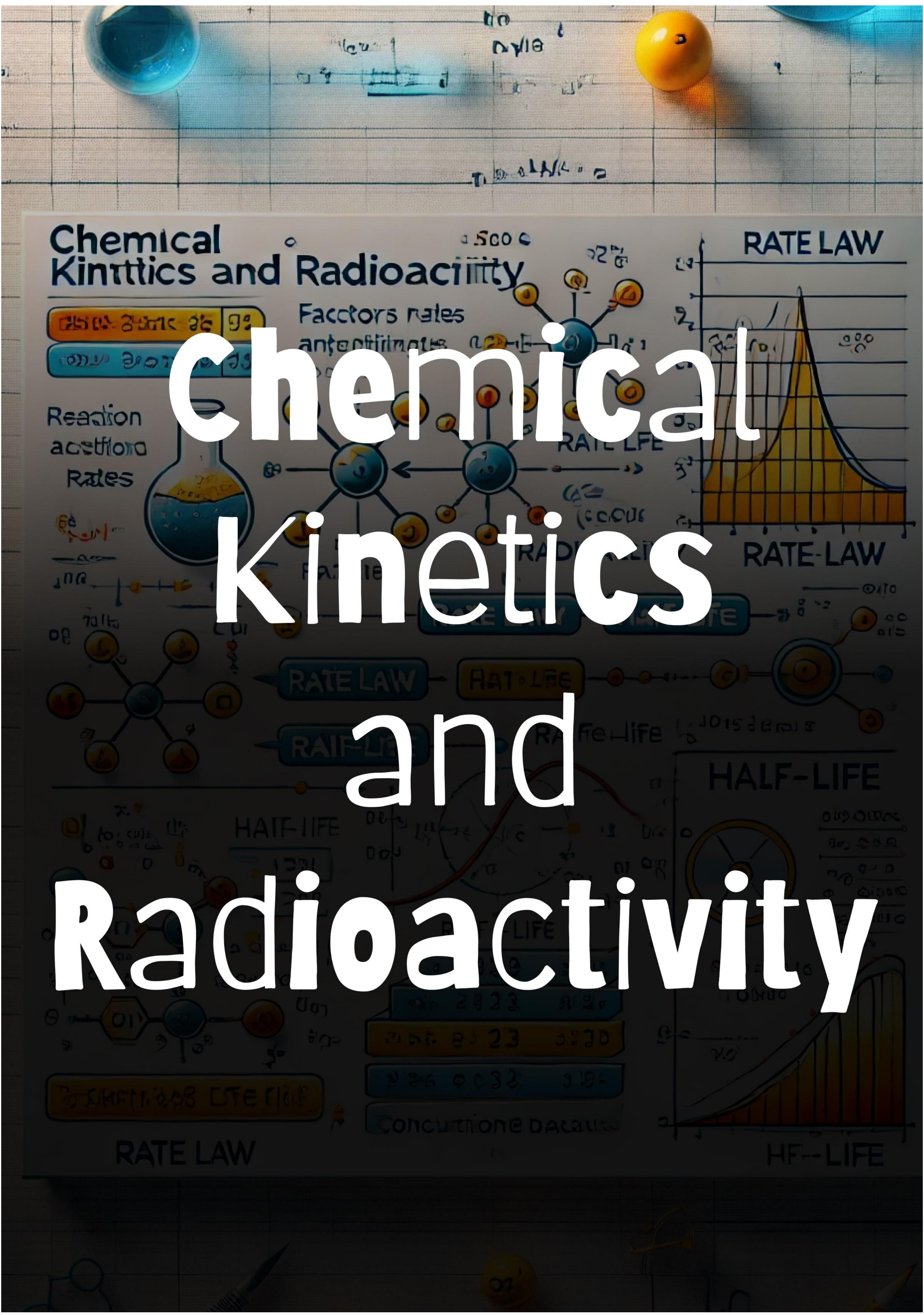


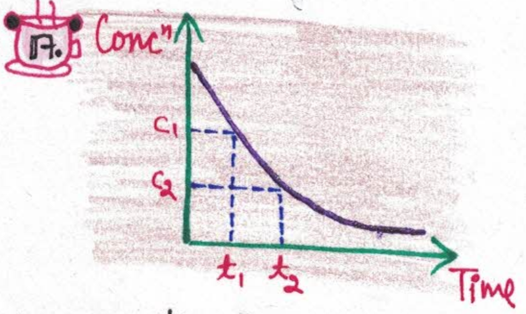
Chemical Kinetics and Radioactivity

CHEMICAL KINETICS

RATE OF A REACTION

$A \rightarrow B$ $\qquad (\text{Rate})_A = \frac{-dc_A}{dt} \qquad (\text{Rate})_B = \frac{+dc_B}{dt}$

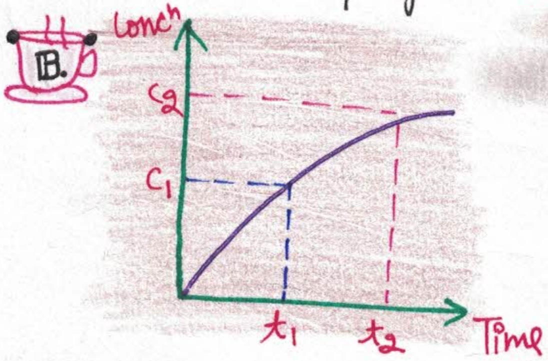
Same can be done for pressure as it is directly proportional.



$$\text{Average rate} = -\left(\frac{c_2-c_1}{t_2-t_1}\right) = -\left(\frac{\Delta c}{\Delta t}\right)$$

$$\text{Instantaneous rate} = -\frac{dc}{dt}$$

It represents the slope of the "c" v/s "t" graph.



$$\text{Rate} = \left(\frac{c_2-c_1}{t_2-t_1}\right) = \left(\frac{\Delta c}{\Delta t}\right)$$
$$= \left(\frac{dc}{dt}\right)$$

We can also write $\frac{dc}{dt} = \frac{1}{V}\left(\frac{dn}{dt}\right)$ $\qquad \{n = \text{moles}\}$

$$aA + bB \longrightarrow cC + dD$$

$$\frac{\text{Male of A}}{a} = \frac{\text{Male of B}}{b} = \frac{\text{Male of C}}{c} = \frac{\text{Male of D}}{d}$$

$$\text{Rate of reaction} = -\frac{1}{a}\frac{dc_A}{dt} = -\frac{1}{b}\frac{dc_B}{dt} = \frac{1}{c}\frac{dc_C}{dt} = \frac{1}{d}\frac{dc_D}{dt}$$

$\frac{-dc_A}{dt}$ = Rate of disappearance of (A)

$\frac{dc_C}{dt}$ = Rate of appearance of (C)

Ques. $N_2 + 3H_2 \longrightarrow 2NH_3$ rate of disappearance of $H_2(g)$ is 12 M sec^{-1} what will be rate of rxⁿ r_{NH_3} , r_{N_2} = ?

$R = 4\ m\,sec^{-1}$
$r_{N_2} = 4\ msec^{-1}$
$r_{NH_2} = 8\ msec^{-1}$

Ans. $R = r_{N_2} = 4 = \frac{1}{2} r\,NH_2$

NOTE Rate of the reaction depands on:-

- Concentration
- Temprature
- Pressure
- pH of solⁿ
- Catalyst

Concentration

$\boxed{Rate \propto (concentration)^n}$ → where n is the order of the reaction

$aA + bB \longrightarrow cC + dD$

$$\boxed{R = \frac{1}{a}\frac{dC_A}{dt} = \frac{-1}{b}\frac{dC_B}{dt} = \frac{1}{c}\frac{dC_c}{dt} = \frac{1}{d}\frac{dC_d}{dt}} = KC_A^x C_B^y$$

Rate = $K[con^n]^n$

Here K = rate constant.
x = order of the rxⁿ w.r.to A
y = order of the rxⁿ w.r. to B.

$\boxed{(x+y) = \text{Overall order of the reaction}}$.

Molecularity = x+y [$x + y \geq 0$]

Imp. point Order of rxⁿ can be calculated experimentally or mechanism of any reaction.

$2A + 3B \longrightarrow C + D$, K is defined as rate constant or velocity constant or specific reaction rate.

