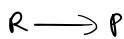


Rate of reaction

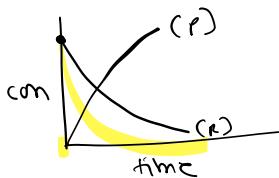
$\gamma = \frac{\text{change in conc. of any one of the reactant/product}}{\text{time}}$

units of rate =  $\text{M L}^{-1} \text{T}^{-1}$

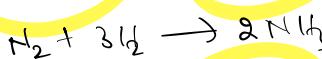


$$\text{Avg. rate} = -\frac{\Delta [R]}{\Delta t} = \frac{\Delta (P)}{\Delta t}$$

$$\text{Instantaneous rate} = -\frac{d(R)}{dt} = \frac{d(P)}{dt}$$

\* Rate expression

$$-\frac{1}{a} \frac{\Delta(A)}{\Delta t} = -\frac{1}{b} \frac{\Delta(B)}{\Delta t} = \frac{1}{c} \frac{\Delta(C)}{\Delta t}$$



$$-\frac{\Delta(N_2)}{\Delta t} = -\frac{1}{3} \frac{\Delta(H_2)}{\Delta t} = \frac{1}{2} \frac{\Delta(NH_3)}{\Delta t}$$

\* In the combustion of  $S_0_2$ , if the rate of disappearance of oxygen is  $2 \times 10^{-2} \text{ mol.lit}^{-1} \text{s}^{-1}$  then what would be the rate of appearance of  $S_0_3$ ?



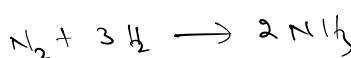
$$-\frac{1}{2} \frac{\Delta(S_0_3)}{\Delta t} = -\frac{1}{1} \frac{\Delta(O_2)}{\Delta t} = \frac{1}{2} \frac{\Delta(S_0_2)}{\Delta t}$$

$$\text{given, } -\frac{\Delta(O_2)}{\Delta t} = 2 \times 10^{-2}$$

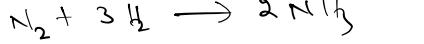
$$\frac{1}{1} \times 2 \times 10^{-2} = \frac{1}{2} \times \frac{\Delta(S_0_2)}{\Delta t}$$

$$\frac{\Delta(S_0_3)}{\Delta t} = 2 \times 2 \times 10^{-2} = 4 \times 10^{-2} \text{ M L}^{-1} \text{ s}^{-1}$$

\* In the Haber's process, if the rate of appearance of ammonia is  $4 \times 10^{-4} \text{ m}^{-1} \text{s}^{-1}$  then what will be the rate of disappearance of  $H_2$ ?



$$-\frac{1}{3} \frac{d(H_2)}{dt} = \frac{1}{2} \frac{d(NH_3)}{dt}$$

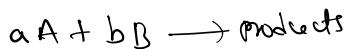


$$-\frac{1}{3} \frac{d(H_2)}{dt} = \frac{1}{2} \frac{d(NH_3)}{dt}$$

$$-\frac{1}{3} \frac{d(H_2)}{dt} = \frac{1}{2} \times 4 \times 10^{-4}$$

$$-\frac{d(H_2)}{dt} = \frac{3}{2} \times 4 \times 10^{-4} \Rightarrow 6 \times 10^{-4} \text{ mol s}^{-1}$$

\* Law of mass action :— By Waage & Guldberg



$$r \propto (A)^a (B)^b - \text{law of mass action}$$

$$r = k(A)^a (B)^b$$

$k$  = rate constant — dependent on temperature and activation energy

$a+b$  = order of reaction

units of  $k$  will be dependent on overall order of reaction.

$$\text{For } n\text{th order, } k = m^{\frac{1}{n}} L^{n-1} T^{-1}$$

$$\text{For zero order, } k = m^{-1} T^{-1} \Rightarrow \text{units of rate}$$

$$\text{For first order, } k = T$$

$$\text{For second order, } k = m^{\frac{1}{2}} L T^{-1}$$

practically, order can be +ve, -ve, zero & fraction

\* practical determination of rate law & order :—

Initial rate method is useful to determine order of reaction

Eg if consider the following practical data for the reaction  $2A + B \rightarrow P$

Exp.-No	[A] in mol/L	[B] mol/L	rate ( $\text{mol s}^{-1}$ )
①	0.1	0.1	$2 \times 10^{-4}$
②	0.2	0.1	$8 \times 10^{-4}$
③	0.2	0.2	$16 \times 10^{-4}$

Find the rate law and overall order of reaction

$$\text{let, } r = k(A)^a (B)^b$$

$$\frac{②}{①} = \frac{8 \times 10^{-4}}{2 \times 10^{-4}} = \frac{k(0.2)^a (0.1)^b}{k(0.1)^a (0.1)^b}$$

$$4 = \frac{(0.2)^a}{(0.1)^a}$$

$$\frac{③}{②} = \frac{16 \times 10^{-4}}{8 \times 10^{-4}} = \frac{k(0.2)^a (0.2)^b}{k(0.2)^a (0.1)^b}$$

$$\frac{1}{2} = 2^b$$

$$2^{-1} = 2^b$$

$$4 = \frac{c}{(0.1)^a}$$

$$4 = 2^a$$

$$a = 2$$

$$\text{rate law} = r = k(A)^a(B)^{-1}$$

$$\text{order of reaction} = 2 - 1 = 1$$

$$2^{-1} = 2^b$$

$$b = -1$$

[ ]

