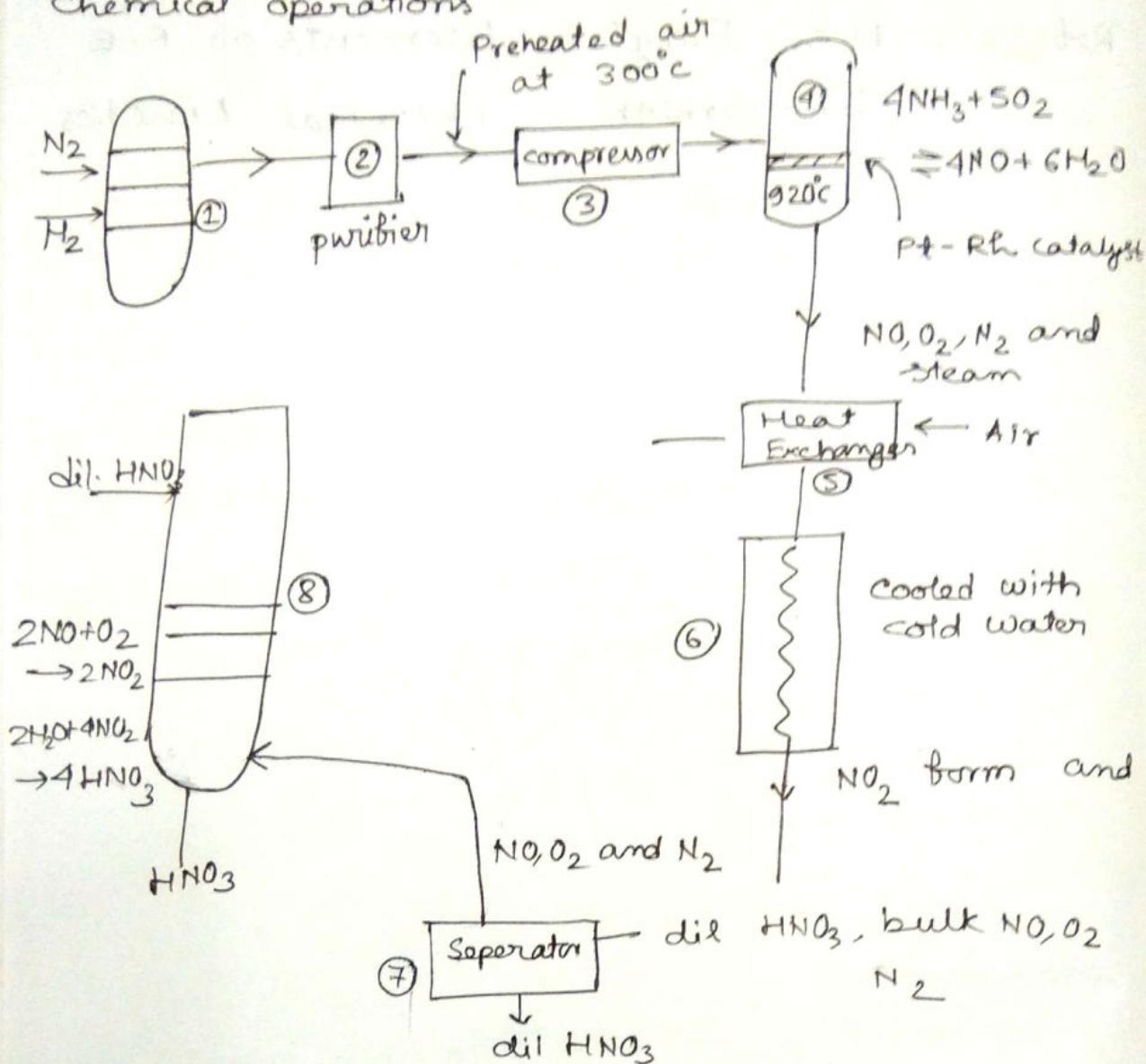


Chemical processes

chemical operations



steps

i) kinetic study

ii) Molar balance \Rightarrow size of the vessel



$$R_1 = \frac{k_1 [\text{A}][\text{B}]}{1 + k_2[\text{B}] + k_3[\text{C}]} \quad \text{Non-elementary reaction}$$

$$R_2 = k_1 [\text{A}][\text{B}]$$

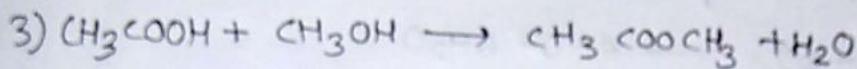
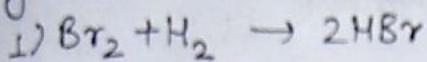
$$R_3 = k_2 [\text{A}][\text{B}] - \frac{k_3}{K_e} \frac{[\text{C}]}{k_1} \left\{ \begin{array}{l} \text{elementary} \\ \text{reaction} \end{array} \right.$$

↑ Eqbm. const

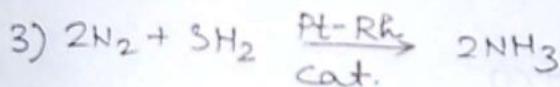
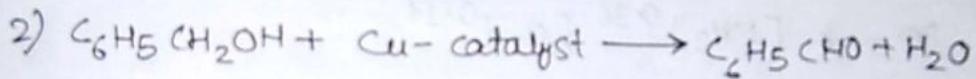
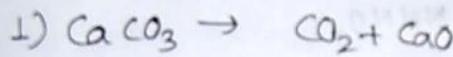
Various Chemical Reactions

→ Homogeneous
→ Heterogeneous

Homogeneous:



Heterogeneous:



Rate of reaction kmole/m³.s

$$i) -r_A = -\frac{1}{V} \frac{dC_A}{dt} = kC_A \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{For homogeneous reaction}$$

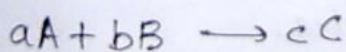
$$ii) -r_A' = \frac{1}{W} \frac{dN_A}{dt} = k'C_A \quad \left. \begin{array}{l} \text{kmole/kg.s} \\ \end{array} \right\} \text{For heterogeneous}$$

$$iii) r_A'' = \frac{1}{S} \frac{dC_A}{dt} = k''C_A \quad \left. \begin{array}{l} \text{reaction} \\ \text{kmole/m}^2.\text{s} \end{array} \right.$$

V → volume of the reactor, (m³)

W → weight of catalyst, (kg)

S → surface area of interface per unit volume of reactor, (m²/volume of reactor)



$$-r_A = -\frac{a}{b} r_B = \frac{a}{c} r_C$$

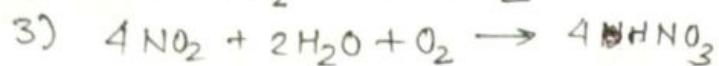
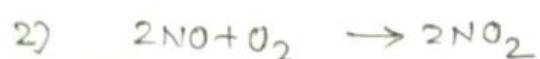
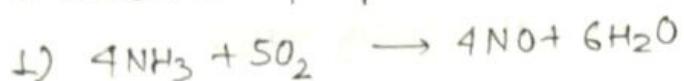
For solid catalyst,

$$S = (\text{external area} + \text{internal area})/\text{kg catalyst}$$

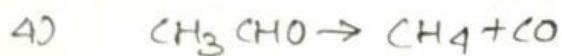
Elementary reaction

Reaction kinetics upto 3rd order

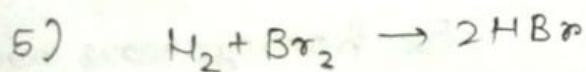
Industrial preparation of nitric acid



$$r_o = k [\text{NH}_3]^{0.36} [\text{O}_2]^{0.14}$$



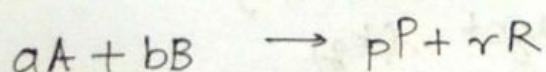
$$-r_{\text{CH}_3\text{CHO}} = k [\text{CH}_3\text{CHO}]^{3/2}$$



$$-r_{\text{HBr}} = \frac{k_1 [\text{H}_2] [\text{Br}_2]}{[\text{HBr}] + k_2 [\text{Br}]}^{3/2}$$

} Non elementary
kinetics with
product inhibition

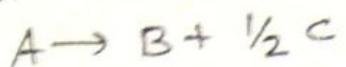
Homogeneous Reaction



$$-r_A = k C_A^a C_B^b \rightarrow \text{General form of rate kinetics.}$$

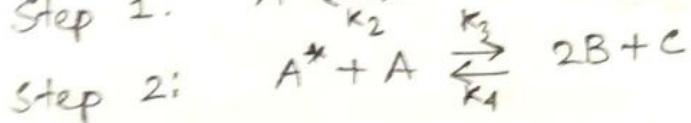
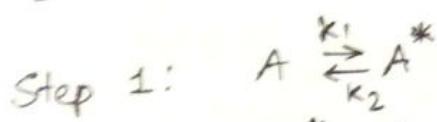
Empirical Kinetics

Non-elementary



$$-r_A = \frac{k C_A^2}{1 + K' C_A}$$

composite catalyst: $Al_2O_3 + SiO_2 + Cr_2O_3$: used in petroleum industry.



we have, $-r_A = k_1 C_A - k_2 C_A^* + k_3 C_A C_A^* - k_4 C_B^2 C_C$

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

The rate of formation of A^* is assumed to be negligible.

