

Date | 19 | Aug | 2019

CHEMICAL KINETICS

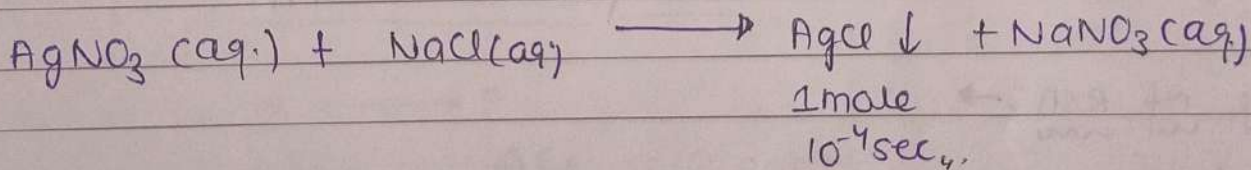
Deals with rate of reactions & the factors affecting reaction rate. It also help in determination of reaction mechanism.

The study of rate is macroscopic study & the study of mechanism is microscopic study of reaction.

Classification of Rxn.

① Macroscopic level (on basis of rate)

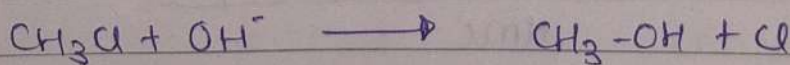
(i) Instantaneous or very fast rate



(ii) very slow rate:

Rusting of iron, Fermentation rxn.

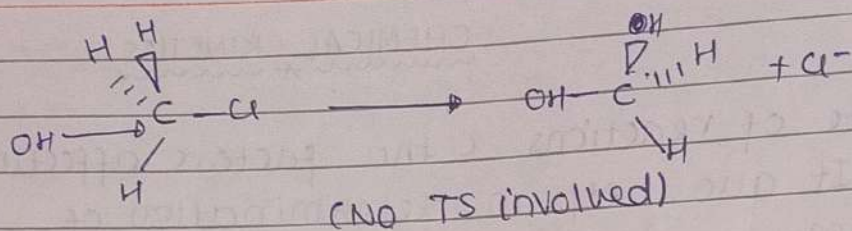
(iii) Moderate rxn: Neither too fast nor very slow.



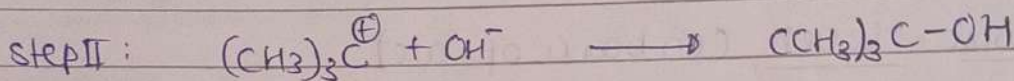
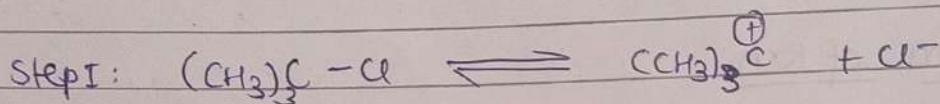
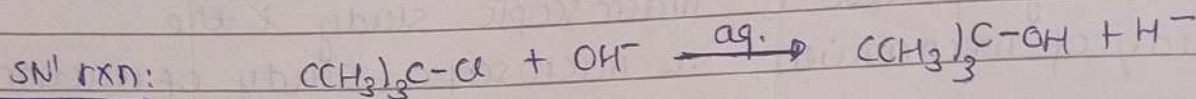
② Microscopic level: (on basis of mechanism)

① Simple or Elementary rxn: single step rxn.

Ex: SN^2 rxn



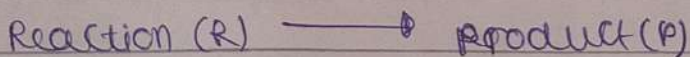
② Complex Rxn: Multi-step rxn



Intermediates are species other than reactant & product which are formed in rxn.

Rate of rxn: \rightarrow

It represents the change in amount of the reaction components per unit time.



$$r_{\text{rxn}} = \frac{\text{decrease in amount of R}}{\text{time}}$$

$$= \frac{\text{increase in amount of P}}{\text{time}}$$

The amount of components may be represented by mass, moles, molar concentration, partial pressure etc. Molar conc. & partial pressure should be used only when rxn is occurring at constant volume (which is normally maintained in kinetical analysis).

The rate is measured by measuring any observable property like mass, conc., partial pressure, total pressure, colour, optical rotation etc. which may be measured easily & accurately.

Expression of Rate: \rightarrow

① Average & instantaneous rate:

$$R \longrightarrow P$$

$$r_{\text{rxn}} = \frac{-\Delta C_R}{\Delta t} = \frac{\Delta C_P}{\Delta t}$$

$$\text{where } \frac{\Delta C}{\Delta t} = \frac{C_2 - C_1}{t_2 - t_1}$$

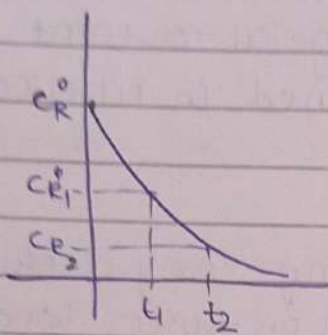
C_1 : moles conc. at t_1

C_2 : moles conc. at t_2

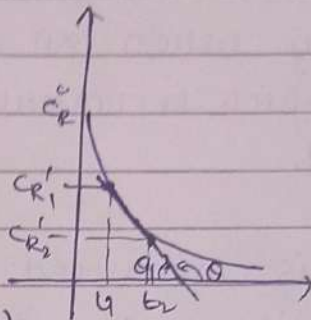
For most of the reaction rate decreases with time. The above expressions are only average rate in the given time interval.

At any time, the rate should be expressed as instantaneous rate.

$$r_{\text{inst}} = -\frac{dc_R}{dt} = \frac{dc_P}{dt}$$



(symbolic graph)



$$r_{\text{avg}} = \frac{c_{R_2} - c_{R_1}}{t_2 - t_1} \quad \text{Actual graph depends on order}$$

$$r_{\text{inst}} = -\frac{dc_R}{dt} = -\frac{c_{R_2} - c_{R_1}}{t_2 - t_1}$$

$$= \frac{c_{R_1} - c_{R_2}}{t_2 - t_1}$$

c_{R_1} is not on graph but on tangent.

• r_{inst} & r_{avg} ~~becomes~~ becomes equal

(i) order of rxn = 0

(ii) $\Delta t \rightarrow 0$

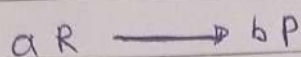
In each time interval, a time always exist at which instantaneous rate is equal to the average rate in that time interval.

② Different stoichiometric coefficient:



$$r_{\text{rxn}} = -\frac{dc_R}{dt} = \frac{dc_P}{dt}$$

If the coefficients are different than 1, the overall rate of reaction has no significance. The rate must be expressed in terms of individual components.



$$\text{Rate of disappearance of R} = r_R = -\frac{dc_R}{dt}$$

$$\text{Rate of appearance of P} = r_P = \frac{dc_P}{dt}$$

If required the overall rate of rxn is given as

Rate of individual component per unit stoichiometric coefficient.

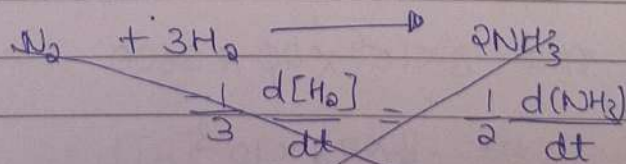
$$r_{\text{rate}} = \frac{1}{a} \frac{-dc_R}{dt} = \frac{1}{b} \frac{dc_P}{dt}$$

$$r_{\text{rate}} = \frac{r_R}{a} = \frac{r_P}{b}$$

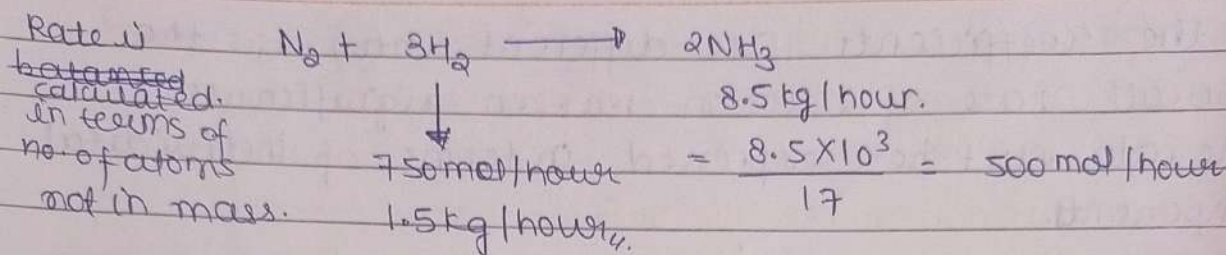
Ques. ① In the Haber's process, the rate of formation of ammonia gas is 8.5 kg/hour. What is the rate of consumption of H_2 gas.

HW
EX(1) LS
EX(2) LS
EX(3) SS

Soln:



$$\frac{d[H_2]}{dt} = \frac{-3}{2} \times 8.5 = -3 \times 4.25 = -12.75 \text{ kg/hour}$$



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Ques. For the reaction $2\text{A} + 3\text{B} \longrightarrow 5\text{C}$, the rate of disappearance of B is $1.2 \times 10^{-5} \text{ mol/L sec}$.

(i) What is the rate of rxn.

Solⁿ: $r = -\frac{1}{3} \frac{d[\text{B}]}{dt} = \frac{1}{3} \times 1.2 \times 10^{-5} = 0.4 \times 10^{-5} = 4 \times 10^{-6} \text{ mol L}^{-1} \text{ sec}^{-1}$

(ii) What is the rate of appearance of C.

Solⁿ $2 \times 10^{-5} \text{ mol/L sec}$. $r_{\text{rxn}} = \frac{1}{5} \frac{d[\text{C}]}{dt}$

(iii) If the rxn is occurring at constant volume of 20L at constant rate, how many moles of A will react in one hour.

Solⁿ $r_{\text{rxn}} = -\frac{1}{2} \frac{d[\text{A}]}{dt}$ $\frac{d[\text{A}]}{dt} = 8 \times 10^{-6} \text{ mol/L sec}$

$$n = 8 \times 10^{-6} \times 20 \times 3600$$

$$8 \times 72 \times 10^{-3}$$

$$496 \times 10^{-3}$$

$$= 0.496$$

Ques. For the reaction $2A \rightarrow 3B + \frac{1}{2}C$. The concentration of A at any time 't' is represented as

$$[A] = [A]_0 e^{-kt}$$

$[A]_0$: Initial concentration of A = 0.2 M

k : Constant = 10^{-3} sec^{-1} .

(i) What is concentration of A, B & C at $t = 1000 \text{ sec}$.

Solⁿ: $[A]_t = 0.2 e^{-10^{-3} \times 10^3} = 0.2 e^{-10} = \frac{0.2}{e^{10}} \text{ M}$

$$[B] = \frac{3}{2} [A]_0 - [A]_t = \frac{3}{2} \left[0.2 - \frac{0.2}{e^{10}} \right]$$

$$[C] = \frac{1}{4} \left[0.2 - \frac{0.2}{e} \right]$$

(ii) What is average rate of disappearance of A in first 1000 seconds.

Solⁿ: - Avg rate = $\frac{C_{Ai} - C_{Af}}{\Delta t} = \frac{0.2 - \frac{0.2}{e}}{1000} = \left(2 - \frac{2}{e}\right) \times 10^{-4}$

$$\text{Avg rate} = 2 \left(1 - \frac{1}{e}\right) 10^{-4} \text{ M/sec}$$

(iii) What is the instantaneous rate of rxn at $t = 1000 \text{ sec}$.

Solⁿ: $\text{rxn} = -\frac{1}{2} \frac{d[A]}{dt} = \frac{1}{2} [A]_0 e^{-kt} (k)$

$$= \frac{1}{2} \times 0.2 e^{-1} (10^{-3}) = \frac{2 \times 10^{-4}}{2e} \text{ M/sec}$$

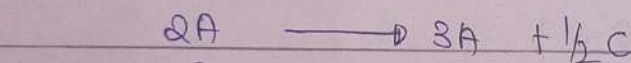
(iv) At what time, the instantaneous rate of disappearance of A will be equal to its average rate in first 1000 sec.

Solⁿ → $\frac{d[A]}{dt} = [A]_0 e^{-kt} (-k) = 2(1 - \frac{1}{e}) \times 10^{-4}$

$$= 0.2 \times 10^{-3} e^{-10^3 \times t} = 2 \times 10^{-4} (1 - \frac{1}{e})$$

(v) Express the conc. of C as fn of time.

Solⁿ $\frac{-1}{2} \frac{d[A]}{dt} = \frac{d[C]}{dt}$



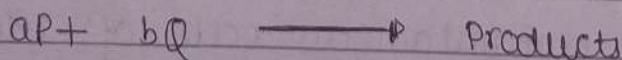
$$t=0 \quad [A]_0$$

$$t=t \quad [A]_0 - x \quad \frac{3}{2}x \quad \frac{x}{4}$$

$$\therefore x = [A]_0 (1 - e^{-kt})$$

$$[C] = \frac{x}{4} = \frac{[A]_0}{4} (1 - e^{-kt})$$

RATE LAW:



$$r \propto [P]^a [Q]^b$$

The rate of rxn is directly proportional to the active masses of reactants raised to some experimentally

determined powers.