\* Find the order & rate law for the reaction  $2A + 3B + C \rightarrow P$  with following data:

exp. No	[A] m/L	[B] m/L	[C] m/L	Rate (mL <sup>-1</sup> s <sup>-1</sup> )
①	0.1	0.1	0.1	0.8
②	0.4	0.1	0.1	1.6
③	0.1	0.2	0.1	0.8
④	0.1	0.2	0.2	0.4

$$r = k(A)^a(B)^b(C)^c$$

$$\frac{\textcircled{2}}{\textcircled{1}} = \frac{1.6}{0.8} = (4)^a \quad \frac{\textcircled{3}}{\textcircled{1}} = \frac{0.8}{0.8} = 2^b \quad \frac{\textcircled{4}}{\textcircled{3}} = \frac{0.4}{0.8} = 2^c$$

$$2 = 4^a \quad 1 = 2^b \quad \frac{1}{2} = 2^c$$

$$a = \frac{1}{2} \quad b = 0 \quad c = -1$$

$$\text{rate law} = r = k(A)^{\frac{1}{2}}(B)^0(C)^{-1}$$

$$\therefore r = k(A)^{\frac{1}{2}}(C)^{-1}$$

$$\text{order of reaction} = \frac{1}{2} - 1 = -\frac{1}{2}$$

\* The reaction  $a+b \rightarrow c$  having rate law  $r = k(a)^{\frac{v}{2}}(b)^{\frac{1}{2}}$ .

If the concentration of  $a$  is doubled then rate will be

- (1) increase by 4 times   (2) decrease by 4 times  
 (3) increase by 2 times   (4) decrease by 2 times.

$$r_1 = k(a)^{\frac{v}{2}}(b)^{\frac{1}{2}}$$

$$r_2 = k(2a)^{\frac{v}{2}}(b)^{\frac{1}{2}}$$

$$r_2 = 2^{\frac{v}{2}} \cdot k(a)^{\frac{v}{2}}(b)^{\frac{1}{2}}$$

$$r_2 = 4 \cdot r_1$$

\* The rate of reaction  $A+B \rightarrow C$  is quadrupled when the

\* The rate of reaction  $A+B \rightarrow C$  is quadrupled when the concentration of A is doubled and rate become 16 times when concentrations of both A & B are doubled. Then the order of reaction will be —

- ① 1    ② 2    ③ 3    ④ 4

$$r_1 = k(A)^a(B)^b$$

$$4r_1 = k(2A)^a(B)^b$$

$$4r_1 = 2^a k(A)^a(B)^b$$

$$4r_1 = 2^a r_1$$

$$4 = 2^a$$

$$a=2$$

$$16r_1 = k(2A)^a(2B)^b$$

$$16r_1 = k(2A)^2(2B)^b$$

$$16r_1 = 4 \times 2^b \times k(A)^2(B)^b$$

$$16 = 4 \times 2^b$$

$$4 = 2^b$$

$$b=2$$

$$\text{order} = 2+2 = 4$$

\* The volume of vessel which contain gaseous reactants with rate law  $r = k(A)^{\frac{1}{2}}(B)^3$  is doubled. Then the rate of reaction will become —

- ①  $\frac{1}{4}$  times    ④  $\frac{1}{32}$  times    ③ 4 times    ⑤ 32 times.

$$r_1 = k(A)^{\frac{1}{2}}(B)^3$$

$$r_2 = k\left(\frac{A}{2}\right)^{\frac{1}{2}}\left(\frac{B}{2}\right)^3$$

$$r_2 = \left(\frac{1}{2}\right)^{\frac{1}{2}} \times \left(\frac{1}{2}\right)^3 \cdot k(A)^{\frac{1}{2}}(B)^3$$

$$r_2 = \frac{1}{32} r_1$$

\* The rate constant of  $2A+B \rightarrow C$  is  $2 \times 10^{-4} \text{ mol}^{-1} \text{ lit}^{-1} \text{ s}^{-1}$ . Then find the most appropriate rate law of the reaction from the following:

- ①  $r = k(A)(B)$     ②  $r = k(A)^{\frac{1}{2}}(B)$     ③  $r = k(A)^{\frac{1}{2}}(B)^{\frac{3}{2}}$

$$④ r = k(A)^3(B)^{-2}$$

Based on units of  $k$ ,  $\text{order} = 2 \therefore \text{③ is correct } \frac{1}{2} + \frac{3}{2} = 2$

\* For a chemical reaction  $A+B \rightarrow \text{product}$ , the order is 1 with respect to A and B.

rate (mol.lit <sup>-1</sup> s <sup>-1</sup> )	$(A)$ mol.lit <sup>-1</sup>	$(B)$ mol.lit <sup>-1</sup>
0.1	20	0.5
x	y	0.5

0.1	20	0.5
0.4	X	
0.8	40	Y

Find x & y values

- ① 80, 2    ② 40, 4    ③ 80, 4    ④ 160, 4

$$\textcircled{2} \frac{\textcircled{1}}{\textcircled{1}} = \frac{0.4}{0.1} = \frac{x^1 \times 0.4^1}{20^1 \times 0.1^1} \quad \textcircled{3} \frac{\textcircled{2}}{\textcircled{2}} = \frac{0.8}{0.4} = \frac{40^1 \times y^1}{80^1 \times 0.4^1}$$

$$4 = \frac{x}{20} \quad y = \frac{40 y^1}{40}$$

$$x = 80 \quad y = 2$$

\* Find the units of rate constant for the following rate laws:

