

Topics

→ chemical kinetics

- Introduction

- Rate of Rxn.

- Order & Molecularity

- Integrated rate law.

→ zeroth order rxn

→ 1st order

→ 2nd order

→ General n-th order rxn.

- Fractional order rxns.

- Determination of order of rxn.

Why rxn Kinetics?

• Thermodynamics predicts :-

- feasibility of a given rxn

- relative amounts of reactants & products at eq.

- Effect of experimental conditions on amount of product at eq.

• Thermodynamics cannot predict

- Rate of rxn.

- Effect of varying conc. on rate of rxn.

- Effect of exptl condition on rate of rxn.

• Chemical kinetics deals with rate of rxn and its dependence on conc. of reactants & experimental condition.

• It helps to establish the mechanism of the rxn - step by step pathway.

Rate of a reaction

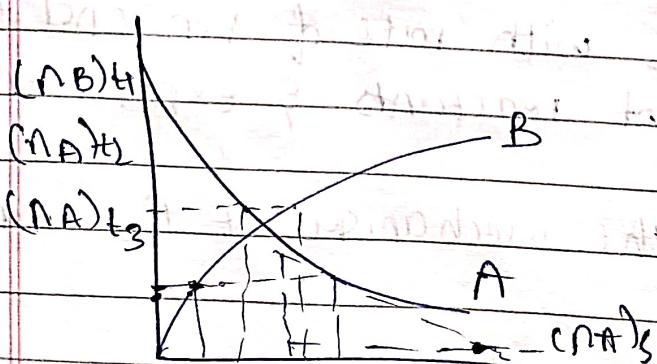
- Extremely fast rxns - instantaneous rxns:
 - Reaction b/w a strong acid & a strong base
- Extremely slow rxns:
- $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$
- $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$
- $\text{C}(\text{graphite}) + \text{O}_2 \rightarrow \text{CO}_2(\text{g})$
- B/w these two extremes, we have rxns those proceed with measurable speed.
- Rate of rxn means rate of change of amount of a reactant or a product in unit time. Thus, unit of rate of rxn is mol·sec⁻¹.

Average & instantaneous rate

Average rate is the rate of change of conc. in a time interval.

$$r_{\text{avr}} = -\frac{\Delta n_A}{\Delta t} = -\frac{n_A(t) - n_A(t')}{t - t'}$$

$$r_{\text{avr}} = \frac{\Delta n_B}{\Delta t} = \frac{n_B(t) - n_B(t')}{t - t'}$$

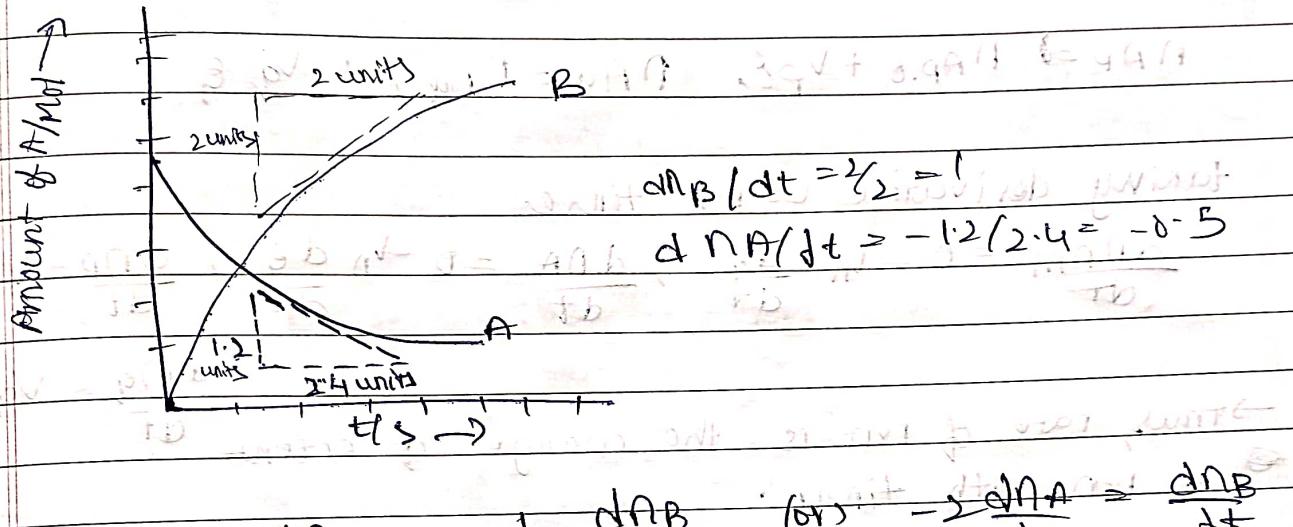


* Δn_A & Δn_B are the change in amount of A & B at a particular time.

$$r_{\text{inst}} = \lim_{\Delta t \rightarrow 0} -\frac{\Delta n_A}{\Delta t}$$

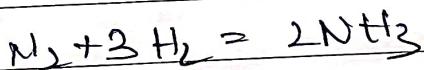
$$\text{rate} = -\frac{dN_A}{dt} = \frac{dN_B}{dt}$$

Average & instantaneous rate



General reaction

For the reaction

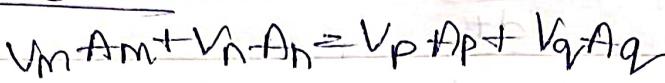


$$\text{rate} = -\frac{dN_2}{dt} = -\frac{1}{3} \frac{dN_{H_2}}{dt} = \frac{1}{2} \frac{dN_{NH_3}}{dt}$$

Gen for a general rxn

v_i = stoichiometric coefficient

$$\text{Rate} = -\frac{1}{v_n} \frac{dN_{A,n}}{dt} = -\frac{1}{v_n} \frac{dN_A}{dt} = \frac{1}{v_0} \frac{dN_{A,0}}{dt} = \frac{1}{v_p} \frac{dN_{A,p}}{dt}$$

General reaction

If ϵ be the extent of reaction, i.e;

$$\Delta A_m = A_{m,0} - V_m \epsilon, \Delta A_n = A_{n,0} - V_n \epsilon,$$

$$\Delta A_p \Rightarrow \Delta A_{p,0} + V_p \epsilon, \Delta A_q \Rightarrow \Delta A_{q,0} + V_q \epsilon$$

taking derivative w.r.t time

$$\frac{d\Delta A_m}{dt} = 0 - V_m \frac{d\epsilon}{dt}, \frac{d\Delta A_n}{dt} = 0 - V_n \frac{d\epsilon}{dt}, \frac{d\Delta A_p}{dt} = V_p \frac{d\epsilon}{dt}, \frac{d\Delta A_q}{dt} = V_q \frac{d\epsilon}{dt}$$

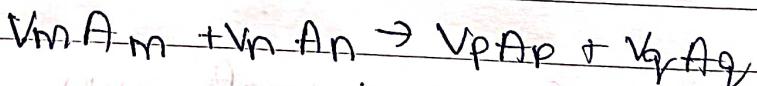
thus, rate of rxn is the change of extent of rxn with time.

conveniently, amount is replaced by concentration (amount per unit volume). thus

$$\text{rate of rxn} = r = \frac{d(\frac{\epsilon}{V})}{dt} = \frac{dx}{dt} = -\frac{1}{V_m} \frac{d[A_m]}{dt} = -\frac{1}{V_n} \frac{d[A_n]}{dt}$$

Order of Reaction

for the rxn



law of mass action predicts the rate of forward reaction.

experimentally,

$$r \propto [A_m]^{m_m} [A_n]^{n_n}$$

where

$$m_m \neq V_m, n_n \neq V_n$$

$$m_m \neq V_m, n_n \neq V_n$$

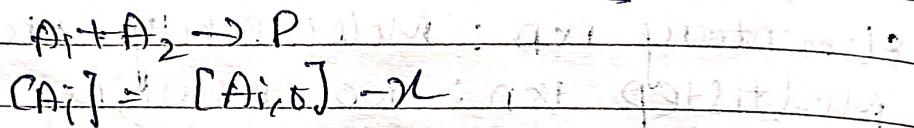
m_m, n_n are called order of the rxn w.r.t A_m & A_n

③ Half-life: $t_{1/2} = \text{time in which } [A_i] = \frac{1}{2} [A_0]$

Thus,

$$t_{1/2} = \frac{[A_0]}{2 k_i K_0}$$

Integrated rate law - first order rxn



Rate

$$r = \frac{d[A_i]}{dt} = -k_i \frac{d[A_i]}{dt} = k_i [A_i]$$

$$\int_{[A_i, 0]}^{[A_i]} \frac{d[A_i]}{[A_i]} = -k_i \int_{t=0}^t dt$$

$$[A_i] = [A_i, 0] e^{-k_i t}$$

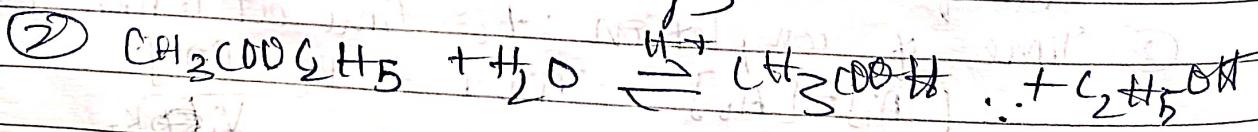
Characteristics of 1st order rxn

- ① Unit of k_i is s^{-1}
- ② First order rxn does not go for completion
- ③ Half life

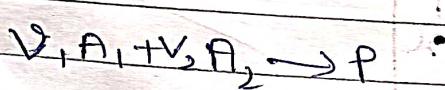
$$= t_{1/2} = \frac{0.693}{k_i}$$

Eg: of 1st order rxn.