Here: x & y are experimentally determined values called order of rxn w.r.t P & Q respectively.

$$\text{or, } r = k [P]^x [Q]^y$$

where k = rate constant or velocity const or specific rxn rate

k is the rate of rxn at unit active masses of the reactants.

For a particular reaction, k depends only on temperature and catalytic condition at

$$k = A e^{-E_a/RT} \quad \text{Arrhenius Equation.}$$

Active mass \Rightarrow It represents amount of components actively participating in the reaction at that time.

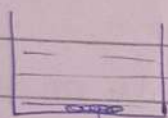
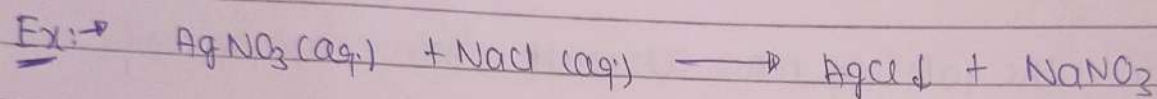
Active mass = ~~Amount~~ Amount \times Activity coefficient
 \downarrow
 Fraction of total amt. of the component actively participating is the rxn at that moment.

When $c \rightarrow 0$, activity coefficient $\rightarrow 1$ & hence, the molar conc. or partial pressure may be taken as active mass.

Substance is ~~solid~~ ^{solution}: Active mass = Molar conc.

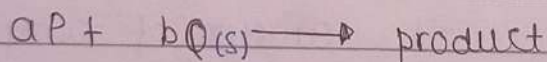
Substance is gas = Active mass = Molar conc. or partial pressure

Substance is solid or pure liquid = Active mass = Constant, independent of its amount



$$[\text{AgCl}(\text{s})] = \frac{n_{\text{AgCl}(\text{s})}}{V_{\text{AgCl}(\text{s})}} = \frac{W_{\text{AgCl}}/M_{\text{AgCl}}}{W_{\text{AgCl}}/d_{\text{AgCl}}} = \frac{d_{\text{AgCl}}}{M_{\text{AgCl}}} = \text{const.}$$

↳ volume is seen only same phase



$$r = k [P]^x [Q]^y = k' [P]^x$$

where $k' = k [Q]^y$ = Pseudo or apparent rate constant

and k = true rate constant.

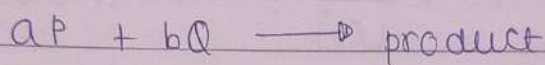
As the conc. of solid or pure liquid is constant, they do not influence reaction rate & hence, the kinetics is always defined in terms of pseudo rate constant. To avoid confusions, normally

We take unit active mass for solid & pure liquid.

Due to similar reason, the order w.r.t any component in large excess is taken as zero.

In all such cases, the active mass of that component remain clubbed in that rate constant.

Order of Rxn \rightarrow



$$\text{Rate Law, } r = k[P]^x[Q]^y$$

Order of rxn w.r.t P = x

Order of rxn w.r.t Q = y

And overall order of rxn = x + y

* Order is always experimental value, independent from the stoichiometry of reaction.

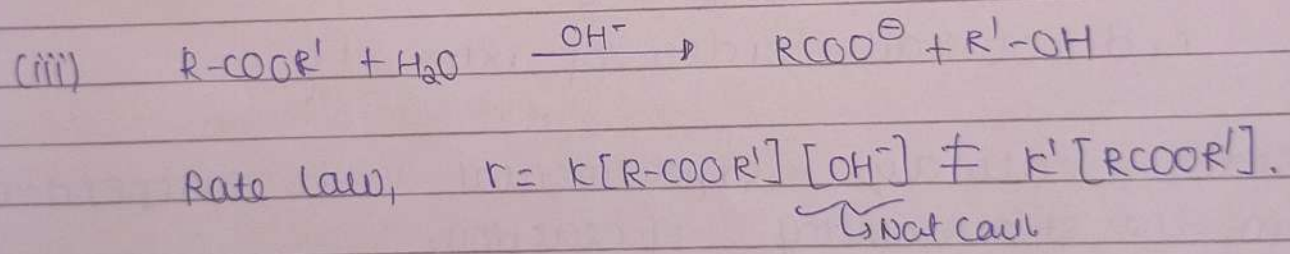
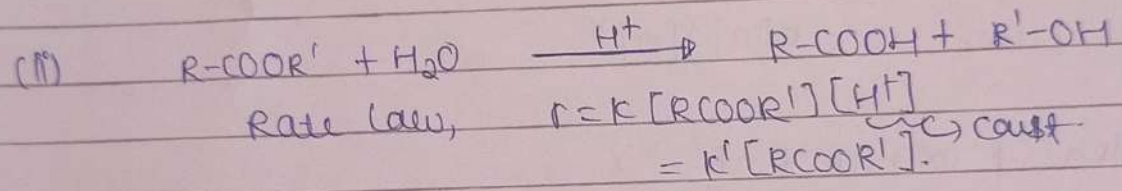
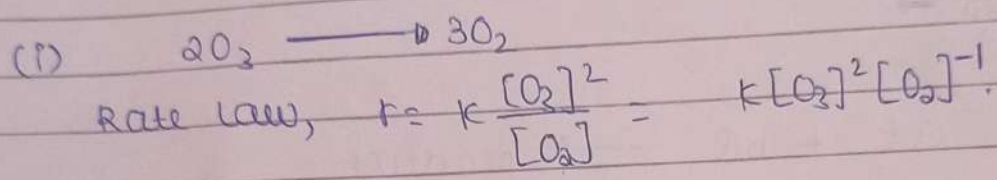
* Order w.r.t any component may be integer or fractional, positive or negative, zero.

* Normally, order of any rxn is a fixed value independent from conditions but there may be some rxn for which order may change by changing the condition.

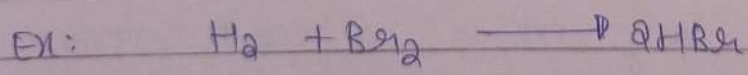
Ex: S_N1 rxn may become S_N2 on ↑ring the nucleophile conc.

$S_N1 : r_1 = k_1 [R-L]$
 $S_N2 : r_2 = k_2 [R-L][Nu]$

* There may be some reaction in which product or catalyst appears in the rate law expression.



* Some reactions has complicated rate law for which overall order may not be defined.



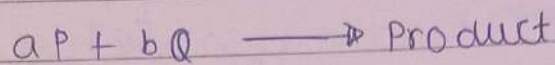
$$r_1 = \frac{k [H_2] [Br_2]^{1/2}}{1 + k' \frac{[HBr]}{[Br_2]}}$$

Order WRT $H_2 = 1$
 But order WRT Br_2 or HBr are not defined.

HW
 15: Interact
 P.V.M.D
 Ex(Ord) SS
 Pg. 192
 NCERT

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LAW OF MASS ACTION:

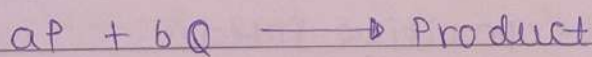


$$r \propto [P]^a [Q]^b$$

where a, b are called molecularity of rxn w.r.t P & Q respectively. And
Overall molecularity of rxn = $a+b$.

The correct rate of any rxn must be given by rate law.
Law of mass action may be used directly in the following cases:

Case I: For elementary rxns, the rate law & law of mass action is normally identical.

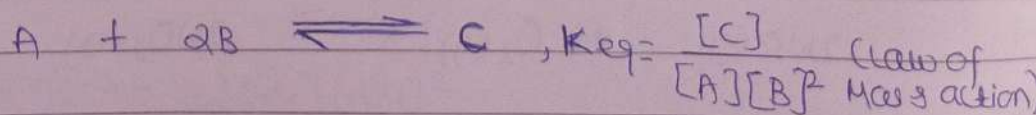


$$\text{Rate law: } r = k[P]^x [Q]^y$$

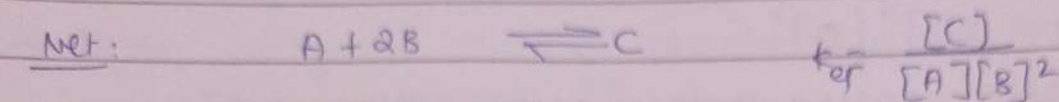
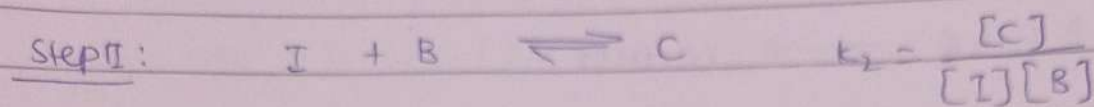
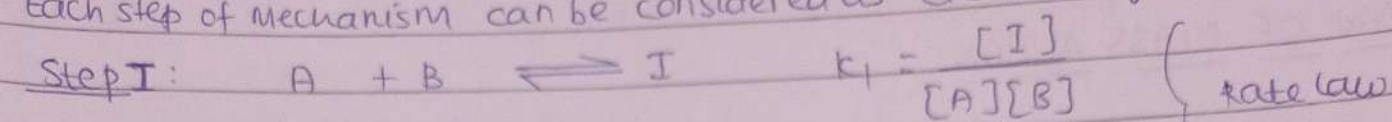
$$\text{Law of mass action: } r = k[P]^a [Q]^b$$

$$a=x, \quad y=b \\ \Rightarrow \text{Molecularity} = \text{order}$$

Case II: In the determination of equilibrium composition.



Each step of mechanism can be considered as elementary.



MOLECULARITY →

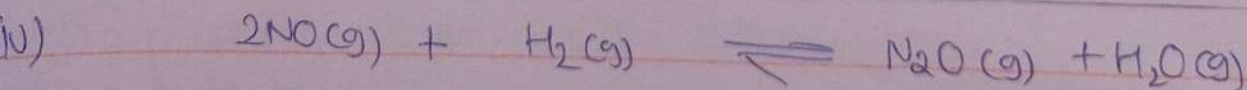
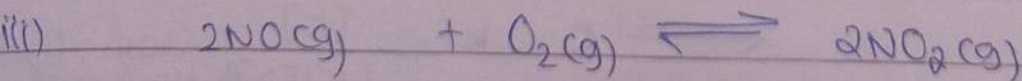
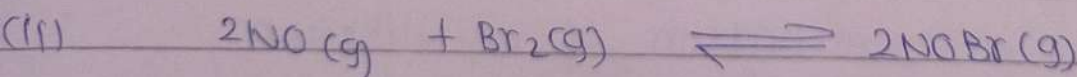
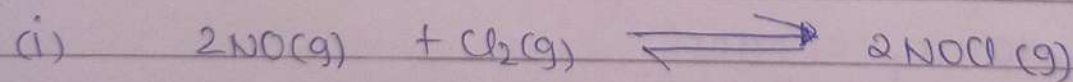
For an elementary reaction, the molecularity represents the number of reactant particles participating in the reaction.

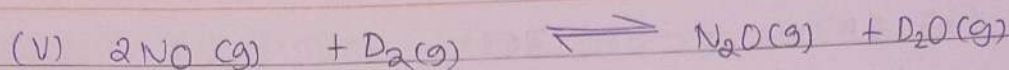
* For a complex reaction, the overall molecularity has no significance & hence it is not defined. But in OC, the molecularity of RDS is taken as the overall molecularity of reaction.

* Molecularity must be positive integer.

* The molecularity of the rxn may have the value 1, 2 & 3.

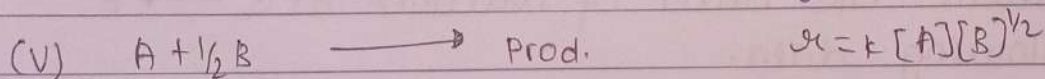
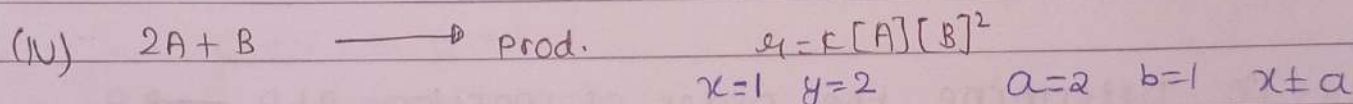
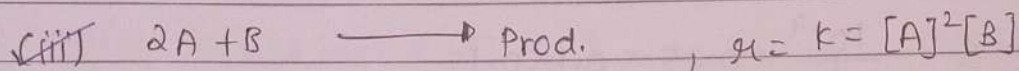
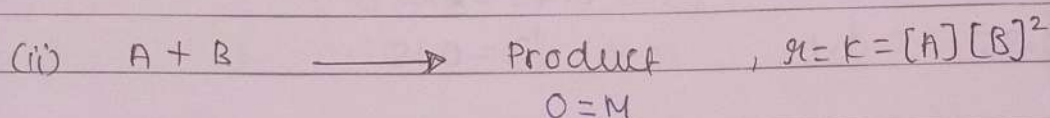
Termolecular reactions are also very rare reaction. The only ^{termolecular} 5 rxn in gaseous state are:





* The reactions having zero, negative or fractional order or total no. of reactant molecules more than 3 must be complex reaction.