① $r = k(A)^{\frac{1}{2}}(B)^{\frac{1}{2}}$	② $r = k(A)^{\frac{1}{2}}(B)^{\frac{1}{2}}$	③ $r = k(A)^{\frac{1}{2}}(B)^{\frac{1}{2}}(C)^{\frac{1}{4}}$
$\delta \Delta n = \frac{1}{2} + 2 = \frac{5}{2}$	$\delta \Delta n = 1 - 1 = 0$	$\delta \Delta n = \frac{1}{2} + \frac{1}{2} + \frac{1}{4} = \frac{5}{4}$
$k = m^{1-n} L^{-n} T^{-1}$	$k = m^{1-0} L^{0-1} T^{-1}$	$k = m^{1-\frac{5}{4}} L^{\frac{5}{4}-1} T^{-1}$
$= m^{-\frac{3}{2}} L^{\frac{3}{2}} T^{-1}$	$= m^{\frac{1}{2}} T^{-1}$	$= m^{-\frac{1}{4}} L^{\frac{1}{4}} T^{-1}$

\* collision theory → by max trautz and william lewis



- ① There must be collisions between reactant molecules to form products.
- ② In any typical gas phase reaction, the collision frequency will be in very high order.
- ③ But, all the collisions does not lead to the formation of products. only few collisions will form products at ordinary conditions. Those collisions are called fruitful/effective collisions.
- ④ Reactant molecules must have some energy to have effective collisions which is called threshold energy.
- ⑤ The fraction of molecules having threshold energy are very less at ordinary conditions.
- ⑥ so, reactant molecules must absorb some extra energy to reach threshold energy barrier. That is called activation energy ( $E_a$ )

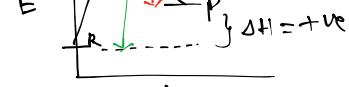
Energy profile diagrams :-





Reaction progression  
exothermic

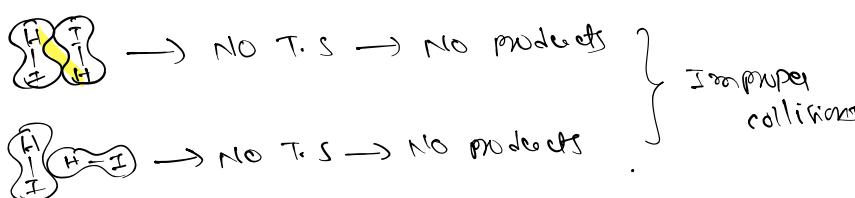
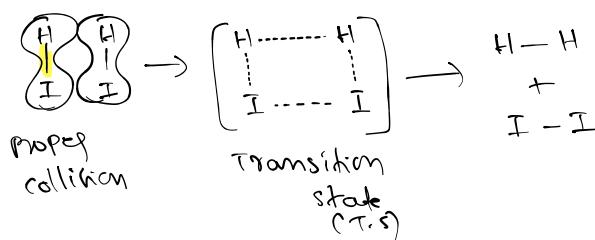
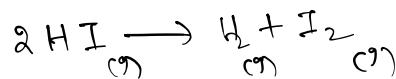
$E_a$  of forward <  $E_a$  of backward  
 $\Delta H = -ve$  ( $\because E_p < E_R$ )



Reaction  
progression  
Endothermic

$E_a$  of forward >  $E_a$  of backward  
 $\Delta H = +ve$  ( $\because E_p > E_R$ )

Orientation factor :



collision b/w reactant molecules must be done in proper orientation to form products.

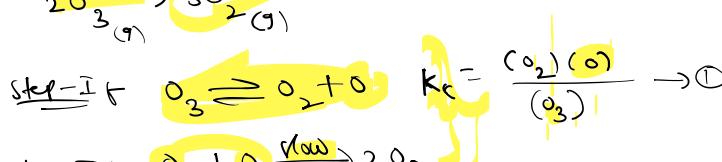
The complex reactions will not complete in single step. They will proceed through multiple steps in which the slowest step is called rate determining step (rds).

The no. of molecules involved in rds is called molecularity. which is always a non-zero positive integer.

order vs molecularity

order	molecularity
Practical	Theoretical
can be +ve, -ve, 0, fraction	only non-zero positive integer.

\* consider the following mechanism for the decomposition of ozone



then find the rate law and order of decomposition of ozone





$$r = k [O_3] [O]$$

From ①  $\Rightarrow [O] = \frac{k_c \cdot [O_3]}{[O_2]}$  — sub. in above rate (as)

$$r = k [O_3] \cdot k_c \frac{[O_3]}{[O_2]}$$

$$r = k [O_3]^2 [O_2]$$

$$\delta n = 2 - 1 = 1$$

### \* Factors affecting rate of reaction :

① concentration of reactants  $\rightarrow$  rate  $\propto$  (Reactants)

② Nature of reactants  $\rightarrow$  reactions with different reactants will have different energies. so, rates also different

③ physical state of reactants  $\rightarrow$  rate in gas phase > liquid phase > solid phase.

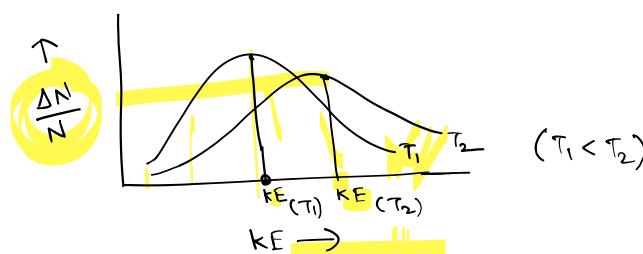
In solid phase, rate in powder form (fine form) is more when compared with bulk form (coarse form). since, in finely divided form surface area is more.

