = k\,[\text{ester}]$$

☆ Pseudo first order kinetics:

⇒ When in a second order reaction one of the reactant is in excess the rate depends on the less one. and become first order w.r.t ~~that~~ the less one.

This is called Pseudo first order kinetics.

eg: $kt = \frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)}$

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☆ n^{th} order kinetics:

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

$t=0$. $\quad C_0$

$t=t$. $\quad C_t$

$$-\frac{dC_A}{dt} = K(C_A)^n.$$

$$\int_{C_0}^{C_t} \frac{-dC_A}{(C_A)^n} = \int_0^t K\,dt$$

$$-\int_{C_0}^{C_t} (C_A)^{-n}\, dC_A = Kt$$

$$\left[\frac{C_A^{-n+1}}{n-1}\right]_{C_0}^{C_t} = Kt.$$

✓ $$\boxed{\frac{1}{n-1}\left[\frac{1}{(C_t)^{n-1}} - \frac{1}{(C_0)^{n-1}}\right] = Kt.}$$ $n \neq 1$

$n \rightarrow$ overall order of reaction.

$$A \longrightarrow \text{product}$$

$t=0$ a

$t=t$ $a-x$

$$\frac{1}{n-1}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right] = kt$$

Half life:

$$t_{1/2} = \frac{1}{n-1}\left[\frac{2^{n-1}-1}{K(C_0)^{n-1}}\right]$$

$t_{1/2} \propto C_0^{1-n}$