So, that $r_A^* = 0$ and

$$C_A^* = \frac{k_1 C_A + k_4 C_B^2 C_C}{k_2 + k_3 C_A} \quad \text{--- (1)}$$

Substituting C_A^* in Eqⁿ (1), we have

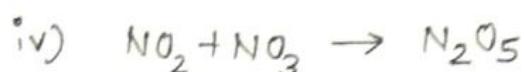
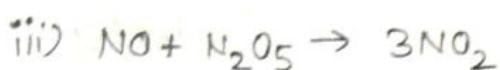
$$-r_A = \frac{k C_A^2}{1 + K' C_A} \quad \text{--- (2)}$$

Where, k_4 is assumed to be zero,

$$K = \frac{2k_1 k_3}{k_2} \quad \text{and} \quad K' = \frac{k_3}{k_2}$$

If the second term in denominator of eqⁿ (1) is neglected as $k_1 \gg k_2$

Decomposition of N_2O_5



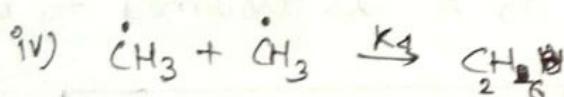
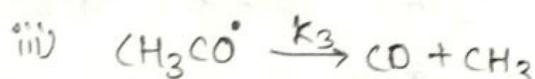
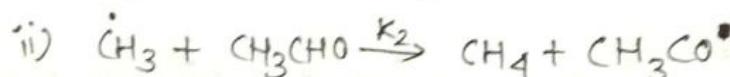
Free radical
formation
mechanism

$$-\frac{dc_{\text{N}_2\text{O}_5}}{dt} = k \cdot c_{\text{N}_2\text{O}_5}$$

²



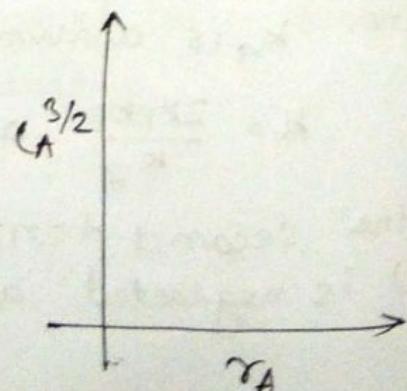
²



$$\begin{aligned} -\frac{dc_{\text{CH}_3\text{CHO}}}{dt} &= k_2 \left(\frac{k_1}{k_4} \right)^{1/2} c_{\text{CH}_3\text{CHO}}^{3/2} \\ &= k' c_{\text{CH}_3\text{CHO}}^{3/2} \end{aligned}$$

$$\gamma_A = K C_A^{3/2}$$

$$\ln(-\gamma_A) = \ln K + \frac{3}{2} \ln C_A$$



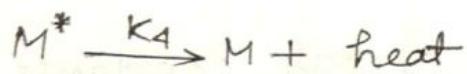
Three Body reactions

If two species A and B forms the intermediate as in the activated compound AB.



forward rate constant = k_1

backward rate constant = k_2



The overall reaction is



$$\frac{d[AB]}{dt} = k_3 [AB^*] [M]$$

$$\frac{d[AB]}{dt} = k_1 [A][B] - k_2 [AB^*] - k_3 [AB^*] [M] \approx 0$$

$$[AB^*] = \frac{k_1 [A][B]}{k_2 + k_3 [M]}$$

$$-r_A = -\frac{d[A]}{dt} = \frac{d[AB]}{dt} = \frac{k_1 k_3 [A][B][M]}{k_2 + k_3 [M]}$$

Langmuir - Hinshelwood type rkⁿ



$$r_A = \frac{k_1 [P_A P_B - \frac{P_R P_S}{k_e}]}{[1 + k_A P_A + k_B P_B + k_R P_R + k_S P_S]^2}$$

Rate parameters:

$$k_1, k_e, k_A, k_B, k_R, k_S$$

Temperature dependence of rate constants

* Collision Theory

frequency of collision

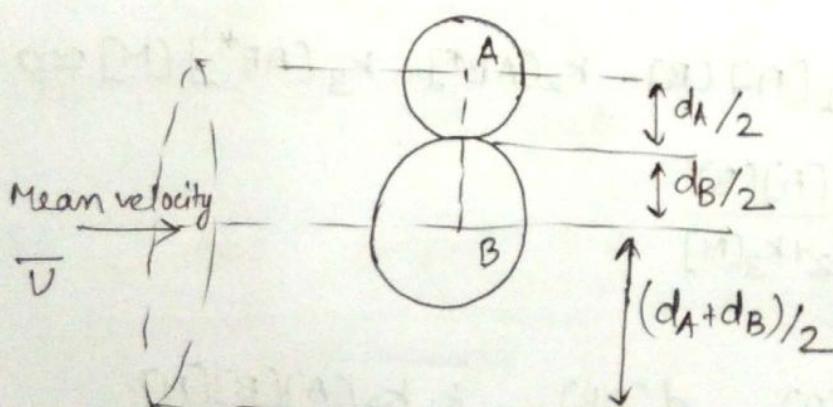


Fig: Swept volume for bimolecular collision

$$\sigma_{AB} = \frac{\pi}{4} d_{AB}^2$$

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

$$\frac{1}{m_{AB}} = \frac{1}{M_A} + \frac{1}{M_B}$$

$$\sigma_{AB} \bar{u} = \frac{\pi}{4} d_{AB}^2 \left(\frac{8k_B T}{\pi m_{AB}} \right)^{1/2}$$

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

↑
collision frequency

The reaction rate

$$= [\text{rate of collisions between A and B}] \times e^{-\frac{E}{RT}}$$

(successful collisions for reaction)

$$= [10^6 N_A^2 C_A C_B \left(\frac{\pi}{4} d_{AB}^2 \right) \left(\frac{8k_B T}{\pi m_{AB}} \right)^{1/2}] \times [e^{-\frac{E}{RT}}]$$

$$= [10^6 N_A^2 \left(\frac{\pi}{4} d_{AB}^2 \right) \left(\frac{8k_B T}{\pi m_{AB}} \right)^{1/2}] \times [e^{-\frac{E}{RT}}] C_A C_B$$

$$= K C_A C_B$$

unique in collision theory

Therefore,

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

$e^{-\frac{E}{RT}}$ is the Boltzmann expression for evaluating the fraction having energy excess over E

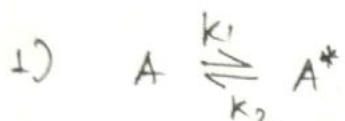
Arrhenius theory: $-r_A = k_0 e^{-\frac{E}{RT}} C_A C_B = K_1 C_A C_B$

Collision theory: $-r_A = k_0 T^{1/2} e^{-\frac{E}{RT}} C_A C_B$

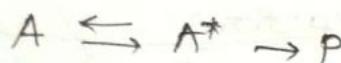
$$= K_1 C_A C_B$$

Transition State Theory (Activated state theory)

In reaction path, there will be initial change of energies of the reacting molecules to reach the maximum energy level to transition complex.



If first step is RDS, kinetics will follow collision theory. If 2nd step is RDS, kinetics will follow transition state theory.



$$\ln k = -\frac{\Delta G}{RT} = -\frac{\Delta H + T\Delta S}{RT}$$

eqbm. const.

$$K = \frac{[A^*]}{[A]} \quad [A^*] = K[A]$$

$$k = e^{\frac{\Delta S}{R}} e^{-\frac{\Delta H}{RT}}$$

$$\frac{dP}{dt} = k'[A] = k_1[A^*] = k_1 K[A] = k'[A]$$

from statistical and quantum mechanics

$$k_1 = \frac{kRT}{N\hbar}$$

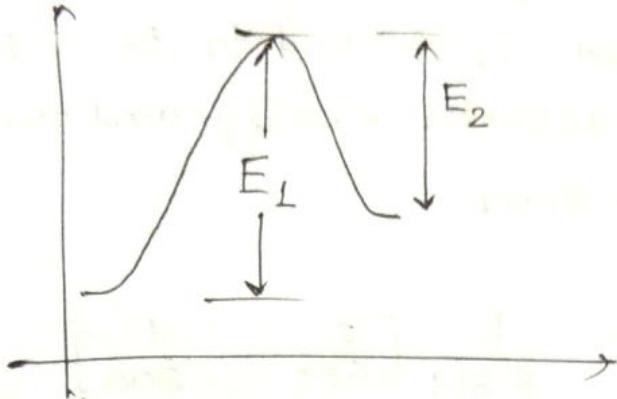
AVOGADRO NO. \rightarrow Planck const.

$$K' = 2 \times 10^{10} T e^{\Delta S / R} e^{-\Delta H / RT} s^{-1}$$

Eyring equation

$e^{\Delta S / R} \rightarrow$ less temperature sensitive

$$k_1 \propto T e^{-\Delta H_1^*/RT} \quad k_2 \propto T e^{-\Delta H_2^*/RT}$$



$$\Delta H_1^* - \Delta H_2^* = \Delta H_r = \text{heat of reaction}$$

$$E_1 \approx \Delta H_1^* \text{ and } E_2 \approx \Delta H_2^*$$

Therefore

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

For collision theory the step 1 is the slowest step and rate depends on the bimolecular collision. Whereas, in the transition state theory, step-2 is RDS. Combining both theories

$$k \propto T^m e^{-E/RT} \quad \text{and } 0 \leq m \leq 1$$

$$-r_A = k_0 T e^{-E/RT} \quad C_A C_B = k_1 C_A C_B$$

From

transition state theory

Arrhenius theory

$$\ln \frac{K_1}{K_2} = -\frac{E}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

(Q11)

The rate const. for the reaction

$H_2(g) + I_2(g) \rightarrow 2HI(g)$ is 5.6×10^{-4} at $618K$. At $600K$ the rate const. is found to be 2.8×10^{-2} . Calculate the activation energy and the rate constant at high temp.

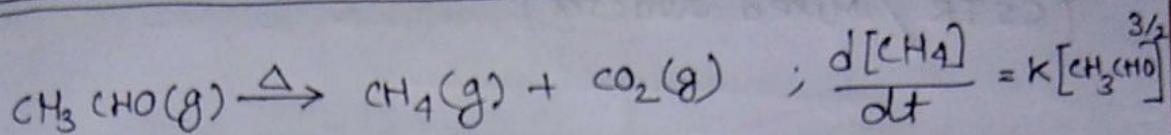
$$\ln \frac{5.6 \times 10^{-4}}{2.8 \times 10^{-2}} = -\frac{E}{8.314} \left[\frac{1}{600} - \frac{1}{818} \right]$$

$$E = 1.59 \times 10^5 \text{ J/mol}$$

24/07/17

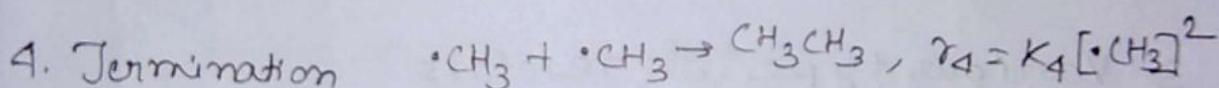
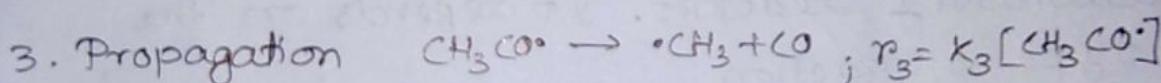
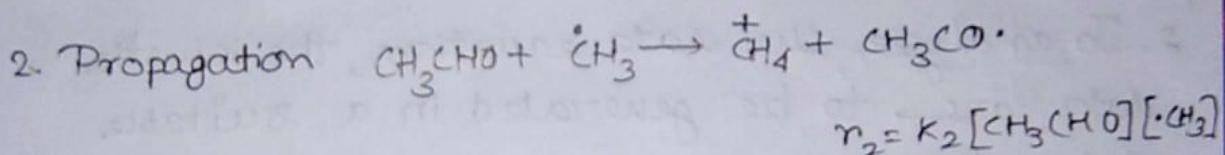
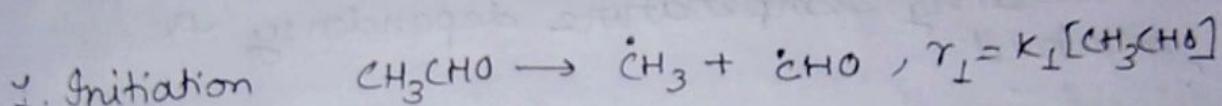
JKB

