

Reaction Engineering

Homogeneous Rxn: and Heterogeneous Rxn:

Single phase rxn: are homogeneous rxn:

- Eg:-
- ① $\text{Br}_2 + \text{H}_2 \rightarrow 2\text{HBr}$
 - ② $\text{N}_2\text{O} \rightarrow \text{N}_2 + \frac{1}{2}\text{O}_2$
 - ③ $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$

Multiphase Rxn: are heterogeneous rxn:

- Eg:-
- ① $\text{CaCO}_3 \rightarrow \text{CO}_2 + \text{CaO}$
 - ② $2\text{N}_2 + 3\text{H}_2 + \text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{H}_2\text{O}$

Rate of Rxn:

The rate of rxn in various forms are expressed as

$$-r_A = -\frac{1}{V} \frac{dCA}{dt} = k' CA$$

\uparrow

Representing consumption of A

$$-r_A' = -\frac{1}{W} \frac{dNA}{dt} = k'' CA$$

\uparrow

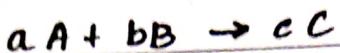
Single prime comes when we are considering
rate / weight

$$-r_A'' = -\frac{1}{S_i} \frac{dNA}{dt} = k''' CA$$

\uparrow

Double prime appears when we are considering
rate / surface area

Consider the rxn:

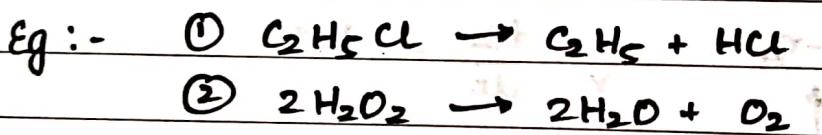


$$-\dot{r}_A = -\frac{a}{b} \dot{r}_B = \frac{a}{c} \dot{r}_C$$

Elementary Rxn:

If one molecule of species A is involved in the rxn, $A \rightarrow B$, it is unimolecular.

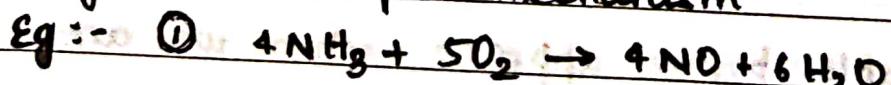
If the rxn stoichiometry is $2A \rightarrow B$, it is second order and bimolecular.



These are mono molecular rxn's and the rate of these rxn's are described by first order kinetics.

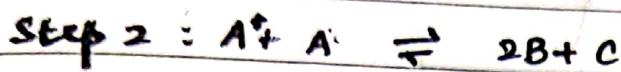
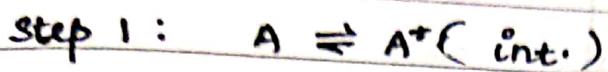
Non-elementary Rxn:

Non-elementary rxn take place in multiple steps and all individual steps may be elementary. They have complex mechanism.



$$r = k [NH_3]^{0.36} [O_2]^{0.14}$$

Derivation of rate Models



$$-r_A = k_1 C_A - k_2 C_A^+ + k_3 C_A C_A^+ - k_4 C_B^2 C_C$$

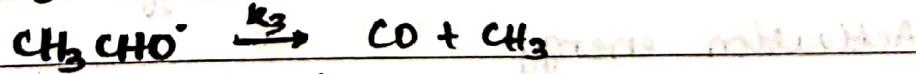
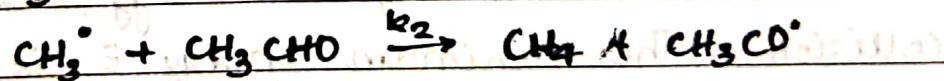
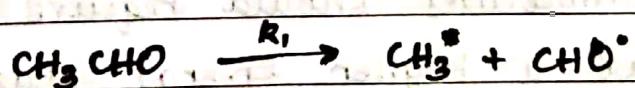
$$-r_{A^+} = k_1 C_A - k_2 C_A^+ - k_3 C_A C_A^+ + k_4 C_B^2 C_C$$

$$-r_A^+ = 0 \Rightarrow C_A^+ = \frac{k_1 C_A + k_4 C_B^2 C_C}{k_2 + k_3 C_A}$$

$$\therefore -r_A = \frac{k C_A^2}{1 + k' C_A}, \quad k = \frac{2k_1 k_3}{k_2}, \quad k' = \frac{k_3}{k_2}$$

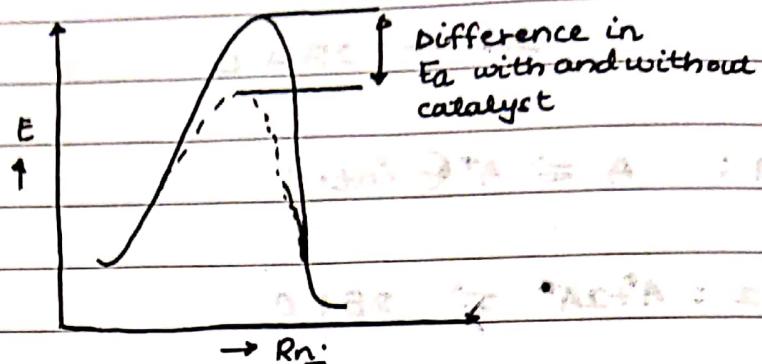
The rate of r_A can be approximated to 2nd-order kinetics.

Decomposition of Acetylaldehyde



On solving, $-r_{\text{CH}_3\text{CHO}} = k' [\text{CH}_3\text{CHO}]^{3/2}$

Catalytic Rn[±]



Catalyst reduces the activation energy, thereby enhancing the rate

Rate const. and Specific m³ rate

$$\text{specific rate} = k \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

unit: $(\text{dm}^3)^{-1} (\text{kmol})^{1-n} \text{s}^{-1}$

Temp. dependency of rate const.

The reacting molecules should require a min energy E to reach at a higher energy state, to perform collision. The minimum energy E is known as Activation energy.