Ques ① Which of the following reactions may be elementary reaction?



Molecular Fractional X.

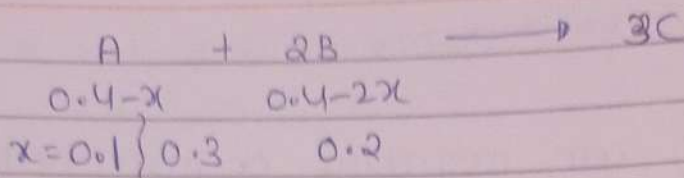
Ques ② For the elementary rxn $A + 2B \longrightarrow 3C$, the rate is $4 \times 10^{-5} \text{ mol l}^{-1} \text{ sec}^{-1}$ when $[A] = [B] = 0.4 \text{ M}$. Calculate the rate of rxn, when

$$(i) \quad [A] = 0.3 \text{ M}$$



$$4 \times 10^{-5} = k[0.4][0.4]^2$$

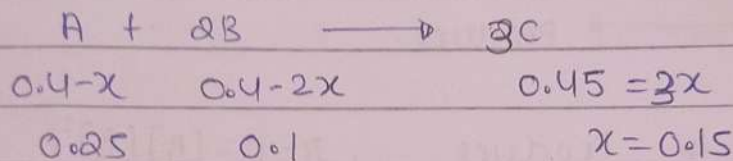
$$k = \frac{4 \times 10^{-5}}{4^3 \times 10^{-3}} = \frac{10^{-2}}{16}$$



$$\text{Rate} = \frac{10^{-2}}{16} \times 3 \times 10^{-1} \times 2 \times 2 \times 10^{-2}$$

$$\frac{3}{4} \times 10^{-5}$$

(ii) $[C] = 0.45M$



$$\text{Rate} = \frac{10^{-2}}{16} \times 0.25 \times 0.1 \times 0.1$$

Ques. 3 Determine the order of reaction $A+B \longrightarrow P$ from the following data.

[A]	[B]	initial rate
0.1M	0.2M	$4.0 \times 10^{-5} \text{ Ms}^{-1}$
0.1M	0.4M	$8.0 \times 10^{-5} \text{ Ms}^{-1}$
0.2	0.2M	$2.0 \times 10^{-5} \text{ Ms}^{-1}$

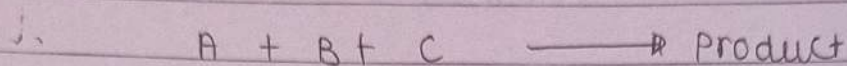
Soln

WRT A = ~~2~~ -1 WRT B = 1

Order = zero.

$$r = k[A]^x[B]^y$$

Ques ④ Determine the rate constant for the reaction



from following data.

P_A (/atm)	P_B (/atm)	P_C (/atm)	Initial Rate (atm min ⁻¹)
0.05	0.02	0.01	8×10^{-7}
0.05	0.02	0.02	8×10^{-7}
0.05	0.01	0.03	4×10^{-7}
0.10	0.02	0.04	3.2×10^{-6}

solⁿ Order w.r.t C = 0
 order w.r.t B = 1
 Order w.r.t A = 2.
 order of rxn = 3.

$$r = k P_A^2 P_B^1 P_C^0$$

$$4 \times 10^{-7} = k [0.05]^2 [0.01] [0.03]^0$$

$$4 \times 10^{-7} = k \times 25 \times 10^{-4} \times 10^{-2}$$

$$k = \frac{4}{25} \times 10^{-7} = \frac{40}{25 \times 10^2} = \frac{8}{5} \times 10^{-2} = \frac{0.08}{5} "$$

$$k = 1.6 \times 10^{-2} \text{ atm}^{-2} \text{ min}^{-1}$$

Ques ⑤ For the reaction $A \longrightarrow \text{Prod.}$

The rate constant is $0.04 \text{ mol}^{-1} \text{ L min}^{-1}$ what is order of reaction.

solⁿ:

$$r = k[A]^n$$

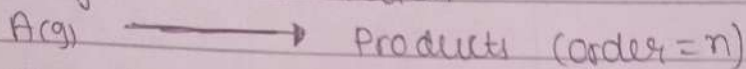
$$k = \frac{r}{[A]^n}$$

$$k = \frac{x}{[A]^n} = \frac{\text{mol l}^{-1} \text{ min}^{-1}}{(\text{mol l}^{-1})^n}$$

Unit of $k = (\text{mol l}^{-1})^{1-n} \text{ min}^{-1}$

Hence order of rxn = 2.

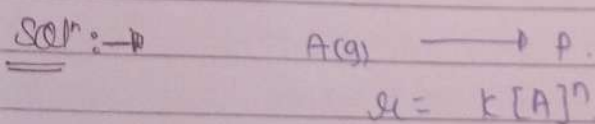
Ques 6 For a gaseous reaction



The rate may be expressed as

$$(i) \quad -\frac{1}{V} \frac{dn_A}{dt} = k_1 C_A^n \quad (ii) \quad -\frac{dp_A}{dt} = k_2 P_A^n$$

Relate k_1 & k_2 .



$$\left(-\frac{1}{V}\right) \frac{dn_A}{dt} = k_1 [A]^n$$

Volume = const.

$$-\frac{1}{V} \frac{dn_A}{dt} = r$$

$$k_1 C_A^n = k_2 P_A^n$$

$$P_A = \frac{n_A}{V} RT \quad \Rightarrow \quad P_A = C_A RT$$

$$\frac{dp_A}{dt} = \frac{RT}{V} \frac{dn_A}{dt}$$

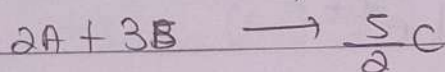
$$= +k_2 P_A^n = \frac{RT}{V} (+x k_1 C_A^n)$$

$$\frac{k_2}{k_1} = RT \left[\frac{C_A}{P_A} \right]^n$$

$$\frac{k_2}{k_1} = RT \left(\frac{1}{RT} \right)^n = (RT)^{1-n}$$

Note: It is the only first order reaction for which the numerical value of rate constant is independent from the unit used to express the quantity of component.

Ques 7 For the reaction,



The rate is expressed as

$$(i) -\frac{d[A]}{dt} = k_1 [A] [B]^2$$

$$(ii) -\frac{d[A]}{dt} = k_2 [A] [B]^2$$

$$(iii) +\frac{d[C]}{dt} = k_3 [A] [B]^2$$

Relate k_1 , k_2 & k_3 .

Solⁿ: $r_{rxn} = \frac{1}{2} \frac{-d[A]}{dt} = \frac{1}{3} \frac{-d[B]}{dt} = \frac{2}{5} \frac{d[C]}{dt}$

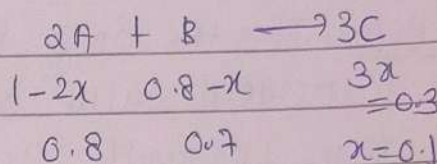
$$k_1 = \frac{1}{2} k_2 = \frac{1}{3} k_3 = \frac{2}{5} k_3$$

$$k_{rxn} = \frac{k_1}{2} = \frac{k_2}{3} = \frac{2k_3}{5}$$

Ques 8 For the reaction $2A + B \rightarrow 3C$, the rate is expressed as $-\frac{d[A]}{dt} = (2 \times 10^{-3} \text{ s}^{-1}) \times [A]$.

Calculate the rate of reaction when conc. of C is 0.3M, if $[A_0] = 1.0M$ & $[B_0] = 0.8M$.

Soln:
$$-\frac{d[A]}{dt} = (2 \times 10^{-3} \text{ s}^{-1}) [A]$$



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

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$[A]_t = [A]_0 e^{-kt}$$

$$-\frac{d[A]}{dt} = 2 \times 10^{-3} \text{ sec}^{-1} \times 0.8 M$$

HW
 Race-4,5
 PYQ(S)
 Ex(5-2) } ss
 Ex(10-2)
 Half life
 Avg life

Rate of rxn = $2 \times 10^{-3} \times 0.8 \text{ M s}^{-1}$
2.

Date | 26 | Aug | 2019

Integrated Rate Law :->

It is used to determine the conc. of any component at any given time.

Case I: $A \rightarrow \text{Products (order} = n)$.

Rate Law:

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

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

$$[A]_0 = [A]_0 = a M$$

$$[A] = [A]_t = [A]_t = (a-x) M$$

$n=1$

$$kt = \ln \frac{[A]_0}{[A]}$$

$$\Rightarrow [A] = [A]_0 e^{-kt} \quad (\text{Wilhelmy's Equation})$$

 $n \neq 1$

$$kt = \frac{[A]_0^{1-n} - [A]^{1-n}}{1-n}$$

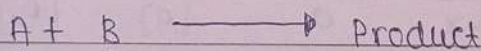
 $n=0$

$$kt = [A]_0 - [A]$$

 $n=2$

$$kt = \frac{1}{[A]} - \frac{1}{[A]_0}$$

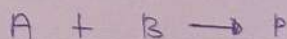
Note: If rxn & kinetics are not defined, rxn is always considered for single reactant.

Case II:

And rate law; $a-x$ $b-x$

$$r = k[A][B]$$

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

 $t=0$ 

a b

 $t=t$

$a-x$ $b-x$

 x

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

$$-\frac{d[a-x]}{dt} = k[a-x][b-x]$$

$$\frac{dx}{dt} = k[a-x][b-x]$$

$$\int_0^x \frac{dx}{[a-x][b-x]} = \int_0^t k dt$$

if $a \neq b$

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

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

$$\frac{1}{b-a} \ln \left| \frac{b-x}{a-x} \right|_0^x = kt$$

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

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

if $a = b$

$$kt = \frac{1}{a-x} - \frac{1}{a} = \frac{1}{[A]} - \frac{1}{[A_0]}$$

$$kt = \frac{1}{[A]} - \frac{1}{[A_0]}$$

if $a \ll b$

$$(b-a) \approx b \quad (b-x) \approx b$$

~~$$kt \ln \frac{a \times b}{b \times (a-x)}$$~~

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

$$kt \approx \frac{1}{b} \ln \frac{a \times b}{b \times (a-x)}$$

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

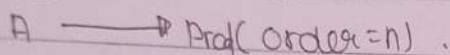
$$\Rightarrow kt = \ln \frac{[A_0]}{[A]}$$

where $k' = k_b$

= pseudo or apparent rate constant.

In such case, the second order rxn start obeying first order kinetics. Such rxn is called pseudo unimolecular rxn.

Ques. Calculate the time of completion of reaction



Soln: \rightarrow

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

$$\int_{[A_0]}^{[A]} \frac{-d[A]}{[A]^n} = \int_0^t k dt$$

$$[A]^{1-n} k t = \frac{[A_0]^{1-n} - [A]^{1-n}}{1-n}$$

$n=1$

$$t = \frac{1}{k} \ln \frac{[A_0]}{[A]} = \frac{1}{k} \ln \frac{[A_0]}{0} = \infty.$$

$n \neq 1$

$$t = \frac{[A_0]^{1-n} - [A]^{1-n}}{(1-n)k} = \frac{[A_0]^{1-n} - (0)^{1-n}}{k(1-n)}$$

$n < 1$

$$t = \frac{[A_0]^{1-n}}{k(1-n)}$$

$n > 1$

$$t = \infty \text{ (infinite)}$$

Final Ans: $t_{100\%} = \frac{[A_0]^{1-n}}{k(1-n)}$ (when $n < 1$)
 $= \text{infinite}$ when $n > 1$.

Note: In reality, none of the reaction occur completely.

Half life time period ($t_{1/2}$): \rightarrow

It is the time in which half of the amount of reactant reacts.

(i) If no. of reactants are two or more, individual half life for all components may be defined. If required the overall half life is the time in which half of the amount of limiting reagent get reacted.

(ii) $A \rightleftharpoons B$ For a reversible reaction,
 $a \qquad \qquad \qquad 0$
 $t_{1/2} \quad t - \frac{x_e}{2} \qquad \frac{x_e}{2}$ $t_{1/2}$ is the time in which
 $t_{100\%} \quad t - x_e \qquad x_e$ half of the amount of reactant
 which should react upto
 equilibrium has been reached.