- ① All radioactive decays



Integrate Rate law - 2nd order reaction



Two cases:-

- 1) when order is 2 w.r.t A_1 or A_2
- 2) when order is 1 w.r.t each of A_1 & A_2

Case 1:-

$$r = \frac{dx}{dt} = -\frac{1}{V_1} \frac{d[A_1]}{dt} = k_2 [A_1]^2 = k_2 (A_{1,0} - V_1 x)^2$$

Case 2:-

$$r = \frac{dx}{dt} = -\frac{1}{V_1} \frac{d[A]}{dt} = k_2' [A_1][A_2] = k_2' [A_{1,0} - V_1 x][A_{2,0} - V_2 x]$$

On integration

Case 1 :- $\frac{dx}{dt} = k_2 (A_{1,0} - V_1 x)^2$

$$\int \frac{1}{(A_{1,0} - V_1 x)^2} dx = \int k_2 dt$$

$$-\frac{1}{V_1} \left[\frac{-1}{(A_{1,0} - V_1 x)} \right]_0^x = k_2 [t]_0^+$$

$$\left[\frac{1}{(A_{1,0} - V_1 x)} \right]_0^x = V_1 k_2 t + C$$

Case 2:-

$$\frac{dx}{dt} = -k_2' [A_{1,0} - V_1 x][A_{2,0} - V_2 x]$$

$$\int_0^x \frac{dx}{[A_{1,0} - V_1 x][A_{2,0} - V_2 x]} = \int k_2' dt$$

$$-\frac{1}{V_1 V_2} \left[\frac{1}{(A_{1,0} - V_1 x)} - \frac{1}{(A_{2,0} - V_2 x)} \right]_0^x = k_2' t$$

Unit of k_n is $\text{mol}^{1-n} \text{dm}^{3(n-1)} \cdot \text{s}^{-1}$

Half-life

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

Example of fractional order rxn

i) Reaction b/w H_2 & D_2

$$\frac{dx}{dt} = K_p \text{P}_{\text{H}_2} (\text{P}_{\text{D}_2})^{1/2}$$

ii) Conversion of para H_2 to ortho H_2 at high pressure.

$$\frac{dx}{dt} = K_p (\text{P}_{\text{H}_2})^{1.5}$$

iii) The rxn $\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$ follows

$$-\frac{d[\text{CH}_3\text{CHO}]}{dt} = K [\text{CH}_3\text{CHO}]^{1.5}$$

iv) The rxn $\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$ follows

$$-\frac{d[\text{CH}_3\text{CHO}]}{dt} = K [\text{CH}_3\text{CHO}]^{1.5}$$

v) The rxn $\text{O}_2 \rightarrow 2\text{O}_2$, has -ve order w.r.t $[\text{O}_2]$, it follows

$$-\frac{1}{2} \frac{d[\text{O}_2]}{dt} = K \frac{[\text{O}_2]^2}{[\text{O}_2]}$$

Determination of order of reaction

Based on the type of reaction various methods can be used to determine its order.

① Integration method:

- Suitable data from expt are substituted into the integrated rate eqns for different order reactions
- The eqn giving almost a const value of rate const decides the order of rxn.

2. Graphical method:

Suitable data from expt are plotted according to different integrated rate eqns to give a st line.

- The rate const. of the rxn is calculated from the slope of the resultant st line plot

Kinetics	st-line	slope of the plot
(i) 1 st order	$\log [A]_t \text{ vs } t$	$-k_1$ 2.303

ii) 2nd order with equal conc of reactants $\frac{1}{[A]_t} \text{ vs } t$ k_2

iii) 2nd order with diff conc of reactants $\log \left(\frac{[B]_0 - x}{[A]_0 - x} \right) \text{ vs } t$ $([B]_0 - [A]_0) k$
 2.303

iv) 3rd order with equal conc of reactants $\frac{1}{[A]^2} \text{ vs } t$ $2 k_3$

v) 3rd order with equal conc. of two of reactants $\frac{2x(2[B]_0 - [A]_0)}{[A]_0([A]_0 - 2x)} \text{ vs } t$ $k_3(2[B]_0 - [A]_0)$
 $+ \ln \frac{[B]_0([A]_0 - 2x)}{[A]_0([B]_0 - x)} \text{ vs } t$

3. Half life method

- Applicable only when the rate law involves only one conc term.

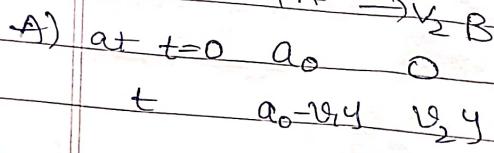
$$t_{1/2} = \frac{1}{k_n(n-1)} \frac{2^{n-1} - 1}{[A]_0^{n-1}}$$

n can be determined graphically

$$\log(t_{1/2}) = \log \left(\frac{2^{n-1} - 1}{kn(n-1)} \right) + (1-n) \log [A]_0$$

$\log(t_{1/2}) \text{ vs } \log [A]_0$ will give a st line with slope $(1-n)$

(1)

 $y \rightarrow$ extent of dissociation

$$\left(\frac{dy}{dt} \right) = k(a_0 - v_1 y)^1$$

$$PV_0 = a_0 RT$$

$$PV = (a_0 - v_1 y + v_2 y) RT$$

$$y = \left[\frac{PV}{RT} - a_0 \right] / (v_2 - v_1)$$

$$\left(\frac{dy}{dt} \right) = \frac{P}{(v_2 - v_1) RT} \cdot \frac{dv}{dt}$$

$$\frac{P}{(v_2 - v_1) RT} \cdot \frac{dv}{dt} = k(a_0 - v_1) \left[\frac{PV}{RT} - a_0 \right]$$

$$\frac{P}{(v_2 - v_1) RT} \cdot \frac{dv}{dt} = k \left[\frac{PV_0}{RT} - v_1 \left[\frac{PV}{RT} - \frac{PV_0}{RT} \right] \right]$$

$$\frac{P}{(v_2 - v_1) RT} \cdot \frac{dv}{dt} = \frac{k}{RT} \left[PV_0 V_2 - PV_0 V_1 - PV_1 V_2 + PV_0 V_1 \right]$$

$$\frac{dv}{dt} = k(V_0 V_2 - V_0 V_1)$$

$$\int_{V_0}^{V_1} \frac{dv}{V_0 V_2 - V_0 V_1} = k \int_0^t dt$$

$$\Rightarrow -\frac{1}{V_1} \left[\ln(V_0 V_2 - V_0 V_1) \right]_{V_0}^V = k t$$

$$\Rightarrow K + V_1 = \ln(V_0 V_2 - V_0 V_1)$$

$$\frac{V_0 V_2 - V_0 V_1}{V_0 V_2 - V_0 V_1}$$

$$\Rightarrow V = V_0 \left[\left(\frac{V_2}{V_1} \right) - \left(\frac{V_2 - V_1}{V_1} \right) e^{-V_1 K t} \right]$$

(A)

$$(a_0 - v_1 y) = a_0 e^{-v_1 k t}$$

$$[A]_t \propto V = [A]_0 \times e^{-v_1 k t}$$

$$[A]_t = [A]_0 \cdot e^{-v_1 k t}$$

$$\left(\frac{V_2}{V_1} - \left(\frac{V_2}{V_1} - 1 \right) e^{-k t v_1} \right)$$

case 1:

when $v_1 = v_2 = 1$

$$V = V_0 \Rightarrow [A]_t = [A]_0 \cdot e^{-v_1 k t}$$

case 2:-

when $v_1 = 1, v_2 = 2$

$$V = 2V_0 - V_0 \cdot e^{-v_1 k t} = V_0 (2 - e^{-v_1 k t})$$

$$[A]_t = [A]_0 \cdot e^{-v_1 k t}$$

$$e^{-v_1 k t} < 1$$

$$[A]_t (2) = [A]_t (1) \cdot \frac{1}{2 - e^{-v_1 k t}}$$

since at time $t=0$

$$2 - e^{-v_1 k t} > 1$$

 $[A]_t$ is $< [A]_0$

→ The gaseous rxn $V_1 A(g) \rightarrow V_2 B(g)$ is 1st order w.r.t A.