Collision Theory

Acc. to this theory, the $r \propto$ no. of effective collisions per unit vol per unit time.

$$\bar{u} = \left(\frac{8RT}{\pi M} \right)^{1/2}$$

Let the diameter of A, B be d_A, d_B . The collision diameter $d_{AB} = \underline{d_A + d_B}$. The area of cross section for collision b/w two molecules = area of circle of radius $\frac{d_{AB}}{2}$.

$$f = N_A N_B \cdot \frac{\pi}{4} d_{AB}^2 \left(\frac{8k_B T}{\pi m_{AB}} \right)^{1/2}$$

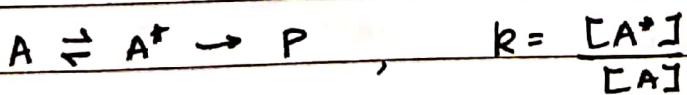
$$\text{rate of collision} \propto C_A C_B T^{1/2}$$

$$\begin{aligned} \therefore \text{Rate of m} &= [\text{rate of collision}] \times [\text{successful collisions}] \\ &= \left[10^6 N_A V \frac{\pi}{4} d_{AB}^2 \left(\frac{8k_B T}{\pi m_{AB}} \right)^{1/2} \right] e^{-E/RT} \\ &= k C_A C_B \end{aligned}$$

$$\therefore -r_A \propto C_A C_B T^{1/2} e^{-E/RT}$$

Transition State Theory

Acc. to this theory, the reacting molecules will reach the max. energy level to form an activated complex.



$$\ln K = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H + T\Delta S}{RT}, \quad K = e^{\Delta S/R} e^{-\Delta H/RT}$$

$$\frac{dp}{dt} = k'[A] = k_1 [A^*] \quad -r_A = k_1 [A^*] = k_1 K[A]$$

$$k_1 = \frac{k RT}{N h}$$

$$-r \propto C_A C_B T e^{-\Delta E/RT}$$

Arrhenius law

$$k = k_0 e^{-E/RT}$$

$$-r_A \propto T^n e^{-E/RT}$$

$$\text{Rate} = \left[\frac{(T_0)^n}{(T_1)^n} \right] \text{Rate}_0 \times \text{Rate}_0 = ?$$

$$\text{Rate}_0 = ?$$

$$\text{Rate} = k^n T^n \propto k^n T^n \propto RT^n$$

Pressure state coefficient

Arrhenius equation, written with pressure coefficient

$$\frac{P_A}{P_A^0} = ?$$

$$P_A = P_A^0 \cdot ?$$

$$P_A^0 = P_A^0 \cdot 1$$

$$\frac{P_A}{P_A^0} = \frac{P_A}{P_A^0} \cdot \frac{P_A^0}{P_A^0} = ?$$

$$P_A^0 = P_A^0 \cdot 1$$

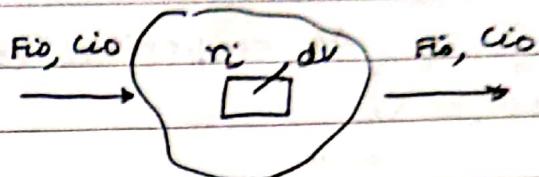
$$\frac{P_A}{P_A^0} = ?$$

Hole Balances & Kinetic study

General mole balance

$$[\text{Rate of In}] - [\text{Rate of Out}] + [\text{Rate of regeneration}] = [\text{Rate of accumulation within vol.}]$$

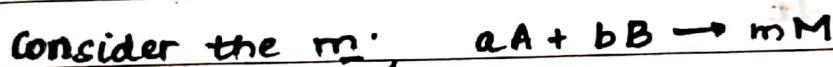
$$\text{Rate of gen.} = R_i = \int_0^V r_i dv$$



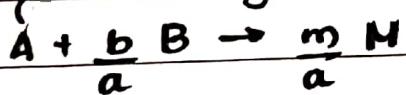
$$F_{i0} - F_0 + \int r_i dv = \frac{dN_i}{dt}$$

$$\text{At steady state, rate of acc.} = 0 \Rightarrow \frac{dN_i}{dt} = 0$$

Batch Reactor



→ limiting reactant



Initial no. of moles of A → N_{AO}

Initial no. of moles of B → N_{BO}

$$x_A = \frac{N_{AO} - N_A}{N_{AO}} \quad b = \frac{\text{Moles of A reacted}}{\text{Initial Moles of A}}$$

For batch reactor, $F_{i0} = 0$, $F_0 = 0$, but there is accumulation.

$$\int_0^V r_i dv = \frac{dN_i}{dt}$$

$$\Rightarrow \int_0^V r_A dv = \frac{dN_A}{dt} = -N_{AO} \frac{dx_A}{dt}$$

$$N_A = N_{AO}(1 - x_A)$$

$$-\tau_A = \frac{k_1 C_A}{1 + k_2 C_A}$$

For the rxn, $A \rightarrow B$

The estimation of k_1, k_2 is known as kinetic analysis.

An empirical eqn' is also used,

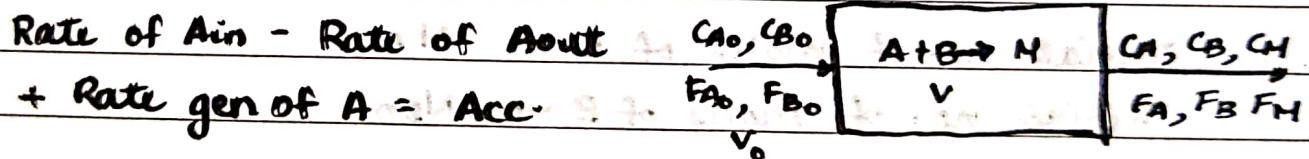
$$-\tau_A = k C_A^p, \quad k, p \text{ are parameters}$$

$$-\tau_A V = N_{AO} \frac{dx_A}{dt}$$

$$\frac{N_{AO}}{V} \frac{dx_A}{dt} = -\tau_A$$

$$\frac{C_{AO}}{V} \frac{dx_A}{dt} = -\tau_A \quad (\text{for } V \text{ const.})$$