④ physical form  $\rightarrow$  different physical forms will have different energy. so, rates will be different.

E.g. white-p is more reactive than red-p

⑤ Temperature :— rate  $\propto$  temp.

Effect of temp. on rate of reaction can be studied by using maxwell-Boltzmann distribution curves.



From the above graph,

(i) Fraction of molecules having very low KE and very high KE is less at given temp.

(ii) If temp. is increased, fraction of molecules have low KE decrease and fraction of molecules having high KE increase i.e. fraction of fruitful collisions will increase

Fraction of fruitful collisions will increase

(ii) Area under the curve remains same even though temp. is changed

(iv) For every  $10^\circ$  raise in temp. fraction of molecules having threshold energy will be doubled (sometimes tripled). Hence, For every  $10^\circ$  raise rate of reaction also will be doubled or tripled.

$$u_T = \frac{k_{T+10}}{k_T} = 2 \text{ or } 3 = \text{Temp. coefficient}$$

$$\frac{k_2}{k_1} = (u_T)^{\frac{10}{T_2 - T_1}}$$

$k_2$  = rate constant at  $T_2$  (higher temp)

$k_1$  = rate constant at  $T_1$  (lower temp)

Arrhenius equation

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

$$A = \text{Pre-exponential factor} = P \cdot Z_{AB}$$

P = orientation/probability/steric factor

$Z_{AB}$  = collision frequency

$E_a$  = Activation energy

$e^{-\frac{E_a}{RT}}$  = fraction of molecules having energy  $\geq$  Activation energy

$$K = P \cdot Z_{AB} \cdot e^{-\frac{E_a}{RT}}$$

units of A = units of K = depends upon order of reaction

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

$$\ln k = \ln A - \frac{E_a}{R} \left( \frac{1}{T} \right)$$

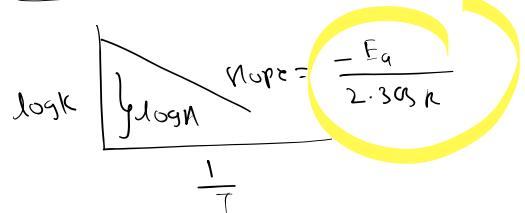
$$\ln k \quad \text{Nlope} = -\frac{E_a}{R}$$

$$\ln k = \ln A - \frac{E_a}{R} \left( \frac{1}{T} \right)$$

$$2.303 \log k = 2.303(\log A - \frac{E_a}{R} \left( \frac{1}{T} \right))$$

$$\ln k_1 - \ln k_2 = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\log k = \log A - \frac{E_a}{2.303 R} \left( \frac{1}{T} \right)$$



let,  $k_1$  = rate constant at  $T_1$  temp.

$$\log k_1 = \log A - \frac{E_a}{2.303 R} \left( \frac{1}{T_1} \right) \rightarrow ①$$

$k_2$  = rate constant at  $T_2$  temp.

$$\log k_2 = \log A - \frac{E_a}{2.303 R} \left( \frac{1}{T_2} \right) \rightarrow ②$$

$$② - ① = \log \left( \frac{k_2}{k_1} \right) = \frac{E_a}{2.303 R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Note if  $E_a$  can't be -ve & zero.

### \* Numerically ↴

$$① \text{ For the reaction } A \rightarrow B \quad k_1 = 10 e^{-\frac{15}{T}} \\ C \rightarrow D \quad k_2 = 10 e^{-\frac{16}{T}}$$

Then find the temp. at which both rate constants become equal.

$$k_1 = k_2$$

$$10 e^{-\frac{15}{T}} = 10 e^{-\frac{16}{T}}$$

$$\frac{10^{-15}}{10^{-16}} = \frac{e^{-\frac{16}{T}}}{e^{-\frac{2000}{T}}}$$

$$10 = e^{\frac{-16}{T} + \frac{2000}{T}}$$

$$10 = e^{\frac{1000}{T}}$$

$$\ln 10 = \frac{1000}{T}$$

$$2.303 \log 10 = \frac{1000}{T}$$

$$2.303 = \frac{1000}{T}$$

$$T = \frac{1000}{2.303} \approx 434 \text{ K}$$

$$T = \frac{1000}{2.303} \approx 434 \text{ K}$$

\* The rate constant of a reaction is  $k_1$  at  $10^\circ\text{C}$  and  $k_2$  at  $100^\circ\text{C}$ . Then the correct relation between  $k_1$  and  $k_2$  is —

- ①  $k_1 = 10k_2$  ②  $k_2 = 10k_1$  ③  $k_2 = 512k_1$  ④  $k_2 = 18k_1$

$$\frac{k_2}{k_1} = (e^{\frac{E_a}{RT}})^{\frac{T_2 - T_1}{10}} = 2^{\frac{100 - 10}{10}} = 2^9$$

$$k_2 = 2^9 k_1$$

\* The rate of reaction was quadrupled by raising the temp. from  $300\text{K}$  to  $400\text{K}$ . Then find the activation energy of that reaction. ( $\log 2 = 0.3$ ,  $R = 8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ )

$$\log \left( \frac{k_2}{k_1} \right) = \frac{E_a}{2.303 R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