Calculation of Half life: $A \rightarrow \text{Product (order} = n)$

when, $t = t_{1/2}$, then $[A] = [A]_0 - \frac{[A]_0}{2} = \frac{[A]_0}{2}$

$n=1$ $t = \frac{1}{k} \ln \frac{[A]_0}{[A]} \Rightarrow t_{1/2} = \frac{1}{k} \ln 2$

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

$n \neq 1$

$$t = \frac{[A_0]^{1-n} - [A]^{1-n}}{k(1-n)}$$

$$\Rightarrow t_{1/2} = \frac{[A_0]^{1-n} - \left(\frac{[A_0]}{2}\right)^{1-n}}{k(1-n)}$$

$$\Rightarrow t_{1/2} = \frac{[A_0]^{1-n} (1 - 2^{n-1})}{k(1-n)}$$

$n=0$

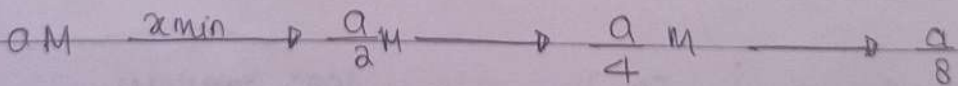
$$t_{1/2} = \frac{[A_0]}{2k}$$

$n=2$

$$t_{1/2} = \frac{1}{k[A_0]}$$

* In general: $t_{1/2} \propto [A_0]^{1-n}$

* It is the only first order reaction for which $t_{1/2}$ is independent from initial concentration.



$n=1$

$x \text{ min}$

$x \text{ min}$

$n=0$

$\frac{x}{2} \text{ min}$

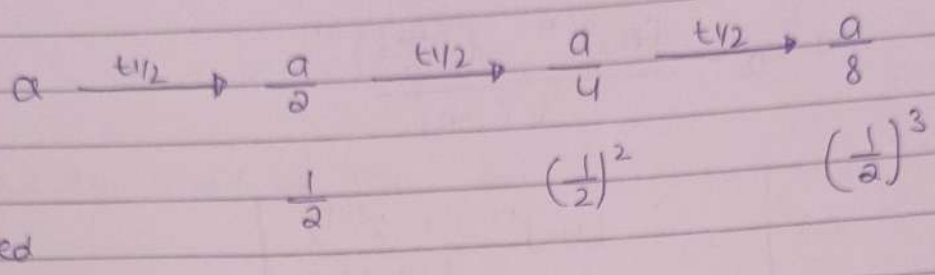
$\frac{x}{4} \text{ min}$

$n=2$

$2x \text{ min}$

$4x \text{ min.}$

* It is the only for which any percentage progress of reaction is independent from initial concentration.



in general,
 Fraction remained = $\left(\frac{1}{2}\right)^x = \frac{[A]}{[A_0]}$

x: No. of half lives.

% Rxn	50%	75%	87.5%
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* $t_{1/2} \propto \frac{1}{k}$

HW
 RARE 67
 JUNA SS (Review)
 EX-15)

Date [28] Aug [20] 19

Average or Mean Life: \rightarrow

It is the average time upto which a molecule remain unreacted.

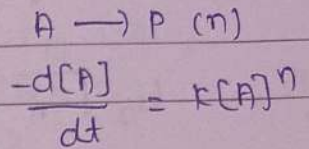
t = 0	[A ₀]	1000 particles
⋮		
t = t ₁	[A ₁]	990 particles
t = t ₁ + dt	[A ₁] + d[A ₁]	988 particles
⋮		
t = t ₂	[A ₂]	956 particles
t = t ₂ + dt	[A ₂] + d[A ₂]	999 particles

Annotations:
 -d[A₁] particles have life, t₁.
 -d[A₂] particles have life, t₂.

$$T_{avg} = \frac{(-d[A])t_1 + (-d[A_2])t_2 + \dots}{[A]_0}$$

$$= \frac{1}{[A]_0} \int_0^{t_{100\%}} t (-d[A])$$

$$= \frac{1}{[A]_0} \int_0^{t_{100\%}} t (k[A]^n dt)$$



$$T_{avg} = \frac{k}{[A]_0} \int_0^{t_{100\%}} t [A]^n dt$$

For $n=0$

$$T_{avg} = \frac{k}{[A]_0} \frac{t^2}{2} = \frac{k}{[A]_0} \left(\frac{[A]_0}{k} \right)^2 \frac{1}{2} = \frac{[A]_0}{2k}$$

$$\left. \right\} T_{avg} = \frac{[A]_0}{2k}$$

For $n=1$

$$T_{avg} = \frac{k}{[A]_0} \int_0^{\infty} t \cdot [A] dt$$

$$[A] = [A]_0 e^{-kt}$$

$$T_{avg} = k \int_0^{\infty} t e^{-kt} dt$$

$$\left. \right\} T_{avg} = \frac{1}{k}$$

Ques. ① For a rxn $A \longrightarrow \text{Product}$ the half life depends on initial conc. of A as $\sqrt{C_A^0} \cdot t_{1/2} = K$. What is the order of rxn.

Sol: $t_{1/2} \sqrt{C_A^0} = K$

$$t_{1/2} = \frac{K}{\sqrt{C_A^0}}$$

$$t_{1/2} \propto [A_0]^{1-n}$$

$$1-n = \frac{-1}{2}$$

$$\} n = 3/2 \rightarrow \text{order of rxn.}$$

Ques. ② For a gaseous rxn $A \longrightarrow \text{Product}$ the following data is observed.

Initial Partial Pressure of A (atm)	0.4	0.8	1.6
Initial $t_{1/2}$ (min)	20	10	5

What is order of rxn.

Sol: $t_{1/2} \propto [A_0]^{1-n}$

$$t_{1/2} = K(0.4)^{1-n}$$

$$\frac{20}{10} = \left(\frac{0.4}{0.8}\right)^{1-n}$$

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

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

$$\} n = 2 \checkmark$$

Ques 3) The following data are obtained for rxn
 $A + B \rightarrow \text{Prod.}$, $r = k[A]^2[B]$

$[A_0]$	$[B_0]$	Initial $t_{1/2}$ (min)
0.002 M	2.0 M	20
0.004 M	2.0 M	x
4.0 M	0.001 M	80
4.0 M	0.002 M	y
2.0 M	0.004 M	z

Determine values of x, y, z.

Solⁿ:

$$t_{1/2} \propto [A]^{-1}$$

$$x = 10 \quad y = 80.$$

In first 2 cases,

$$r = k[A]^2[B]$$

$$= k'[A]^2$$

$$t_{1/2} = \frac{1}{k'[A_0]}$$

In last 2 cases

$$r = k[A]^2[B]$$

$$= k''[B]$$

$$t_{1/2} = \frac{1}{k''[B]} \quad \boxed{y = 80}$$

~~$$t_{1/2} = \frac{k}{[A]}$$~~

~~$$k = \frac{t_{1/2}[A]}{1}$$~~

~~$$20(0.002) =$$~~

4x

~~$$k = x \times 10^{-2} = \frac{x \times 10^{-3}}{1}$$~~

~~$$x = 10$$~~

~~$$4 \times 10^{-2} = \frac{4}{1}$$~~

$$r = k[A]^2[B]$$

$$= k''[B]$$

$$t_{1/2} = \frac{\ln 2}{k''} = \frac{\ln 2}{k[A_0]^2}$$

For z, conc. of A is changing

$$z = 320.$$

Ques 4) For the rxn $A \rightarrow 3B$ follows zero order kinetics. The rxn is started with 0.2 M A.

(i) If after 20 minutes, the conc. of A becomes 0.04 M, calculate the rate constant of rxn.

Soln: $[A]_0 - [A] = kt$
 $k = \frac{0.2 - 0.04}{20} \text{ M min}^{-1} = \frac{0.16}{20} = \frac{4}{5} \times 10^{-2}$
 $= 8 \times 10^{-3}$

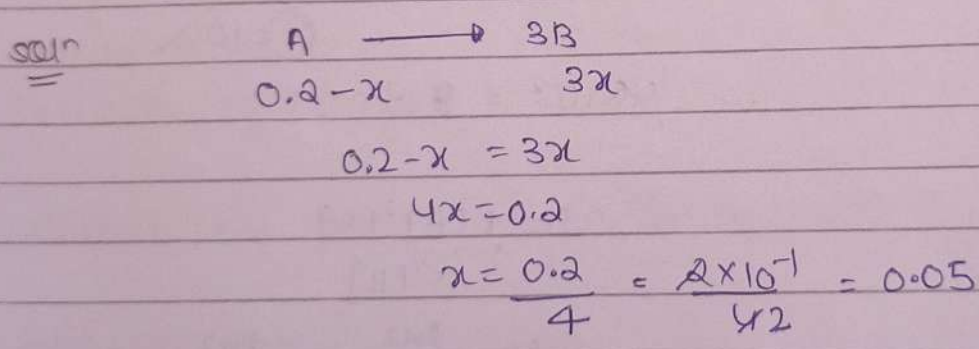
(ii) Calculate the initial half life of rxn.

Soln: $t_{1/2} = \frac{[A]_0}{2k} = \frac{0.2}{2 \times 8 \times 10^{-3}} = 12.5 \text{ min}$

(iii) In what time the rxn will complete.

Soln: $t_{1/2} = \frac{[A]_0}{k} = 25 \text{ min.}$

(iv) In what time the conc. of A & B becomes equal.



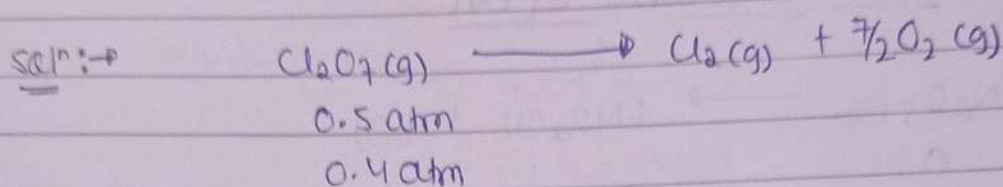
$t = \frac{0.2 - 0.15}{k} = \frac{5 \times 10^{-2}}{8 \times 10^{-3}}$

$t = \frac{50}{8} = \frac{25}{4} \text{ min.}$
 $= 6.25 \text{ min}$

(v) Calculate conc. of A & B at t=30 min.

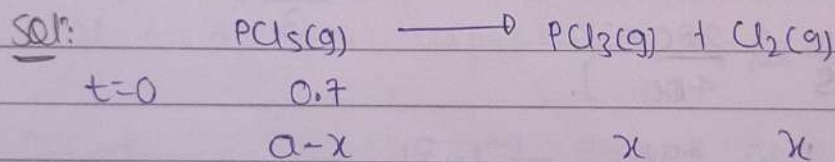
Soln: $A = 0$ $B = 0.6$

Ques ③ The reaction $\text{Cl}_2\text{O}_7(\text{g}) \longrightarrow \text{Cl}_2(\text{g}) + \frac{7}{2}\text{O}_2(\text{g})$ follows first order kinetics. If partial pressure of $\text{Cl}_2\text{O}_7(\text{g})$ drops from 0.5 atm to 0.4 atm in 20 minutes calculate the rate constant of rxn.



$$k = \frac{1}{t} \ln \frac{P_{\text{Cl}_2\text{O}_7}^0}{P_{\text{Cl}_2\text{O}_7}} = \frac{1}{20} \ln \frac{0.5}{0.4}$$

Ques ④ The reaction $\text{PCl}_5(\text{g}) \longrightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ follows first order kinetics. The reaction is performed at constant volume & temperature. If the total pressure of the system was 0.7 bar at $t=0$ and 0.9 bar at $t=45$ min. Calculate specific rxn rate.



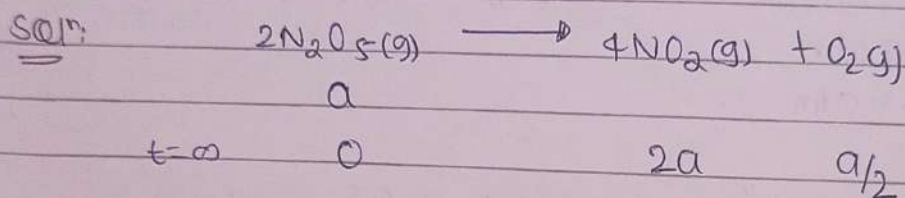
$$a = 0.7$$

$$a + x = 0.9$$

$$x = 0.2$$

$$k = \frac{1}{45} \ln \frac{7}{5}$$

Ques ① The rxn $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ follows first order kinetics. After 25 min, from the start of rxn pressure of system was 500 torr and after a very long time the pressure becomes 700 torr. Calculate the rate constant of rxn.



$$2a + a/2 = 700$$

$$5a = 1400$$

$$a = 280 \text{ torr}$$

$$t = 25 \text{ min} \quad a - x \quad \quad \quad 2x \quad \quad \quad x/2$$

$$280 - \frac{440}{3} \quad a + \frac{3x}{2} = 500$$

$$\frac{840 - 440}{3} - \frac{400}{3} \quad \frac{3x}{2} = 220 \quad 3x = 440$$

$$x = \frac{440}{3}$$

$$\left\{ k = \frac{1}{25} \ln \frac{280 \times 3}{400} \right\}$$

$$\frac{1}{25} \ln \frac{840}{400} = \frac{1}{25} \ln \frac{21}{10}$$

$$K_{\text{rxn}} = \frac{k}{2} = \frac{1}{50} \ln \frac{21}{10}$$

Ques ② For a first order rxn, the rate is $4 \times 10^{-5} \text{ mol l}^{-1} \text{ s}^{-1}$ at $t = 20 \text{ min}$ & $3 \times 10^{-5} \text{ mol l}^{-1} \text{ s}^{-1}$ at $t = 30 \text{ min}$. Calculate the rate constant.