Contin. Stirred Tank Reactor



$$\dot{V}_0 (C_{AO} - C_A) - \dot{V}_0 (C_A + \tau_A V) = \frac{d(C_A V)}{dt}$$

Acc = 0, steady state

$$\dot{V}_0 (C_{AO} - C_A) = -\tau_A V$$

$$\therefore T_m = \frac{V}{\dot{V}_0} = \frac{C_{AO} - C_A}{-\tau_A} \quad \begin{cases} \text{Const. vol.} \\ \text{process} \end{cases}$$

$$F_{AO} = v_0 C_{AO}, \quad F_A = v C_A, \quad v_0 = v$$

$$-r_A = \frac{F_{AO} - F_A}{v} = \frac{F_{AO} x_A}{v}$$

Plug flow reactor

→ Velocity along the radius is same

$$F_A + (F_A + dF_A) + \int A_C r dr dz$$

$$= \frac{dN_A}{dt}$$

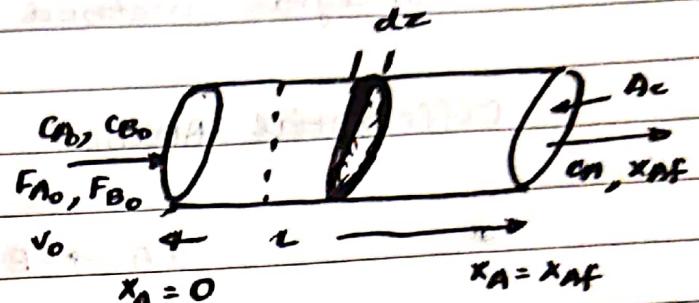
$$\text{Considering, } \frac{dN_A}{dt} = 0, \quad A_C dz = dv$$

$$-dF + \int_0^r r_A dv = 0$$

$$\frac{dF_A}{dv}$$

$$F_{AO} \left(\frac{dx_A}{dv} \right) = -r_A$$

$$\frac{v}{F_{AO}} = \int_0^{x_f} \frac{dx_A}{-r_A}, \quad T_p = \frac{v}{v_0} = C_A \int_0^x \frac{dx}{-r_A}$$

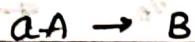


Kinetic Analysis of Batch Reactor

There are two methods,

- Differential method
- Integral method

Differential Method



$$-r_A = -\frac{dC_A}{dt} = k C_A^p$$

Taking log on both sides,

$$\ln(-r_A) = \ln\left(\frac{-dC_A}{dt}\right) = \ln k + p \ln C_A$$

The r_A rates at diff. C_A are available. Then $\ln(-r_A)$ and $\ln(C_A)$ are calculated and $\ln(-r_A)$ is plotted against $\ln(C_A)$ resulting in st. line.

$p \rightarrow \text{slope}$ $\ln k \rightarrow \text{intercept}$

Rate by graphical method

Tangents are drawn at diff. mⁿ times or diff. conc. on C_A vs t and the slopes of tangents are determined from the graph. Slope will be $-r_A = -\frac{dC_A}{dt}$.

The derivative b/w the points $(t_{n-1}, C_{A,n-1})$ and $(t_n, C_{A,n})$

$$-\frac{dC_A}{dt} = -\frac{\Delta C_A}{\Delta t} = \frac{C_{A,n-1} - C_{A,n}}{t_n - t_{n-1}}$$

Simplified method

$$\ln(-r_{A1}) = \ln k + p \ln(C_{A1})$$

$$\ln(-r_{A2}) = \ln k + p \ln(C_{A2})$$

Eq:- The initial rate data at 30°C obtained for $A + B \rightarrow C + D$ is given. Find a rate eqn. Find rate law for m at 300 K

Run no. $\frac{C_{A0}}{C_{B0}} = \frac{m}{n} = \frac{-r_{A0}}{-r_{B0}}$

1	1.125	2.250	9.2
2	1.125	1.125	3.58
3	2.250	2.250	86.78

$$-r_A = k C_{A0}^n C_{B0}^m$$

$$\frac{-r_{A0_1}}{-r_{A0_2}} = \frac{9.2}{3.58} = 1^n \left(\frac{2.25}{1.125} \right)^m$$

$$\therefore m = 1$$

Similarly, $n = 2$

$$-r_A = k C_{A0}^2 C_{B0}^1, \text{ using run 1, } k = 0.306 \text{ (mol/L)}^2$$

Numerical method

From Taylor series

$$f'(x_0) = \frac{(x_0 + h) - x_0}{h} - \frac{h^2}{2} f''(c)$$

Neglecting the truncation

$$f'(x_0) = \frac{(x_0 + \Delta x) - x_0}{\Delta x}$$

For our case, we use,

At t_0 , initial rate

$$\frac{c_0 - c_{t_0}}{\Delta t} = - \frac{3c_{t_0} + 4c_{t_1} - c_{t_2}}{2\Delta t} \quad (\text{using three point method})$$

$$\Delta t = t_1 - t_0$$

Polynomial adjusted method

$$c_A = \alpha + \beta t + \gamma t^2 + \dots + \eta t^N$$

where $\alpha, \beta, \gamma, \dots, \eta$ are unknown

$$\frac{dc_A}{dt} = \beta + 2\gamma t + 3\delta t^2 + \dots + \eta N t^{N-1}$$

Then the diff. at various t can be calculated by substituting diff. t -values.