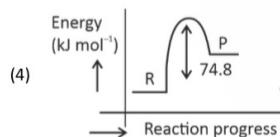
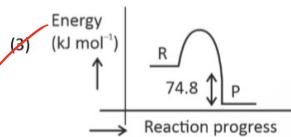
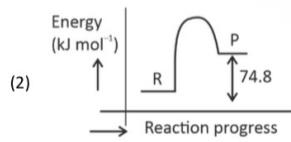
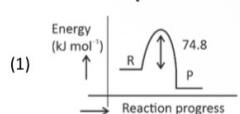
$$\log 4 = \frac{E_a}{2.303 \times 8.314} \left( \frac{1}{300} - \frac{1}{400} \right)$$

$$0.6 = \frac{E_a}{2.303 \times 8.314} \left( \frac{400 - 300}{400 \times 300} \right)$$

$$E_a = \frac{0.6 \times 2.303 \times 8.314 \times 400 \times 300}{100}$$

$$E_a = 13786 \text{ J} = 13.786 \text{ kJ}$$

64.  $\text{C(s)} + 2\text{H}_2\text{(g)} \rightarrow \text{CH}_4\text{(g)}$ ;  $\Delta H = -74.8 \text{ kJ mol}^{-1}$ . Which of the following diagrams gives an accurate representation of the above reaction? [R → reactants; P → products]



\* Activation energy of any chemical reaction can be calculated if one knows the value of

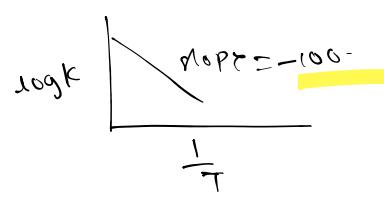
- ① rate constant at standard temp.

- ② probability of collision

- ③ orientation of reactants during collisions

- ↵ probability of collision  
 ③ orientation of reactants during collisions  
 ↵ rate constant at two diff. temp-

\* consider the following graph:



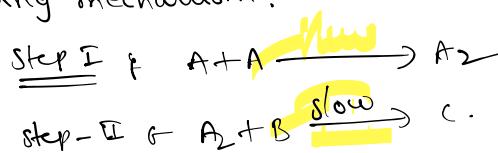
Then the activation energy of that reaction is —

$$\text{slope} = \frac{-E_a}{2.303R} = -100$$

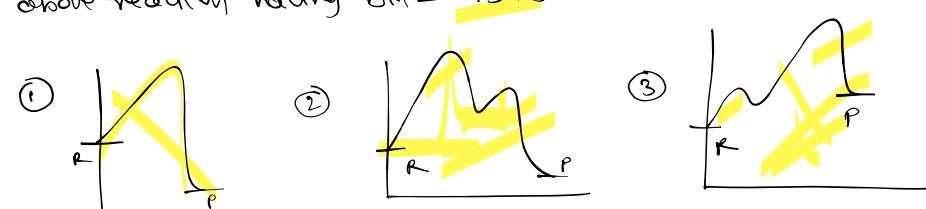
$$E_a = 100 \times 2.303 \times 8.314$$

$$E_a = 1915 \text{ J}$$

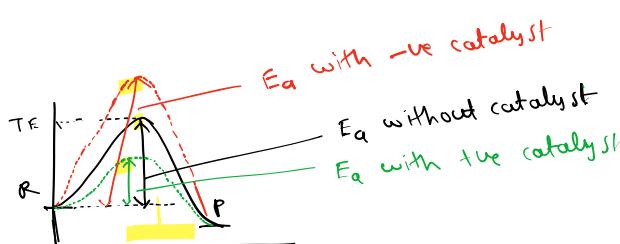
\* consider the reaction  $2A + B \rightarrow C$  which is having the following mechanism:



Then choose the most appropriate energy profile diagram of above reaction having  $\Delta H = -73 \text{ kJ}$



### ⑤ Effect of catalyst $\leftarrow R \rightarrow P$



catalyst will alter the rate of reaction by forming a complex with reactants in an alternate path in which activation energy is different.

activation energy is different.

### characteristics of catalyst :

- ① catalyst will not change the energy of reactants / products
- ② catalyst will not change  $\Delta H$  of reaction
- ③ catalyst will never initiate the reaction
- ④ catalyst will never alter the yield of products.
- ⑤ positive catalyst will increase the rate of reaction by decreasing activation energy. on the other hand, negative catalyst will decrease the rate of reaction by increasing activation energy.

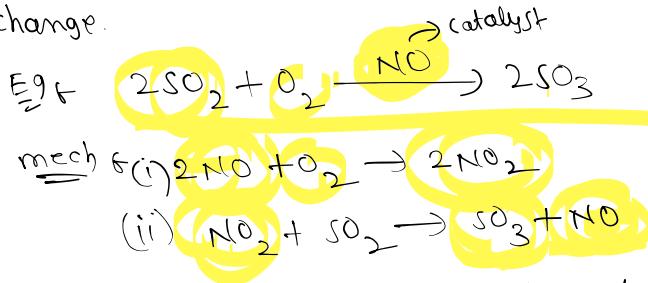
- ⑥ chemical substances which enhance the catalyst power are called promoters. In case of enzymes, promoters are called co-enzymes.

Eg: Mo will be used as promoter to increase the power of Fe-catalyst in Haber's process

- ⑦ chemical substances which will decrease the catalyst activity are called poisons. In case of enzymes, poisons are also called inhibitors.