Unit of K ⇒ $\boxed{K = \left(\frac{mole}{lit}\right)^{1-n} sec^{-1}}$

Unit of K	Order
$\left(\frac{mol}{lit}\right) sec^{-1}$	0
sec^{-1}	1
$lit.\ mol^{-1} sec^{-1}$	2

Zero Order Reaction

$A \longrightarrow$ Product.

t=0 C_0

t=t C_t

$$-\frac{dA}{dt} = K(C_A)^0 \Rightarrow \int_{C_0}^{C_t} dC_A = K\int_0^t dt$$

$$\boxed{C_0 - C_t = KT} \Rightarrow C_0 = C_t + KT$$

$A \longrightarrow$ Product.

t=0 a 0

t=t a-x x

$$-\frac{dA}{dt} = K(C_A)^0$$

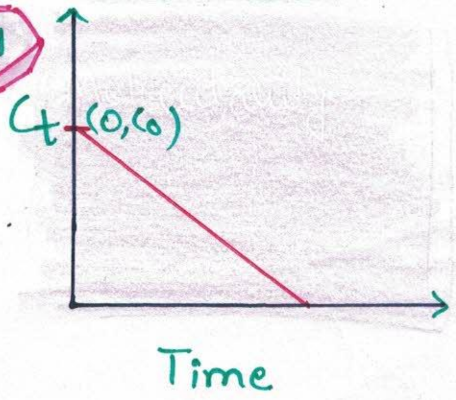
$$-\frac{d(a-x)}{dt} = K(a-x)^0 \Rightarrow \int_0^x dx = K\int_0^t dt$$

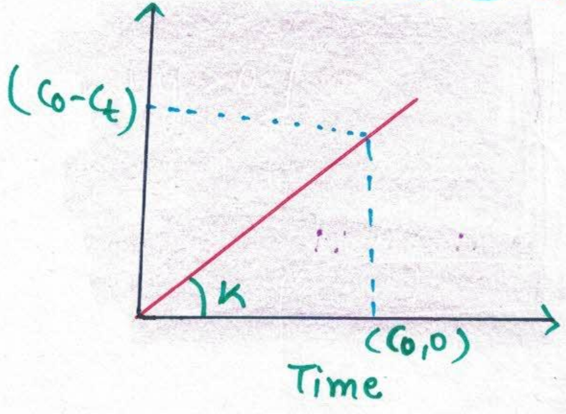
Zero order reaction increase the concn of reacting species.

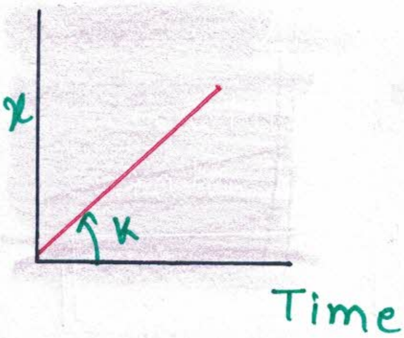
$$\boxed{x = KT}$$

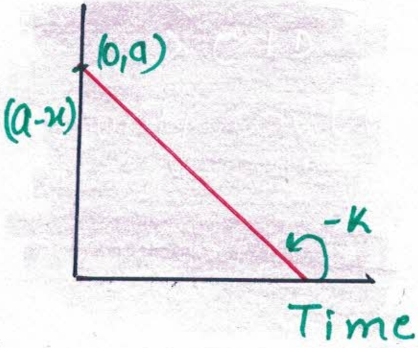
Not speed up the rate of rxn.

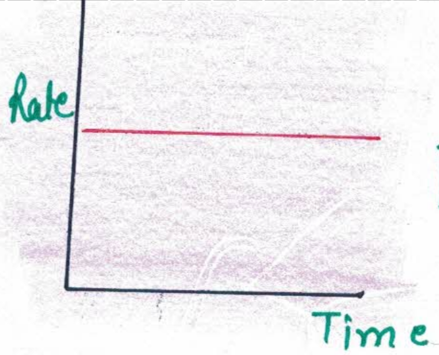
GRAPH











$\boxed{r = K}$

* At time $= \frac{C_0}{K}$, then we'll have conc^n ended.

Half Life

[$t_{1/2}$ or $t_{50\%}$ or $t_{0.5}$]

When half of reactant gets reacted in the reaction is called half life of reaction.

Therefore - $\frac{C_0}{2} = C_t$ $\quad C_0 - \frac{C_0}{2} = K t_{1/2}$ $\quad T_{1/2} = \frac{C_0}{2K}$

NOTE

$$\boxed{t_{100\%} = \frac{C_0}{K} = 2 t_{1/2}}$$ Zero order

If $t_{3/4}$ asked then $C_t = \frac{1}{4} C_0$; $\boxed{C_0 - \frac{C_0}{4} = K t_{3/4}}$ $\quad \boxed{t_{3/4} = \frac{3}{4K}}$

Quest. for a rx^n, rate = K[A°]. If initial concentration of A was (C_0), then C_t = ?

Ans. $2A \longrightarrow$ Product $\quad -\frac{1}{2}\frac{dC_A}{dt} = K \Rightarrow C_0 - C_t = 2Kt$

t=0 C_0

t=t a

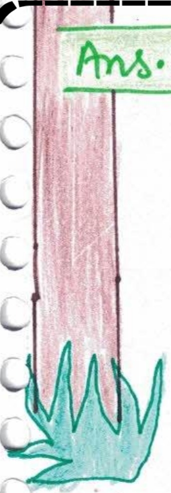
$$\boxed{C_t = C_0 - 2Kt}$$

Quest. for a rx^n $(\text{rate})_A \longrightarrow K[A]^\circ$ If $[A_i] = 0$ then C_t = ?

Ans.

$$-\frac{dC_A}{dt} = K \Rightarrow \boxed{C_0 - C_t = Kt}$$

Questi. $2A + 3B \longrightarrow C + 4D$ Rate $= K[C_A]^0[C_B]^0$ [A = a moles, B = b moles] find the $(t_{1/2})_A$ and $(t_{1/2})_B$. Also if we have $(t_{1/2})_A = (t_{1/2})_B$ then find a : b = ?



Ans. $2A + 3B \longrightarrow C + 4D$

$t=0 \quad a \quad b$

$t=t \quad a-x \quad b-\frac{3}{2}x$

We take as (x) because then the limits of integrⁿ had to changed

$$-\frac{1}{2}\left(\frac{dC_A}{dt}\right) = K \Rightarrow -\frac{1}{2}\frac{d}{dt}(a-x) = K$$

$$\boxed{x = 2Kt}$$

$[A]_t = a - 2Kt$

$[B]_t = b - 3Kt$

for $t_{1/2}$ we have $\Rightarrow [A]_{t_{1/2}} = a/2$

$[B]_{t_{1/2}} = b/2$

$\frac{a}{2} = a - 2Kt$ $\quad \boxed{(t_{1/2})_a = \frac{a}{4K}} \quad \boxed{(t_{1/2})_B = \frac{b}{6K}}$

given $= \frac{a}{4K} = \frac{b}{6K}$ $\quad \boxed{\frac{a}{b} = \frac{2}{3}}$

First Order Kinetics

$A \longrightarrow$ Product

$t=0 \quad C_0$

$t=t \quad C_t$

$$-\frac{dC_A}{dt} = K(C_A) \Rightarrow -\int_{C_0}^{C_t}\frac{dC_A}{C_A} = K\int_0^t dt \Rightarrow \boxed{\ln\frac{C_0}{C_t} = KT}$$

$$\boxed{C_t = C_0 e^{-KT}} \quad , \quad \boxed{C_0 - C_t = C_0(1-e^{-KT}}$$

$A \longrightarrow$ Product

$t=0 \quad a$

$t=t \quad a-x$

] In moles

$$\Rightarrow -\frac{d}{dt}(a-x) = K(a-x) \Rightarrow \int_{C_0}^{C_t}\frac{dx}{a-x} = K\,dt \Rightarrow -\ln[a-x] = K(a-x)$$

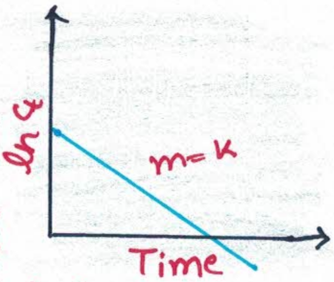
$$\Rightarrow -\ln(a-x)_0^x = Kt \Rightarrow \frac{\ln a}{\ln(a-x)} = Kt$$