- 1Q) it is studied at a constant pressure with a_0 as the initial amount of A. Show that the volume of the system & the concentration of A at time t are given by the expression.

$$V = V_0 \left[\left(\frac{V_2}{V_1} \right) - \left(\frac{V_2}{V_1} - 1 \right) e^{-v_1 k t} \right]$$

$$[A]_t = [A]_0 \left[\frac{e^{-v_1 k t}}{\left(\frac{V_2}{V_1} \right) - \left(\frac{V_2}{V_1} - 1 \right) e^{-v_1 k t}} \right]$$

→ V_0 - volume of system at $t=0$. Assume ideal behaviour for the gasses. Derive the exprsn for $V \cdot \epsilon_1 [A]$ for the system where $v_1 = v_2 = 1$ $\epsilon_1 = 1$ $v_1 = 1$ $\epsilon_1 v_2 = 2$

② The gaseous rxn



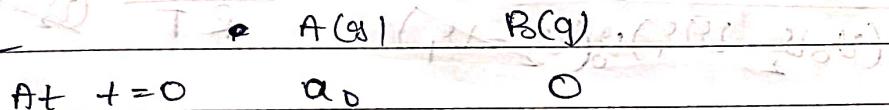
is a 2nd order rxn w.r.t A. It is studied at a const pressure with a_0 as the initial amount of A. Show that the volume of the system and the concentration of A at time t are given by the expression.

$$V = V_0 \left(\frac{1 + v_2 k a_0 t}{1 + v_1 k a_0 t} \right)$$

$$\frac{1}{[A]_t} = \left(\frac{1}{[A]_0} + v_1 V_0 k t \right) \left(\frac{1 + v_2 k a_0 t}{1 + v_1 k a_0 t} \right)$$

where V_0 is the volume of the system at $t=0$. Assume ideal behaviour for the gases. Derive the expression for V and $[A]$ for the system where $v_1 = v_2 = 1$ and $v_1 = 1$ & $v_2 = 2$

So,



$$At \quad t=0 \quad a_0 \quad 0$$

$$At \quad t=t \quad a_0 - v_1 y \quad v_2 y$$

$$\frac{dy}{dt} = k(a_0 - v_1 y)^2$$

$$PV_0 = a_0 RT$$

$$PV = (a_0 - v_1 y + v_2 y) RT$$

$$y = \frac{\left[\frac{PV}{RT} - a_0 \right]}{(v_2 - v_1)}$$

$$\frac{dy}{dt} = \frac{P}{v_2 - v_1 (RT)} \frac{dv}{dt}$$

$$\frac{P}{(v_2 - v_1) RT} \cdot \frac{dv}{dt} = k \left(a_0 - \frac{v_1}{v_2 - v_1} \left[\frac{PV}{RT} - a_0 \right] \right)^2$$

$$\frac{P}{(V_2 - V_1)RT} \cdot \frac{dV}{dt} = \frac{k}{V_1} \left[\frac{PV_0}{RT} - \frac{V_1}{V_2 - V_1} \left[\frac{PV}{RT} - \frac{PV_0}{RT} \right] \right]$$

$$\frac{P}{(V_2 - V_1)RT} \cdot \frac{dV}{dt} = \frac{k}{RT} \left[\frac{PV_0V_2 - PV_0V_1 - PVV_1 + PV_0V_1}{(V_2 - V_1)^2} \right]$$

$$R \cdot \frac{dV}{dt} = \frac{k}{RT} P^2 \frac{(V_0V_2 - V_1V_1)^2}{(V_2 - V_1)}$$

$$\frac{1}{(V_0V_2 - V_1V_1)} \frac{dV}{dt} = \frac{KP}{RT} dt \times \frac{1}{V_2 - V_1}$$

$$\Rightarrow \left[\frac{1}{(V_0V_2 - V_1V_1)} \right] \frac{dV}{V_0} = \frac{KP}{RT} t \times \frac{1}{(V_2 - V_1)}$$

$$\frac{1}{(V_0V_2 - V_1V_1)} = \frac{V_1 K P t \times 1}{RT (V_2 - V_1)}$$

$$\frac{V_0V_2 - V_0V_1 - V_1V_2 + V_1V_1}{(V_0V_2 - V_1V_1)V_0(V_2 - V_1)} = \frac{V_1 K P t \times 1}{RT (V_2 - V_1)}$$

$$\frac{V - V_0}{(V_0V_2 - V_1V_1)(V_2 - V_1)} = a_0 K t$$

$$V - V_0 = a_0 K t V_0 V_2 - a_0 K t V_1 V_1$$

$$V = V_0 \left[1 + a_0 K t \frac{V_2}{V_1} \right]$$

AJ_t

$$\frac{1}{[AJ_t]} - \frac{1}{[AJ_0]} = V_1 K_1 t \quad a_0 t = [AJ_t] V$$

$$\frac{1}{a_0 t} - \frac{1}{[AJ_0]} = V_1 K_2 t \quad a_0 = [AJ_0] V_0$$

$$\frac{1}{[A]_t} = \frac{1}{[A_0]_0} + v_1 K_2 t$$

$$\frac{1}{[A]_t} = \frac{1}{[A_0]_0} + v_1 K_2 t$$

$$\frac{1}{[A]_t} = \left(\frac{1}{[A_0]} + v_1 V_0 K t \right) \left[\frac{1 + v_2 K a_0 t}{1 + v_1 K a_0 t} \right]$$

Case 1: $v_1 = v_2 = 1$

$$v = v_0$$

$$\frac{1}{[A]_t} = \left(\frac{1}{[A_0]} + v_0 K t \right)$$

case 2: $v_1 = 1$ $v_2 = 2$

$$v = v_0 \left[1 + 2 a_0 K t \right]$$

$$v = v_0 \left[2 - \frac{1}{1 + K a_0 t} \right] > 1$$

③ The half-life period & the initial conc. for a reaction are as follows.

What is the order of the reaction? calculate the rate const.

$t_{1/2}$ s	42.5	27.5	94.1
a_0 mm Hg	354	540	158

Plot required

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

$\log(t_{1/2})$ vs. $\log[A_0]$ will be a st. line with slope $(1-n)$.

- ii) what is the rate ~~of~~ const of the rxn?
 iii) what is the rate of rxn at $t = 500\text{ s}$?
 iv) what will be concentration of N_2O_5 at 200 s ?
 v) what is the avg rate over the period 0 s to 200 s ?

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

Test - 1

$$k = \frac{2.303}{200} \log \frac{0.250}{0.223} = 0.0005715487$$

Test - 2

$$k = \frac{2.303}{400} \log \frac{0.250}{0.198} = 0.00058308977$$

\Rightarrow rxn is 1st order

ii) $k = 0.00058$

7314823444

iii) $\text{rate} = \frac{dx}{dt} = k [\text{N}_2\text{O}_5]$
 $= 0.00058 \times [\text{N}_2\text{O}_5] = 0.00058 \times 0.18796$
 $= 0.0001090168$

$$0.000583 = \frac{2.303}{500} \log \frac{0.250}{[\text{A}]_{500}}$$

$$6.126574 = \log \frac{0.250}{[\text{A}]_{500}}$$

$$1.33 = \frac{0.250}{[\text{A}]_{500}} \quad [\text{A}]_{500} = \frac{0.250}{1.33} = 0.1879$$

iv)

$$0.000583 = \frac{2.303}{2000} \log \frac{0.250}{[\text{A}]_{2000}}$$

$$0.5062961 = \log \frac{0.250}{[\text{A}]_{2000}}$$

$$\text{Solve } 3 \cdot 20845 = 0.250 \\ \text{Let } [A]_{2000} = 0.0760942351$$

$$[A]_{2000} = 0.0760942351$$

Avg rate $0 \leftrightarrow 200$

$$\text{Avg rate} = \frac{0.027}{200} = 0.000135$$

(*) let a be a rational $\Rightarrow a = \frac{p}{q}$
 b be irrational

Assume $a \times b = \text{rational}$

$$a \times b = \frac{m}{n}$$

$$\frac{p}{q} \times b = \frac{m}{n}$$

$$\therefore b = \left(\frac{m}{n} \times \frac{q}{p} \right) \Rightarrow \left(\frac{q}{p} \right) \text{ form (rational)}$$

contradiction.