The Rice-Herzfeld mechanism for
pyrolysis of acetaldehyde in absence of air



Some ethane is also detected

This reaction proceeds according the Rice-Herzfeld mechanism as below



$$i) \frac{d[\cdot\text{CH}_3]}{dt} = k_1[\text{CH}_3\text{CHO}] - k_2[\text{CH}_3\text{CHO}][\cdot\text{CH}_3] + k_3[\text{CH}_3\text{CO} \cdot] - 2k_4[\cdot\text{CH}_3]^2 = 0$$

$$ii) \frac{d[\text{CH}_3\text{CO} \cdot]}{dt} = k_2[\text{CH}_3\text{CHO}][\cdot\text{CH}_3] - k_3[\text{CH}_3\text{CO} \cdot] = 0$$

from i) and ii)

$$k_1[\text{CH}_3\text{CHO}] - 2k_4[\cdot\text{CH}_3]^2 = 0$$

the steady state conc. of methyl radical is

$$[\cdot\text{CH}_3] = \sqrt{\frac{k_1}{2k_4}} [\text{CH}_3\text{CHO}]^{\frac{1}{2}}$$

$$\frac{d[\text{CH}_4]}{dt} = k_2[\text{CH}_3\text{CHO}][\cdot\text{CH}_3] = k_2 \sqrt{\frac{k_1}{2k_4}} [\text{CH}_3\text{CHO}]^{\frac{3}{2}}$$

Ideal reactors

Batch reactor

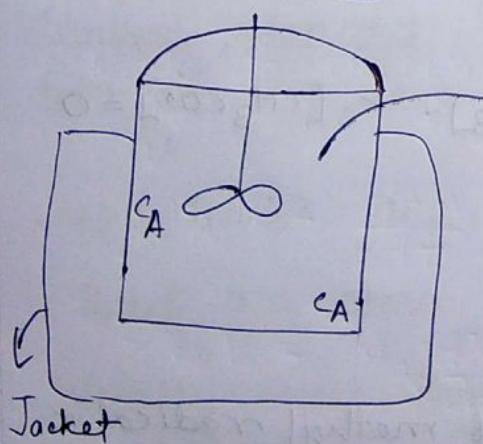
Plugflow reactor

(CSTR / Mixed reactor)

Kinetic study and analysis of Rate models

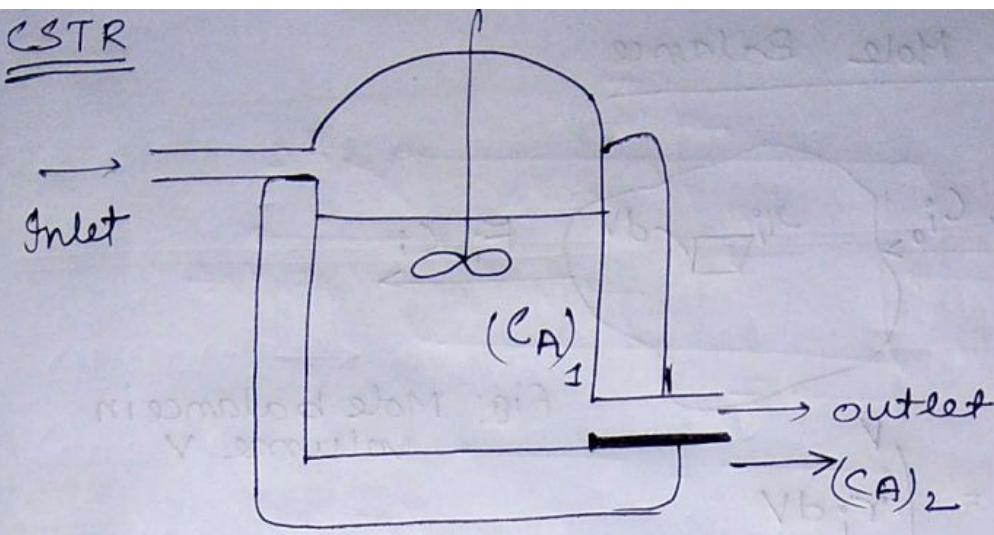
1. The rate equation for a reaction with detail knowledge of kinetic parameters including temperature dependency is required
2. To analyze the rate equations, the kinetic data are to be generated in a suitable laboratory reactors. It depends on the type of reaction
3. Various type of reactors

Batch reactor



* No in flow / out flow
uniform conc. throughout the bulk

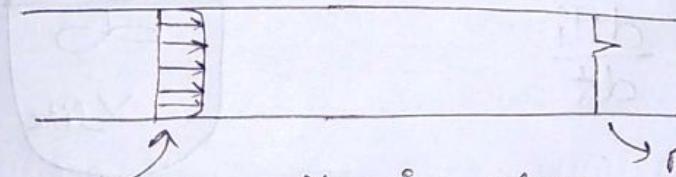
* Batch reactor data
concentration $\rightarrow f(t)$
 f of time



$$[(C_A)_1 = (C_A)_2] \Leftrightarrow \text{Ideal CSTR}$$

Stirrer speed \Rightarrow determines ideality/non ideality of reactor

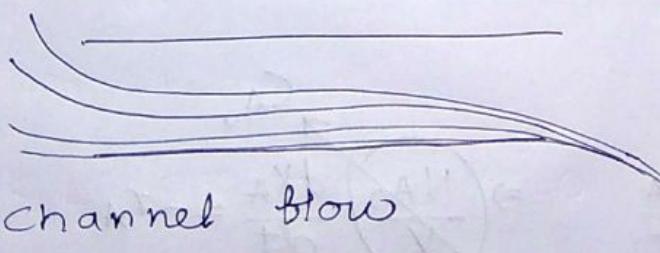
Plug flow reactor



velocity profile in plug

micro mixing
(Due to flow rate change)

- # No velocity variation in the axial direction
- # No micro mixing



channel flow

micro mixing may occur due to channeling of flow and dead spot etc.