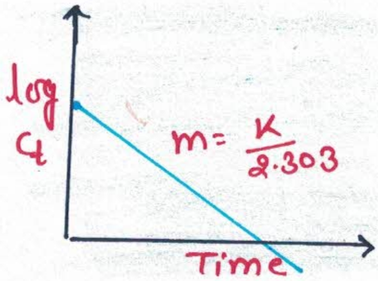
$$\Rightarrow \ln a - x = ae^{-Kt} \quad \Rightarrow \boxed{x = a[1-e^{-KT}}$$

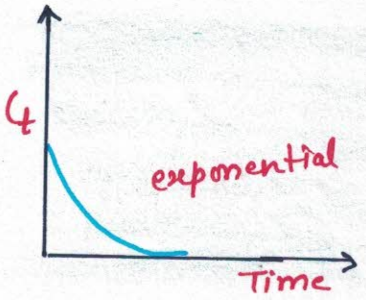
$\ln\left(\frac{C_0}{C_t}\right) = Kt \Rightarrow \ln C_0 - \ln C_t = KT \Rightarrow C_t = C_0(e^{-Kt})$

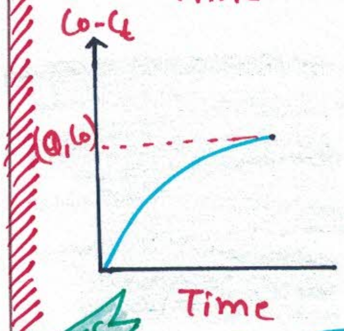
$$\boxed{\log C_t = \log C_0 - \frac{Kt}{2.303}}$$

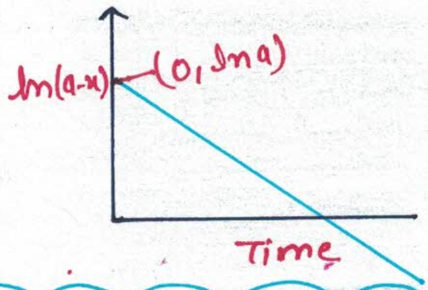
GRAPHS

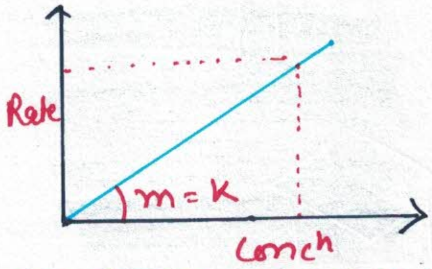












NOTE

The first order kinetics reaction never gets completed Half life is Independent of Initial concn.

$2A \longrightarrow P$ If rate of $rx^n = KC_A'$

$t=0 \quad C_0$

$t=t \quad C_t$

$-\frac{1}{2}\frac{dC_A}{dt} = KC_A \Rightarrow -\frac{1}{2}\ln(C)_{C_0}^{C_t} = Kt$

$$\boxed{\ln\frac{C_0}{C_t} = 2Kt}$$

$2A \longrightarrow P$ If rate of $rx^n = KC_A$

$t=0 \quad C_0$

$t=t \quad C_t$

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

$$\boxed{\ln\frac{C_0}{C_t} = KT}$$

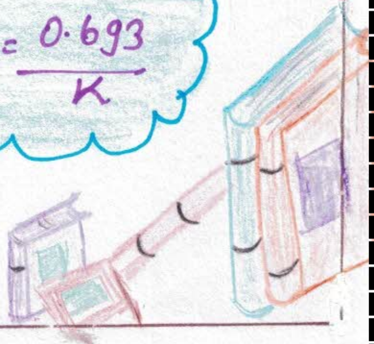
for Ist order rxn

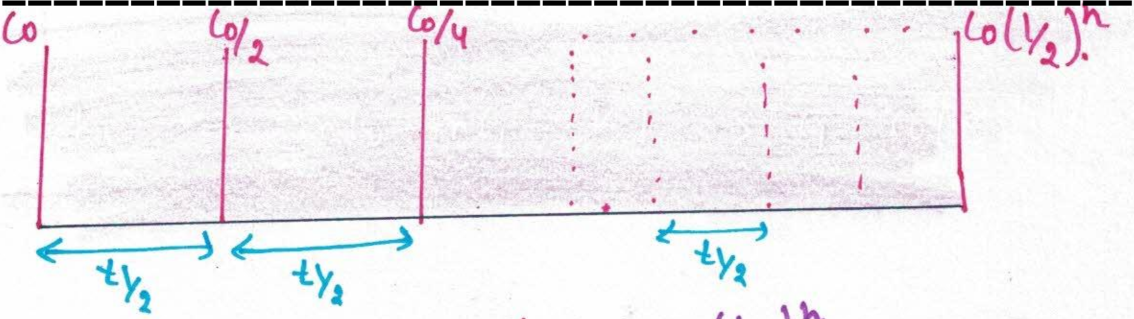
Half life :- $\ln\frac{C_0}{C_0/2} = Kt_{1/2}$

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

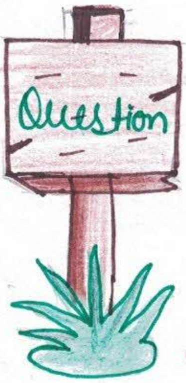
NOTE

$T_{1/2} = \frac{0.693}{K}$





Concentration after 'n' half life = $C_0(1/2)^n$



$2A + 3B \longrightarrow C + 4D$ At $t=0$, we have $A = a$, $B = b$ $R = KC_A^1 C_B^0$, what will be conc^n of A and B at any time t? what will be half life of 'A' and 'B'? what should be the initial mole ratio for getting $(t_{1/2})_A = (t_{1/2})_B$?

$$2A + 3B \longrightarrow C + 4D$$

t=0 $\quad a \quad b$

t=t $\quad a-x \quad b-3/2\,x$

$\Rightarrow -\frac{1}{2}\frac{d(a-x)}{dt} = K(a-x) \Rightarrow \int_0^x \frac{dx}{2(a-x)} = K\int dt$

$\Rightarrow -\frac{1}{2}\Big[\ln(a-x)\Big]_{x}^{0} = Kt \Rightarrow \boxed{\frac{\ln a}{\ln(a-x)} = 2KT}$ — Ⓐ

From Eq. Ⓐ $\boxed{x = a(1-e^{-2KT})}$ $\Rightarrow -\frac{1}{3}\frac{d}{dt}\left(b-\frac{3}{2}x\right) = K(a-x)$

$\Rightarrow \frac{1}{2}\int_0^x \frac{dx}{(a-x)} = K\int dt$

$[A]_t = a-(a-ae^{-Kt(2)}) = ae^{-2KT}$

$[B]_t = b-\left(\frac{3}{2}-(a-ae^{-2KT}\right) = b-\frac{3}{2}(1-e^{-2KT}) \Rightarrow \boxed{\frac{\ln a}{a-3/2\,x} = 2KT}$

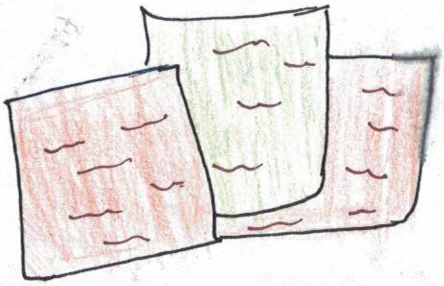
$\Rightarrow$ for $[t_{1/2}]_A = \frac{a}{2} = (a)\,2^{-2KT} \Rightarrow \boxed{(t_{1/2})_A = \frac{\ln 2}{2K}}$

$\Rightarrow$ for $[t_{1/2}]_B = \frac{b}{2} = b-\frac{3}{2}a[1-e^{-2KT}] \Rightarrow \frac{3}{2}a(1-e^{-2KT}) = b/2$