22/8/23

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classmate

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$$\text{Q) } t_{\text{mean}} = \frac{\int_{A_0}^{A_\infty} t dA}{\int_{A_0}^{A_\infty} dA} \quad A_\infty \rightarrow 0$$

$$\text{To prove: } t_{\text{mean}} = \frac{1}{K_n}$$



$$t = -\frac{1}{K_1} \ln \frac{A}{A_0}$$

$$t_{\text{mean}} = \frac{\int_{A_0}^{A_\infty} -\frac{1}{K_1} \ln \frac{A}{A_0} dA}{\int_{A_0}^{A_\infty} dA}$$

$$\int \ln x \cdot 1$$

$$x \ln x - x$$

$$\Rightarrow -\frac{1}{K_1} \frac{A_0}{A_0} \left[A \ln \frac{A}{A_0} \right]$$

$$\Rightarrow -\frac{1}{K_1} \frac{A_0}{A_0} \left[\int_{A_0}^{A_\infty} (\ln A) dA - \int_{A_0}^{A_\infty} dA \right]$$

$$0 - A_0$$

$$= f \frac{1}{K_1} \left[[A \ln A - A] \Big|_{A_0}^0 + \ln A \Big|_{A_0}^0 \right]$$

$$+ A_0$$

$$- A_0 \ln A_0 + A_0 + A_0 \ln A_0$$

$$K_1$$

$$= \frac{1}{K_1} //$$

* Reaction order and Reaction mechanism

- ① Opposed elementary rxn or reversible elementary rxn.
- ② Side or concurrent elementary rxn.

$$\Rightarrow K_1 ([A]_0 - x_{eq}) = K_2 x_{eq}$$

x_{eq} = extent of rxn divided by volume at eq.

$$\Rightarrow K_2 = \frac{K_1 [A]_0}{x_{eq}} - K_1$$

$$(or) \quad K_1 + K_2 = \frac{K_1 [A]_0}{x_{eq}}$$

$$\frac{dx}{dt} = K_1 ([A]_0 - x) - \left(\frac{K_1 [A]_0}{x_{eq}} - K_1 \right) x$$

$$\frac{dx}{dt} = K_1 [A]_0 \left(1 - \frac{x}{x_{eq}} \right)$$

$$(or) \quad \frac{dx}{dt} = \frac{K_1 [A]_0}{x_{eq}} (x_{eq} - x)$$

$$\Rightarrow \int \frac{dx}{x_{eq} - x} = \frac{K_1 [A]_0}{x_{eq}} \int dt$$

$$\Rightarrow -\ln(x_{eq} - x) = \frac{K_1 [A]_0 t}{x_{eq}} + C$$

at $t=0, x=0$

$$\Rightarrow -\ln x_{eq} = C$$

$$\Rightarrow \ln \frac{x_{eq}}{x_{eq} - x} = \frac{K_1 [A]_0 \cdot t}{x_{eq}}$$

$$\Rightarrow \frac{x_{eq} - x}{x_{eq}} = e^{-\frac{K_1 [A]_0 \cdot t}{x_{eq}}}$$

$$\Rightarrow x = x_{eq} \left[1 - e^{-\frac{K_1 [A]_0 t}{x_{eq}}} \right]$$

Earlier we got:

$$K_1 + K_2 = \frac{K_1 [A]_0}{x_{eq}}$$

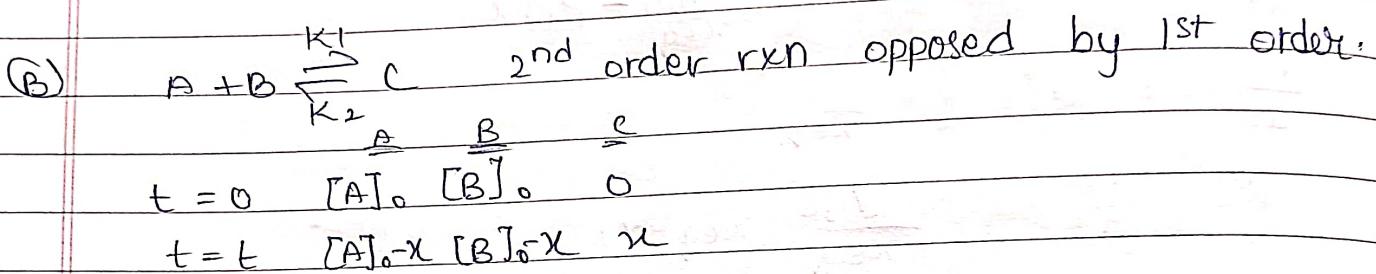
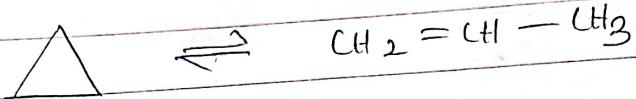
$$\Rightarrow x = \frac{K_1 [A]_0}{K_1 + K_2} \left[1 - e^{-(K_1 + K_2)t} \right]$$

↳ Integrated rate law of a reversible rxn $A \rightleftharpoons B$

$$\therefore \frac{K_2}{K_1} = K_{eq}$$

$$[A] = [A]_0 \cdot \frac{1}{1 + K_{eq}} [K_{eq} + e^{-(K_1 + K_2)t}]$$

Example:- isomerism of cyclopropane into propene.



rate law, $-\frac{dx}{dt} = K_1([A]_0 - x)([B]_0 - x) - K_2 \cdot x$

$$\ln \left[\frac{x_{eq} ([A]_0^2 - x_{eq})}{[A]_0^2 (x_{eq} - x)} \right] = K_1 \frac{[A]_0^2 - x_{eq}^2}{x_{eq}}$$

Eg:-



$$-\frac{dx}{dt} = K_1([A]_0 - x)([B]_0 - x) - K_2 \cdot x$$

At eq:-

$$K_1([A]_0 - x_{eq})([B]_0 - x_{eq}) = K_2 x_{eq}$$

$$\Rightarrow K_2 = \frac{K_1([A]_0 - x_{eq})([B]_0 - x_{eq})}{x_{eq}}$$

$$-\frac{dx}{dt} = K_1([A]_0 - x)([B]_0 - x) - \frac{K_1([A]_0 - x_{eq})([B]_0 - x_{eq})}{x_{eq}}$$

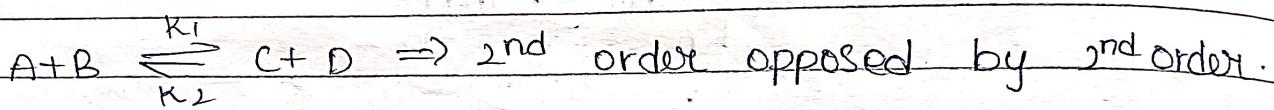
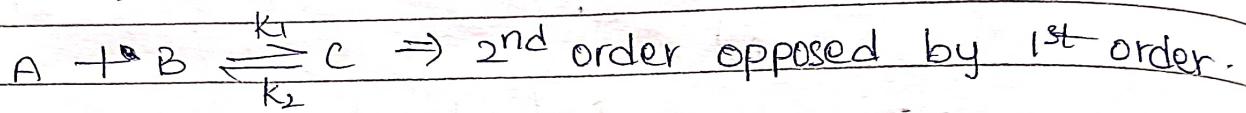
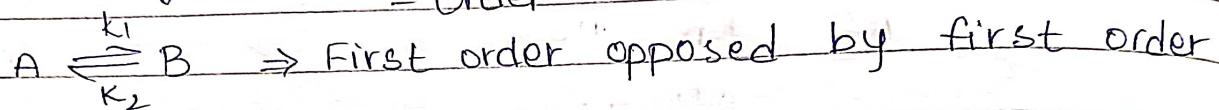
③ Consecutive or sequential rxn.

a) Derive rate law & integrated rate law for such elementary rxn.

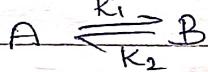
① Opposed or reversible elementary rxn.



Elementary rxn \Rightarrow molecularity = order
= order



② First order opposed by 1st order



rate of rxn = rate of forward rxn - rate of backward rxn

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

If x = extent of rxn divided by volume, at any time, then,

$$[A] = [A]_0 - x$$

$$[B] = x$$

|| we assume no B was present at the beginning.

$$\Rightarrow -\frac{d}{dt} \{[A]_0 - x\} = k_1([A]_0 - x) - k_2 x$$

$$\Rightarrow \frac{dx}{dt} = k_1[A]_0 - (k_1 + k_2)x$$

At "Equilibrium,"

rate of forward rxn = rate of backward rxn.

$$\log \frac{425}{275} = \log \left(\frac{2^{n-1}-1}{kn(n-1)} \right) + (1-n) \log \frac{354}{540}$$

$$\log \frac{275}{425} = \log \left(\frac{2^{n-1}-1}{kn(n-1)} \right) + (1-n) \log \frac{540}{354}$$

$$\log \frac{\frac{161}{805}}{\frac{1125}{55}} = (1-n) \log \frac{354}{540} \quad (-0.42227)$$

$$(-0.1833) \quad (-0.221848)$$

$$-2.759 = 1-n$$

$$n = 3.7 = \underline{\underline{4}}$$

$$\log \frac{425}{275} = (1-n) \log \frac{354}{540}$$

$$1-n = -1$$

$$n=2$$

- ④ The decomposition of N_2O_5 at 318 K acc to the eqn $\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$

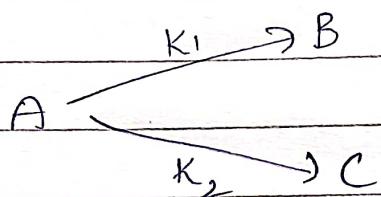
The following concentration data were obtained:

t/sec (n-1)	0	200	400	600	800	1000	1200
$[\text{N}_2\text{O}_5]/\text{mol dm}^{-3}$	0.256	0.223	0.198	0.174	0.152	0.134	0.120

Answer the following.