Soln:

$$r = k[A]$$

$$4 \times 10^{-5} =$$

$$k = \frac{1}{t} \ln \frac{[A]_0}{[A]}$$

$$r = k[A]$$

$$\frac{4}{8} = \frac{30}{20} \times 4 \times 10^{-5} = \frac{1}{20} \ln$$

Shortcut:

$$k = \frac{1}{t} \ln \frac{r_0}{r}$$

$$t = 20 \text{ min} \quad 0 \text{ min}$$

$$t = 30 \text{ min} \quad 10 \text{ min}$$

$$k = \frac{1}{10} \ln \frac{4 \times 10^{-5}}{3 \times 10^{-5}}$$

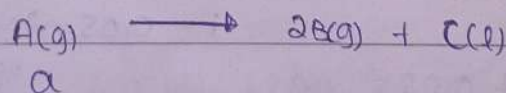
Detailed

$$t_1 = \frac{1}{k} \ln \frac{r_0}{r_1}$$

$$t_2 = \frac{1}{k} \ln \frac{r_0}{r_2}$$

$$t_2 - t_1 = \frac{1}{k} \left[\ln \frac{r_1}{r_2} \right]$$

Ques 9) For the first order reaction $A(g) \rightarrow 2B(g) + C(l)$ the pressure of system was 40 cm Hg at $t=0$ & 52.5 cm Hg at $t=10$ min. Calculate the pressure of system at $t=20$ min. Vap. pressure of $C(l) = 2.5$ cm Hg.

Soln: →

a

a-x

2x

$$a = 40$$

$$a + x + 2.5 = 52.5$$

$$x = 10$$

$$k = \frac{1}{10} \ln \frac{40}{30}$$

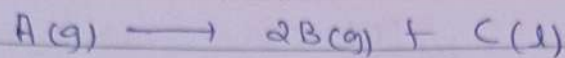
$$k = \frac{1}{20} \ln \frac{40}{P}$$

$$\cancel{\frac{1}{10}} \ln \frac{40}{30} = \cancel{\frac{1}{20}} \ln \frac{40}{P}$$

$$\left(\frac{40}{30}\right)^2 = \frac{40}{P}$$

$$2 \ln \frac{40}{30} = \ln \frac{40}{P}$$

$$P = \frac{900}{40} = \frac{45}{2} = 22.5$$



$$a - y \qquad 2y$$

$$= 22.5$$

$$y = 40 - 22.5$$

$$= 17.5$$

$$P = 22.5 + 35 + 2.5$$

$$= 60\%$$

HW
EX(5-1)
1-22CK

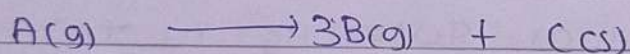
LS EX(6-11)

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Ques. (10) The reaction $A(g) \longrightarrow 3B(g) + C(s)$ follows first order kinetics. Determine the rate constant of rxn from following data.

Time (min)	0	10	∞
P_{total} (bar)	0.4	0.75	1.25

Soln:



$$0.4$$

$$0.4 - x$$

$$0$$

$$3x$$

$$3(0.4)$$

$$P$$

$$P$$

$P = 0.05 \rightarrow$ vap. pressure of solid.

$$0.4 + 2x + 0.05 = 0.75$$

$$2x = 0.30$$

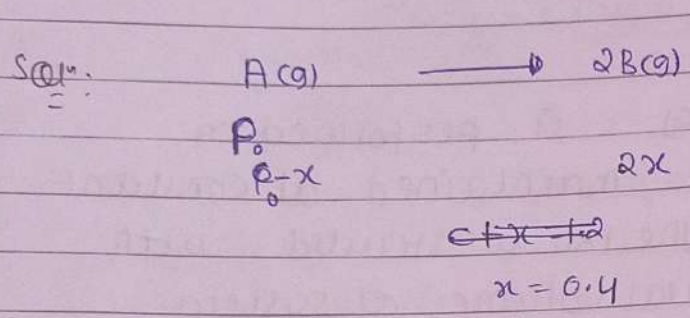
$$x = 0.15$$

$$k = \frac{1}{10} \ln \frac{0.4}{0.25}$$

$$\left[k = \frac{1}{10} \ln \frac{8}{5} \text{ min}^{-1} \right]$$

Ques. (11) The reaction $A(g) \longrightarrow 2B(g)$ follows first order kinetics. Determine its rate constant from the following data.

Time (min)	0	25	∞
P_{total}	0.8	1.2	1.5



Pinert gas.
 $(0.8 - P_0)$

$$P_0 + x + (0.8 - P_0) = 1.2$$

$$x = 0.4$$

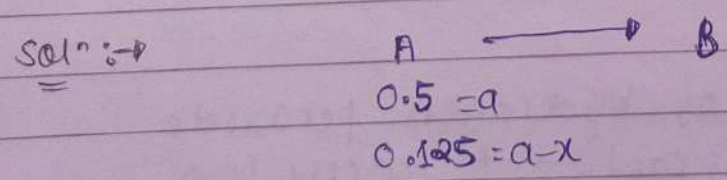
$$k = \frac{1}{25} \ln \frac{0.7}{0.3}$$

$$2P_0 + 0.8 - P_0 = 1.5$$

$$P_0 = 0.7$$

$$k = \frac{1}{25} \ln \frac{7}{3}$$

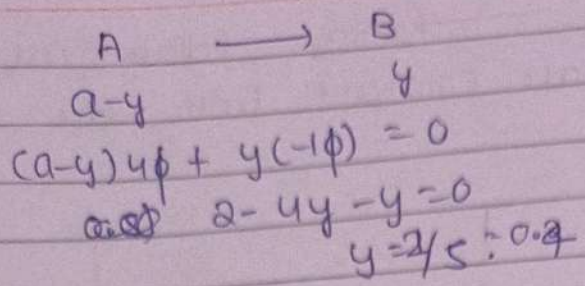
Ques. (12) In a process of mutarotation, an optically active compound A converts into its isomeric form B by first order kinetics. The specific rotations of A & B are $+40^\circ$ & -10° per mole respectively. The initial optical rotation of the sample was $+20^\circ$. If the rotation of sample becomes $+5^\circ$ at $t = 20$ min, calculate the rate constant. Also, calculate the time in which sample becomes optically inactive.



$$(a - x)40 + x(-10) = 5$$

$$x = 0.3$$

$$k = \frac{1}{20} \ln \frac{0.5}{0.2}$$

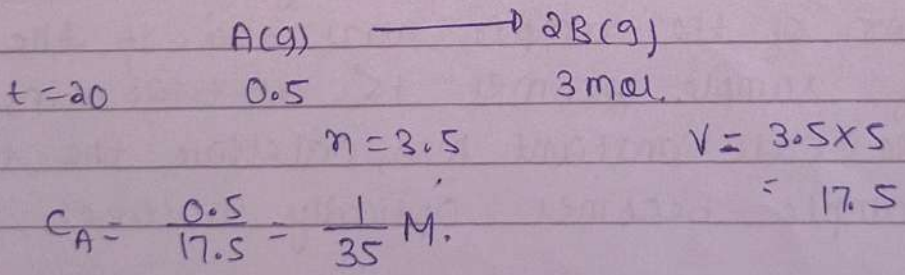


$$t = \frac{1}{k} \ln \frac{0.5}{0.1}$$

Ques 13) $A(g) \xrightarrow{k=0.0693 \text{ min}^{-1}} 2B(g)$ is performed in cylinder piston arrangement maintained at constant pressure & temperature. The rxn is started with 2 moles of $A(g)$ & the initial volume of system was 10L. Calculate the concentration of A at $t=20 \text{ min}$.

Sol: $n \propto V$
 $A(g) \xrightarrow{k=0.0693 \text{ min}^{-1}} 2B(g)$

$$t_{1/2} = \frac{0.693}{0.0693} = \frac{693 \times 10^{-3}}{693 \times 10^{-4}} = 10 \text{ min.}$$



Ques 14) The decomposition of hydrogen peroxide may be represented as $H_2O_2(aq) \longrightarrow H_2O(l) + \frac{1}{2}O_2$. From the following data determine the order of rxn.

Time (min)	0	10	30
Vol. of KMnO_4 sol ⁿ needed (ml)	25	16	7.3

Solⁿ →

$$n_{\text{eq H}_2\text{O}_2} = n_{\text{eq KMnO}_4} \text{ (fixed)}$$

$$\frac{N_1 V_1}{1000} = \frac{N_2 V_2}{1000}$$

Every time taken in fixed amt

$$N_1 \propto V_2$$

} Data
Random, so don't
Cross check
} V_1 & N_2
are kept const.

∴ conc. of $\text{H}_2\text{O}_2 \propto$ Volume of KMnO_4

Hint & trial

Assuming 1st order

$$k = \frac{1}{t} \ln \frac{[\text{H}_2\text{O}_2]_0}{[\text{H}_2\text{O}_2]_t} = \frac{1}{t} \ln \frac{V_0}{V_t}$$

$$k_1 = \frac{1}{10} \ln \frac{25}{16}$$

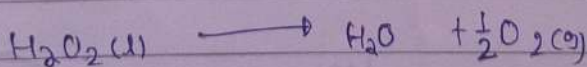
$$k_2 = \frac{1}{30} \ln \frac{25}{7.3}$$

If $k_1 \approx k_2$, then order is 1.

Ques. (15) From the following data show that the decomposition of H_2O_2 follows first order kinetics.

Time (min)	10	15	∞
Volume of O_2 (g) produced at STP (ml)	25	32	45

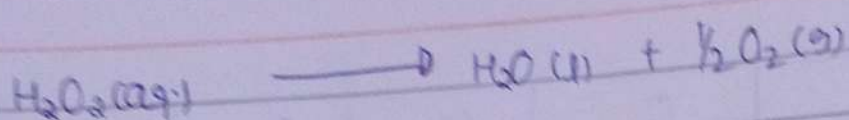
Solⁿ



$$k = \frac{1}{t} \ln \frac{[\text{H}_2\text{O}_2]_0}{[\text{H}_2\text{O}_2]_t}$$

conc. of $\text{H}_2\text{O}_2 \propto$ Volume of KMnO_4

To prove.
$$= \frac{1}{t} \ln \frac{V_\infty}{V_\infty - V_t}$$



$$t=0 \quad a \text{ mole}$$

$$t=t \quad (a-x) \text{ mole}$$

$$\frac{x}{2} \text{ mole} = \frac{PV_x}{RT}$$

$$t=\infty$$

$$0$$

$$\frac{a}{2} = \frac{PV_0}{RT}$$

$$k = \frac{1}{t} \ln \frac{a}{a-x} = \frac{1}{t} \ln \frac{\frac{2PV_0}{RT}}{\frac{2PV_0}{RT} - \frac{2PV_t}{RT}}$$

Do not cross
check data
Random.

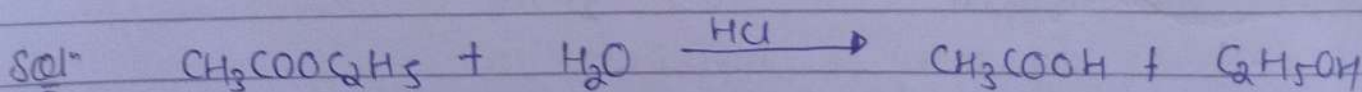
$$\left\{ k = \frac{1}{t} \ln \frac{V_0}{V_0 - V_t} \right\}$$

Hence proved.

Ques. (6) The following data is obtained for the hydrolysis of ethyl acetate in presence of HCl catalyst

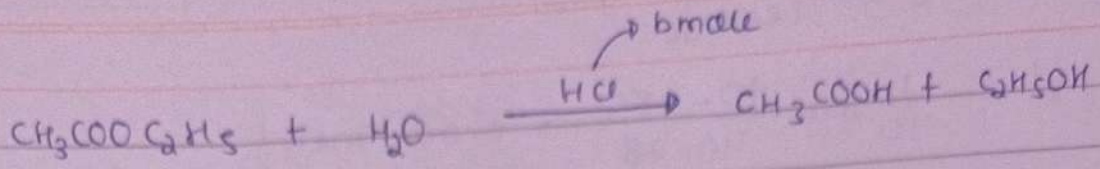
Time (min)	0	10	25	∞
Volume of NaOH sol ⁿ needed (ml)	12	14.2	15.7	18.3

Show that the hydrolysis of ester follows first order kinetics.



$$k = \frac{1}{t} \ln \frac{[\text{conc}]_0}{[\text{conc}]_t}$$

$$\text{To prove: } k = \frac{1}{t} \ln \frac{V_0 - V_a}{V_0 - V_t}$$



t=0	a	0
t=t	a-x	x
t=∞	0	a

neg NaOH = neg acids

$$t=0 \quad \frac{NV_0}{1000} = bx1 \rightarrow \text{①}$$

$$t=t \quad \frac{V_1N}{1000} = bx1 + x1 \rightarrow \text{②}$$

$$t=\infty \quad \frac{V_\infty N}{1000} = bx1 + ax1 \rightarrow \text{③}$$

$$k = \frac{1}{t} \ln \frac{a}{a-x} = \frac{1}{t} \ln \frac{V_\infty - V_0}{V_\infty - V_t}$$

Ques. 17) The following data is obtained for the hydrolysis of 0.3M ethyl acetate in presence of HCl catalyst.