Eg:-



$t, \text{ min}$

0

0.2

0.4

0.6

0.8

1

$C_A, \text{ mol/L}$

1.02

0.775

0.6

0.468

0.368

0.295

$t, \text{ min}$

1.2

1.4

1.6

1.8

2.0

$C_A, \text{ mol/L}$

0.242

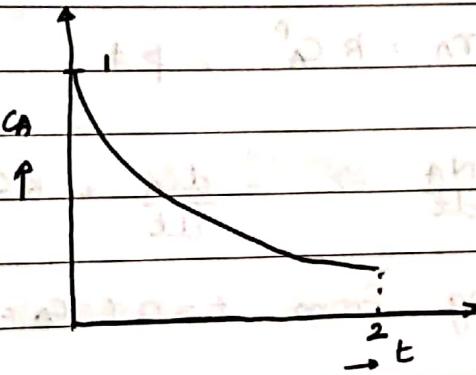
0.197

0.165

0.138

0.12

On plotting,



① By graphical method,

$$\text{At } t=0, -\frac{\Delta C_A}{\Delta t} = -1.225 \text{ mol/min L}$$

$$\text{At } t=0.6 \text{ min}, -\frac{\Delta C_A}{\Delta t} = \frac{0.368 - 0.6}{0.4} = -0.58 \text{ mol/min L}$$

②

Numerically

$$\text{At } t=0, -r_{A0} = -\frac{3C_{A0} + 4C_A_1 - C_{A2}}{2\Delta t} = -1.4 \text{ mol/min L}$$

③

By polynomial adjusted method,

$$C_A = 0.0577t^4 - 0.3672t^3 - 0.9708t^2 - 1.384t + 1.0189$$

$$-\frac{dC_A}{dt} = 0.2309t^3 - 1.1015t^2 + 1.9415t - 1.3840$$

At all that time we get the values of $-r_A$

(4) $\ln C_A$ vs $\ln(-r_A)$ are plotted

Then, $p = 1.2518$ $\ln k = 1.2518$

$$\Rightarrow k = 1.4258$$

- Diff methods

$$k = \frac{-r_{A0}}{(C_{A0})^{1.252}} = \frac{1.3840}{(1.0189)^{1.252}} = 1.3519 \text{ mol/min}$$

Integral method

$$-r_A = k C_A^p, p \neq 1$$

$$-r_A = -\frac{1}{v} \frac{dC_A}{dt} \Rightarrow -\frac{dC_A}{dt} = k C_A^p$$

On integrating from $t=0$ ($C_A = C_{A0}$), $t=t$ ($C_A = C_t$)

$$\frac{1}{C_t^{p-1}} - \frac{1}{C_{A0}^{p-1}} = (p-1)kt$$

This fn. is plotted against t for determining k from slope. In this method p should be specified

For eg., order = 2

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt$$

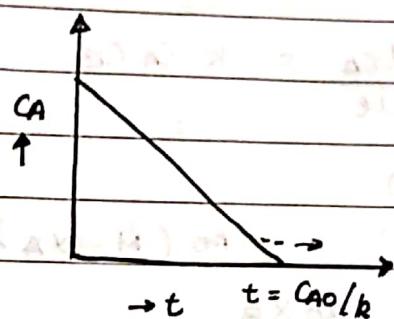
Zero order kinetics

$$-r_A = \frac{1}{V} \frac{dC_A}{dt} = k$$

On integration $t=0, C_A = C_{A0}, t=t, C_A = C_A$
 At $t \rightarrow \infty, C_A$ is 0 - (2)

$$C_A = C_{A0} - kt$$

However, eqn: is satisfied only if $C_A = 0$



First Order Kinetics

$$-r_A = k C_A$$

$$-r_A = -\frac{dC_A}{dt} = k C_A$$

$$\int \frac{dC_A}{C_A} = k \int dt \Rightarrow \ln \frac{C_A}{C_{A0}} = kt$$

$$X_A = 1 - e^{-kt} \quad \text{or, } C_A = C_{A0} e^{-kt}$$

$$\therefore -\ln(1-X_A) = kt$$

Plot $-\ln(C_A/C_{A0})$ to get k (slope) or X_A vs can also be used

$$x_A = 1 - e^{-kt}, \quad C_A = C_{A0} e^{-kt}$$

$$\text{At } t = \frac{1}{k}, \quad C_A = \frac{C_{A0}}{e}$$

$$\text{At } t = \frac{2}{k}, \quad C_A = \frac{C_{A0}}{e^2}$$

Second Order rx



$$-r_A = -\frac{dC_A}{dt} = k C_A C_B$$

$$C_A = C_{A0} (1 - x_A)$$

$$M = C_{B0}/C_{A0}$$

$$C_B = C_{B0} (1 - x_B) = C_{A0} (M - x_A)$$

$$\therefore C_{A0} x_A = C_{B0} x_B$$

$$-r_A = C_{A0} \frac{dx_A}{dt} = k C_{A0}^2 (1 - x_A) (M - x_A)$$

$$\int_{x_A}^{x_A} \frac{dx_A}{(1 - x_A)(M - x_A)} = \int_0^t k C_{A0} dt$$

$$\ln \left[\frac{(M - x_A)}{(M - 1)} \right] = C_{A0} (M - 1) kt$$

$$= (C_{B0} - C_{A0}) kt$$

If $M = 1$,

$$-r_A = -\frac{dC_A}{dt} = k C_A^2$$

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = 2kt$$

$$-\tau_A = C_{A0} \frac{dx_A}{dt} = C_{A0}^2 (1-x_A)^2$$

On integration,

$$\frac{x_A}{1-x_A} = C_{A0} k t$$

Plot $\frac{x_A}{1-x_A}$ versus t , slope will give k

Negative or fractional order n :

$$-\tau_A = k C_A^n$$

$$C_A = C_{A0} \left[1 + (n-1) k C_{A0}^{n-1} t \right]^{1/(1-n)}$$

$$\text{As } t \rightarrow \infty, C_A = 0, \Rightarrow t \geq \frac{1}{(1-n) k C_{A0}^{n-1}}$$