- i) what is the order of the rxn?

② Side or concurrent elementary rxn:

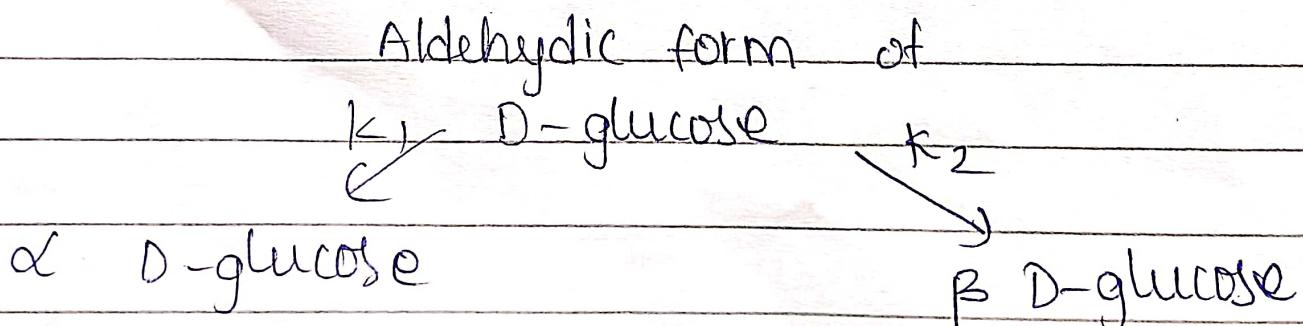


Rate of disappearance of A:

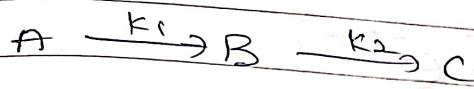
$$\Rightarrow -\frac{d[A]}{dt} = k_1[A] + k_2[A]$$
$$= (k_1 + k_2)[A]$$

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

Example:



② Consecutive or sequential rxn.



$$[AJ]_0 = [AJ] + [BJ] + [C] \text{ at any time } t \quad \text{at } t=0 \quad \text{at } t=t$$

$$-\frac{d[AJ]}{dt} = k_1[AJ] \rightarrow \textcircled{2}$$

$$\frac{d[BJ]}{dt} = k_1[AJ] - k_2[BJ] \rightarrow \textcircled{3}$$

$$\frac{d[C]}{dt} = k_2[BJ] \rightarrow \textcircled{4}$$

$$\text{From } \textcircled{1}, [AJ] = [AJ]_0 \cdot e^{-k_1 t} \quad \textcircled{5}$$

$$\text{from } \textcircled{2}, \frac{d[BJ]}{dt} + k_2[BJ] = k_1[AJ]$$

$$\therefore \frac{d}{dt} \{ [BJ] \cdot e^{k_2 t} \} = e^{k_2 t} \cdot \frac{d[BJ]}{dt} + [BJ] \cdot k_2 \cdot e^{k_2 t}$$

$$= e^{k_2 t} \left\{ \frac{d[BJ]}{dt} + k_2 [BJ] \right\}$$

$$\Rightarrow \frac{d}{dt} \{ [BJ] \cdot e^{k_2 t} \} = e^{k_2 t} \cdot \frac{d[BJ]}{dt} + k_1[AJ]$$

$$\therefore [AJ] = [AJ]_0 \cdot e^{-k_1 t}$$

$$\Rightarrow \frac{d}{dt} \{ [BJ] \cdot e^{k_2 t} \} = k_1[AJ]_0 \cdot e^{(k_2 - k_1)t}$$

$$\Rightarrow \int d \{ [BJ] e^{k_2 t} \} = k_1[AJ]_0 \int e^{(k_2 - k_1)t} dt$$

$$\Rightarrow [BJ] \cdot e^{k_2 t} = \frac{k_1}{k_2 - k_1} [AJ]_0 \cdot e^{(k_2 - k_1)t} + c$$

$$\text{at } t=0 \quad [BJ]=0$$

$$\Rightarrow c = -\frac{k_1}{k_2 - k_1} [AJ]_0$$

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

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

$$\therefore [A]_0 > [A] + [B] + [C]$$

$$\Rightarrow [C] = [A]_0 - [A] - [B]$$

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

$$\Rightarrow [C] = [A]_0 \left\{ 1 - e^{-K_1 t} - \frac{K_1}{K_2 - K_1} e^{-K_1 t} + \frac{K_1}{K_2 - K_1} e^{-K_2 t} \right\}$$

$$\Rightarrow [C] = \frac{[A]_0}{K_2 - K_1} \left[K_2 - K_1 - K_2 e^{-K_1 t} + K_1 e^{-K_2 t} - K_1 e^{-K_1 t} + K_1 e^{-K_2 t} \right]$$

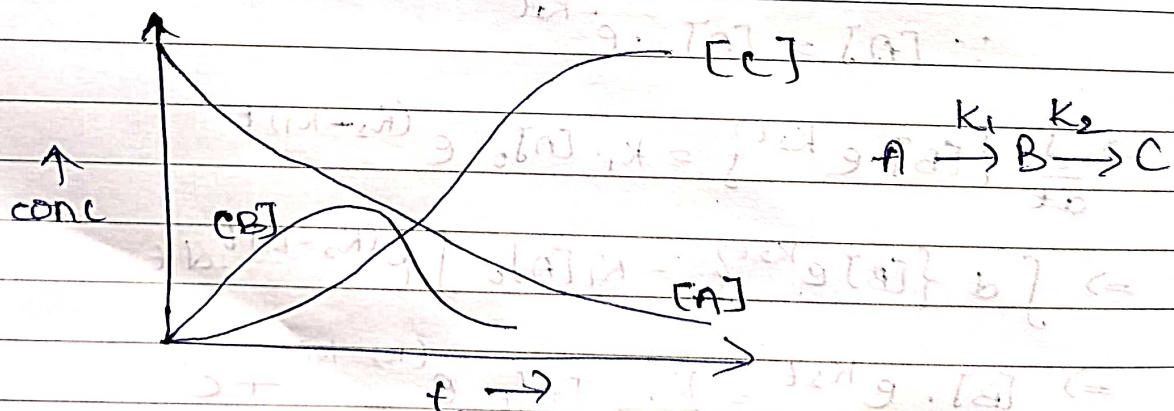
$$\Rightarrow [C] = [A]_0 \left\{ 1 + \frac{K_1 e^{-K_2 t} - K_2 e^{-K_1 t}}{K_2 - K_1} \right\}$$

Thus,

$$[A] = [A]_0 \cdot e^{-K_1 t}$$

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

$$[C] = [A]_0 \left\{ 1 + \frac{K_1 \cdot e^{-K_2 t} - K_2 \cdot e^{-K_1 t}}{K_2 - K_1} \right\}$$



what would be the max conc. of B i.e. $[B]_{\text{max}}$

$$\Rightarrow \frac{d[B]}{dt} = 0 \quad \& \quad \frac{d^2[B]}{dt^2} < 0$$

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

$$\Rightarrow \frac{d[B]}{dt} = [A]_0 \cdot \frac{k_1}{k_2 - k_1} (-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}) = 0$$

$$\Rightarrow \frac{k_1}{k_2} = e^{(k_1 - k_2)t_{\max}}$$

$$\Rightarrow t_{\max} = \frac{1}{k_1 - k_2} \ln \left(\frac{k_1}{k_2} \right)$$

$$\frac{d^2[B]}{dt^2} = [A]_0 \cdot \frac{k_1}{k_2 - k_1} (k_1^2 e^{-k_1 t} - k_2^2 e^{-k_2 t})$$

For $\frac{d^2[B]}{dt^2} < 0$

(i) $k_2 - k_1 < 0$ & $k_1^2 e^{-k_1 t} > k_2^2 e^{-k_2 t}$

\Downarrow

$$k_2 < k_1$$

\Downarrow

$$k_1 > k_2 \Rightarrow k_1^2 e^{-k_1 t} > k_2^2 e^{-k_2 t}$$

True.