Time & volume of NaOH

Time (min)	0	10	∞
Volume of NaOH sol ⁿ needed (ml)	25	28	40

The rate of rxn may be represented as

$$r = k[\text{ester}][\text{H}^+] = k'[\text{ester}]$$

(ln 5 = 1.6 ln 2 = 0.7)

(i) Calculate k & k'.

$$k' = \frac{1}{t} \ln \frac{[ester]_0}{[ester]_t}$$

$$k' = \frac{1}{10} \ln \frac{40-25}{40-28} = 0.02 \text{ min}^{-1}$$

$[H^+] = b$
previous derivation.

$$k[H^+] = k'$$

$$k = \frac{k'}{[H^+]} = \frac{0.02 \text{ min}^{-1}}{0.3}$$

$$k = 0.04 \text{ mol}^{-1} \text{ min}^{-1}$$

$$\left. \begin{array}{l} \frac{b}{a} = \frac{V_0}{V_\infty - V_0} \end{array} \right\}$$

$$\frac{[H^+]}{0.3} = \frac{25}{40-25}$$

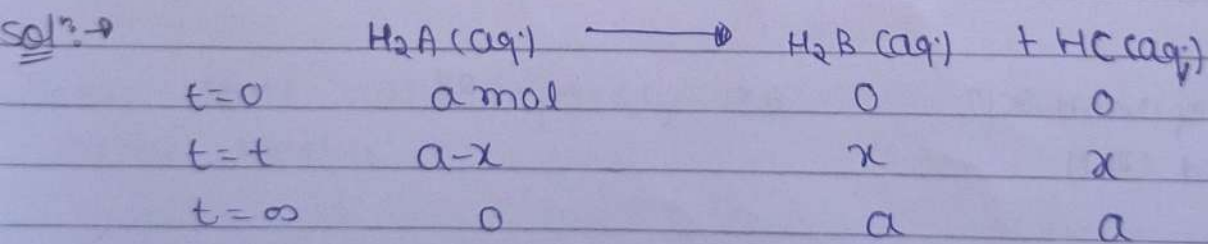
(ii) What is the half life of rxn?

Solⁿ → $t_{1/2} = \frac{\ln 2}{k'} = \frac{0.7}{0.02} = \frac{70}{2} = 35 \text{ min.}$

HW
papers
(KCH)

Date] 02 [Sept] 2019

Ques 18) The reaction $H_2A(aq) \longrightarrow H_2B(aq) + HC(aq)$ follows first order kinetics if the volume of standard NaOH solution needed for the titration of fixed volume of rxn mixture is 20 ml at $t = 90 \text{ min}$ & 25 ml at $t = \infty$. Calculate the rate constant of reaction.



$\text{Neg NaOH} = \text{Neg total acid}$

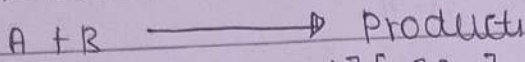
$$t=t = \frac{V_t \cdot N}{1000} = 2(a-x) + 2x + x$$

$$t=\infty = \frac{V_\infty N}{1000} = 2a + a$$

$$k = \frac{1}{t} \ln \frac{a}{a-x} = \frac{1}{t} \ln \frac{0_0 - 0_\infty}{0_t - 0_\infty}$$

Hence proved.

Ques. 20 For the reaction



The rate is $[2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}] [A][B]$.

Calculate the conc. of A at $t = 10 \text{ min}$ if the initial conc. are

(i) $[A]_0 = 0.4 \text{ M}$, $[B]_0 = 0.6 \text{ M}$.

Sol:

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

$$2 \times 10^{-3} \times 10 \times 60 = \frac{1}{0.2} \ln \frac{0.4(0.6-x)}{0.6(0.4-x)}$$

$$[A] = 0.4 - x$$

(ii) $[A]_0 = 0.4 \text{ M}$ $[B]_0 = 0.4 \text{ M}$

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

$$\frac{1}{[A]_t} = \frac{1}{0.4} + 2 \times 10^{-3} \times 10 \times 60$$

(iii) $[A]_0 = 0.02 \text{ M}$ $[B]_0 = 2.0 \text{ M}$

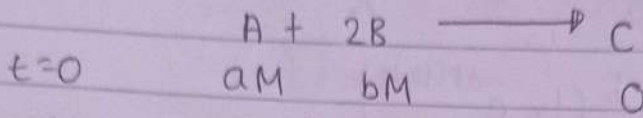
$b \gg a$,

pseudo first order rxn.

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

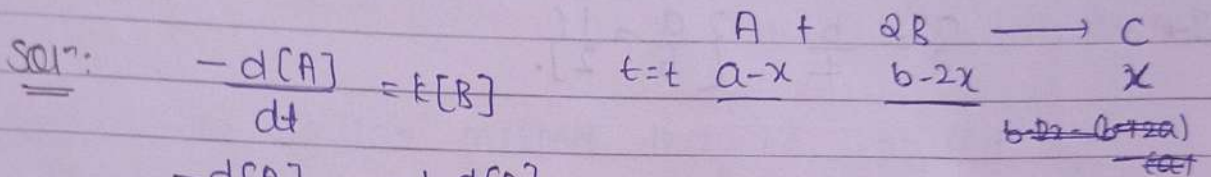
$$2 \times 10^{-3} \times 10 \times 60 = \frac{1}{2} \ln \frac{0.4}{0.4-x}$$

Ques. (a) For the reaction



rate law, $-\frac{d[A]}{dt} = k[B]$

(i) Derive the expressions for conc. of ~~[A]~~, ~~[B]~~ A, B & C at any time t .



$$-\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = k[B]$$

$$-\frac{d[B]}{dt} = 2k[B]$$

$$[B] = [B]_0 e^{-2kt}$$

$$x = \frac{[B]_0}{2} (1 - e^{-2kt})$$

$$[A]_t = a - x$$

$$[A]_t = [A]_0 - \frac{[B]_0}{2} (1 - e^{-2kt})$$

M-Q

$$-\frac{d[a-x]}{dt} = k[b-2x]$$

$$\frac{dx}{dt} = k(b-2x)$$

$$\int_0^x \frac{dx}{b-2x} = \int_0^t kt$$

(ii) Derive the expressions for $(t_{1/2})_A$ & $(t_{1/2})_B$.

Solⁿ: $(t_{1/2})_B = \frac{\ln 2}{2k}$; ~~$(t_{1/2})_A = \frac{\ln 2}{k}$~~

$$\frac{a}{a} = \frac{b}{a} (1 - e^{-ak(t_{1/2})_A})$$

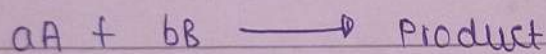
$$\text{for } (t_{1/2})_B = \frac{b}{a} = \frac{b}{a} (1 - e^{-ak(t_{1/2})_B})$$

(iii) Derive the relation between A & B for which $(t_{1/2})_A = (t_{1/2})_B$.

Sol: $\rightarrow \frac{a}{2} = \frac{b}{4} \quad \left\{ \frac{a}{b} = \frac{1}{2} \right\}$

EXPERIMENTAL DETERMINATION OF ORDER OF RXN: \rightarrow

① Initial Rate Method or Von't off's differential method or ratio variation method.



$$\text{Rate law, } r = k[A]^m[B]^n$$

The order w.r.t (A) may be determined by performing the rxn with same initial conc. of B but different initial conc. of A and measuring the initial rate of reaction.

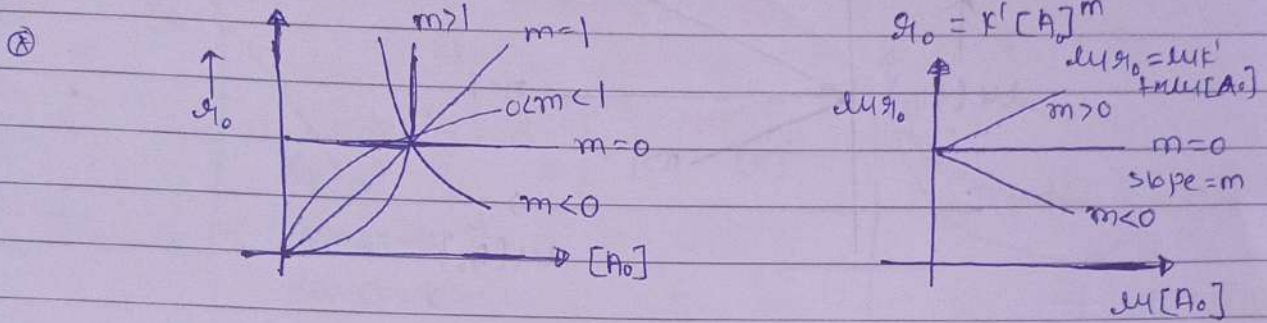
$$\text{Now, initial rate, } r_1 = k[A_0]^m[B_0]^n = k'[A_0]^m$$

where $k' = k[B_0]^n$

$$r_1 = k'[A_0]^m$$

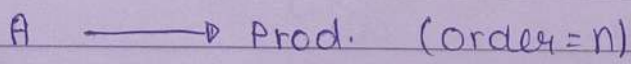
$$\frac{(r_1)_1}{(r_1)_2} = \left(\frac{[A_0]_1}{[A_0]_2} \right)^m$$

$$m = \frac{\ln\left(\frac{r_{10}}{r_{20}}\right)}{\ln\left(\frac{[A_0]_1}{[A_0]_2}\right)} = \frac{\ln(r_{10})_1 - \ln(r_{10})_2}{\ln[A_0]_1 - \ln[A_0]_2}$$



Note ⇒ The similar method may be applied by taking B in large excess and comparing the rate at any moment at different conc. of A. [OSTWALD'S ISOLATION METHOD].

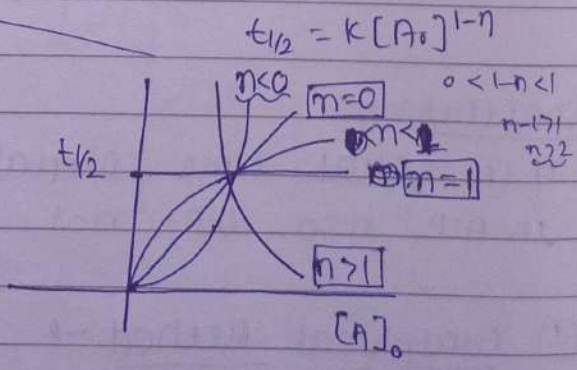
⊗ Half life method:



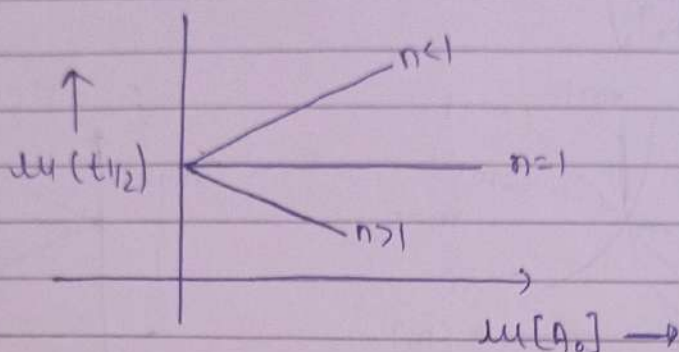
$$t_{1/2} \propto [A_0]^{1-n}$$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{[A_0]_1}{[A_0]_2}\right)^{1-n}$$

$$\therefore n = 1 - \frac{\ln\left(\frac{(t_{1/2})_1}{(t_{1/2})_2}\right)}{\ln\left(\frac{[A_0]_1}{[A_0]_2}\right)}$$



$$\ln(t_{1/2}) = \ln C + (1-n) \ln[A_0]$$



③ Hit & trial Method: →

It is used when the amount of components are directly or indirectly given at different time. The rxn is assumed for a particular order and rate constant is calculated from all the given time. For correct order, all the rate constants calculated must be same.

$$0, \quad t, \quad 2t, \quad 3t, \quad \dots$$

$$[A]_0, \quad [A]_t, \quad [A]_{2t}, \quad [A]_{3t} \quad \text{AP} = n=0$$

$$\text{GP} = n=1$$

$$\text{HP} = n=2$$

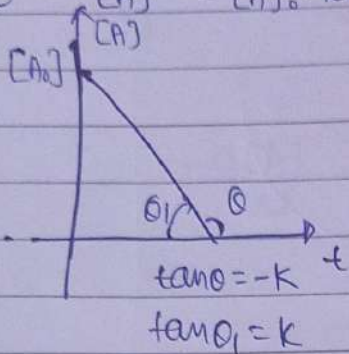
Shortcut:

If in equal time interval, the consecutive conc. are in A.P. $n=0$, GP; $n=1$, HP; $n=2$.