gives rise to non-ideality

For ideal CSTR

- no channeling
- uniform concentration
- no micromixing

General Mole Balance

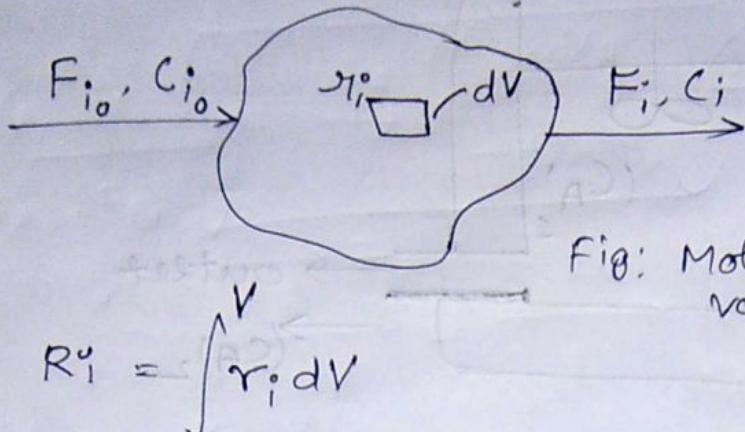


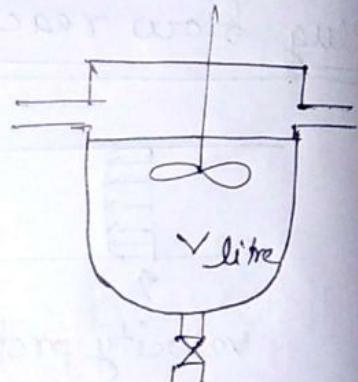
Fig: Mole balance in volume V

at steady state, the rate of accumulation of i is

$$\frac{dN_i}{dt} = 0$$

Batch reactor

$$\int_V r_i dV = \frac{dN_i}{dt}$$



Rate of generation of A

= Rate of accumulation of A

$$\int_V r_A dV = \frac{dN_A}{dt}$$

$$-r_A V = N_{A_0} \frac{dx_A}{dt}$$

$$C_{A_0} \frac{dx_A}{dt} = -r_A$$

$$\Rightarrow \cancel{\left(\frac{N_{A_0}}{V} \right)} \frac{dx_A}{dt} = -r_A$$

$$x_A = \frac{C_{A_0} - C_A}{C_{A_0}}$$

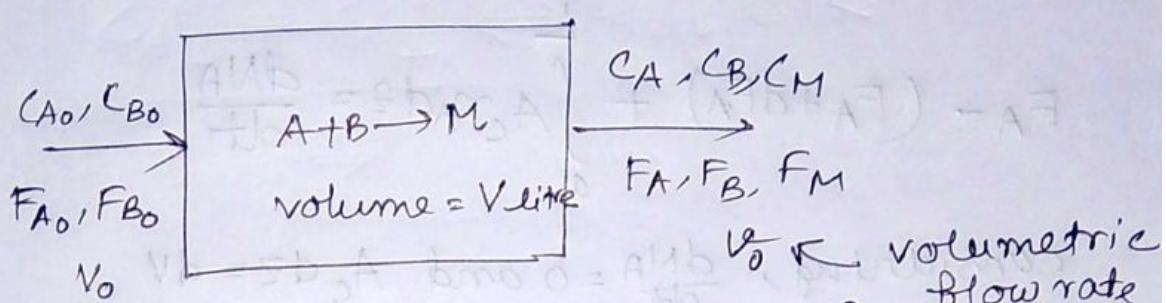
$$C_A = k C_{A_0} (1 - x_A)$$

CSTR

$$C_A \frac{dx_A}{dt} = k(C_{A_0}(1-x_A))$$

CSTR

F_A molar flow rate



$$V_0 C_{A_0} - V_0 C_A + r_A V = \frac{d}{dt} (r_A V)$$

↑ ↑ ↑
 Rate in Rate out Rate of gen

$$V_0 (C_{A_0} - C_A) + r_A V = 0$$

$$T_m = \frac{V}{V_0} = \frac{C_{A_0} - C_A}{-r_A}$$

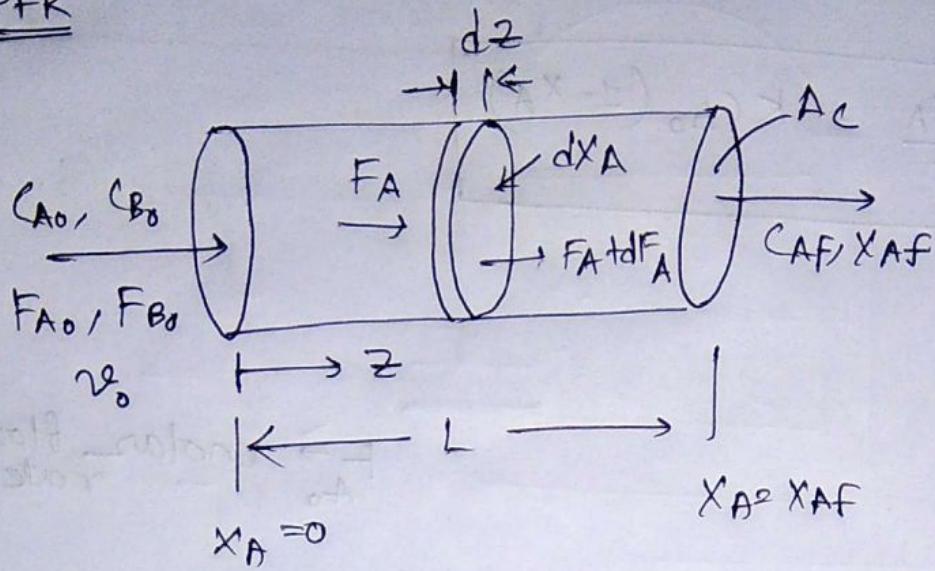
Space time

$$F_{A_0} = V_0 C_{A_0}; F_A = V C_A$$

and $V_0 = V$ if there is no volume change by the reactant

$$-r_A = \frac{F_{A_0} - F_A}{V} = \frac{F_{A_0} x_A}{V}$$

PFR



$$F_A - (F_A + dF_A) + \int_0^L A_c x_A dz = \frac{dN_A}{dt}$$

Considering, $\frac{dN_A}{dt} = 0$ and $A_c dz = dV$

$$-dF_A + \int_0^{V_t} r_A dV = 0$$

$$\boxed{-\frac{dF_A}{dV} = -r_A} \quad \text{PFR mole balance}$$

$$F_A = F_{A0} (1 - x_A)$$

25/07/17
JKB

$$\int_0^V \frac{dV}{F_{A_0}} = \int_0^{X_A} \frac{dx_A}{-r_A}$$

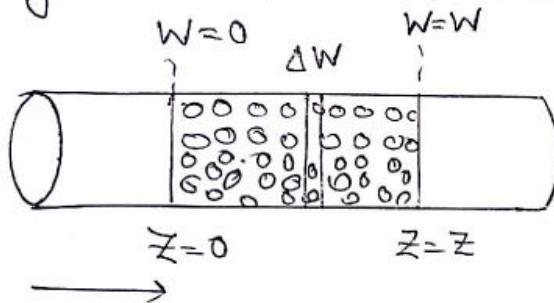
$$\frac{V}{F_{A_0}} = \int_0^{X_A} \frac{dx_A}{-r_A}$$

$$r_A = \frac{k_1 C_{A_0}(1-X_A)}{1 + K_A C_{A_0}(1-X_A)}$$

$$F_{A_0} \frac{dx_A}{dV} = -r_A = f(x_A) = \frac{k_1 C_{A_0}(1-X_A)}{1 + K_A C_{A_0}(1-X_A)}$$

$$T_p = \frac{V}{V_0} = C_{A_0} \int_0^{X_f} \frac{dx_A}{-r_A}$$

Heterogeneous



$$-\frac{dF_A}{dW} = -\frac{r_A'}{kg\ mol\ hr}$$

Kinetic analysis of batch reactor

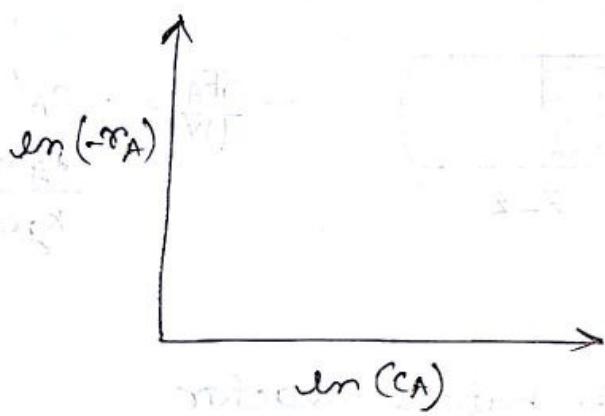
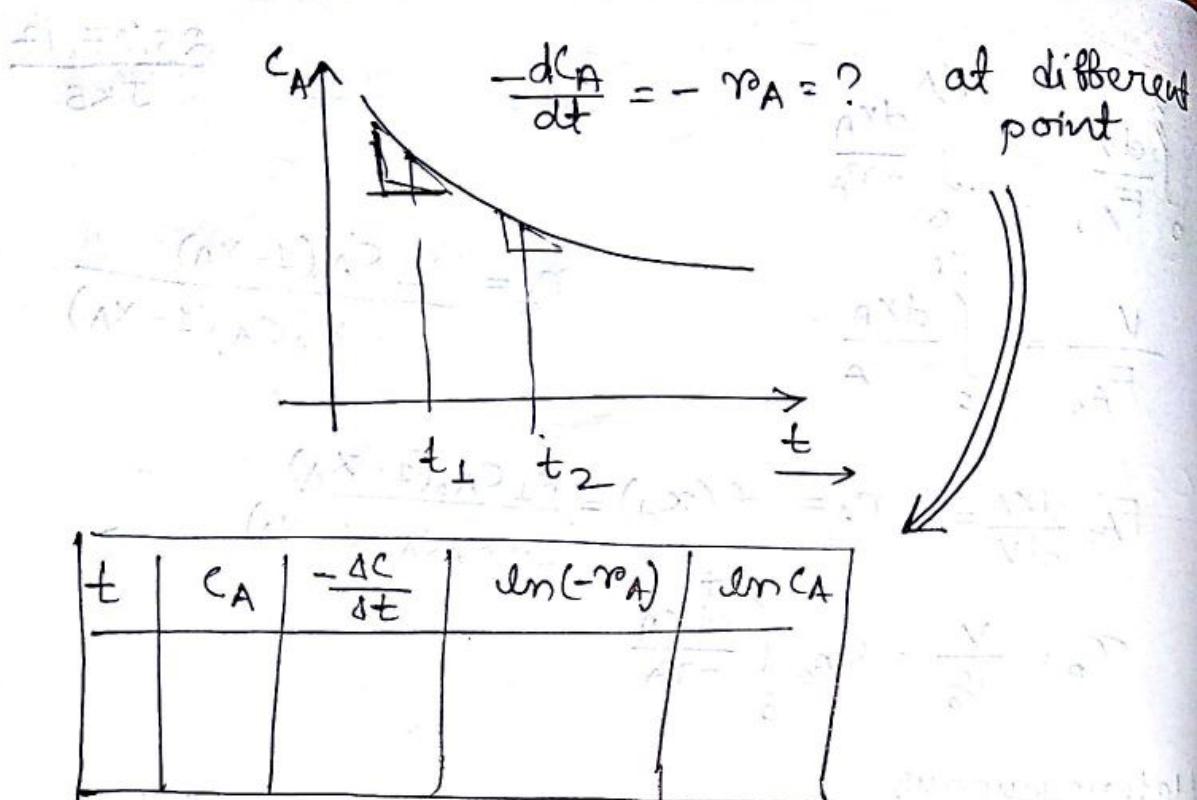
1) Differential method 2) Integral method

\rightleftharpoons Diff^n method
 $A \rightarrow B$

If the order of reaction is assumed to be p and the kinetic eqⁿ used is

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

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



$$-\frac{dc_A}{dt} = -\frac{\Delta c_A}{\Delta t} = \frac{c_{A,n-1} - c_{A,n}}{t_n - t_{n-1}}$$

If two rates are available,

Example : 4.1



find the rate law at 300K

Run number	$C_{A_0}, \frac{\text{mol}}{\text{L}}$	$C_{B_0}, \frac{\text{mol}}{\text{L}}$	$-\frac{dC_A}{dt}, \frac{\text{mol/L sec}}{}$
1	1.125	2.250	9.2
2	1.125	1.125	3.58
3	2.250	2.250	36.78

$$-r_A = K C_A^n C_B^m$$

$$\frac{-r_{A01}}{-r_{A02}} = \frac{9.2}{3.58} = \left(\frac{1.125}{1.125}\right)^n \left(\frac{2.25}{1.125}\right)^m$$

$$2.008 = 1^n 2^m ; m=1$$

$$\frac{-r_{A03}}{-r_{A01}} = \frac{36.78}{9.2} = \left(\frac{2.25}{1.125}\right)^n \left(\frac{2.25}{2.25}\right)^m$$

$$-r_A = K C_A^2 C_B^{\frac{1}{2}}$$

$$y'(x) = \frac{-3*y(x) + 4*y(x+h) - y(x+2h)}{2*h}$$

considering
centred diff
method

At $t=0$, initial rate

$$-r_{A_0} = \frac{-3C_{A_0} + 4C_{A1} - C_{A2}}{2\Delta t}$$

Polynomial fitting

$$C_A = \alpha + \beta t + \gamma t^2 + \delta t^3 + \dots + \mu t^n$$

$\alpha, \beta, \gamma, \delta, \dots, \mu$ are unknown

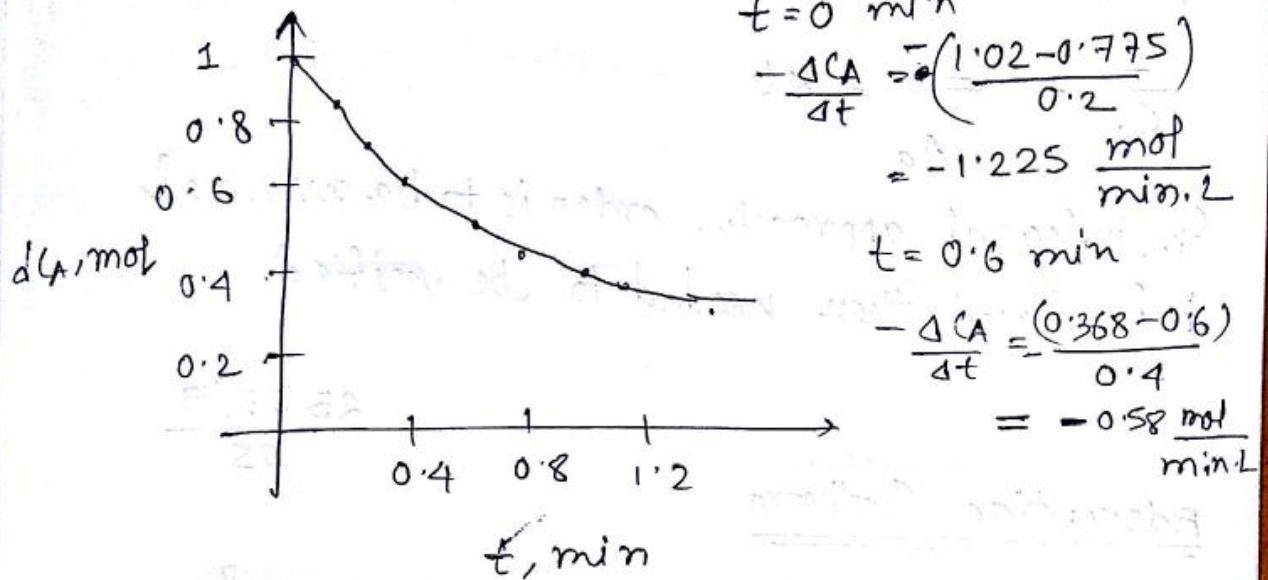
$$\frac{dC_A}{dt} = \beta + 2\gamma t + 3\delta t^2 + \dots + \mu \cdot n \cdot t^{n-1}$$