(or)

(ii) $k_2 - k_1 > 0$ & $k_1^2 e^{-k_1 t} < k_2^2 e^{-k_2 t}$

$$k_2 > k_1$$

\Downarrow

$$k_1 < k_2 \Rightarrow k_1^2 e^{-k_1 t} < k_2^2 e^{-k_2 t}$$

$$\Rightarrow [B]_{\max} = [A]_0 \cdot \frac{k_1}{k_2 - k_1} (e^{-k_1 t_{\max}} - e^{-k_2 t_{\max}})$$

\vdots

Simplify

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

① Rate determining step

② Steady-state approximation

Rate-determining step:

Who is controlling $[C]$, k_1 or k_2 ?

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

Case 1: When $k_2 \gg k_1$

$$\Rightarrow e^{k_2 t} \gg e^{k_1 t}$$

$$\Rightarrow e^{-k_2 t} \ll e^{-k_1 t}$$

$$\Rightarrow k_2 \cdot e^{-k_1 t} \gg k_1 \cdot e^{-k_2 t}$$

$$\Rightarrow k_2 - k_1 \approx k_2$$

$$\text{&} k_2 \cdot e^{-k_1 t} - k_1 \cdot e^{-k_2 t} \approx k_2 \cdot e^{-k_1 t}$$

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

$$\Rightarrow [C] \approx [A]_0 \left(1 - e^{-k_1 t} \right)$$

so, $[C]$ is controlled by k_1 , i.e. rate const of slowest step as $k_2 \gg k_1$

Case 2: When $k_1 \gg k_2$

$$\Rightarrow e^{k_1 t} \gg e^{k_2 t}$$

$$\Rightarrow e^{-k_1 t} \ll e^{-k_2 t}$$

$$\Rightarrow k_1 \cdot e^{-k_2 t} \gg k_2 \cdot e^{-k_1 t}$$

$$\Rightarrow k_2 - k_1 \approx -k_1$$

$$\text{&} k_2 \cdot e^{-k_1 t} - k_1 \cdot e^{-k_2 t} \approx -k_1 \cdot e^{-k_1 t}$$

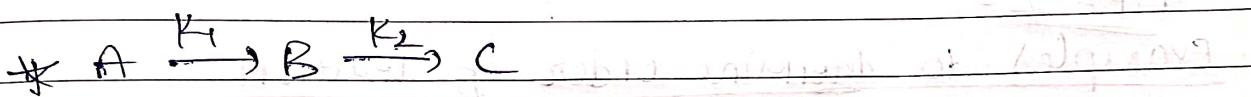
$$\Rightarrow [C] = [A]_0 \left\{ 1 - \frac{1}{(-k_1)} \cdot (-k_1 e^{-k_2 t}) \right\}$$

$$\Rightarrow [C] = [A]_0 \cdot (1 - e^{-k_2 t})$$

Again $[C]$ is controlled by rate const of slowest step as $k_1 \gg k_2$

Thus the production of C depends upon the rate const of slowest step (\Rightarrow slowest step is rate determining step)

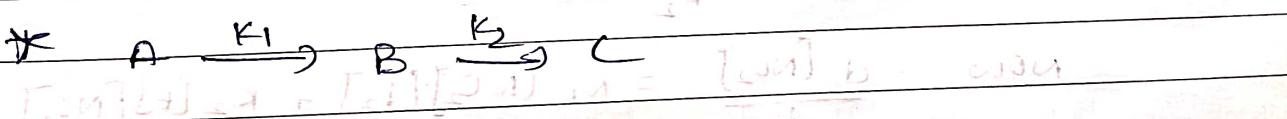
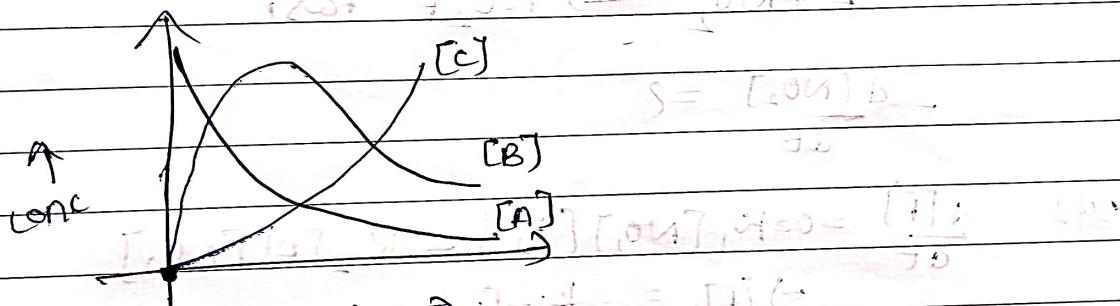
Steady State Approximation:-



If $k_1 \gg k_2$

\Rightarrow Rate of formation of B is much larger than its decomposition.

$\Rightarrow B$ will accumulate in the rxn mixture

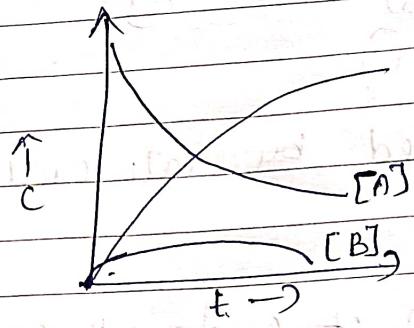


If $k_2 \gg k_1$

\Rightarrow decomposition of B is much faster than its formation.

\Rightarrow As soon as B is formed, it is decomposed to C .

$\Rightarrow B$ will not accumulate in rxn mixture

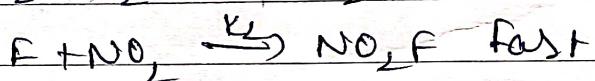
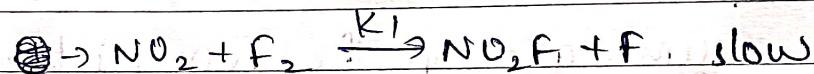


Thus if $k_2 \gg k_1$, $[B]$ is almost fixed for appreciable amount of time \Rightarrow Steady-state approximation

$\frac{d[B]}{dt} = 0$; B is a ~~non~~reactive intermediate.

TYPE-1:

Examples to determine order of reaction



$$-\frac{d[\text{NO}_2]}{dt} = ?$$

$$\text{S.Q. } \frac{d[\text{F}]}{dt} = 0 = k_1 [\text{NO}_2][\text{F}_2] - k_2 [\text{F}][\text{NO}_2]$$

$$\Rightarrow [\text{F}] = \frac{k_1 [\text{F}_2]}{k_2}$$

$$\text{Now } -\frac{d[\text{NO}_2]}{dt} = k_1 [\text{NO}_2][\text{F}_2] + k_2 [\text{F}][\text{NO}_2]$$

$$= 2k_1 [\text{NO}_2][\text{F}_2]$$

$$-\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = k_1 [\text{NO}_2][\text{F}_2]$$

so the rxn is 2nd order w.r.t $[NO_2]$

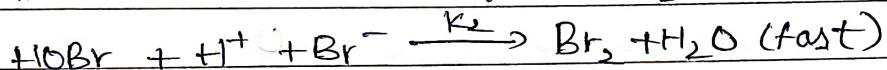
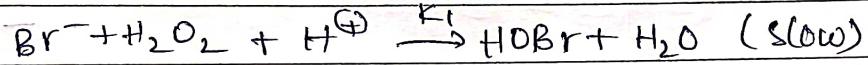
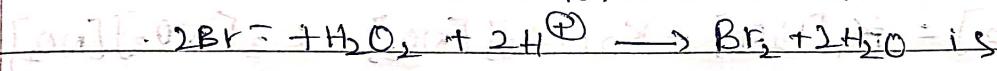
$$\text{so:- } \frac{d[NO_3]}{dt} = k_1 [NO_2]^2 - k_2 [NO_3][CO] = 0$$

$$-\frac{d[NO_2]}{dt} = k_1 [NO_2]^2 - k_2 [NO_3][CO] = 0$$

$$\text{rate } \frac{dx}{dt} = -\frac{d[CO]}{dt} = k_2 [NO_3][CO] \approx k_1 [NO_2]^2$$

$$-\frac{d[NO_2]}{dt} \quad (2)$$

(B) Proposed Mechanism for the rxn.



