

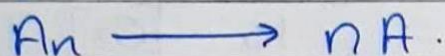
★ Some examples based on First order Kinetics.

I ✦ When we have only gaseous reactant and product.

↳ at constant  $V, T$   
 $\therefore P \propto n$ .

data provided for total pressure

Time	0	t	----- $\infty$
Total pressure.	$P_0$	$P_t$	$P_\infty$



$$t=0. \quad P_0$$

$$t=t. \quad P_0 - P \quad nP$$

$$t=\infty \quad \times \quad nP_0$$

$$P_t = P_0 - P + nP = P_0 + (n-1)P.$$

$$P = \frac{P_t - P_0}{n-1} \quad \dots (1)$$

$$P_\infty = nP_0. \quad \dots (2)$$

$$\ln \left( \frac{P_0}{P_0 - P} \right) = kt. = \ln \left[ \frac{P_0}{P_0 - \left( \frac{P_t - P_0}{n-1} \right)} \right]$$



$$kt = \ln \left( \frac{nP_0 - P_0}{nP_0 - P_t} \right)$$

$$\therefore \ln \left( \frac{P_\infty - P_0}{P_\infty - P_t} \right) = kt$$

2)  $P$  &  $T$  is constant.

$\therefore V \propto n$ .

Time	0	t	...	$\infty$
Total volume	$V_0$	$V_t$	...	$V_\infty$

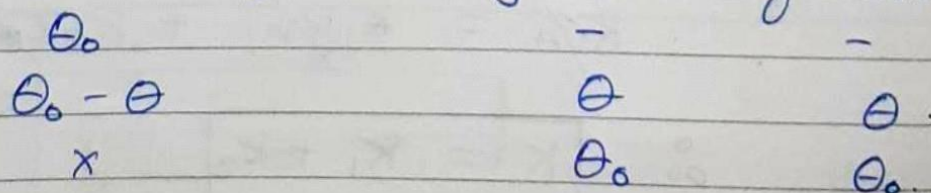
similarly.

$$\therefore \ln \left( \frac{V_\infty - V_0}{V_\infty - V_t} \right) = kt$$

3) Optical rotation  $(\theta) \propto n$ .

$$\therefore \ln \left( \frac{\theta_\infty - \theta_0}{\theta_\infty - \theta_t} \right) = kt$$

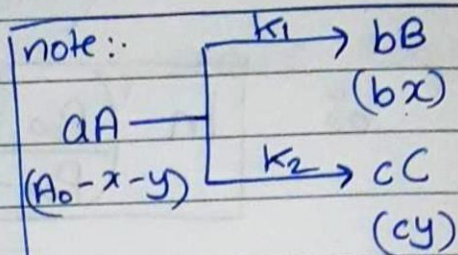
eg: Sucrose +  $H_2O$   $\longrightarrow$  glucose + fructose.



Note:- All radioactive disintegrations are first order kinetics.



### Parallel <sup>first order</sup> Kinetics:



$$a_{Keg} = K_1 + K_2 \quad \#$$

$$-\frac{dC_A}{dt} = k_{CA}$$

$$\frac{dx}{dt} = \frac{dC_B}{dt} = k_1 C_A$$

$$\frac{dy}{dt} = \frac{dC_c}{dt} = K_2 C_A.$$

but  $\frac{-dc_a}{dt} = -\frac{d(a-x-y)}{dt} = \frac{dx}{dt} + \frac{dy}{dt}$

$$K_{CA} = K_1 [C_A] + K_2 [B_A]$$

$$K = K_1 + K_2$$

$$-\frac{dCA}{dt} = k CA$$



$$\therefore \int_0^t \frac{d[A]}{[A]} = \int_0^t -k dt$$

$$\therefore [A]_t = [A]_0 e^{-(k_1+k_2)t}$$

$$\int d[C] = \int k_1 [A] dt$$

$$\int d[C] = \int k_1 [A]_0 e^{-(k_1+k_2)t} dt$$

$$[B]_t = - \frac{k_1 [A]_0}{k_1+k_2} \left[ e^{-(k_1+k_2)t} \right]_0^t$$

$$\therefore \# [B]_t = \frac{k_1 [A]_0}{k_1+k_2} \left[ 1 - e^{-(k_1+k_2)t} \right]$$

$$\therefore [C]_t = \frac{k_2 [A]_0}{k_1+k_2} \left[ 1 - e^{-(k_1+k_2)t} \right]$$

$$\therefore \# \frac{[B]_t}{[C]_t} = \frac{k_1}{k_2}$$

$$\therefore \# \% [B] = \frac{k_1}{k_1+k_2} \times 100$$

$$\# \% [C] = \frac{k_2}{k_1+k_2} \times 100$$



$$k = k_1 + k_2$$

$$\frac{\ln 2}{T_{\text{half}}} = \frac{\ln 2}{T_{1 \text{ half}}} + \frac{\ln 2}{T_{2 \text{ half}}}$$

$$\therefore \# \boxed{\frac{1}{t} = \frac{1}{t_1} + \frac{1}{t_2}} \quad t \rightarrow \text{overall half life.}$$

$$k = k_1 + k_2$$

$$A e^{-E_a/RT} = A_1 e^{-E_{a1}/RT} + A_2 e^{-E_{a2}/RT}$$

differentiating w.r.t 'T' temperature.