t , min	C_A , mol/L	t , min	C_A , mol/L
0	1.02	1.2	0.242
0.2	0.775	1.4	0.197
0.4	0.6	1.6	0.165
0.6	0.468	1.8	0.138
0.8	0.368	2.0	0.12
1	0.295		

a) Calculate the initial reaction rate and rate at 0.6 min time

b) Find rate eqⁿ



Numerically,

$$@ t = 0$$

$$-\gamma_{A_0} = \frac{-3C_{A_0} + 4C_{A_1} - C_{A_2}}{2At} = \frac{-3 \times 1.02 + 4 \times 0.775 - 0.6}{2 \times 0.2}$$

$$= -1.4 \text{ mol/min.L}$$

$$C_A = 0.0577t^4 - 0.3672t^5$$

$$\rho = 1.2518, \text{ rate const} = 1.4258 \text{ mol/L.min}$$

Integral Method

$$-r_A = kC_A^P \quad \text{where } P \neq 1$$

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = -\frac{dC_A}{dt} = kC_A^P$$

$$\int_{C_A}^{C_A} \frac{dC_A}{kC_A^P} = \int_0^t dt \Rightarrow \frac{1}{C_A^{P-1}} - \frac{1}{C_{A_0}^{P-1}} = (P-1)kt$$

$p=2$

$$\frac{1}{C_A} - \frac{1}{C_{A_0}} = kt$$

In integral approach, order is to be assumed beforehand, then needed to be verified.

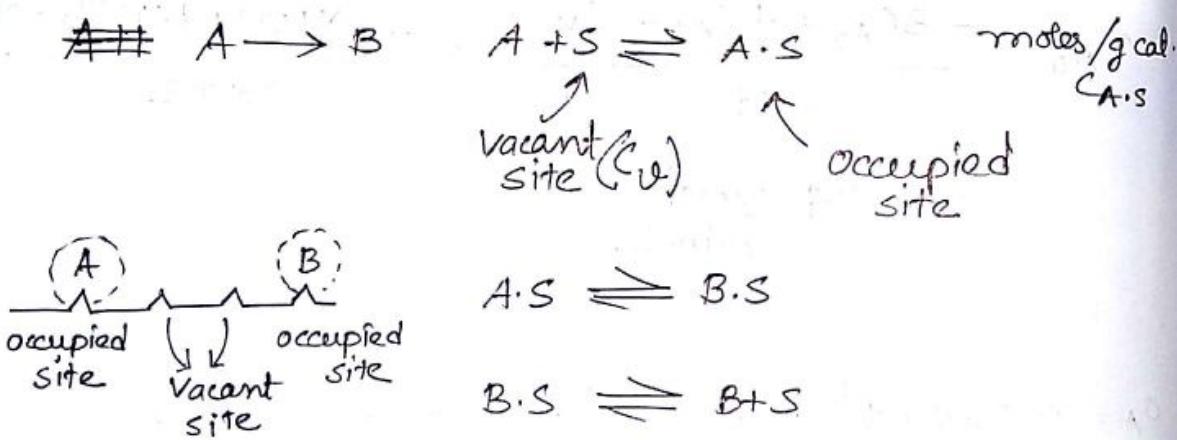
25/07/17

SS

Adsorption Isotherm

'S' → active site on the catalyst surface

$$\frac{\text{no. of active sites}}{\text{unit mass of catalyst}} \times \frac{1}{N_A} = \frac{\text{moles}}{\text{g catalyst}}$$



total site concentration (C_t)

$$: C_t = C_V + C_{A \cdot S} \quad \text{site balance}$$

Amount of non reacting gas absorbed at same temperature but @ different pressure

constructs adsorption isotherm

(JKB) 31/07/17

Q The pyrolysis of ethane proceeds with an activation energy of about 75,000 cal. How much faster is the decomposition at 650°C than at 500°C.

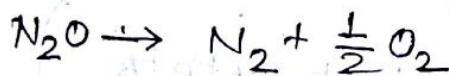
$$\frac{K_{650}}{K_{500}} = \frac{\cancel{A} e^{-\frac{E_a}{R \cdot 923}}}{\cancel{A} e^{-\frac{E_a}{R \cdot 773}}}$$

Assumption:
Activation energy is const. for given variation of temp

$$\frac{K_{650}}{K_{500}} = e^{\frac{E_a}{R} \left(\frac{1}{773} - \frac{1}{923} \right)} = e^{\frac{150 E_a}{R \cdot 773 \cdot 92}}$$

$$K_{650} = 2.218 K_{500} \quad 2879 \cdot 7396 K_{500}$$

Q Experiment shows that the preliminary reaction in the homogeneous decomposition of nitrous oxide proceeds with stoichiometry



$$\text{rate} = -r_{N_2O} = \frac{k_1 [N_2O]^2}{1 + k_2 [N_2O]} \frac{\text{mol}}{\text{lit. min}}$$

$$k_1 = 10^{19.39} e^{-81800/RT}$$

$$k_2 = 10^{8.69} e^{-28400/RT}$$

- What is the activation for the reaction?
- Sketch the curve you expect to obtain in an ~~an~~ Arrhenius plot

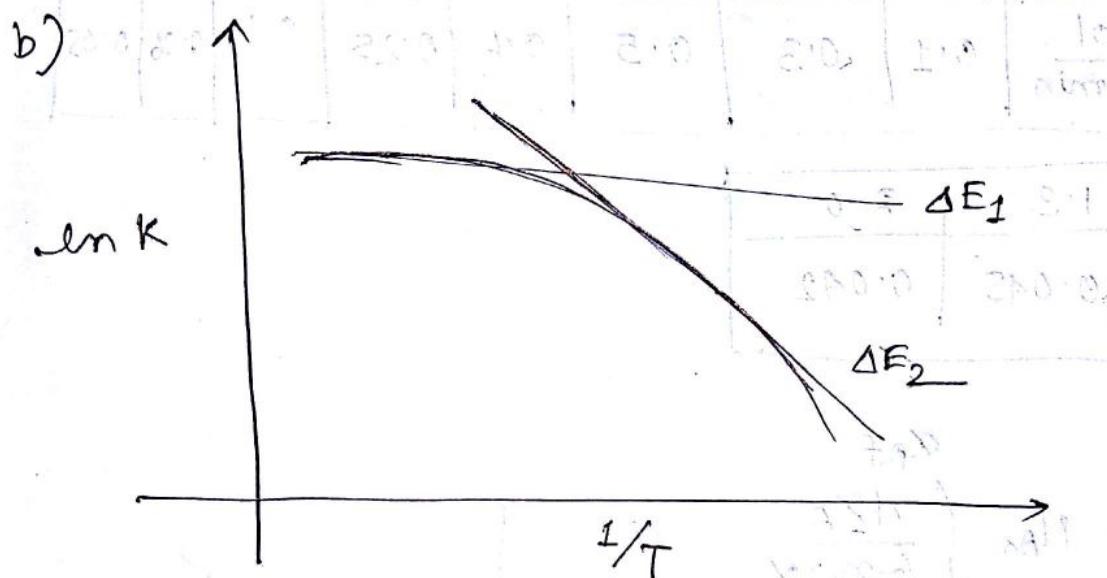
at low temp

$$K_2 [N_2O] \ll 1$$

$$\Rightarrow -r_{N_2O} = \frac{K_1 [N_2O]^2}{1} = K_1 [N_2O]^2 \Rightarrow \text{2nd order}$$

a) Activation energy (ΔE_a)

$$= 81800 \frac{\text{cal}}{\text{mol}}$$



at high temp

$$-r_{N_2O} = \frac{K_1 [N_2O]^2}{K_2 [N_2O]} = \frac{K_1}{K_2} [N_2O]$$

$$= 10^{10.7} e^{-\frac{53400}{RT}} [N_2O]$$

a) activation energy = $53400 \frac{\text{cal}}{\text{mol}}$

b) Combination of 2 straight lines \Rightarrow gives curve

We are planning to operate a batch reactor to convert A into R. This is a liquid reaction the stoichiometry is $A \rightarrow R$ & the rate of reaction is given in the following table. How long must we react each batch for the concentration to drop from $C_{A_0} = 0.3 \text{ mol/L}$

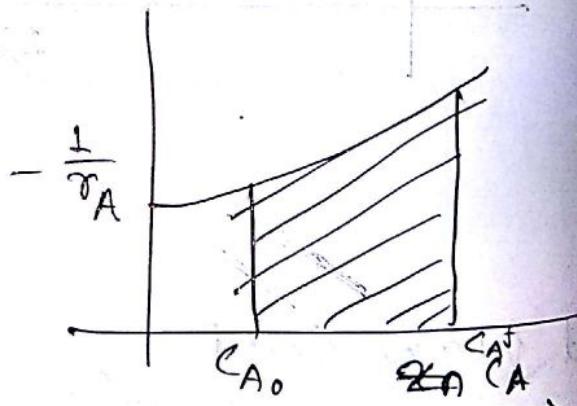
$C_A, \frac{\text{mol}}{\text{L}}$	0.1	0.2	0.3	0.4	0.6	0.7	0.8	1.0
$-r_A, \frac{\text{mol}}{\text{L min}}$	0.1	0.3	0.5	0.6	0.25	0.10	0.06	0.05