④ Graphical Method: →

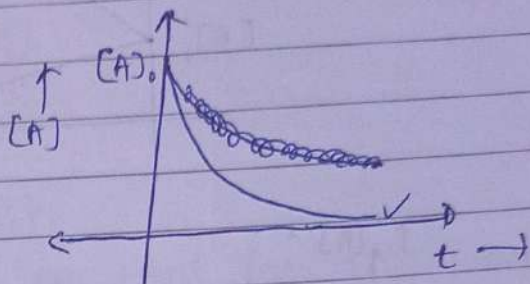
conc. vs time for rxn $A \rightarrow \text{Prod. (order} = n)$

$n=0$ $[A] = [A]_0 - kt$

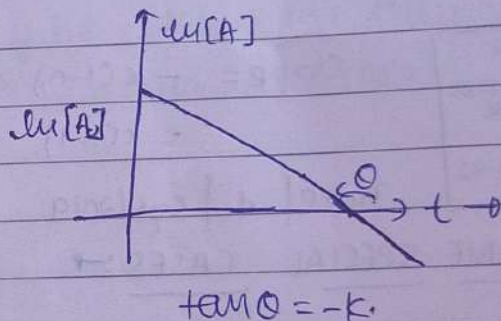


$\frac{[A]_0}{k} = t_{100\%}$

$[A]_t = [A]_0 e^{-kt}$



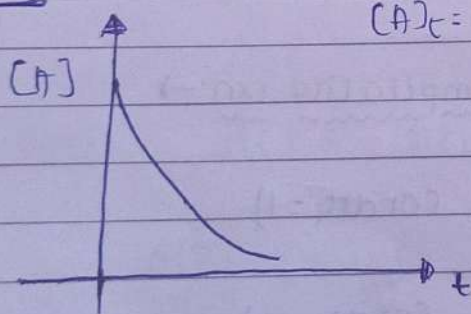
$\ln[A]_0 - kt = \ln[A]$



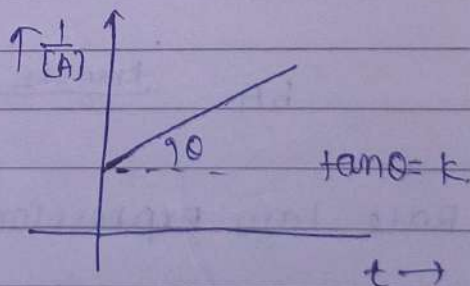
$n=2$

$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$

$[A]_t = \frac{1}{kt + \frac{1}{[A]_0}}$



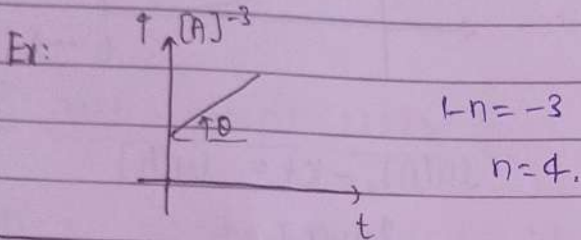
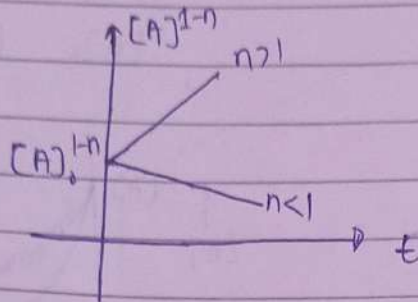
$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$



n^{th} order rxn ($n \neq 1$)

$\frac{[A]_0^{1-n} - [A]_t^{1-n}}{1-n} = kt$

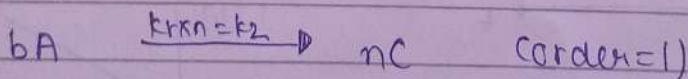
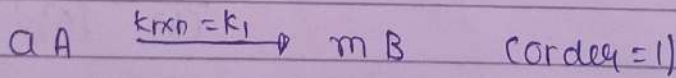
$$[A]^{1-n} = [A_0]^{1-n} - k(1-n)t$$



HW EX(5-1)23-33 CK	Slope = $-k(1-n)$ = $kn-1$
EX(6-1) 1-42 CK	Date 4 Sept/2019

SOME SPECIAL CASES :->

① Parallel or simultaneous or Competative rxn :->



① Rate law expression:

$$r_1 = -\frac{1}{a} \frac{d[A]}{dt} = +\frac{1}{m} \frac{d[B]}{dt} = k_1[A] \rightarrow \textcircled{1}$$

$$r_2 = -\frac{1}{b} \frac{d[A]}{dt} = +\frac{1}{n} \frac{d[C]}{dt} = k_2[A] \rightarrow \textcircled{2}$$

② Net rate of disappearance of A:

$$-\frac{d[A]}{dt} = ak_1[A] + bk_2[A]$$
$$= (ak_1 + bk_2)[A]$$

$$\text{or } -\frac{d[A]}{dt} = k[A] \rightarrow \textcircled{3}$$

$$\text{where } k = ak_1 + bk_2$$

= overall rate constant for disappearance of A.

The overall rate constant may be expressed only when all parallel reactions are of same order.

③ Composition of products:

$$\text{Eqn (1): } d[B] = mk_1[A] dt$$

$$\text{Eqn (2): } d[C] = nk_2[A] dt$$

$$\frac{d[B]}{d[C]} = \frac{mk_1}{nk_2}$$

$$\int_0^{[B]} d[B] = \int_0^{[C]} \frac{mk_1}{nk_2} d[C]$$

$$\therefore \frac{[B]}{[C]} = \frac{mk_1}{nk_2}$$

The composition of product is time independent when all parallel reactions are of same order.

④ Conc. of A, B & C at any time t :

From eqⁿ ③ $-\frac{d[A]}{dt} = k[A]$

$$[A]_t = [A]_0 e^{-kt}$$

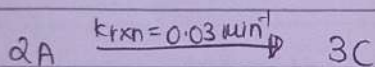
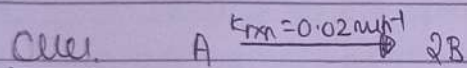
FOR B:

$$\frac{d[B]}{dt} = m k_1 [A] dt$$

$$\int_0^t d[B] = \int_0^t m k_1 [A]_0 e^{-kt} dt$$

$$[B] = \frac{m k_1 [A]_0}{k} (1 - e^{-kt})$$

$$[C] = \frac{n k_2 [A]_0}{k} (1 - e^{-kt})$$



At $t=0$, $[A_0] = 0.2 \text{ M}$; $[B] = [C_0] = 0$

(i) What is the rate constant for the disappearance of A?

Solⁿ: $k = a k_1 + b k_2$

$$k = 0.02 + 0.06 = 0.08 \text{ min}^{-1}$$

(ii) What % of total product is B at $t=10 \text{ min}$.

Solⁿ: $\frac{[B]}{[C]} = \frac{2 \times 0.02}{3 \times 0.03} = \frac{4}{9}$

$$[B] = [C] \frac{4}{9}$$

$$\% \text{ of B} = \frac{4}{13} \times 100 = \frac{400}{13}$$

(iii) Calculate the conc. of A, B & C at $t = 12.5 \text{ min}$.

Soln

$$k t = \ln \frac{[A]_0}{[A]_t}$$

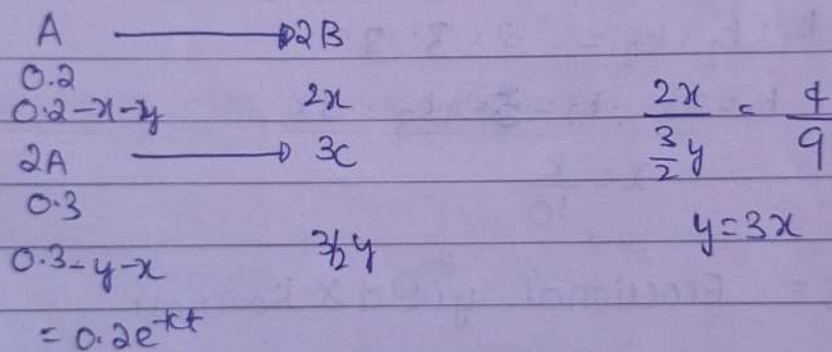
$$0.08 \times 12.5 = \ln \frac{0.02}{[A]_t}$$

$$-1 = \ln \frac{0.02}{[A]_t}$$

$$[B] = \frac{2 \times 0.02 \times 0.2}{0.08} (1 - e^{-0.08 \times 12.5})$$

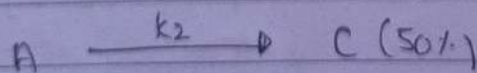
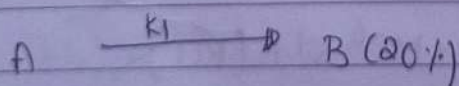
$$[C] = \frac{3 \times 0.03 \times 0.2}{0.08} (1 - e^{-0.08 \times 12.5})$$

M-Q

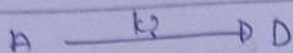
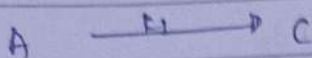
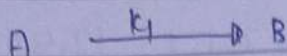


$$x + y = 0.2 (1 - \frac{1}{e})$$

Ques.



If the conc. of A drops to $\frac{1}{4}$ th of initial conc. in 20 min. calculate k_1, k_2, k_3 .

Soln.

$$k = \frac{1}{20 \text{ min}} \ln \frac{[A]_0}{[A]_0/4}$$

$$t_{1/4} \rightarrow 10 \text{ min}$$

$$t_{1/2} \rightarrow 20 \text{ min}$$

$$k = \frac{\ln 4}{20} \text{ min}^{-1}$$

$$k = k_1 + k_2 + k_3$$

$$[B] : [C] : [D] = k_1 : k_2 : k_3$$

$$k_1 : k_2 : k_3 = 2 : 3 : 3$$

$$k_1 = 2x ; k_2 = 3x ; k_3 = 3x$$

$$x = \frac{k}{10}$$

$$k_{\text{path}} = \text{Fractional yield} \times k_{\text{overall}}$$

Ques. $\text{CH}_3 - \overset{\text{Cl}}{\text{C}} - \text{CH}_3 + \text{OH}^- \xrightarrow{\text{aq}} \text{CH}_3 - \overset{\text{OH}}{\text{C}} - \text{CH}_3 + \text{Cl}^-$
follows the following pathways.

$$\text{SN}^1 \text{ path: } r_1 = (2 \times 10^{-6} \text{ s}^{-1}) [\text{RCl}]$$

$$\text{SN}^2 \text{ path: } r_2 = (4 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}) [\text{RCl}] [\text{OH}^-]$$

predict the dominant pathway if $[\text{OH}^-] = 0.02 \text{ M}$.

$$r_2 = (4 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}) [\text{RCl}] 0.02 \text{ M}$$

$$r_1 >> r_2$$

SN¹

(ii) At what minimum OH^- conc., the dominant pathway will become SN^2 .

Solⁿ $r_1 = r_2$
 $4 \times 10^{-7} [\text{RCl}][\text{OH}^-] = 2 \times 10^{-6} [\text{RCl}]$
 $[\text{OH}^-] = \frac{10}{2} = 5\text{M}$.

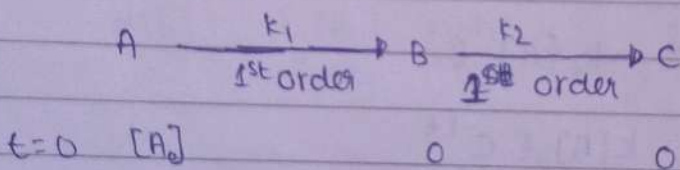
(iii) Calculate the % of alcohol formed by SN^2 pathway when OH^- conc. = 0.5M .

Solⁿ: % product by SN^2 path = $\frac{r_2}{r_1 + r_2} \times 100\%$ (in unit time).

$$\frac{k_2 [\text{RCl}][\text{OH}^-]}{k_1 [\text{RCl}] + k_2 [\text{RCl}][\text{OH}^-]} \times 100$$

$$= \frac{100}{11}$$

(B) STATE SEQUENTIAL OR SUCCESSIVE RXN: \rightarrow



① conc. of A, B and C at any time t

$$[A] = [A]_0 e^{-k_1 t} \quad -\frac{d[A]}{dt} = k_1 [A]$$

$$+\frac{d[B]}{dt} = k_1 [A] - k_2 [B]$$

or $\frac{d[B]}{dt} + k_2 [B] = k_1 [A]$

$$\frac{d[B]}{dt} + k_2 [B] = k_1 [A]_0 e^{-k_1 t} \quad \text{I.F.} = e^{\int k_2 dt} = e^{k_2 t}$$

Multiply both sides with $e^{k_2 t}$

$$e^{k_2 t} \frac{d[B]}{dt} + k_2 [B] e^{k_2 t} = k_1 [A]_0 e^{-k_1 t} e^{k_2 t}$$

$$\text{or } \frac{d}{dt} ([B] e^{k_2 t}) = k_1 [A]_0 e^{(k_2 - k_1)t}$$

$$\int_0^t d([B] e^{k_2 t}) = \int_0^t k_1 [A]_0 e^{(k_2 - k_1)t} dt$$

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

If $k_1 \neq k_2$,

$$[B] e^{k_2 t} = \frac{k_1 [A]_0}{k_2 - k_1} [e^{(k_2 - k_1)t} - 1]$$

$$\therefore [B] = \frac{k_1 [A]_0}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}]$$

If $k_1 = k_2 = k$

$$[B] e^{k_2 t} = k_2 [A]_0 t$$

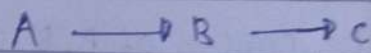
$$[B] = k [A]_0 t e^{-k t}$$

for c: net rate of formation of c.