$\Rightarrow 1-e^{-2KT} = \frac{b}{2a} \Rightarrow e^{-2KT} = 1-\frac{b}{2a} \Rightarrow \boxed{(t_{1/2})_B = \ln\frac{3a}{3a-b}}$

for $(t_{1/2})_A = (t_{1/2})_B \Rightarrow \ln 2 = \left(\ln \frac{2a}{2a-b}\right) \Rightarrow 4a - 2b = 4a$

$$\boxed{\frac{a}{b} = \frac{2}{3}}$$



IInd Order Kinetics

I A $\longrightarrow$ P

t=0 C_0
t=t C_t

completion at t=∞

$$-\frac{dC_A}{dt} = K(C_A)^2 \Rightarrow \boxed{\frac{1}{C_t} - \frac{1}{C_0} = Kt}$$

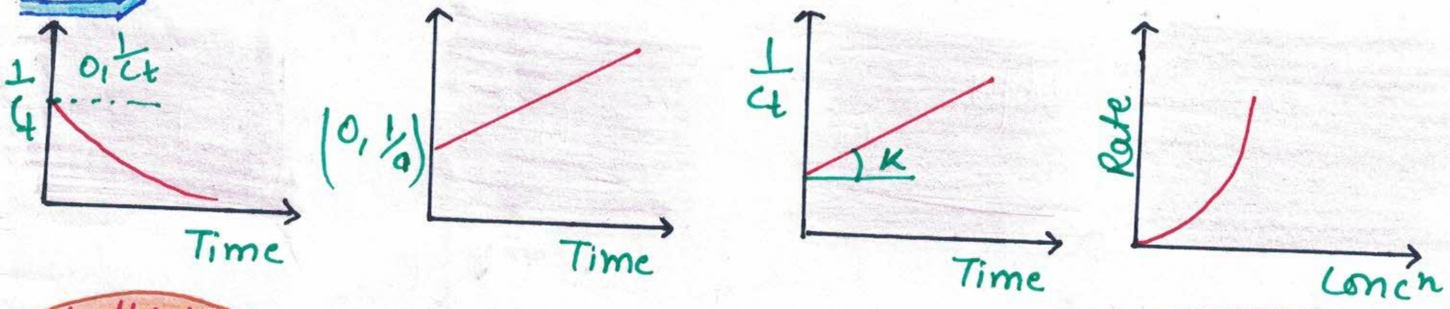
II A $\longrightarrow$ P

t=0 a
t=t a−x

$$\int_0^x \frac{dC_A}{dt} = K\int_0^t dt$$

$$\boxed{\frac{1}{a-x} - \frac{1}{a} = Kt}$$

GRAPHS



Half life.

$$K(t_{1/2}) = \frac{2}{C_0} - \frac{1}{C_0} \Rightarrow \frac{1}{C_0} \Rightarrow \boxed{t_{1/2} = \frac{1}{C_0K}}$$

$$K(t_{3/4}) = \frac{3}{C_0} \Rightarrow \boxed{t_{3/4} = \frac{3}{C_0K}}$$

III 2A $\longrightarrow$ P

t=0 C_0
t=t C_t

$$R = K(C_A)^2$$

$$-\frac{1}{2}\int_{C_0}^{C_t} \frac{dC_A}{(C_A)^2} = K\int dt \Rightarrow \left(\frac{1}{2}\right)\left(\frac{1}{C}\right)_{C_0}^{C_t} = Kt$$

$$\boxed{2Kt = \frac{1}{C_t} - \frac{1}{C_0}}$$

Pseudo Ist Order Kinetics

A + B $\longrightarrow$ P

t=0 a b
t=t a−x b−x

Rate = $KC_A^{1}C_B^{1}$

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

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

If b is in excess b>>> a

If a is in excess a>>> b

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

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

$$\boxed{k't = \ln\left(\frac{a}{a-x}\right)}$$

↳ Thus the rx^n behaves as the Ist order with respect to 'a'

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

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

↳ Thus the reaction behaves as the Ist order with respect to 'b'

Thus if we've 'B' in the excess, then rx^n is Ist order w.r.to 'a'. If 'A' is in the excess, then rx^n is Ist order, w.r.to 'B'. Overall order was second Order, such rx^n are called Pseudo order Kinetics.

Example:- Inversion of Sugar Cane ... H_2O in excess, grounded by ester.

nth - Order Kinetics

$$A \longrightarrow P$$

t=0 C_0

t=t C_t

$$-\frac{dC_A}{dt} = KC_A^{\,n} \Rightarrow \int^{C_t} C_A^{-n}\,dC_A = -K\int_0^t dt$$

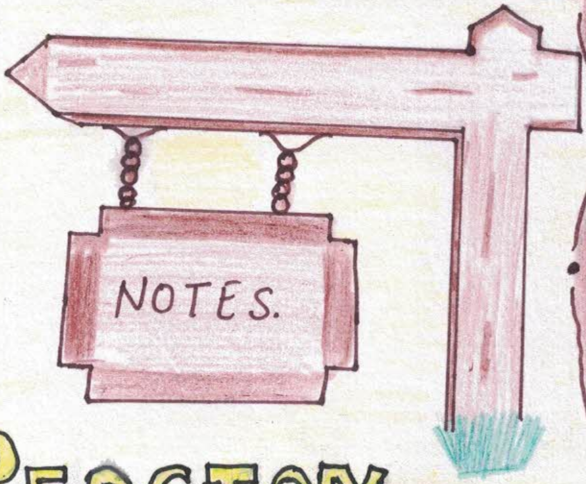
$$\boxed{Kt = \frac{1}{(n-1)}\left[\frac{1}{C_t^{\,n-1}} - \frac{1}{C_0^{\,n-1}}\right]}$$

Half Life:- $\frac{1}{(n-1)}\left[\frac{2^{n-1}}{(C_0)^{n-1}} - \frac{1}{(C_0)^{n-1}}\right] \Rightarrow \frac{2^{n-1}-1}{C_0^{\,n-1}(n-1)K}$

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

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

Order	∝ $t_{1/2}$
0	C_0
1	constant
2	C_0^{-1}
⋮	⋮
n	$(C_0)^{1-n}$



ORDER OF REACTON

Were following methods to determine the order of the reaction.

① Initial rate Law method ③ Half life method
② Integrated rate Law method. ④ Graphical method
⑤ Ostwald Isolation method

Initial Rate Law Method.

We can understand this method by Question

$$2A + 3B + 5C \longrightarrow P$$

	[A]	[B]	[C]	Rate [M sec⁻¹]
Ex-1	0.02	0.02	0.02	8×1.0^{-6}
Ex-2	0.02	0.04	0.02	16×10^{-5}
Ex-3	0.01	0.02	0.02	8×10^{-6}
Ex-4	0.02	0.02	0.08	3.2×10^{-5}

ⓐ What will be the order of the rxn w.r.to [A], [B], [C] and overall order of reaction?

ⓑ What will be rate of disappearance of [A], [B] [C] if concn of each [A] [B] [C] is 0.03 M

ⓒ What is the value of specific reaction rate?

ⓐ Soln ① $(2)^x = 1$ $\boxed{x = 0}$ ② $(B)^y = \frac{1.6 \times 10^{-5}}{8 \times 10} = \boxed{y = 1}$

③ $\left(\frac{1}{4}\right)^z = \frac{1}{4}$ $\boxed{z = 1}$

Overall rate = 2

$\boxed{Rate = K(C_A)^0(C_B)^1(C_c)^1}$

b $-\frac{1}{2}\frac{dC_A}{dt} = R \Rightarrow \left(\frac{1}{2}\right)(2\times10^{-2})(0.03)^2 = 36\times10^{-6}\ M\,sec^{-1}$

$-\frac{1}{3}\frac{dC_B}{dt} = R \Rightarrow \left(\frac{1}{3}\right)(2\times10^{-2})(0.03)^2 = 54\times10^{-6}\ M\,sec^{-1}$

$-\frac{1}{5}\frac{dC_c}{dt} = R \Rightarrow \left(\frac{1}{5}\right)(2\times10^{-2})(9\times10^{-4}) = 90\times10^{-6}\ M\,sec^{-1}$

C $(8\times10^{-6}) = K(0.02)(0.02) \Rightarrow K = 2\times10^{-2}\ mol^{-1}\,lit\,sec^{-1}$

Initial Rate Law Method

It is a hit and trial method.

Time	0	t_1	t_2	....	t_n
order	C_0	C_1	C_2	....	C_n

Let zero order:-

$C_t = C_0 - Kt \Rightarrow \boxed{K = \frac{C_0 - C_t}{t}}$

Let first order:-

$\boxed{K = \frac{1}{t}\ln\frac{C_0}{C_t}}$

If we have K = constant; then we've that order.