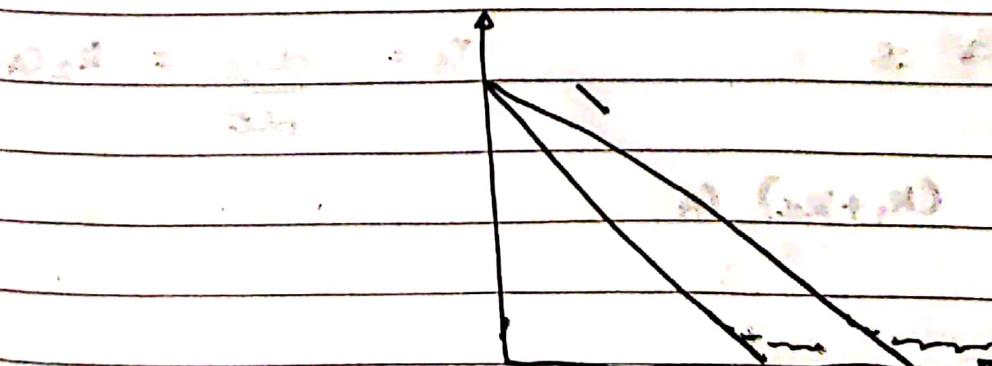
$$\text{At } t = n = 1/2$$

$$C_A = C_{A0} \left[1 - \frac{1}{2} k t C_{A0}^{-1/2} \right]^2$$

$$C_A = 0 \text{ for } \frac{1}{2} k t C_{A0}^{-1/2} = 1 \Rightarrow t = 2 C_{A0}^{1/2} / k$$

$$\text{Similarly for } n^{\text{th}} \text{ order } t = \frac{1}{(n-1)} k C_{A0}^{n-1}$$

$$t \geq \frac{1}{(n-1)} k C_{A0}^{n-1}; C_A = 0$$



Half life period

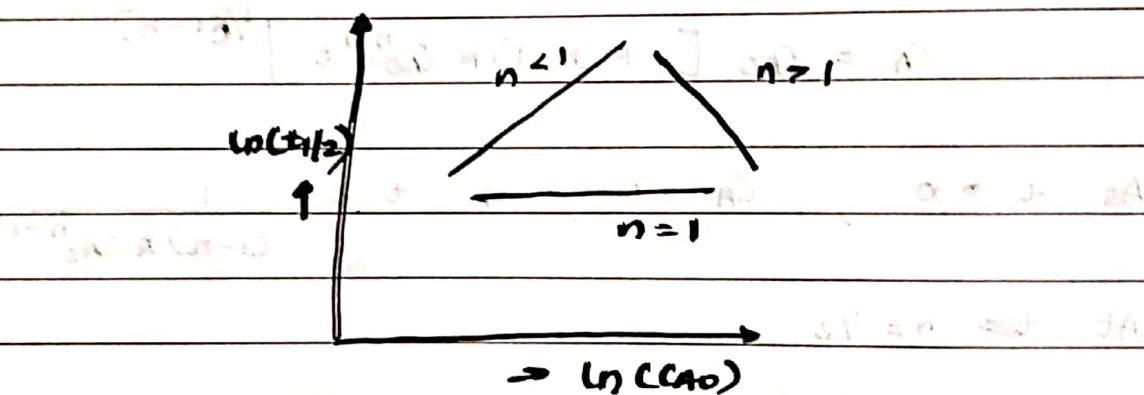


$$\frac{c_B}{c_A} = \frac{b}{a}, \quad -\frac{dc_A}{dt} = k c_A^a \left(\frac{b}{a}\right)^b c_A^b$$

$n \neq 1$,

$$c_A^{1-n} - c_{A0}^{1-n} = k(n-1)t$$

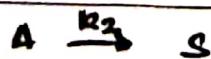
$$\text{At } t_{1/2} = \frac{0.5^{1-n} - 1}{k(n-1)} c_{A0}^{1-n}$$



Irrev. parallel m.

Consider,

$$A \xrightarrow{k_1} R \quad r_R = \frac{dc_R}{dt} = k_1 c_A$$



$$r_S = \frac{dc_S}{dt} = k_2 c_A$$

$$-r_A = (k_1 + k_2) c_A$$

At $t=0$, $C_A = C_{AO}$; $C_{RO} = C_{SO} = 0$

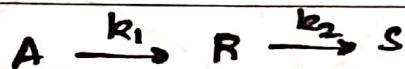
$$-\ln \frac{C_A}{C_{AO}} = (k_1 + k_2)t = k't$$

k' is obtained from the plot of $-\ln \frac{C_A}{C_{AO}}$ vs t

$$\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_1}{k_2} \Rightarrow \frac{C_R - C_{RO}}{C_S - C_{SO}} = k''$$

If we know C_S , C_R at diff. t , then we plot C_R v/s C_S to get k''

Series m:



$$r_A = \frac{dC_A}{dt} = -R_1 C_A$$

$$-\ln \frac{C_A}{C_{AO}} = k_1 t$$

$$r_R = \frac{dC_R}{dt} = -k_1 C_A - k_2 C_R$$

$$\frac{dC_R}{dt} + k_2 C_R = k_1 C_{AO} e^{-k_1 t}$$

$$r_S = \frac{dC_S}{dt} = k_2 C_R \quad (3)$$

For (3), (2)

$$C_R e^{\int k_2 dt} = \int (k_1 C_{AO} e^{-k_1 t} e^{\int k_2 dt}) dt + C$$

$$\text{At } t=0, C_{RO} = 0 \Rightarrow C = -\frac{k_1 C_{AO}}{k_2 - 1}$$

$$C_R = C_{AO} k_1 \left[\frac{e^{-k_1 t}}{k_2 - k_1} + \frac{e^{-k_2 t}}{k_1 - k_2} \right]$$

$$\text{As, } C_{AO} = C_A + C_R + C_S$$

$$C_S = C_{AO} \left[1 + \frac{k_2}{k_1 - k_2} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right]$$

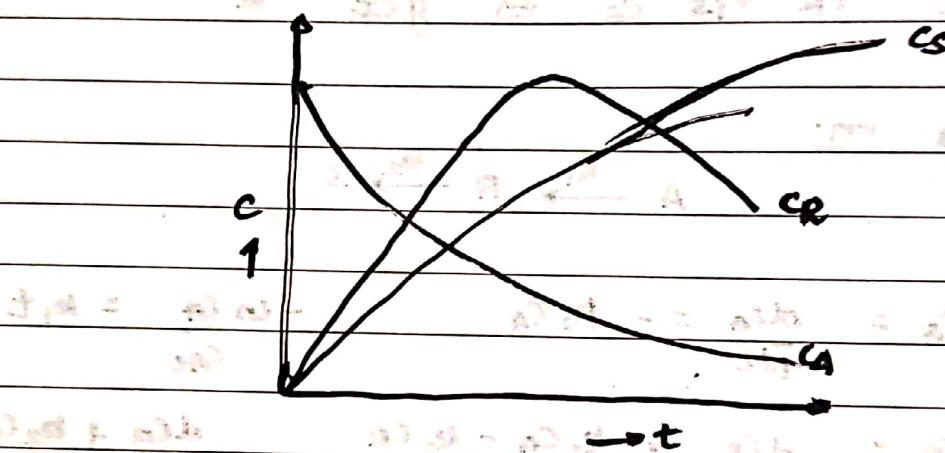
Neglecting k_2 when $k_2 \gg k_1 \Rightarrow C_S = C_{AO} (1 - e^{-k_1 t})$