Eg:  $\text{BaSO}_4$  will be used as poison of pd-catalyst during hydrogenation of alkynes.

- ⑧ catalyst may/may not participate in chemical reaction. If catalyst participated in the chemical reaction then it will come in the last step without any permanent chemical change.

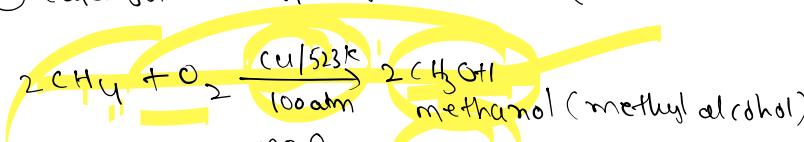


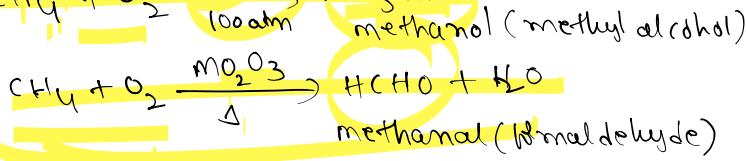
- ⑨ As there is no net consumption of catalyst, small amount of catalyst is enough to catalyse reaction.

- ⑩ catalysts can be effected by temperature &  $P^H$ .

For enzymes, the optimum conditions are :  $35 - 40^\circ\text{C}$ ,  $P^H = 5 \text{ to } 7.5$

- ⑪ catalysts are specific in nature





\* Integrated rate law : study of variation in concentration of reactants as a function of time



$$t=0 \quad a = (R^0)$$

$$t=t \quad a-x = (R^t)$$

$$\text{rate} = -\frac{d(R)}{dt} = -\frac{d(a-x)}{dt}$$

$$= -\frac{da}{dt} + \frac{dx}{dt}$$

$$= 0 + \frac{dx}{dt}$$

$$\text{rate} = \frac{dx}{dt}$$

zero order reactions :- rate is independent on reactant concentration

$$r = k(R)^0$$

$$\frac{dx}{dt} = k$$

$$dx = k \cdot dt$$

$$\int dx = k \int dt$$

$$x = kt + c \rightarrow ①$$

apply initial conditions to find the value of c.

At initial condition,  $t=0, x=0$  - sub. in ①

$$x = kt + 0$$

$$\therefore x = kt$$

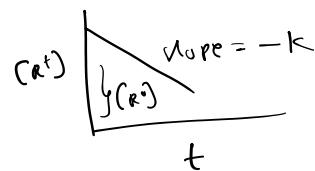
$$k = \frac{x}{t}$$

$$k = \frac{a - (a-x)}{t}$$

$$k = \frac{(R^0) - (R^t)}{t}$$

$$kt = (R^0) - (R^t)$$

$$(R^t) = (R^0) - kt$$



Half-life ( $t_{1/2}$ )

Half-life ( $t_{\frac{1}{2}}$ )

$$t = \frac{x}{k}$$

If  $t = t_{\frac{1}{2}}$  then  $x = \frac{a}{2}$

$$\boxed{t_{\frac{1}{2}} = \frac{a}{2k}}$$

$t_{\frac{1}{2}} \checkmark$

$$t_{\frac{1}{2}} \propto a$$

If  $t = t_{100\%}$  then  $x = a$

$$\boxed{t_{100} = \frac{a}{k}}$$

$$\boxed{t_{100} = 2 \times t_{\frac{1}{2}}}$$

$\therefore$  zero order have two half-lives

Eg - In general, catalytic and photochemical reactions will follow zero order kinetics.

- (i) Decomposition of ammonia over platinum surface at high pressure
- (ii) Thermal decomposition of H<sub>2</sub>I over gold surface.

### \*First order $\gamma$

$$\gamma = k(R)^1$$

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

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

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

$$-\ln(a-x) = kt + c \rightarrow ①$$

If  $t=0$  then  $x=0$

$$\therefore -\ln(a-0) = k(0) + c$$

$$\therefore c = -\ln a - \text{sub. in } ①$$

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

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

$$\boxed{kt = \ln \frac{(R^0)}{(R^t)}}$$

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

$$\boxed{kt = 2.303 \log \frac{(R^0)}{(R^t)}}$$

$$kt = 2 \cdot 305 \log \frac{(\text{R}_0)}{(\text{R}_t)}$$

Half-life

$$t = \frac{1}{k} \ln \frac{a}{a-x}$$

If  $t = t_{\frac{1}{2}}$  then  $x = \frac{a}{2}$

$$t_{\frac{1}{2}} = \frac{1}{k} \ln \frac{a}{a-\frac{a}{2}}$$

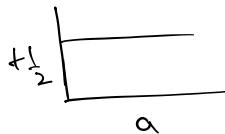
$$t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

$$t_{\frac{1}{2}} = \frac{2 \cdot 305 \log 2}{k}$$

$$t_{\frac{1}{2}} = \frac{2 \cdot 305 \times 0.3010}{k}$$

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

i.e.  $t_{\frac{1}{2}}$  of first order kinetics is independent on initial concentration.