1.3	2.0
0.045	0.042

$$t = N_{A_0} \int_0^{x_{A_f}} \frac{dx_A}{(-r_A) V}$$

$$= C_{A_0} \int_0^{x_{A_f}} \frac{dx_A}{(-r_A)}$$

$$= - \int_{C_{A_0}}^{C_A} \frac{dC_A}{(-r_A)}$$



for 3rd order

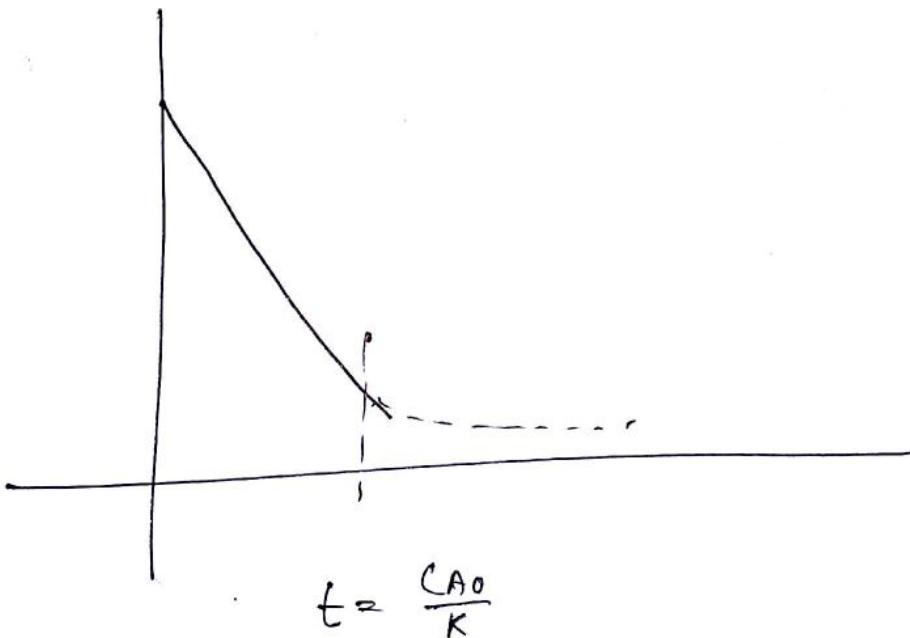
$$\frac{1}{C_A^2} - \frac{1}{C_{A_0}^2} = 2kt$$

zero order $\propto k^n$

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

$$C_A = C_{A_0} - kt \quad \text{valid within}$$

$$t \leq \frac{C_{A_0}}{k} \quad \text{and at } t \geq \frac{C_{A_0}}{k}, C_A = 0$$



Negative or fractional order $\propto k^n$

$$\int_{C_{A_0}}^{C_A} C_A^{-n} dC_A = - \int_0^t k dt$$

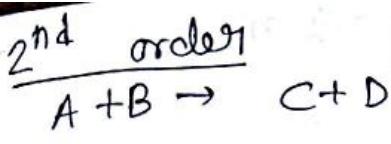
$$\frac{1}{-n+1} (C_A^{-n+1} - C_{A_0}^{-n+1}) = -kt$$
$$C_A = C_{A_0} [1 + (n-1) \frac{k}{C_{A_0}}]^{1/(1-n)}$$

valid for $n = \text{fraction or negative}$

as $t \rightarrow \infty$, $C_A \rightarrow -ve$

for $C_A = 0$ $t \geq \frac{1}{(1-n)k C_{A_0}^{n-1}}$

Beyond $t = \frac{1}{(1-n)k C_{A_0}^{n-1}}$, 1st order kinetics is valid.



01/08/17
JKB

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

$$C_B = C_{B_0} (1 - x_B) = C_{A_0} (M - x_A)$$

$$\int_0^{x_A} \frac{dx_A}{(1-x_A)(M-x_A)} = \int_0^t k C_{A_0} dt$$

$$\ln \left[(M - x_A) / (M - 1) \right] = C_{A_0} (M - 1) kt = (C_{B_0} - C_{A_0}) kt$$

for $M = 1$

$$-r_A = -\frac{dC_A}{dt} = k C_A^2 ; \quad \frac{1}{C_A^2} - \frac{1}{C_{A_0}^2} = 2kt$$

1st order

$$-r_A = -\frac{d [C_{A_0}(1-x_A)]}{dt} = k C_{A_0} (1-x_A)$$

$$\frac{dx_A}{dt} = k C_{A_0} (1-x_A)$$

$$-\ln (1-x_A) = kt$$

Negative order & fractional order

$$-r_A = k C_A^n$$

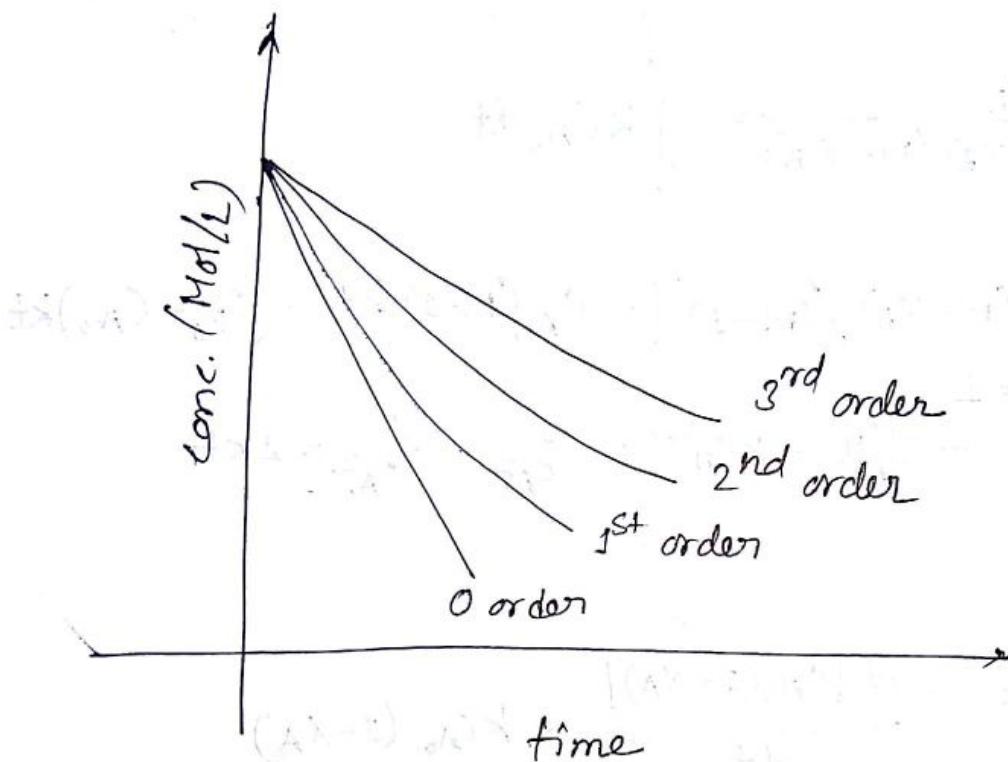
$$\frac{dC_A}{dt} = -k C_A^n$$

$$\frac{1}{-n+1} (C_A^{-n+1} - C_{A_0}^{-n+1}) = -kt$$

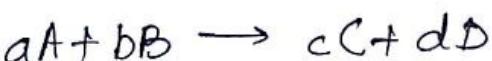
$$C_A = C_{A_0} \left[1 + (n-1)k C_{A_0}^{n-1} t \right]^{1/(1-n)}$$

as $t \rightarrow \infty \quad C_A = -ve$

$$C_A = 0 \text{ for } t \geq \frac{1}{(1-n)k C_{A_0}^{n-1}}$$



Overall Order of reaction by half-life period method



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

performed in stoichiometric ratio throughout period of $\propto k^n$

$$\frac{C_B}{C_A} = \frac{b}{a} \quad \text{and} \quad -\frac{dC_A}{dt} = k C_A^a \left(\frac{b}{a} C_A\right)^b = k \left(\frac{b}{a}\right)^b C_A^{a+b}$$

$$= K' C_A^n$$

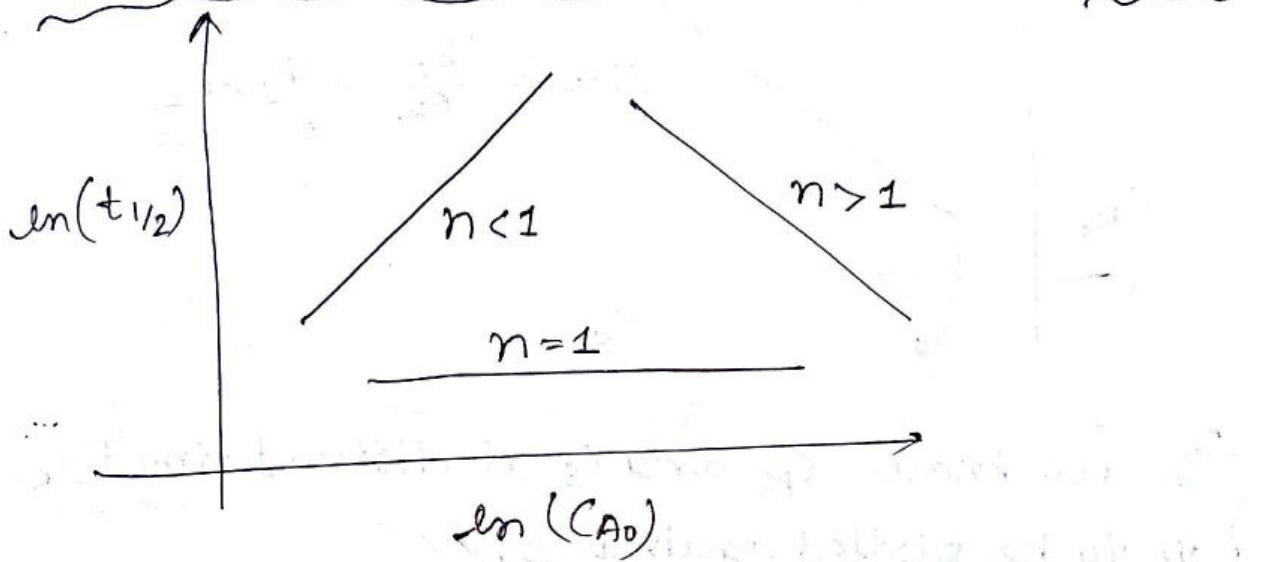
for $n \neq 1$

$$(C_A^{1-n} - C_{A_0}^{1-n}) = K(n-1)t$$

for half life: $t_{1/2}$

$$t_{1/2} = \frac{C_{A_0}}{2}, \quad t_{1/2} = \frac{0.5^{1-n} - 1}{K(n-1)} C_{A_0}^{1-n}$$

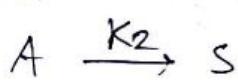
$\ln(t_{1/2})$ vs $\ln(C_{A_0})$ gives a st. line with slope = $\frac{1-n}{n-1}$