The second step is controlling

$$\text{At } \frac{dC_R}{dt} = 0, \quad t_{\max} = \frac{\ln k_2/k_1}{k_2 - k_1}$$

$k_2 \gg k_1$

$$C_{R,\max} = \left(\frac{k_1}{R_2} \right)^{k_2/k_2 - k_1} C_{AO}$$



Ex :- For $A \xrightarrow{k_1} R \xrightarrow{k_2} S$, $k_1 = k_2 = 0.1 \text{ min}^{-1}$, $C_{AO} = 10 \text{ mol/l}$
Derive expression for C_R . Find $C_{R,\max}$ t_{\max}

$$r_A = -\frac{dC_A}{dt} = -k_1 C_A \Rightarrow C_A = C_{AO} e^{-kt}$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A - k_2 C_R \\ = k_1 (C_{AO} e^{-kt} - C_R)$$

$$\frac{dC_R}{dt} + k_2 C_R = k_1 C_{AO} e^{-kt}$$

$$C_R e^{kt} = \int k_1 C_{AO} dt + C$$

$$\text{At } t=0, \quad C_R = 0 \Rightarrow C = 0$$

$$C_R = R_1 C_{AO} e^{-k_1 t}$$

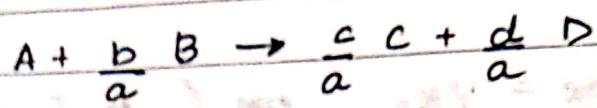
$$\frac{dC_R}{dt} = -k_1^2 C_{AO} e^{-k_1 t} + k_1 C_{AO} e^{-k_1 t} = 0$$

$$\Rightarrow t_{\max} = \frac{1}{k_1} \text{ or } (R_1 C_{AO} e^{-k_1 t} (1 - k_1 t) = 0)$$

$$C_{R,\max} = R_1 C_{AO} \frac{1}{k_1} = 3.679 \text{ mol/L}$$

Variable Volume Rxn:

For Batch Reactor,



$$\text{Let } \theta_B = \frac{N_{BO}}{N_{AO}} = \frac{C_{BO}}{C_{AO}}$$

Similarly θ_C, θ_D

Initial moles	Final Moles	Final Conc.
N_{AO}	$N_A = N_{AO}(1 - x_A)$	$\frac{N_{AO}}{\sqrt{}} (1 - x_A)$
N_{BO}	$N_B = N_{AO} \left(\theta_B - \frac{b}{a} x_A \right)$	$\frac{N_{AO}}{\sqrt{}} \left(\theta_B - \frac{b}{a} x_A \right)$
N_{CO}	$N_C = N_{AO} \left(\theta_C + \frac{c}{a} x_A \right)$	$\frac{N_{AO}}{\sqrt{}} \left(\theta_C + \frac{c}{a} x_A \right)$
N_{DO}	$N_D = N_{AO} \left(\theta_D + \frac{d}{a} x_A \right)$	$\frac{N_{AO}}{\sqrt{}} \left(\theta_D + \frac{d}{a} x_A \right)$

$$\text{Total feed rate, } F_{TO} = F_{AO} (1 + \theta_B + \theta_C + \theta_D)$$

$$\begin{aligned} \text{Total effluent rate, } F_{TE} &= F_{AO} (1 + \theta_B + \theta_C + \theta_D) \\ &\quad + F_{AO} \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right) x_A \end{aligned}$$

$$\text{Let } \delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$$

$$\begin{aligned} \therefore \frac{F_T}{F_{TO}} &= 1 + \frac{F_{AO}}{F_{TO}} \delta x_A \\ &= 1 + \frac{y_{AO}}{F_{TO}} \delta x_A \end{aligned}$$

Similarly for batch reactor

$$N_T = N_{T0} + N_{AO} \delta x \quad ; \quad \frac{N_T}{N_{T0}} = 1 + y_{AO} \delta x_A$$

Assuming $PV = Z N_T RT$

$$V = V_0 \left(\frac{P_0}{P} \right) \left(\frac{T}{T_0} \right) \left(\frac{Z}{Z_0} \right) \frac{N_T}{N_{T0}}$$

$$\vartheta = V_0 \left(\frac{P_0}{P} \right) \left(\frac{T}{T_0} \right) \frac{F_T}{F_{T0}} \left(\frac{Z}{Z_0} \right) \rightarrow 1 \text{ for ideal gas}$$

For no change in pressure and temp change,

$$V = V_0 \frac{N_T}{N_{T0}} = V_0 \left(1 + \frac{N_{AO}}{N_{T0}} \delta x \right)$$

$$\vartheta = V_0 \frac{F_T A}{F_{T0}} = V_0 \left(1 + \frac{F_{AO}}{F_{T0}} \delta x \right)$$

$$\frac{N_{AO}}{N_{T0}} = \frac{F_{AO}}{F_{T0}} = \delta y_{AO} = \epsilon_A \uparrow \text{Volume expansion factor}$$

$$V = V_0 (1 + \epsilon_A x)$$

For j -th species,

$$g_j = \frac{N_j}{V} = \frac{N_{j0} (\theta_j + j/a x_A)}{V_0 (1 + \frac{N_{j0}}{N_{T0}} \delta x)}$$