Determine order of rxn, w.r.t $[H_2O_2]$, $[H^+]$, $[Br^-]$

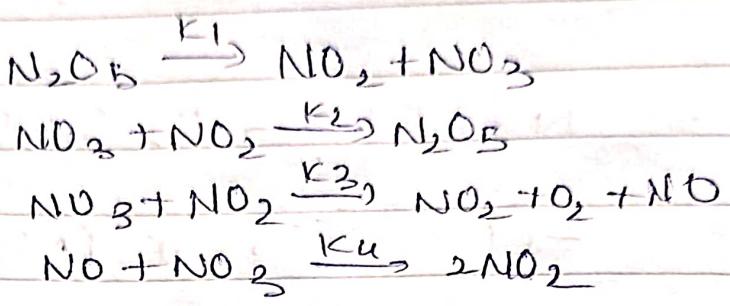
$$\text{so:- } \frac{d[HOBr]}{dt} = k_1 [Br^-][H_2O_2][H^+] - k_2 [HOBr][H^+][Br^-] = 0$$

$$-\frac{d[H_2O_2]}{dt} = k_1 [Br^-][H_2O_2][H^+]$$

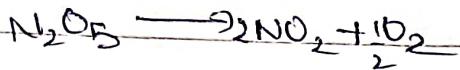
$$-\frac{d[H_2O_2]}{dt} = k_1 [Br^-][H_2O_2][H^+]$$

(g)

The thermal decomposition of N_2O_5 follows the mechanism



$$\text{S.t. : } -\frac{d}{dt} [\text{N}_2\text{O}_5] = \frac{2k_1 k_3 [\text{N}_2\text{O}_5]}{k_2 + 2k_3}$$



For $[\text{NO}_3]$, $[\text{NO}]$ apply steady state approximation.

$$\frac{d}{dt} [\text{NO}_3] = k_1 [\text{N}_2\text{O}_5] - k_2 [\text{NO}_3][\text{NO}_2] - k_3 [\text{NO}_3][\text{NO}_2] - k_4 [\text{NO}][\text{NO}_3] = 0$$

similarly

$$\frac{d}{dt} [\text{NO}] = k_3 [\text{NO}_3][\text{NO}_2] - k_4 [\text{NO}][\text{NO}_3] = 0 \quad \text{--- (2)}$$

$$-\frac{d}{dt} [\text{N}_2\text{O}_5] = k_1 [\text{N}_2\text{O}_5] - k_2 [\text{NO}_3][\text{NO}_2] - \text{--- (3)}$$

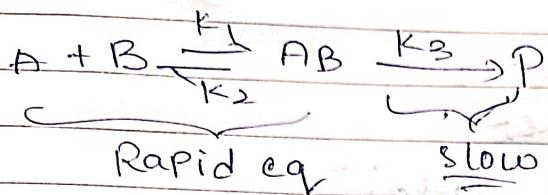
from (1) & (2)

$$k_1 [\text{N}_2\text{O}_5] - k_2 [\text{NO}_3][\text{NO}_2] - 2k_3 [\text{NO}_3][\text{NO}_2] = 0$$

$$\frac{k_1 [\text{N}_2\text{O}_5]}{k_2 + 2k_3} = [\text{NO}_3][\text{NO}_2] \text{ --- Put in eqn 3}$$

$$-\frac{d}{dt} [\text{N}_2\text{O}_5] = \frac{2k_1 k_3 [\text{N}_2\text{O}_5]}{k_2 + 2k_3}$$

Type II :- First step is rapid equilibrium followed by a slow step.



$$\frac{d[P]}{dt} = K_3 [AB]$$

$$\text{Method 1} :- K_{\text{eq}} = \frac{K_1}{K_2} = \frac{[AB]}{[A][B]} \Rightarrow [AB] = \frac{K_1}{K_2} [A][B]$$

$$\Rightarrow \frac{d[P]}{dt} = K_3 \cdot \frac{K_1}{K_2} [A][B].$$

Method 2 :-

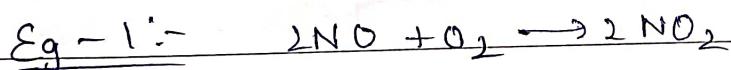
Applying steady state approximation to $[AB]$

$$\frac{d[AB]}{dt} = 0 = K_1[A][B] - K_2[AB] - K_3[AB]$$

$$[AB] = \frac{K_1[A][B]}{K_2 + K_3}$$

$$\begin{aligned} \Rightarrow \frac{d[P]}{dt} &= K_3 [AB] \\ &= K_3 \frac{K_1[A][B]}{K_2 + K_3} = \frac{K_3 K_1}{K_2} [A][B] \end{aligned}$$

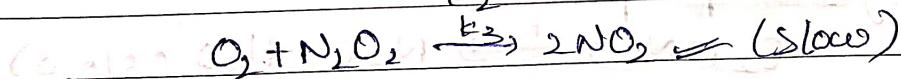
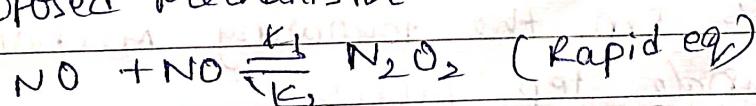
neglected.

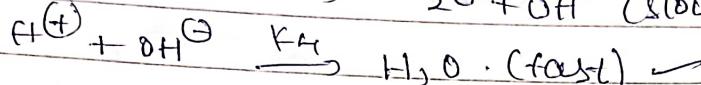
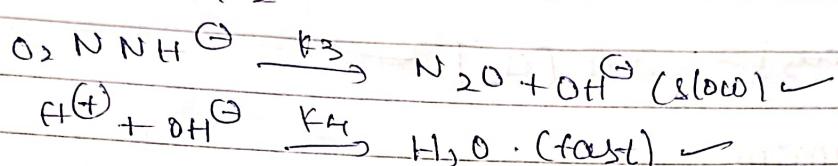
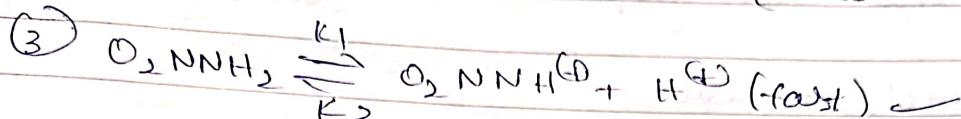
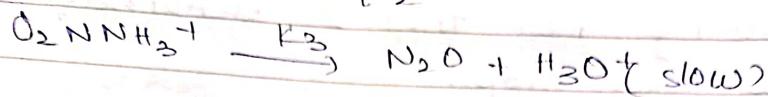
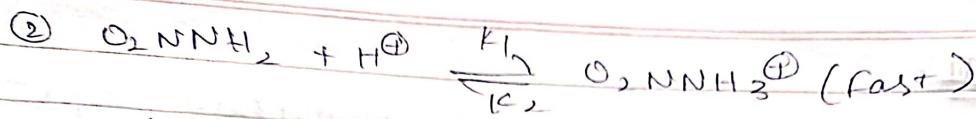


Exp. rate law is $\frac{1}{2} \frac{d[NO_2]}{dt}$

$$= K_1 [NO]^2 [O_2]$$

Proposed mechanism

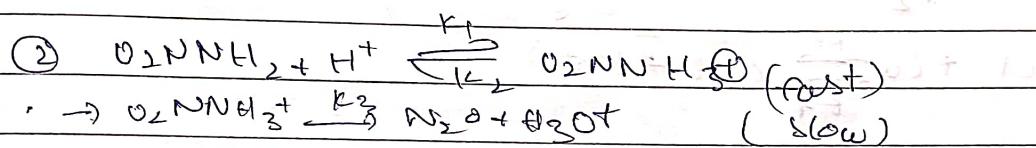




which of the proposed mechanism that obeys expt rate law

sol:- ① single step.

$$\frac{d}{dt} [\text{N}_2\text{O}] = k [\text{O}_2\text{NNH}_2] \times$$



$$\frac{d}{dt} [\text{N}_2\text{O}] = k_3 [\text{O}_2\text{NNH}_3^{\oplus}]$$

$$k_{\text{req}} = \frac{k_1}{k_2} = \frac{[\text{O}_2\text{NNH}_3^{\oplus}]}{[\text{O}_2\text{NNH}_2][\text{H}^{\oplus}]}$$

$$\Rightarrow \frac{d}{dt} [\text{N}_2\text{O}] = k_3 \cdot \frac{k_1}{k_2} \cdot [\text{O}_2\text{NNH}_2][\text{H}^{\oplus}] \times$$

∴

(3) $\frac{d}{dt} [\text{N}_2\text{O}] = k_3 [\text{O}_2\text{NNH}^{\oplus}]$

$$k_{\text{req}} = \frac{k_1}{k_2} = \frac{[\text{O}_2\text{NNH}^{\oplus}][\text{H}^{\oplus}]}{[\text{O}_2\text{NNH}_2]}$$

$$\Rightarrow \frac{d}{dt} [\text{N}_2\text{O}] = k_3 \cdot \frac{k_1}{k_2} \cdot \frac{[\text{O}_2\text{NNH}_2]}{[\text{H}^{\oplus}]}$$