Half Life Method

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

At least 2 experiment, we have to do.

By this method we can calculate only overall order of the rxn but not all over of the rxn.

$$\frac{\text{Exp.1.}\ (t_{1/2})_A}{\text{Exp.2.}\ (t_{1/2})_B} = \left[\frac{(C_0)_A}{(C_0)_B}\right]^{1-n}$$

Ostwald Isolation Method.

$aA + bB \longrightarrow Product$

$Rate = K(C_A)^x(C_B)^y.$

A is in excess;

$Rate = K(C_B)^y$

⇓

get y

B is in excess;

$Rate = K(C_A)^x$

⇓

get x

Thus we can find rate of rxn.

Monitering of Reaction for I^{st} Order Kinetics :-

for gaseous mixture :- $A_n \longrightarrow nA$ V, T ⇒ constant [Data will be of Total Pressure]

$t=0$ a 0

$t=t$ $a-x$ nx

⋮

$t=\infty$ x na

Time	0	t_1	t_2	t_∞
Pressure	P_0	P_1	P_2	P_∞

$a \propto P_0$

$a-x+nx \propto P_t$

$na \propto P_\infty$

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

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

TEMPRATURE EFFECT

Temp. Cofficient. It is defined as the ratio of the rate constant of the reaction when the temprature difference is 10 units.

$$\boxed{\theta = \frac{r_{T+10}}{r_T} = \frac{K_{T+10}}{K_T}}$$

Thus rate always increases, when Temprature is increases

Quest Rate constant at 25°C is 4×10^{-3} sec^{-1}. what will be rate constant at +55°C if $\theta = 2$

Ans. $2 = \frac{x}{4\times10^{-3}} \Rightarrow$

$x = 8\times10^{-3}$ — 35°C

$x = 16\times10^{-3}$ — 45°C

32×10^{-3} — 55°C

NOTE: When we increased 10°c of reaction; rate of the reaction is just doubled.

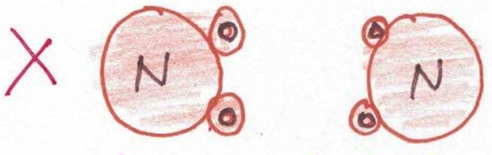
$$\boxed{K_{T_2} = K_{T_1}(\theta)^{\frac{T_2-T_1}{10}}}$$

$$\boxed{r_{T_2} = r_{T_1}(\theta)^{\frac{T_2-T_1}{10}}}$$

Arrhenius Theory

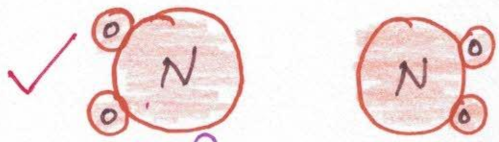
According to this theory reacting molecule collide with each other to form a product. during collision, bonds of reacting molecule will break and for product molecule, bond will be formed. So the collision must be effective for the reacting molecule should have certain amount of energy and proper orientation.

$2NO_2 \rightleftharpoons N_2O_4$



Wrong orientation

$2NO_2 \rightleftharpoons N_2O_4$



Proper orientation

So there are two factor (a) orientation (b) energy. for the formation of product. the fraction of energy that each molecule should've so experimentally;

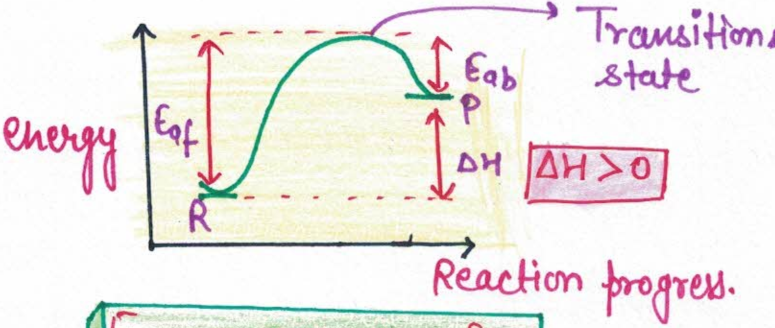
$e^{-E_a/RT}$, where E_a = Activation Energy
R = Gas Constant
T = Temprature.

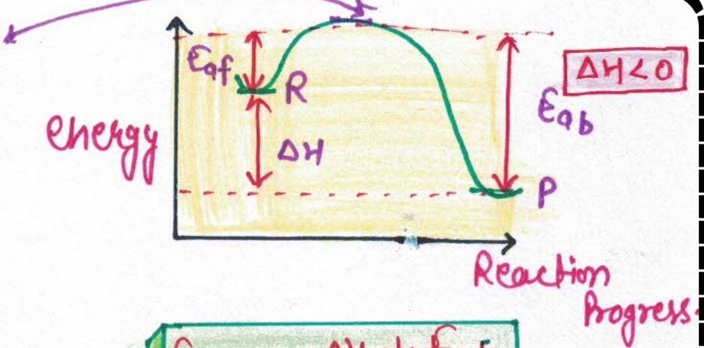
and orientation is represented by pre expontential factor (A) also called frequency factor

Arhenius equation $\boxed{K = Ae^{-E_a/RT}}$

K = Rate constant
A = frequency factor
T = Temprature
E_a = Activation Energy

Whenever not mentioned take activation energy for forward reaction.





$$\boxed{E_{af} = \Delta H + \Delta E_{ab}}$$

Endothermic

$$\boxed{E_{ab} = \Delta H + E_{af}}$$

Exothermic

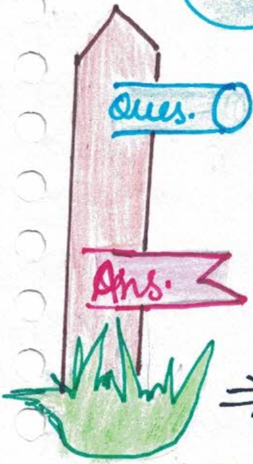
$$K = A\,e^{-E_a/RT} \Rightarrow \ln K = \ln A - \frac{E_a}{RT} \Rightarrow \log K = \frac{-E_a}{2.303RT} + \log A$$

$$\log K_1 = \frac{-E_a}{2.303RT_1} + \log A \quad \text{—①}$$

$$\log K_2 = \frac{-E_a}{2.303RT_2} + \log A \quad \text{—②}$$

① - ②

$$\boxed{\log \frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]}$$

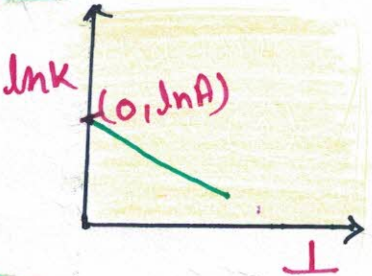


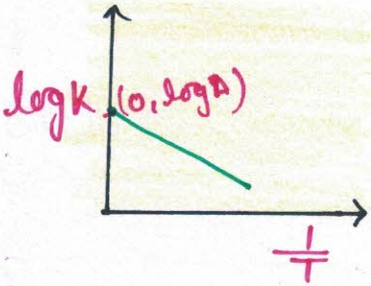
Ques. ① At 27°C rate constant = 4×10^{-3} sec⁻¹. At 37°C $K = 8 \times 10^{-3}$ sec⁻¹
What will be E_a = ?

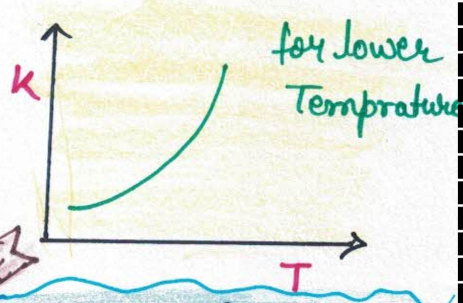
Ans.