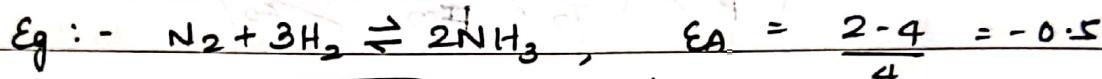
$$\vartheta = \frac{F_j}{V} = \frac{F_j}{V_0 (1 + \frac{F_{j0}}{F_{T0}} \delta x)}$$

For reactant A,

$$EAx = \frac{v}{V_0} - 1 \quad \text{or} \quad x = \frac{\Delta V_{\text{initial}} + v}{V_0 EA}$$

$$C_A = \frac{N_A}{v} = \frac{N_{A0}(1-x_A)}{V_0(1+EAx)}$$

$$C_B = \frac{N_B}{v} = \frac{N_{B0}(b_b - b/a x_A)}{V_0(1+EAx)}$$



If they are added in their stoichiometric ratio

Variable Volume R_V in A Batch Reactor

Considering, first order $r_n = k C_A$

$$-\frac{1}{v} \frac{dN_A}{dt} = k C_A = \frac{k N_A (1-x_A)}{V_0}$$

$$v = V_0(1+EAx_A)$$

$$-\frac{N_A}{V_0(1+EAx_A)} \left(-\frac{dx_A}{dt} \right) = \frac{k N_A (1-x_A)}{V_0(1+EAx_A)}$$

$$C_{A0} \frac{dx_A}{dt} = k C_{A0} (1-x_A)$$

$$\frac{dx_A}{dt} = k (1-x_A)$$

$$-\ln(1-x_A) = \ln \left(1 - \frac{\Delta V}{EAV_0} \right) = kt$$

Mole balance for 2nd order reaction, $2A \rightarrow P$

$$-r_A = k C_A^2$$

$$-r_A = k C_A^2 = k \left[\frac{C_{A0} (1 - x_A)}{1 + E_A x_A} \right]^2$$

$$\frac{C_{A0}}{1 + E_A x_A} \frac{dx_A}{dt} = k \left[\frac{C_{A0} (1 - x_A)}{1 + E_A x_A} \right]^2$$

$$\frac{dx_A}{dt} = k C_{A0} \frac{(1 - x_A)^2}{1 + E_A x_A}$$

On solving,

$$\int_0^{x_A} \frac{dx_A}{(1 - x_A)^2} + \int_0^{x_A} \frac{E_A dx_A}{(1 - x_A)^2} = k C_{A0} \int_0^t dt$$

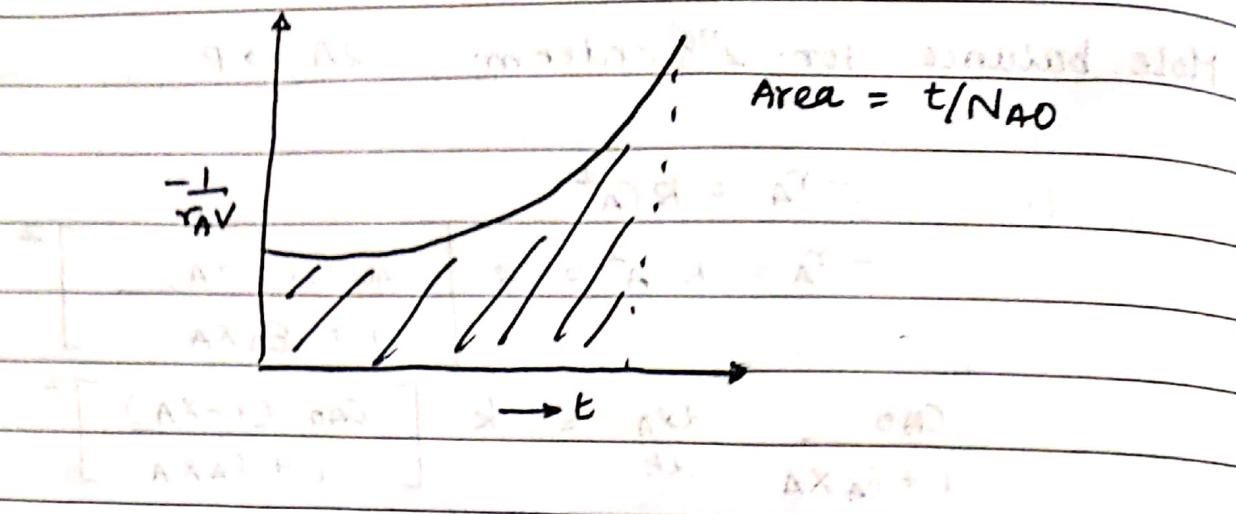
$$\frac{(1 + E_A)x_A}{1 - x_A} + E_A \ln(1 - x_A) = k C_{A0} t$$

$$\text{where, } x_A = \frac{\Delta V}{E_A V_0}$$

$$\text{For } n\text{-th order; } \int_0^{x_A} \frac{(1 + E_A x_A)^{n-1}}{(1 - x_A)^n} = dx_A \frac{C_{A0}^{n-1}}{(-r_A)} dt$$

$$t = N_A \int_0^{x_A} \frac{dx_A}{V(-r_A)} = N_A \int_0^{x_A} \frac{dx_A}{V_0 (1 + E_A x_A) (-r_A)}$$

$$\therefore t = \frac{C_{A0}}{(-r_A)} \int_0^{x_A} \frac{dx_A}{(1 + E_A x_A) (-r_A)}$$



$$t(\Delta A \rightarrow A_0) \Delta t = \Delta A_0$$

$$\frac{t(\Delta A \rightarrow A_0) \Delta t}{\Delta A_0} = \frac{\Delta A_0}{\Delta A_0} = 1$$

$$\frac{t(\Delta A \rightarrow A_0) \Delta t}{\Delta A_0} = \frac{\Delta A_0}{\Delta A_0} = 1$$

$$t(\Delta A \rightarrow A_0) \Delta t = (\Delta A \rightarrow A_0) \Delta t + \Delta A(\Delta A + 1)$$

$$\Delta A = \Delta A_0 + \Delta A_0 \Delta t$$

$$\Delta A = \Delta A_0 + \Delta A_0 \Delta t$$

$$\Delta A = \Delta A_0 + \Delta A_0 \Delta t = \Delta A_0(1 + \Delta t) = \Delta A_0$$

$$\Delta A = \Delta A_0(1 + \Delta t) = \Delta A_0$$

Flow Reactors

They are of two types, ① CSTR ② PFR

Their performances are evaluated by two parameters
 ① Space Time

② Space Vol.