Irreversible Parallel reaction



$$r_R = \frac{dC_R}{dt} = k_1 C_A$$



$$r_S = \frac{dC_S}{dt} = k_2 C_A$$

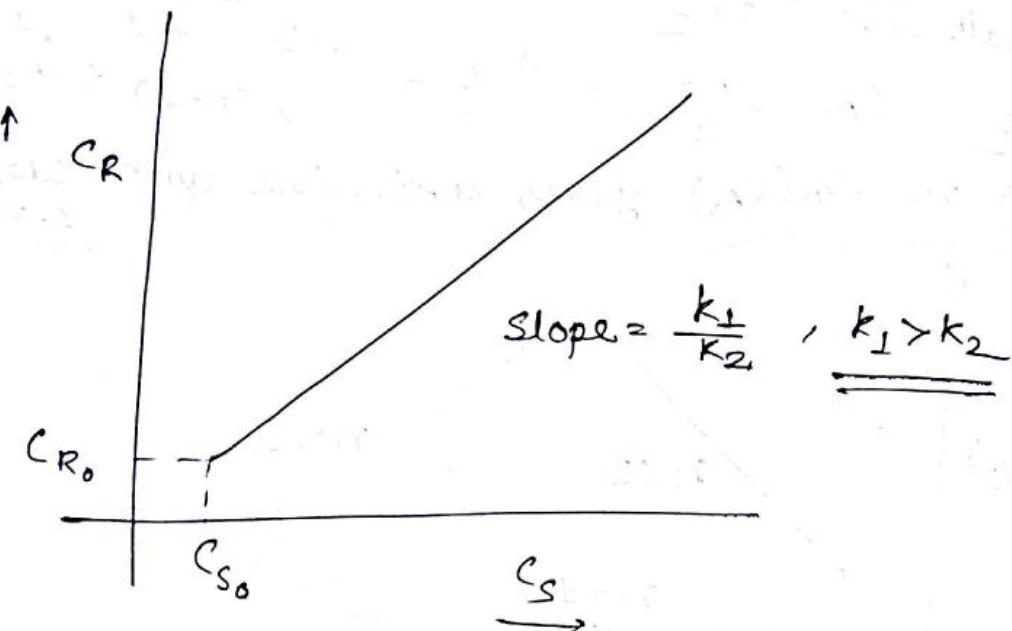
$$-r_A = -\frac{dC_A}{dt} = (k_1 + k_2) C_A$$

$$\text{at } t=0, \quad C_A = C_{A_0}, \quad C_{R_0} = C_{S_0} = 0$$

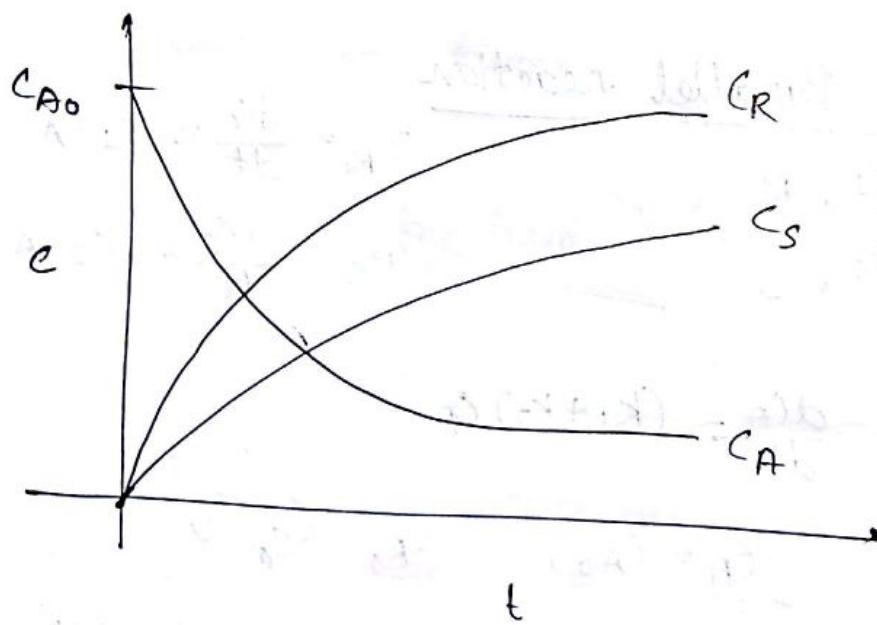
$$-\ln\left(\frac{C_A}{C_{A_0}}\right) = (k_1 + k_2)t = k't$$

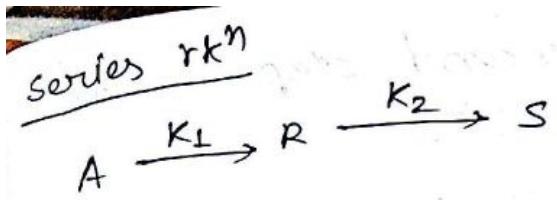
k' is obtained from the plot of $-\ln \frac{C_A}{C_{A_0}}$ vs. t

$$\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_1}{k_2} \Rightarrow \frac{C_R - C_{R_0}}{C_S - C_{S_0}} = k''$$



{ If we know C_R and C_S at different time 't', C_R vs to be plotted against C_S .





$$r_A^{\rho_2} \frac{dC_A}{dt} = -k_1 C_A$$

$$r_R^{\rho_2} = \frac{dC_R}{dt} = -k_2 C_A - k_2 C_R$$

$$r_S^{\rho_2} \frac{dC_S}{dt} = k_2 C_R$$

$$-\ln\left(\frac{C_A}{C_{A_0}}\right) = k_1 t \quad \text{or} \quad C_A = C_{A_0} e^{-k_1 t}$$

$$\frac{dC_R}{dt} + k_2 C_R = k_1 C_{A_0} e^{-k_1 t}$$

$$C_R e^{\int k_2 dt} = \int (k_1 C_{A_0} e^{-k_1 t} e^{\int k_2 dt}) dt + \text{const.}$$

$$C_R e^{k_2 t} = C_{A_0} k_1 \frac{e^{(k_2 - k_1)t}}{k_2 - k_1} + \text{const}$$

$$C_{R_0} = 0$$

$$\text{const} = -\frac{k_1 C_{A_0}}{k_2 - k_1}$$

$$C_R e^{k_2 t} = C_{A_0} k_1 \left[\frac{e^{(k_2 - k_1)t}}{k_2 - k_1} - \frac{1}{k_2 - k_1} \right]$$

$$C_R = C_{A_0} k_1 \left[\frac{e^{-k_1 t}}{k_2 - k_1} + \frac{e^{-k_2 t}}{k_1 - k_2} \right]$$

$$\text{as } C_{A_0} = C_A + C_R + C_S$$

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

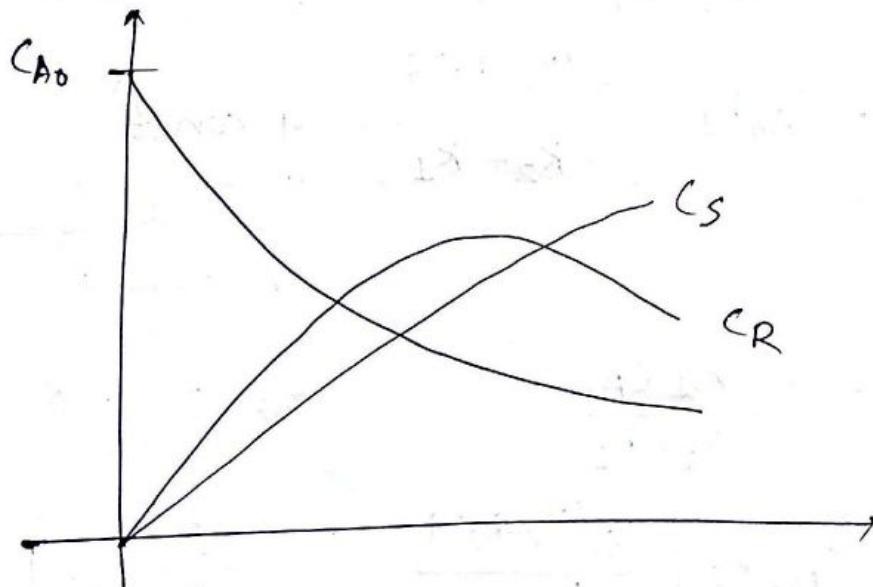
$C_S = C_{A_0} (1 - e^{-k_2 t})$, the second step is the controlling one for $k_1 \gg k_2$

$C_S = C_{A_0} (1 - e^{-k_1 t})$, the first step is controlling for $k_1 \ll k_2$

at $\frac{dC_R}{dt} = 0$

$$t_{\max} = \frac{1}{K_{\log \text{mean}}} = \frac{\ln \left(\frac{k_2}{k_1} \right)}{(k_2 - k_1)}$$

and $\frac{C_{R, \max}}{C_{A_0}} = \left(\frac{k_1}{k_2} \right)^{\frac{k_2}{(k_2 - k_1)}}$





Derive the expression for C_R as a fn of time
Find $C_{R,\max}$ and t_{\max}

$$n_A = \frac{dC_A}{dt} = -k_1 C_A$$

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

$$C_R e^{\int k_1 dt} = \int (k_1 C_{A_0} e^{-k_1 t} - k_2 C_R) dt + I$$

$$C_R = k_1 C_{A_0} e^{-k_1 t}$$

Steps are elementary

$$-\ln \frac{C_A}{C_{A_0}} = k_1 t \quad C_A = C_{A_0} e^{-k_1 t}$$

$$\frac{dC_R}{dt} + k_1 C_R = k_1 C_{A_0} e^{-k_1 t}$$

$$C_R e^{k_1 t} = \int (k_1 C_{A_0}) dt + I$$

$$\text{at } t=0, \quad C_R = 0 \text{ and } I=0$$

$$\frac{dC_R}{dt} = -k_1^2 C_{A_0} e^{-k_1 t} + k_1 C_{A_0} e^{-k_1 t} = 0$$

$$t_{\max} = 1/k_1$$

$$C_{R,\max} = \frac{k_1 C_{A_0}}{2}$$

$$= 3.679 \frac{\text{moles}}{\text{L}}$$

1st order reversible rxn



$$\text{let } M = \frac{C_{R0}}{C_{A0}}$$

$$k_C = \frac{C_{Re}}{C_{Ae}} = \frac{k_1}{k_2}$$

$$\frac{dC_R}{dt} = -\frac{dC_A}{dt} = C_{A0} \frac{dX_A}{dt} = k_1 (A - k_2 C_R)$$

$$\text{at eqbm. } -\frac{dC_A}{dt} = 0$$

$$k_C = \frac{C_{Re}}{C_{Ae}} = \frac{C_{R0} + C_{A0} X_{Ae}}{C_{A0}(1 - X_{Ae})} = \frac{M + X_{Ae}}{1 - X_{Ae}} = \frac{k_1}{k_2}$$

$$\frac{dX_A}{dt} = k_1 (1 - X_A) - k_2 (M + X_A)$$

$$\frac{dX_A}{dt} = \frac{k_1 (1 - X_A) (M + X_{Ae}) - k_2 (1 - X_{Ae}) (M + X_A)}{(M + X_{Ae})}$$

$$\frac{dX_A}{dt} = \frac{k_1 (M + 1)}{(M + X_{Ae})} (X_{Ae} - X_A) = k' (X_{Ae} - X_A)$$

$$\int_0^{\frac{X_A}{X_{Ae} - X_A}} \frac{dX_A}{(X_{Ae} - X_A)} = \int_0^t k' dt$$