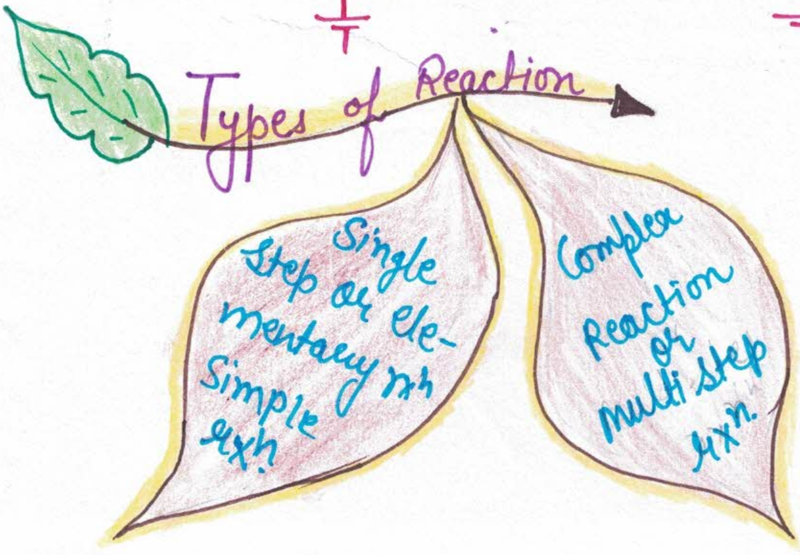
$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \Rightarrow \log \frac{8 \times 10^{-3}}{4 \times 10^{-3}} = \frac{E_a}{2.303 \times 8.3}\left[\frac{1}{310} - \frac{1}{300}\right]$$

$$\Rightarrow E_a = \frac{8.3 \times 3 \times 23 \times 93}{100} = \frac{532611}{10} = \boxed{53.26\,KJ}$$









NOTE

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

$$K = A\,e^{-ax}$$

$$y = \ln A - cx$$

$$\ln K = \ln A - \frac{E_a}{RT}$$

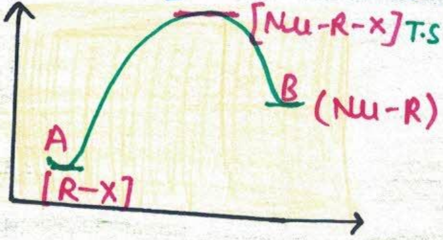
$$\log K = \log A - \frac{E_a}{2.303R}$$

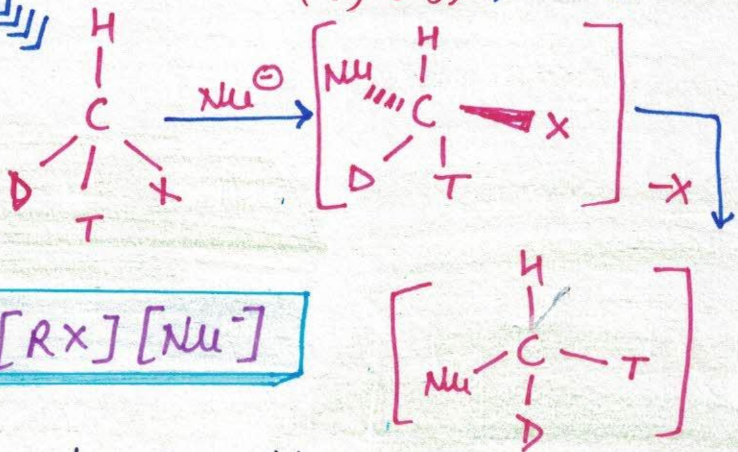
$$y = c - mx$$

Single Step for these type of rx^n, the order of the reaction will be sum of the stoichiometric cofficient. as well as the molecularity of the reaction.

$[A + B \longrightarrow P]$

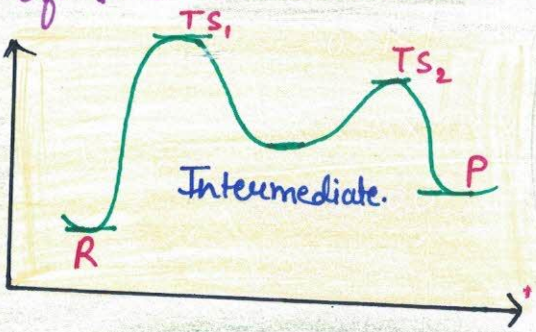
$R = K(C_A)(C_B)$, $n=2$





$$\boxed{\text{Rate} \propto [RX][Nu^-]}$$

Multi-Step. for complex reaction we can't determine molecularity of the rx^n. for the calculation of order of the rx^n we will consider. solwent step as the rate determining step. The order of the rx^n will be the sum of the stoichiometric cofficient of the solwent step.



In the slow step having concentration of Intermediate then order of the rx^n can be fraction. It can be determined by the supporting equillibrium reaction by which we can eliminate intermidiate concentration.

- In the complex rx^n we can define molecularity for the step but not for the overall rx^n.

$$O_3 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} O_2 + O \Rightarrow \text{(Fast)}$$

$$O_3 + O \xrightarrow{K_2} 2O_2 \Rightarrow \text{(Slow)}$$

$$2O_3 \longrightarrow 3O_2$$

$$\frac{K_1}{K_2} = \frac{[O_2][O]}{[O_3]} \Rightarrow [O] = \frac{K_1}{K_2}\frac{[O_3]}{[O_2]} \text{ — ①}$$

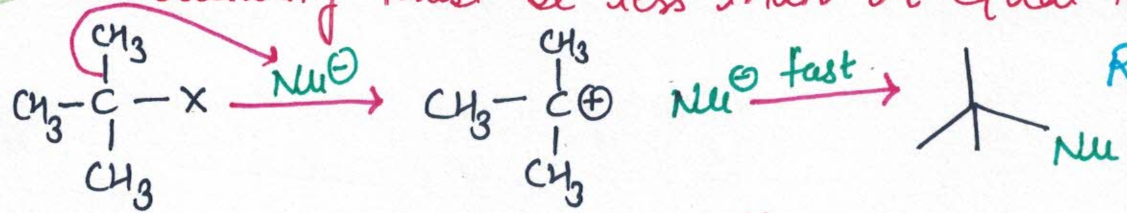
Put eq.(1) in eq.(ii)

$$\Rightarrow R = K_3[O][O_3] \text{ — ②}$$

$$\Rightarrow R = K_3\frac{K_1}{K_2}[O_3]^2[O_2]^{-1}$$

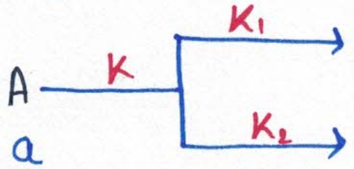
order ⇒ 1
molecularity = N.D

Molecularity must be less than or equal to 3.



Rate ∝ [RX]
It is S_N1 Rxn.

Parallel Kinetics



$B(x) \Rightarrow -\frac{dc}{dt} = KC_A$

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

t=0 a
t=∞ a-x-y

$\frac{d[B]}{dt} = K_1C_A$ $\frac{d[C]}{dt} = K_2C_A$ $K_1(C_A) = K_2(C_A)$

$$\boxed{K = K_1 + K_2}$$

$$-\int\frac{dC}{C_A} = \int_0^t K\,dt \Rightarrow \ln\left(\frac{C_0}{C_t}\right) = Kt \Rightarrow \boxed{[A]_t = ae^{-(K_1+K_2)t}}$$

$$C_t = C_0e^{-Kt} \Rightarrow \boxed{(t_{1/2})_A = \frac{\ln 2}{K_1+K_2}}$$

$$\int_0^x d[B] = \int_0^t K_1ae^{-(K_1+K_2)t}\,dt$$

$$\boxed{[B]_t = \frac{aK_1}{K_1+K_2}\left[1-e^{-(K_1+K_2)t}\right]} \qquad \boxed{[C] = \frac{aK_2}{K_1+K_2}\left[1-e^{-(K_1+K_2)t}\right]}$$

$K = K_1 + K_2$

$$\frac{\ln 2}{T_A} = \frac{\ln 2}{T_B} = \frac{\ln 2}{T_C}$$

$$\left(\frac{1}{T_{1/2}}\right)_A = \left(\frac{1}{T_{1/2}}\right)_B = \left(\frac{1}{T_{1/2}}\right)_C$$

overall activation energy.
Ea_1 ⟶ for B
Ea_2 ⟶ for C

$$\boxed{Ea = \frac{K_1Ea_1 + K_2Ea_2}{K_1+K_2}}$$

Series Kinetics

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C \Rightarrow t_{1/2} = \frac{\ln 2}{K_1}$$

t=0 a

$$-\frac{dC_A}{dt} = KC_A \Rightarrow \int_{C_0}^{C_t} dC_A = -K\int_{C_0}^{C_t} dt \Rightarrow \ln\frac{C_0}{C_t} = K_1t$$

$$C_t = C_0e^{-K_1t} \Rightarrow [A]_t = ae^{-K_1t}$$

$$\boxed{[A_0] = [A]_t + [B]_t + [C]_t}$$

$$\Rightarrow \frac{d[B]}{dt} = K_1[A] - K_2[B] \Rightarrow \frac{d[B]}{dt} + K_2[B] = K_1[A]$$ Linear differential eq^n.