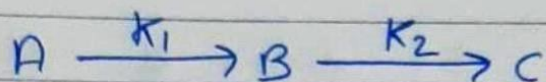
$$A e^{-E_a/RT} \left( \frac{E_a}{RT^2} \right) = A_1 e^{-E_{a1}/RT} \cdot \left( \frac{E_{a1}}{RT^2} \right) + A_2 e^{-E_{a2}/RT} \left( \frac{E_{a2}}{RT^2} \right)$$

$$k E_a = k_1 E_{a1} + k_2 E_{a2}$$

$$\therefore \# \boxed{E_a = \frac{k_1 E_{a1} + k_2 E_{a2}}{k_1 + k_2}} \rightarrow \text{overall activation energy.}$$



### III ~~First~~ First order series/sequential reactions.



$$-\frac{dC_A}{dt} = k_1 [A]$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B$$

$$\frac{dC_C}{dt} = k_2 C_B$$

$$\frac{dC_B}{dt} + k_2 C_B = k_1 C_A$$

$$\# \boxed{[A]_0 = [A]_t + [B]_t + [C]_t}$$

$$-\frac{dC_A}{dt} = k_1 C_A$$

$$\int_{C_0}^{C_t} \frac{-dC_A}{C_A} = \int_0^t k_1 dt$$

$$\ln \left( \frac{C_0}{C_t} \right) = k_1 t$$

$$C_t = C_0 e^{-k_1 t}$$

$$\boxed{[A]_t = [A]_0 e^{-k_1 t}}$$



$$\therefore \frac{dC_B}{dt} + K_2 C_B = K_1 [A]_0 e^{-k_1 t}$$

$$\Rightarrow \frac{dy}{dx} + P_y = Q$$

$$y \cdot (IF) = \int Q \cdot (IF) dx$$

$$IF = e^{\int P dx}$$

$P, Q \rightarrow \text{const. or fcn}$

$$\therefore IF = e^{\int K_2 dt} = e^{K_2 t}$$

$$[B]_t e^{K_2 t} = \int_0^t K_1 [A]_0 e^{(K_2 - K_1)t} dt$$

$$= \frac{K_1 [A]_0}{K_2 - K_1} \left[ e^{(K_2 - K_1)t} \right]_0^t$$

$$= \frac{K_1 [A]_0}{K_2 - K_1} \left[ e^{(K_2 - K_1)t} - 1 \right]$$

$$\therefore [B]_t = \frac{K_1 [A]_0}{K_2 - K_1} \left[ e^{-K_1 t} - e^{-K_2 t} \right]$$



# Time when  $[B]$  is maximum :-

$$\frac{d[B]_t}{dt} = \frac{k_1[A]_0}{k_2 - k_1} \left[ e^{-k_1 t} (-k_1) - e^{-k_2 t} (-k_2) \right] = 0$$

$$k_1 e^{-k_1 t} = k_2 e^{-k_2 t}$$

$$\frac{k_2}{k_1} = e^{(k_2 - k_1)t}$$

$$\ln \left( \frac{k_2}{k_1} \right) = (k_2 - k_1)t$$

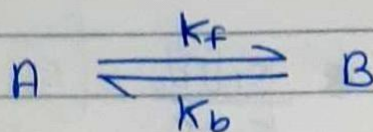
$$\therefore \# \boxed{t_{[B]_{\max}} = \frac{\ln k_2 - \ln k_1}{k_2 - k_1}}$$

$$[B]_{\max} = [A]_0 \left( \frac{k_1}{k_2} \right) e^{-k_1 t}$$

$$\therefore \# \boxed{[B]_{\max} = [A]_0 \left( \frac{k_1}{k_2} \right)^{\left( \frac{k_2}{k_2 - k_1} \right)}}$$



# IV First order reversible reaction.



$$t=0 \quad a \quad -$$

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

$$-\frac{dC_A}{dt} = k_f C_A - k_b C_B$$

$$-\frac{d(a-x)}{dt} = k_f (a-x) - k_b x$$

$$\int_0^x \frac{dx}{a k_f - (k_f + k_b)x} = \int_0^t dt$$

$$-\frac{1}{(k_f + k_b)} \ln [a k_f - (k_f + k_b)x]_0^x = t$$

$$\ln \left( \frac{a k_f}{a k_f - (k_f + k_b)x} \right) = (k_f + k_b)t$$

$$\frac{a k_f}{a k_f - (k_f + k_b)x} = e^{+(k_f + k_b)t}$$

$$\therefore \# \quad x = \frac{a k_f}{k_f + k_b} \left[ 1 - e^{-(k_f + k_b)t} \right]$$



at  $t \rightarrow \infty$ .

$$x = \frac{a K_f}{K_f + K_b}$$

$$\Rightarrow x K_f + x K_b = a K_f$$

$$\therefore \boxed{K_{eq} = \frac{K_f}{K_b} = \frac{x}{a-x}} \rightarrow \text{at } t \rightarrow \infty$$

Note:- In a reaction the fraction of molecule existing in active state is given by

$$\frac{K}{A} = e^{-\frac{E_a}{RT}}$$

$K \rightarrow$  rate constant

$A \rightarrow$  pre-exponential constant

$E_a \rightarrow$  activation energy

$\therefore \frac{K}{A} = e^{-\frac{E_a}{RT}}$  is fraction of molecules existing in activated state.