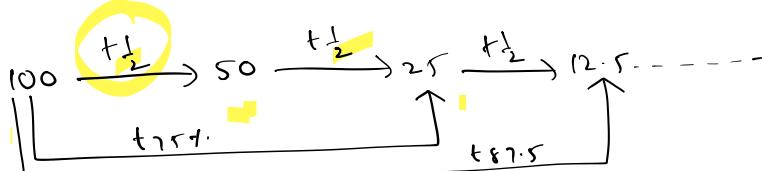


$t_{100\%}$  If  $t = t_{100\%}$ , then  $x = a$

$$t_{100} = \frac{1}{k} \ln \frac{a}{a-a}$$

$$t_{100} = \infty$$

∴ 1st order reactions will have infinite no. of half-lives.



$$t_{75} = 2 \times t_{\frac{1}{2}}$$

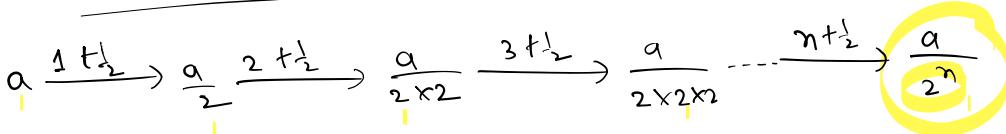
$$(a) \quad t_{\frac{3}{4}} = 2 \times t_{\frac{1}{2}}$$

$$t_{87.5} = 3 \times t_{\frac{1}{2}}$$

$$(b) \quad t_{\frac{7}{8}} = 3 \times t_{\frac{1}{2}}$$

$$t_{99.9} = 10 \times t_{\frac{1}{2}}$$

$$t_{100} = \infty \times t_{\frac{1}{2}}$$



Amount of reactant left after  $n$ -half-lives =  $\left(\frac{1}{2}\right)^n a$

Amount of reactant left after n-half-lives =  $\left(\frac{1}{2}\right)^n$

Fraction of reactant left after n-half-lives =  $\left(\frac{1}{2}\right)^n$

Amount of reactant consumed in n-half-lives =  $\underbrace{\left[1 - \left(\frac{1}{2}\right)^n\right] a}_{\text{fraction}}$

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

$$\frac{t_1}{t_2} = \frac{\log \left( \frac{a}{a-x_1} \right)}{\log \left( \frac{a}{a-x_2} \right)}$$

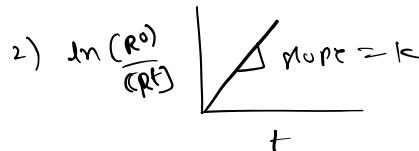
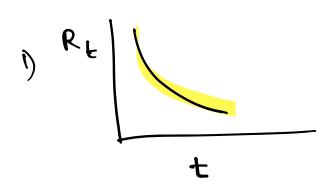
### Graphs of first order r

$$\textcircled{1} \quad kt = \ln \left( \frac{R^0}{R^t} \right)$$

$$e^{kt} = \frac{(R^0)}{(R^t)}$$

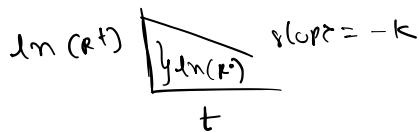
$$\frac{(R^t)}{(R^0)} = e^{-kt}$$

$$(R^t) = (R^0) e^{-kt}$$



$$\textcircled{3} \quad \ln(R^0) - \ln(R^t) = kt$$

$$\ln(R^t) = \ln(R^0) - kt$$



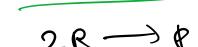
### Eg r

① All radioactive disintegrations

② Decomposition of  $N_2O_5$  and  $N_2O$

③ Hydrogenation of ethene

### second order r



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

$$kt = \left[ \frac{1}{(R^t)} - \frac{1}{(R^0)} \right]$$



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

For nth order ( $n \geq 2$ ) reaction  $nA \rightarrow P$

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

$$kt = \frac{(n-1)}{2} \left[ \frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right]$$

$$t_{\frac{1}{2}} = \frac{(n-1)}{2} \frac{1}{k(n-1)(R^*)^{n-1}}$$

$$t_{\frac{1}{2}} \propto \frac{1}{a^{n-1}}$$

For growth kinetics of first order,

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

### \* Numerically ↗

- ① The initial rate of a zero order reaction  $A \xrightarrow{\text{cat}} 2B_{(g)}$  is 0.02 mol lit<sup>-1</sup> min<sup>-1</sup>. If the initial concentration of A is 0.1M, find the concentration of B after 60s.

For zero order, rate = rate constant = 0.02



$$t=0 \quad a=0.1$$

$$t=1\text{min} \quad 0.1-x \quad 2x$$

$$\text{For zero order} = k = \frac{x}{t}$$

$$0.02 = \frac{x}{1}$$

$$x = 0.02$$

$$(B) = 2 \times 0.02 = 0.04$$

- ② Half life of a first order reaction is 69.3 min. Then find the time required for completion of 90% reaction.