$$\Rightarrow [B]e^{K_2 t} = \int_0^t K_1 a e^{-K_1 t} \cdot e^{-K_2 t} \cdot dt$$

$$\Rightarrow [B]e^{K_2 t} = \left(\frac{K_1 a}{K_2 - K_1}\right)\left[e^{(K_2 - K_1)t} - 1\right]$$

$$\boxed{[B]_t = \frac{K_1 a}{K_2 - K_1}\left[e^{-K_1 t} - e^{-K_2 t}\right]}$$

Now differentiate the $[B]_t$ to find max. value of B at (t)

$$\boxed{\text{Time when } [B] \text{ is max}^m = \left[\frac{\ln K_2 - \ln K_1}{K_2 - K_1}\right]}$$

$$A \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B$$ ⟶ Equilibrium Equation.

t=0 a

t=t a-x x

$$\Rightarrow \frac{dc_A}{dt} = -K_f[A] + K_b[B]$$ This eq^n comes at ∞

$$\Rightarrow -\frac{d(a-x)}{dt} = K_f(a-x) + K_b(x)$$

$$\boxed{K_c = \frac{K_f}{K_b}}$$

$$\Rightarrow \frac{dx}{dt} = aK_f - [K_f + K_B]x \Rightarrow \int_0^x \frac{dx}{dK_f - (K_f + K_b)x} = \int_0^t dt$$

$$\Rightarrow \left[\frac{\ln(aK_f - (K_f + K_b)x}{(-K_f + K_b)}\right]_0^x = t \Rightarrow (K_f + K_b)t = \ln\left(\frac{aK_f}{aK_f - (K_f + K_b)t}\right)$$

$$\boxed{x = \frac{aK_f}{(K_f + K_b)}\left(1 - e^{-(K_f + K_b)t}\right)}$$

At t∞ $x = \frac{aK_f}{(K_f + K_b)}$ $\Rightarrow xK_f + xK_b = aK_f$

$$x\left(\frac{K_f}{K_b}\right) + x = a\left(\frac{K_f}{K_b}\right)$$

$$\boxed{K_c = \frac{x}{a - x}}$$

Catalyst Substance which can increase the rate of the reaction.

[Positive Catalyst]:- Increase the rate of reaction

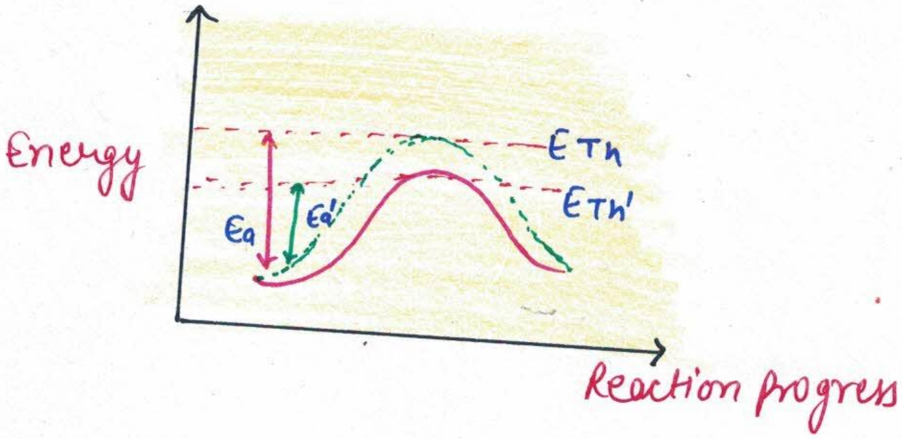
[Negative Catalyst]:- decrease the rate of reaction.

Positive Catalyst ▷ A positive catalyst decrease the Ea Barrier. Thus Ea' will be less for both forward and backward rx^n.

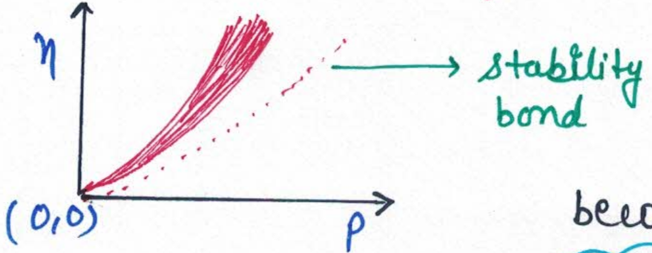
$$\left[K = Ae^{-Ea/RT}\right] \quad \left[K' = Ae^{-\frac{Ea'}{RT}}\right]$$

$$\boxed{\frac{K'}{K} = \left[e^{\frac{(E_a - E_a')}{RT}}\right]}$$

$$\boxed{K' > K}$$



Radioactivity is spontaneous decay of nuclei of any substance cause of radioactivity.



n/p ratio as the n/p ratio ↑es. the nucleus becomes unstable.

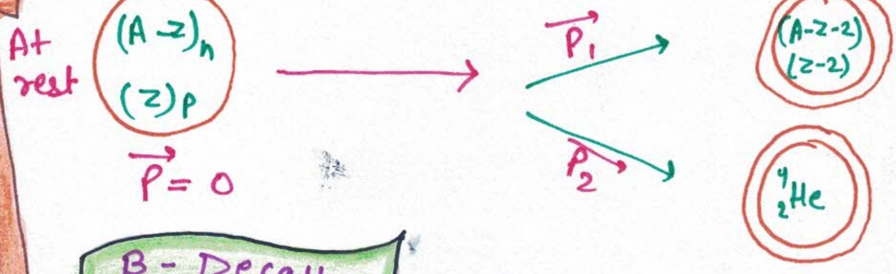
Always n/p = 1 doesn't mean = stable

We will have radioactive decay by which n/p ratio will lie into stability bond

α- Decay

n/p ratio will ↑es.

$$X_Z^A \xrightarrow{\alpha\text{-Decay}} Y_{Z-2}^{A-Y} + He_2^4$$ [maximum amount]



In α- Decay mass no. is reduced by 4 and an atomic No. is reduced by 2.

β - Decay

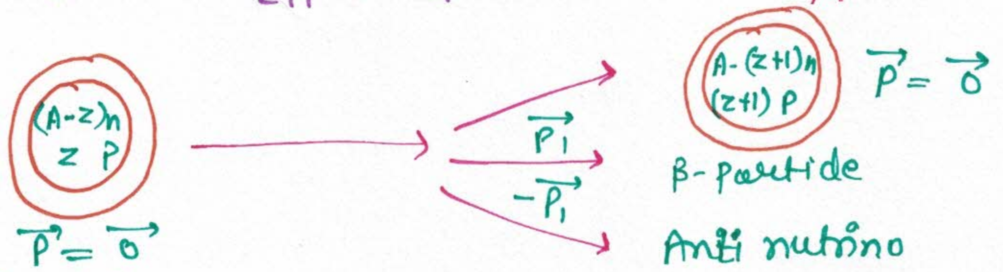
$$_0^1n \longrightarrow {}_{-1}^{0}e + p_1^1$$

It has two Types :-

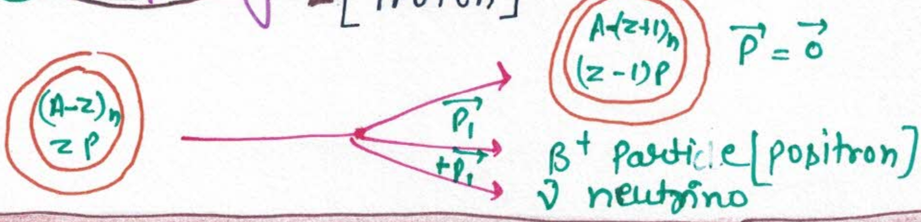
β⁻ decay → When nothing mentioned it is β-decay

$$_0^1n \longrightarrow {}_1^1p + \beta_{-1}^0 + \bar{\nu}$$ → Anti nutrino

$$X_Z^A \longrightarrow X_{Z+1}^A + \beta_{-1}^0 + \bar{\nu}$$ → n/p ratio will decrease



β⁺ Decay → [Proton]



$$_1^1P \longrightarrow n_0^1 + \beta_{+1}^0 + \nu$$

$$X_Z^A \rightarrow Y_{Z-1}^A + \beta_{+1}^0 + \nu$$

Quest. $U^{238}_{92} \xrightarrow[4\beta]{3\alpha} ?$

Solutn $U^{226}_{86} \longrightarrow U^{226}_{90}$ [from 1 α - decay mass no. ↓es by 4 and atomic No. ↓es by 2.]