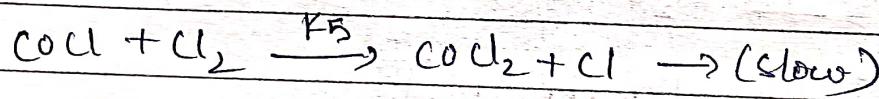
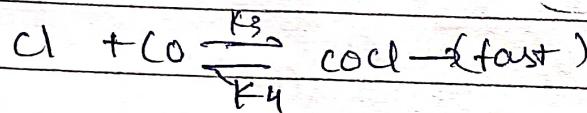
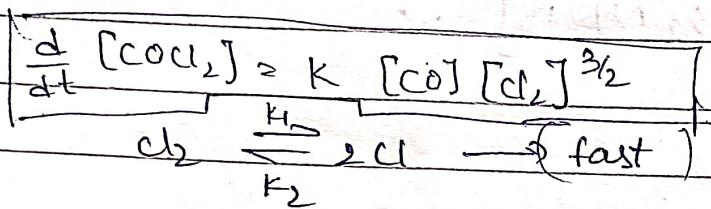
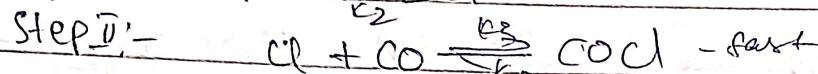
Type - III :-

Rxn involving more than 2. elementary steps with only one slow step.



$$\frac{d[\text{COCl}_2]}{dt} = k[\text{CO}] [\text{Cl}_2]^{3/2}$$

Mechanism



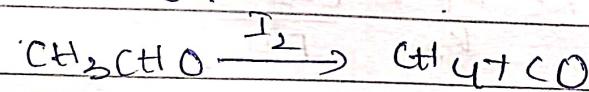
$$\frac{k_1}{k_2} = \frac{[\text{Cl}]^2}{[\text{Cl}_2]} ; \frac{k_3}{k_4} = \frac{[\text{COCl}]}{[\text{Cl}][\text{CO}]}$$

$$\frac{d[\text{COCl}_2]}{dt} = k_5 [\text{COCl}] [\text{Cl}_2]$$

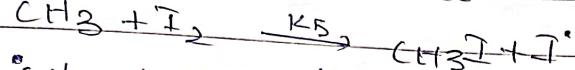
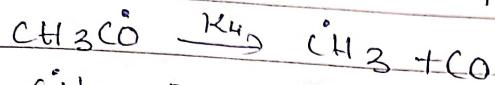
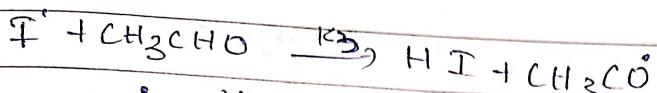
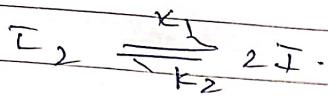
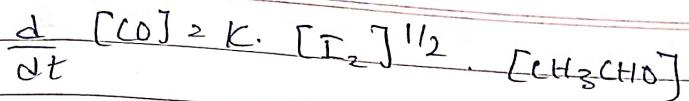
$$= k_5 \frac{k_3}{k_4} [\text{Cl}] [\text{CO}] [\text{Cl}_2]$$

$$= k_5 \cdot k_3 \cdot \left(\frac{k_1}{k_2} \right)^{1/2} [\text{CO}] [\text{Cl}_2]^{3/2}$$

Type - IV :- Rxn involving steps with comparable rate const.



expt rate law.



$$\frac{d}{dt} [I] = 0 ; \frac{d}{dt} [CH_3] = 0 ; \frac{d}{dt} [CH_3CO] = 0 ;$$

$$\Rightarrow \frac{d}{dt} [I] = 0 = 2k_1[I_2] - 2k_2[I]^2 - k_3[I][CH_3CHO]$$

$$+ k_5[CH_3][I_2] + k_6[CH_3][HI] = 0 \quad \textcircled{1}$$

$$\text{Rate} : \frac{d[CO]}{dt} = k_4[CH_3CO]$$

$$\frac{d[CH_2]}{dt} = 0 = k_4[CH_3CO] - k_5[CH_3][I_2] - k_6[CH_3][HI] \quad \textcircled{2}$$

$$\frac{d[CH_3CO]}{dt} = 0 = k_3[I][CH_3CHO] - k_4[CH_3CO] \quad \textcircled{3}$$

$$\frac{d[HI]}{dt} = 0 = k_3[I][CH_3CHO] - k_6[CH_3][HI] \\ - k_7[CH_3I][HI]$$

$$\frac{d[CO]}{dt} = k_4[CH_3CO]$$

from $\textcircled{2}$

from $\textcircled{3}$

$$2k_1[I_2] - 2k_2[I]^2 - k_4[CH_3CO] + k_4[CH_3CO] = 0$$

$$\Rightarrow k_1[I_2] = k_2[I]^2$$

↓

$$\frac{d[CO]}{dt} = k_3[I][CH_3CHO]$$

$$= k_3 \sqrt{\frac{k_1}{k_2}} [I_2]^{1/2} [CH_3CHO]$$

$$\frac{d[CO]}{dt} = k [I_2]^{1/2} [CH_3CHO]$$

$$\text{sof} := \frac{1}{2} \frac{d[N\text{O}_2]}{dt} = K_3 [\text{O}_2][\text{N}\text{O}_2]$$

Eq const.

$$K_{\text{eq}} = \frac{K_1}{K_2} = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}_2]}$$

$$\Rightarrow [\text{N}_2\text{O}_2] = \frac{K_1}{K_2} [\text{NO}_2]^2$$

$$\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = K_3 [\text{O}_2] \times \frac{K_1}{K_2} [\text{NO}_2]^2$$

$$= \left(K_3 \cdot \frac{K_1}{K_2} \right) [\text{O}_2][\text{NO}_2]^2$$

Example - 2 (Pg-194 (K1 Kappor))

In aq. media, nitramide (O_2NNH_2) decomposes slowly in aq. acid soln to N_2O & H_2O . i.e.,



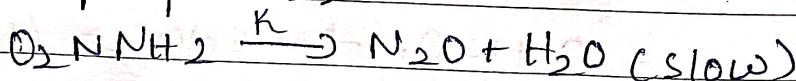
Expt. rate law is

$$\frac{d}{dt} [\text{N}_2\text{O}] = k \frac{[\text{O}_2\text{NNH}_2]}{[\text{H}^+]}$$

* Rate of formation of pdt is first order w.r.t. $[\text{O}_2\text{NNH}_2]$ but ~ 1 w.r.t $[\text{H}^+]$.

For this rxn, the following mechanisms are proposed

① Single step process.



$$\Rightarrow \log \left(\frac{[A_{2,0} - v_2 x]}{[A_{1,0} - v_1 x]} \right) = \log \left(\frac{[A_{2,0}]}{[A_{1,0}]} \right) + v_1 [A_{2,0}] - v_2 [A_{1,0}]$$

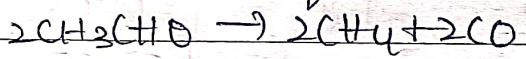
2-303

Half life time for case 1:

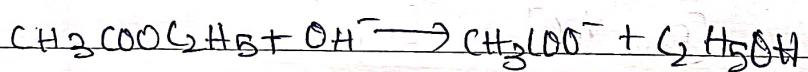
$$t_{1/2} = \frac{1}{k_2 [A_{1,0}]}$$

Examples:-

① Thermal dissociation of acetaldehyde.



② Saponification of an ester.



Integrated rate law - nth order Rxn

Differential rate law - $A \rightarrow \text{Product}$

$$\frac{dx}{dt} = k_n [A]^n = k_n ([A_0] - x)^n$$

On Integration,

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

respectively. $a_m + a_n$ is overall order of rxn.

$a_m + a_n = 0 \Rightarrow$ zeroth order

similarly 1st & 2nd order.

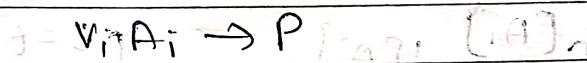
Molecularity of a rxn

No. of molecules taking part in a rxn.

Elementary rxn: Molecularity = order of reaction.

Multi-step rxn: No meaning.

Integrated Law - zeroth order rxn



$$\therefore [A_i] = [A_{i,0}] - v_i t$$

$$\text{Rate } r = \frac{d[A_i]}{dt} = -\frac{1}{V} \frac{d[A_i]}{dt} = k_0 [A_i]^0 = k_0$$

$$[A_i] = [A_{i,0}] - v_i k_0 t$$

$$[A_i] - [A_{i,0}] = -v_i k_0 t$$

$$x = k_0 t$$

Characteristics of zeroth order rxn

① Unit of k_0 is $\text{Mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$

② Time of completion: $t_c \geq$ time at which $[A_i] = 0$

$$\therefore [A_i] - [A_{i,0}] = -v_i k_0 t \Rightarrow t_c = \frac{[A_{i,0}]}{v_i k_0}$$