~~[C]~~

$$\frac{d[C]}{dt} = k_2 [B]$$

$$\int_0^t d[C] = k_2 \int_0^t [B] dt$$



$$t=0 \quad [A]_0 \quad 0 \quad 0$$

$$t=t \quad [A]_0 - x \quad x - y \quad y$$

~~[C]~~

$$[A] + [B] + [C] = [A]_0$$

$$\left. \begin{array}{l} [C] = [A]_0 - [A] - [B] \end{array} \right\}$$

$$\underline{k_1 \neq k_2,}$$

$$[C] = [A_0] \left[1 - \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_2 - k_1} \right]$$

$$\underline{k_1 = k_2}$$

$$\begin{aligned} [C] &= [A_0] - [A] e^{-k_1 t} - [A_0] e^{k_1 t} \cdot t \\ &= [A_0] [1 - e^{-k_1 t} (1 + k_1 t)]. \end{aligned}$$

② Time for max. conc. of [B] : \rightarrow

For $[B]_{\max}$, $\frac{d[B]}{dt} = 0$

$$\underline{k_1 \neq k_2}$$

$$[B] = \frac{k_1 [A_0]}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

Now, $\frac{d[B]}{dt} = 0$

$$\frac{d[B]}{dt} = \frac{k_1 [A_0]}{k_2 - k_1} (e^{-k_1 t} (-k_1) - e^{-k_2 t} (-k_2)) = 0$$

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

$\underline{k_1 = k_2 = k}$: $[B] = k[A_0] t e^{-k t}$

$$\frac{d[B]}{dt} = 0 \Rightarrow \left. \begin{aligned} & \\ & \end{aligned} \right\} t_{\max} = \frac{1}{k}$$

③ Max. conc. of [B] :->

$$k_1 \neq k_2$$

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

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

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

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

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

$$[B] = \frac{k_1 [A]_0}{(k_2 - k_1)} \left(\frac{k_2}{k_1}\right)^{\frac{-k_2}{k_2 - k_1}} \left(\frac{k_2}{k_1} - 1\right)$$

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

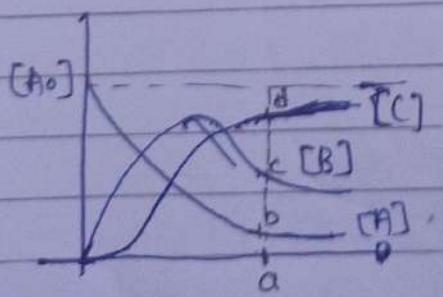
$k_1 = k_2 = k$:

$$[B]_{max} = \frac{[A]_0}{e}$$

HW
Ex (0-2)
Ch
Ex (5-7) 65

Date | 6 | Sept. | 2019

④ Graph :->

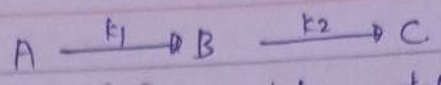


$$[A]_0 = [A] + [B] + [C]$$

$$[A]_0 = ab + ac + ad$$

$$+ \frac{d[C]}{dt} = k_2 [B]$$

⑤ $k_1 \ll k_2$



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

$$= \frac{k_1 [A]_0}{k_2} e^{-k_1 t}$$

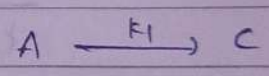
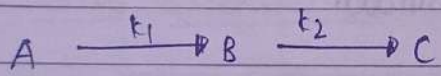
$$[B] = \frac{k_1 [A]}{k_2}$$

Or, $\left\{ k_2 [B] = k_1 [A] \right\}$.

\therefore Rate of formation of A = Rate of disappearance of B.

At this stage, B is called in steady state. C will form stoichiometrically as A reacts.

The reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ may be considered $A \xrightarrow{k_1} C$



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

$[A]_0$	0
$[A]_0 - x$	x
$[A]_0 e^{-k_1 t}$	$[A]_0 (1 - e^{-k_1 t})$

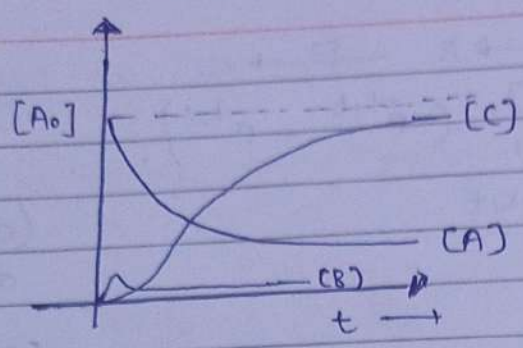
$$[C] = [A]_0 (1 - e^{-k_1 t})$$

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

$$[A]_0 \left(\frac{k_2}{k_1} \right)^{-1} = [A]_0 \left(\frac{k_1}{k_2} \right) \approx \text{very small.}$$

$$t_{max} = \frac{\ln \left(\frac{k_2}{k_1} \right)}{k_2 - k_1} = \text{very small.}$$

$k_2 - k_1 = k_2$
 $e^{-k_2 t} \approx 0$
 $(e^{-k_1 t} - e^{-k_2 t}) = e^{-k_1 t}$
 after sufficient time.
 (As at $t=0$ approx. is not valid).



• It is the case of highly unstable intermediate.

⑥ $k_1 \gg k_2$:

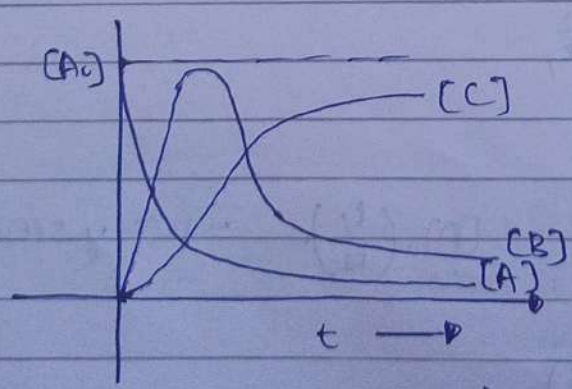
$$[B]_{\max} = [A]_0 \left(\frac{k_2}{k_1} \right)^{\frac{-k_2}{k_2 - k_1}}$$

$$[A]_0 \left(\frac{k_2}{k_1} \right)^{\frac{k_2}{k_1}} \approx [A_0]$$

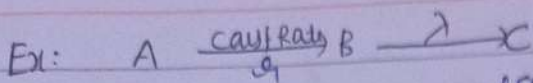
$$\left(\frac{1}{64} \right)^{1/3} = \frac{1}{4} \left(\frac{1}{64} \right)^{1/8} = \frac{1}{2}$$

$$t_{\max} = \frac{\ln \left(\frac{k_2}{k_1} \right)}{k_2 - k_1} = \text{very small.}$$

• In this case the reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ may be considered as $B \xrightarrow{k_2} C$ with the initial conc. of B almost equal to $[A_0]$.



• It is the case of relatively more stable intermediate.



steady state $\frac{d[B]}{dt} = r_1 - \lambda[B] = 0$

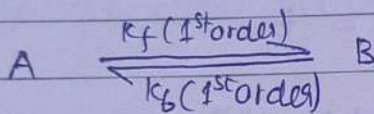
$$[B] = r_1/\lambda$$

$$\int_0^{[B]} \frac{d[B]}{r_1 - \lambda[B]} = \int_0^t dt$$

$$-\frac{1}{\lambda} \ln \frac{r_1}{r_1 - \lambda[B]} = t$$

$$[B] = \frac{r_1}{\lambda} (1 - e^{-\lambda t})$$

③ Reversible or opposing rxn :->



① Rate Law Expressions:

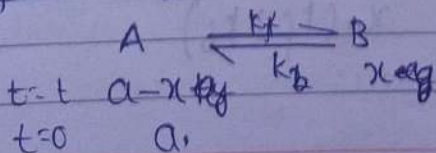
* Rate of forward rxn, $r_f = k_f[A]$

* Rate of backward rxn, $r_b = k_b[B]$

* Net rate of disappearance of A = $-\frac{d[A]}{dt} = k_f[A] - k_b[B]$

* Net rate of appearance of B, $\frac{d[B]}{dt} = k_f[A] - k_b[B]$

② Conc. of [B], [A] at any time t



$$-\frac{d[A]}{dt} = k_f[A] - k_b[B]$$

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

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

$$\frac{dx}{dt} + x(k_f + k_b) = a k_f$$

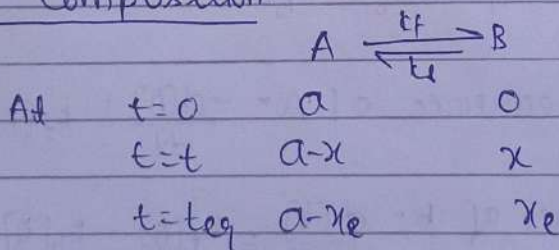
$$\int_0^x \frac{dx}{k_f a - x(k_f + k_b)} = \int_0^t dt$$

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

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

$$x = \frac{k_f a}{k_f + k_b} (1 - e^{-(k_f + k_b)t})$$

③ Conc. of A & B at any time t in terms of equb^m composition:



At equb^m =

$$k_f[A] = k_b[B]$$

$$k_f(a-xe) = k_b(xe)$$

$$\therefore k_f a = xe(k_f + k_b)$$

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

$$(k_f + k_b)t = \ln \frac{x_e}{x_e - x} \rightarrow \text{Learn}$$

(iv) Time of achievement of eqbm.

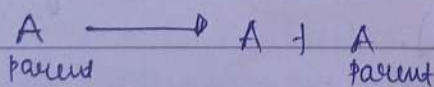
For $t = t_{eq}$, $x = x_e$
 $t = \infty$.

Achievement of eqbm is thermodynamic property of system which can never be related with time.

$$t_{1/2} \Rightarrow x = \frac{x_e}{2}$$

$$\left. \vphantom{t_{1/2}} \right\} t_{1/2} = \frac{\ln 2}{(k_f + k_b)}$$

Bacterial Growth:



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

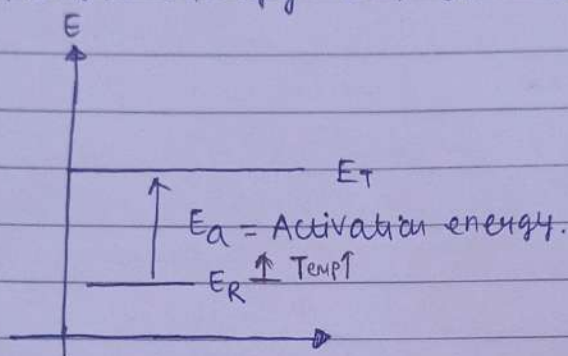
$$kt = \ln \frac{[A]}{[A]_0}$$

Generation time : It is the time in which population becomes double.

Normally, reactions are not so fast. It represents that all the molecular collisions do not result product formation.

② ENERGY BARRIER:

Only those collisions may result a reaction in which the molecules must have a certain minimum energy called threshold energy (E_T) at the time of collision.



$$E_R \approx 0.9$$

$$E_T \approx 90.80$$

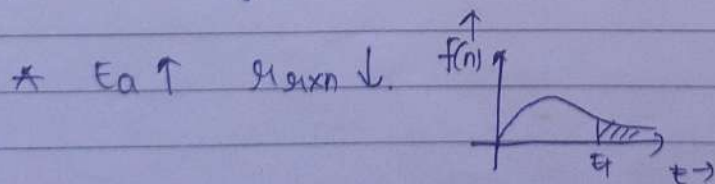
$$E_a = E_T - E_R$$

$$\approx E_T$$

E_T is also temp depend.

Minimum average energy which should be given to reactant molecule in order to make them participating effectively is called activation energy for the rxn.

All the reactant molecules having energy E_a or more may result product formation ($E_a \geq E_T$).



On rising the temp., the activation energy of rxn may or may not change. Normally, the changes remain so small that it is assumed to be temp. independent.

* The fraction of molecules having sufficient energy for rxn is given by Boltzmann factor, $e^{-E_a/RT}$.

HW

Rac-8

Rac-9