K-electron Capture

$e^{0}_{-1} + p^{1}_{1} \longrightarrow {}^{1}_{0}n$

${}^{0}e_{-1} + X^{A}_{Z} \longrightarrow X^{A}_{Z-1}$

γ- Decay

After α and β- decay nucleous become excited. It will relase energy in form of radiation. It is called γ-decay. No mass and energy Involved. Speed of the light is there.

Law of Radioactive Decay

If the 'N' is no. of radioactive nuclei present in a sample at a given instant of time, then the rate of decay will be proportional to 'N'

$\boxed{\text{Rate} \propto N} \Rightarrow -\frac{dN}{dt} \propto N \Rightarrow \boxed{-\frac{dN}{dt} = \lambda N}$ λ = Decay constant

$\boxed{N_t = N_0 e^{-\lambda t}}$

N_t = Remaining Nuclei
N_0 = Initial Nuclei
λ = Decay constant
t = time

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

Average Life

$$\left[\begin{aligned} N &= N_0 e^{-\lambda t} \\ dN &= N_0 e^{-\lambda t}(-\lambda)\,dt \end{aligned}\right]$$

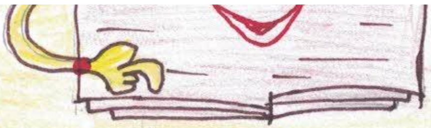
$$\frac{\int_0^\infty t\,dN}{\int_{N_0}^{0} dN} = \int_0^\infty \frac{t(N_0)e^{-\lambda t}\cdot(-\lambda)\,dt}{N_0} \Rightarrow \frac{-N_0 \int_0^\infty t e^{-\lambda t}\cdot dt}{N_0}$$

Average life $= -\lambda\left[-\frac{1}{\lambda^2}\right] \Rightarrow \frac{1}{\lambda}$ $\boxed{\text{Average life } Z = \frac{1}{\lambda}}$

Quest. What will be % remaing nuclei after avegage life

Ans. $-\frac{dN}{dt} = (\lambda)(N) \Rightarrow \int_{N_0}^{N_t} dN = -\lambda \int_0^{1/\lambda} dt \Rightarrow \ln\left(\frac{N_0}{N}\right) = 1$

$\left(N = \frac{N_0}{e}\right)$ % remaing $= \frac{1}{e} \times 100 \Rightarrow \frac{100}{2.718} = \boxed{36.3\%}$



$[A_0 = \lambda N_0]$

Activity :- Rate $= -\frac{dN}{dt} = \lambda N \Rightarrow A = -\frac{dN}{dt} \Rightarrow \lambda N_0 (e^{-\lambda t})$

$A = A_0 e^{-\lambda t} \Rightarrow R = R_0 e^{-\lambda t}$ → disintigration per second.

$N_t = N_0 (1/2)^n \Rightarrow R = R_0 (1/2)^n$

$1\,Ci = 3.7 \times 10^{10}$ dps
$1\,Bq = 1$ dps
$1\,Rd = 10^6$ dps.

Specific Activity:- It is defined for per gram radio active istope.

Special cases for radioactivity

Parallel radioactive Disintegration

$\lambda = \lambda_1 + \lambda_2$

$\frac{N_B}{N_C} = \frac{\lambda_1}{\lambda_2}$ $\left[\frac{1}{T} = \frac{1}{T_1} + \frac{1}{T_2}\right]$

$E_a = \frac{\lambda_1 E_{a_1} + \lambda_2 E_{a_2}}{\lambda_1 + \lambda_2}$; $(N_B)_t = \frac{\lambda N_0}{\lambda_1 + \lambda_2}\left(1 - e^{-(\lambda_1+\lambda_2)t}\right)$

$$\boxed{(N_C)_t = \frac{\lambda_2 N_0}{\lambda_1 + \lambda_2}\left(1 - e^{-(\lambda_1+\lambda_2)t}\right.}$$

Series radioactive disintegration

$[B]_{max} = t = \left[\frac{\ln\lambda_2 - \ln\lambda_2}{\lambda_2 - \lambda_1}\right]$

$$A \xrightarrow{\lambda_1} B \xrightarrow{\lambda_2} C$$

Series	Name of series	Initial element	final element	Nature of series	No. of α, β emittion
4n + 2	Uranium Series	$_{92}U^{238}$	$_{82}Pb^{206}$	Natural	8α 6β
4n+3	Actinium series	$_{92}U^{235}$	$_{82}Pb^{207}$	Natural	7α 6β
4n	Thorium	$_{90}U^{232}$	$_{82}Pb^{208}$	Natural	6α 4β
4n+1	Neptunium	$_{93}U^{237}$	$_{82}Pb^{208}$	Natural	7α 4β

Age determination

Age of Rock

$U^{238} \longrightarrow Pb^{206}$ $(t_{1/2})_{uranium} = 4.5 \times 10^9$ years.

$N_0 = U + Pb$ $N_t = U$

$-\lambda(t) = \ln(N_t/N_0) \Rightarrow (t) = \frac{1}{\lambda}\ln(N_0/N_t)$

$$\boxed{t = \left(\frac{t_{1/2}}{\ln 2}\right)\ln\left(1 + Pb/U\right)}$$

Age of Wood (Carbon-Dating method):- ^{14}C is radioactive element. Ratio of $^{14}C/C^{12}$.

We find the ratio in the fresh wood and in the ratio in the old wood.

$$\boxed{t = \left[\frac{(t_{1/2})_{C^{14}}}{\ln 2}\right]\ln\frac{\text{Ratio fresh}}{\text{Ratio old}}}$$

There are two type of radioactive reaction:-

Nuclear fission → when a heavy nuclear breaks into small nuclei, an exothermic reaction occurs.

$$n_0^1 + U_{92}^{235} \longrightarrow {}^{92}_{36}Kr + {}^{141}_{56}Ba + 3n_0^1 + Heat$$

(Krypton) (Barium

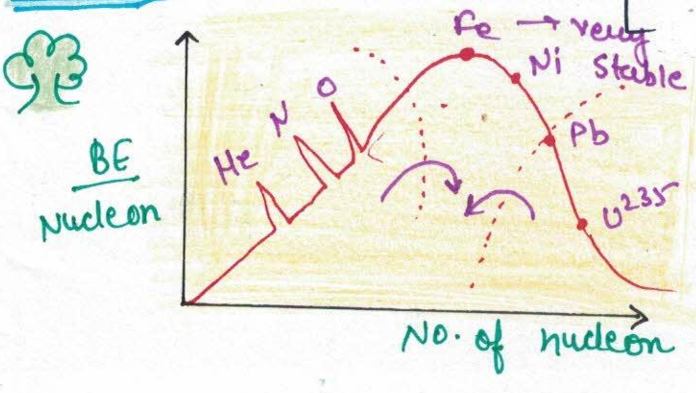
Nuclear fussion → when a small nuclear get fused to make a large nucleus. This reaction is also Exothermic

Mass Defect:- $\Delta m = [Zm_e + Zm_p + (A-Z)m_n] - \text{Atomic mass}$

energy associated with this mass $= (\Delta mc^2)$

Question If mass defect is 1.6×10^{-27} (1amu) B.E = ?

Solution $E = \Delta mc^2 = \left[\frac{1.6\times10^{-27}\times(3\times10^{8})^2}{1.6\times10^{-19}}\right]eV = \boxed{931 MeV}$



NOTE

Magic No are [2, 8, 20, 50, 82, 126) If the no. of nucleon are equal then the nucleous is stable. Generally nucleus contain even no of nucleon are stable.