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

$$t_{90} = \frac{2.303}{k} \log \frac{100}{100-90}$$

$$\text{For first order, } k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{69.3} = 10^{-2} \text{ min}^{-1}$$

$$t_{90} = \frac{2.303}{10^{-2}} \log 10$$

$$t_{90} = 2.303 \times 10^2 = 230 \text{ min}$$

- \* If 90% of first order reaction completes in 100min. Then find the time required for 99.9% completion

$$\frac{t_1}{t_2} = \frac{\log \left( \frac{a}{a-x_1} \right)}{\log \left( \frac{a}{a-x_2} \right)}$$

$$\frac{t_{90}}{t_{99.9}} = \frac{\log \left( \frac{100}{100-90} \right)}{\log \left( \frac{100}{100-99.9} \right)}$$

$$\frac{100}{t_{99.9}} = \frac{1}{3}$$

$$\frac{100}{t_{99.9}} = \frac{1}{3}$$

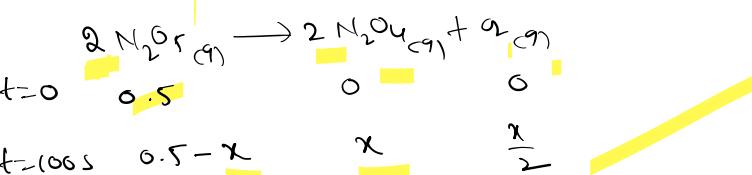
$$t_{99.9} = 300 \text{ min}$$

\* The following data obtained during thermal decomposition of  $\text{N}_2\text{O}_5$  at constant volume with first order kinetics:



SL. NO	time/s	Total pressure/atm
①	0	0.5
②	100	0.512

Then find the value of rate constant ( $\log 1.05 = 0.021$ )



$$\text{Total pressure at } 100s = 0.5 - x + x + \frac{x}{2} = 0.512$$

$$0.5 + \frac{x}{2} = 0.512$$

$$\frac{x}{2} = 0.012$$

$$x = 0.024$$

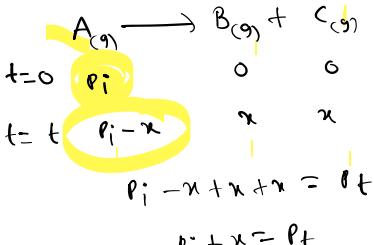
$$k = \frac{2.303}{100} \log \frac{0.5}{0.5 - 0.024}$$

$$k = \frac{2.303}{100} \log 1.05$$

$$k = \frac{2.303}{100} \times 0.021 = 4.8 \times 10^{-5} \text{ s}^{-1}$$

\* For the gaseous <sup>first order</sup> reaction  $A_{(g)} \rightarrow B_{(g)} + C_{(g)}$ , the initial pressure is  $P_i$  and after  $t$  time is  $P_t$ . Then which of the following rate law is correct for this equation?

$$① k = \frac{2.303}{t} \log \frac{P_i}{P_i - P_t}$$



~~②~~ 
$$k = \frac{2.303}{t} \log \frac{P_i}{2P_i - P_t}$$

$$③ k = \frac{2.303}{t} \log \frac{2P_i}{P_i - P_t}$$

$$k = \frac{2.303}{t} \log \frac{P_i}{P_i - x}$$

$$④ k = \frac{2.303}{t} \log \frac{2P_i}{2P_i - P_t}$$

$$k = \frac{2.303}{t} \log \frac{P_i}{P_i - (4-P_i)}$$

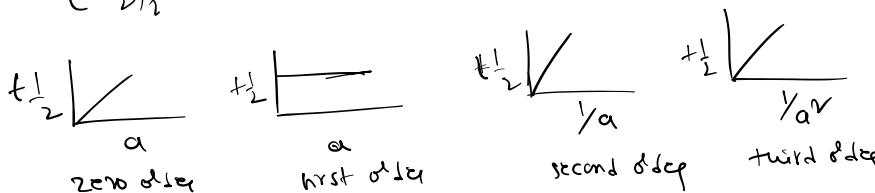
$$k = \frac{2.303}{t} \log \frac{P_i}{2P_i - P_t}$$

Note 6) In a reaction, if one reactant is taken in normal amounts, then rate of

Note 6) In a reaction, if one reactant is taken in normal amount and remaining in large excess amounts then rate of reaction will be dependent only on reactant taken in normal amount.

$$2) t_{\frac{1}{2}} \propto \frac{1}{a^{n-1}}$$

$$\left(\frac{t_{\frac{1}{2}}}{t_{\frac{1}{2}}}\right)_1 = \left(\frac{a_2}{a_1}\right)^{n-1} \quad (n = \text{deg})$$



\* The half-life of a reaction changes to urini from 16 min by doubling the initial concentration of reactant. Then find the order of that reaction.

① 2    ② 3    ③ 4    ④ 0

$$\left(\frac{t_{\frac{1}{2}}}{t_{\frac{1}{2}}}\right)_1 = \left(\frac{a_2}{a_1}\right)^{n-1}$$

$$\frac{16}{4} = \left(\frac{2}{1}\right)^{n-1}$$

$$4 = 2^{n-1}$$

$$n-1 = 2$$

$$n = 3$$

### \* Pseudo first order reactions

① Acidic hydrolysis of ester

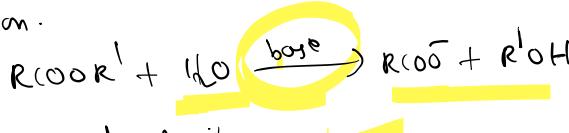


But,  $\text{Rate} \propto [\text{ester}]^1$

$$\text{order} = 1$$

As water is in excess, rate is independent on its concentration

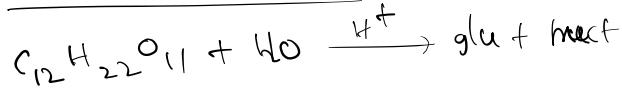
But, basic hydrolysis of ester is normal bi-molecular, second order reaction.



But,  $\text{Rate} \propto [\text{ester}][\text{base}]^1$

$$\text{order} = 2$$

② Inversion of cane sugar by



molecularity = 2

rate  $\propto (\text{Sucrose})^1$

order = 1