Space Time : Time req. to process one reactor vol. of feed at specified cond. Denoted by τ . Unit sec/min

$$\tau = \frac{V}{\dot{V}_0}$$

Space Vol : Number of reactor vol. of feed at specified cond. which can be processed per unit time

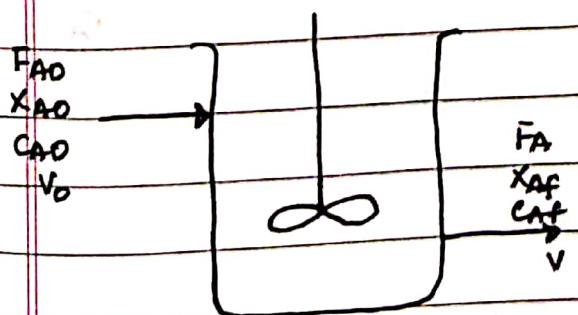
$$S = \frac{1}{\tau}$$

$$\frac{I}{C_{AO}} = \frac{\tau}{V_0 C_{AO}} = \frac{V}{F_{AO}}$$

For catalytic reaction, we use, $\frac{w}{F_{AO}} \rightarrow$ "Time Factor"

w → weight of catalyst

Ideal CSTR or Mixed Flow Reactor



$$F_{AO}(1 - X_{AO}) = F_{AO}(1 - X_A) + (-r_A)$$

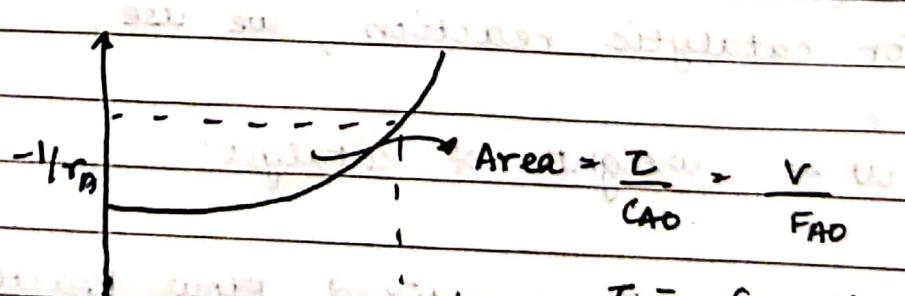
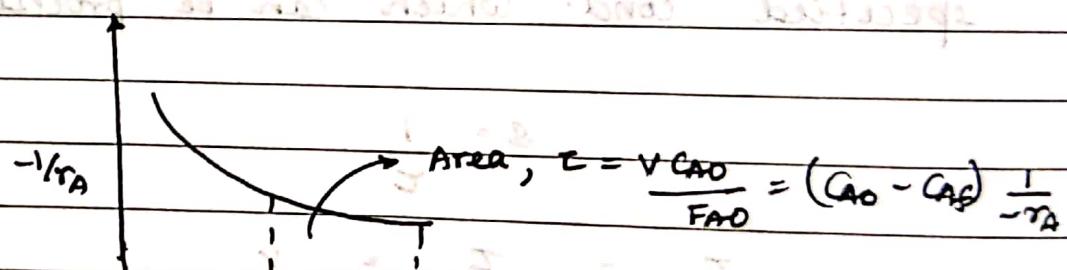
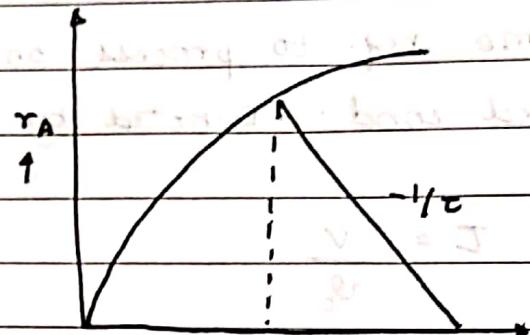
$$\text{At } X_A = 0, \quad F_{AO} X_A = -r_A V$$

$$\frac{V}{F_{AO}} = \frac{X}{-r_A} = \frac{C_{AO} - C_{Af}}{G_{AO}(-r_A)}$$

$$\frac{w}{F_{AO}} = \frac{X_A}{-r_A'}$$

$$\tau = c_{AO} - c_{AF} \quad \text{or} \quad \tau = c_{AO} (K_{AF} - x_{AO})$$

$$-r_A = \left(-\frac{1}{c}\right) (c_{AF} - c_{AO})$$



$$\tau = \frac{c_{AO} \cdot x_{AF} - x_{AO}}{-r_A}$$

Variable Density with first order kinetics.

$$\frac{v}{F_{AO}} = \frac{v_0 (1 + E_A X_A)}{C_{AO} v_0 (1 + E_A X_A)} = \frac{X_A}{k C_{AO} (1 - X_A) \frac{1 + E_A X_A}{1 + E_A X_A}}$$

$$k \tau = \frac{X_A (1 + E_A X_A)}{1 - X_A} = f(X_A)$$

For various τ calculate $f(X_A)$ with X_A values and from the slope of st-line plot k is obtained.

For 2nd order r_n ,

$$-r_A = k C_A^2$$

$$C_A = C_{AO} \frac{(1 - X_A)}{(1 + E_A X_A)}$$

$$\frac{v}{F_{AO}} = \frac{v_0 (1 + E_A X_A)}{C_{AO} v_0 (1 + E_A X_A)} = \frac{X_A}{k C_{AO}^2 \frac{(1 - X_A)^2}{(1 + E_A X_A)^2}}$$

$$k \tau = \frac{X_A (1 + E_A X_A)^2}{k C_{AO} (1 - X_A)^2}$$