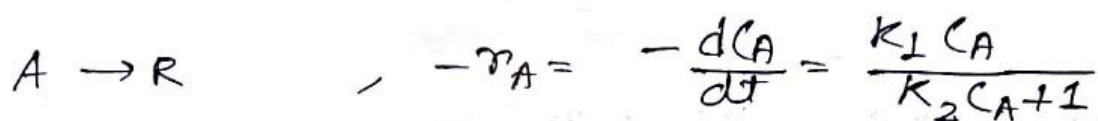
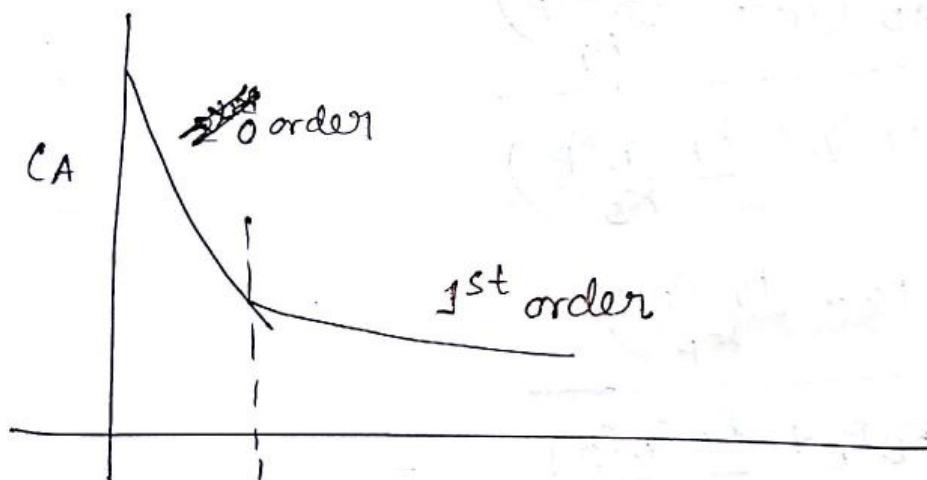
$$-\ln \left[\frac{(X_{Ae} - X_A)}{X_{Ae}} \right] = k't \text{ or } -\ln \left(1 - \frac{X_A}{X_{Ae}} \right) = k'$$

$$k' = \frac{k_1(M+1)}{(M+x_{Ae})}$$

Slope of straight line plot $-\ln\left(\frac{x_{Ae} - x_A}{x_{Ae}}\right)$ vs. t

Shifting of order of $r k^n$

Some cases at different concentrations zone the orders may be different. Order may change from zero to first order, first to 2nd order i.e. lower to higher order as concentration decreases.



at low C_A , $K_2 C_A \ll 1$ and

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A \text{ i.e. } 1^{\text{st}} \text{ order}$$

at high C_A , $K_2 C_A \gg 1$ and

$$-r_A = -\frac{dC_A}{dt} = \frac{k_1}{K_2} \text{ i.e. zero order}$$

for 1st order

$$C_A = C_{A_0} e^{-k_1 t}$$

& 0 order

$$C_{A_0} - C_A = \frac{k_1}{k_2} t$$

transition of order takes place at

$$k_1 C_A = \frac{k_1}{k_2} \quad \text{or} \quad C_A \approx \frac{1}{k_2}$$

01/08/17

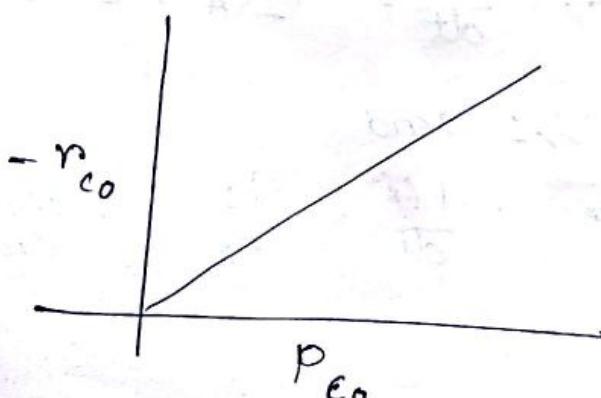
$$-r_c = r_{AD} = k_{AD} \left(P_c - \frac{P_B P_c}{K_p} \right) \left(\frac{C_t}{1 + K_B P_B + \frac{K_B P_B P_p}{K_s}} \right)$$

$$= \frac{C_t k_{AD} \left(P_c - \frac{P_B P_p}{K_p} \right)}{\left(1 + K_B P_B + \frac{K_B P_B P_p}{K_s} \right)}$$

$$\Rightarrow \frac{K \left(P_c - \frac{P_B P_p}{K_p} \right)}{\left(1 + K_B P_B + \frac{K_B P_B P_p}{K_s} \right)}$$

at $t \approx 0$, $r_{c_0} = r_c$

$$r_{c_0} = K P_c \quad P_B = P_p = 0$$



⇒ This plot implies that adsorption is rate controlling step.

08/08/17
JKB

Kinetic Analysis by Total Pressure

Method in a Batch Reactor

Let us consider the stoichiometry as



The stoichiometric table for batch reactor

Species	Initial	change	Final
		Final	
A	N_{A_0}	$-N_{A_0}x$	$N_A = N_{A_0} - N_{A_0}x$
B	N_{B_0}	$-\frac{b}{a}N_{A_0}x$	$N_B = N_{B_0} - \frac{b}{a}N_{A_0}x$
C	N_{C_0}	$+\frac{c}{d}N_{A_0}x$	$N_C = N_{C_0} + \frac{c}{d}N_{A_0}x$
D	N_{D_0}	$+\frac{d}{a}N_{A_0}x$	$N_D = N_{D_0} + \frac{d}{a}N_{A_0}x$
I	N_{I_0}	0	$N_I = N_{I_0}$
Total	N_{T_0}		$N_{T_0} + N_{A_0}x \left(\frac{d}{a} + \frac{c}{d} - \frac{b}{a} - 1 \right)$

$$N_{T_0} + N_{A_0}x \frac{1}{a}(d+c-a-b) = N_{T_0} + N_{A_0}x \frac{1}{a} \Delta n$$

$$N_B = N_{B_0} - \frac{b}{a}N_{A_0}x, \quad N_B = N_{B_0} - y_B N_{A_0}x \quad \text{where} \\ y_B = \frac{b}{a}$$

$$N_i = N_{i_0} - y_i N_{A_0}x$$

assuming a constant volume reactor, V_r

$$c_p = \frac{N_i}{V_p} = (N_{i_0} - y_i N_{A_0}x) \frac{1}{V_r}$$

$$C_A = \frac{N_A}{V_r} = (N_{A_0} - N_{A_0}x) \frac{1}{V_r} = C_{A_0} (1-x)$$

$$N_B = N_{B_0} - \frac{b}{a} N_{A_0} x \rightarrow \gamma_B$$

$$= N_{A_0} \left(\frac{N_{B_0}}{N_{A_0}} - \frac{b}{a} x \right)$$

θ_B

$$N_i = N_{A_0} (\theta_i \pm \gamma_i x)$$

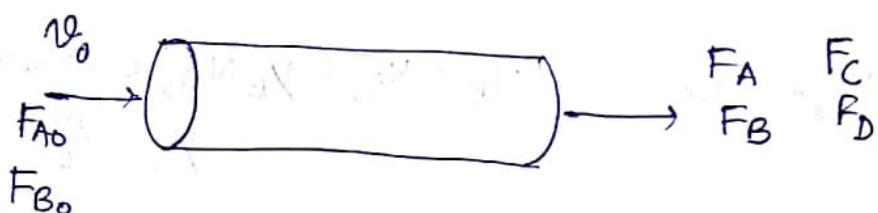
For batch reactor

$$C_A = \frac{N_A}{V_r}, C_B = \frac{N_B}{V_r}$$

For flow reactor

$$F_{A_0}, F_A = F_{A_0} - F_A x$$

$$C_A = \frac{\text{Molar flow rate}}{\text{volumetric flow rate}}$$



$$C_A = \frac{F_A}{v_0}$$

For batch

$$C_B = (N_{B_0} - \gamma_B N_{A_0} x) \frac{1}{V_r} = N_{A_0} [\theta_B - \gamma_B x] \frac{1}{V_r}$$

$$C_C = N_{A_0} [\theta_C - \gamma_C x] \frac{1}{V_r}$$

If the reaction is carried out in a constant volume bomb reactors and total pressure is varying from π_0 to π and the total mole changes from N_{T_0} to N_T

$$N_T = N_{T_0} + N_{A_0} \times \frac{1}{a} \Delta n$$

$$\chi = \frac{N_T - N_{T_0}}{N_{A_0} \Delta n/a} = \frac{N_T - N_{T_0}}{N_{A_0} s}, \quad s = \frac{\Delta n}{a}$$

$$C_A = \frac{N_{A_0}}{V_r} = \frac{N_{A_0} \chi}{V_r} = C_{A_0} - \frac{N_{A_0}}{V_r} \left(\frac{N_T - N_{T_0}}{N_{A_0} \Delta n/a} \right)$$

$$C_{A\text{RT}} = C_{A_0} RT - \frac{N_{A_0} RT}{V_r} \left(\frac{N_T - N_{T_0}}{N_{A_0} \Delta n/a} \right)$$

$$= C_{A_0} RT - \frac{a}{\Delta n} \left(\frac{N_T RT - N_{T_0} RT}{V_r} \right)$$

$$\text{as } C_A = \frac{P_A}{RT} \quad \text{and} \quad \pi = \frac{NRT}{V_r} \equiv \text{total pressure}$$

$$P_A = P_{A_0} - \frac{a}{\Delta n} (\pi - \pi_0), \quad P_B = P_{B_0} - \frac{b}{\Delta n} (\pi - \pi_0)$$

$$P_C = P_{C_0} + \frac{c}{\Delta n} (\pi - \pi_0)$$

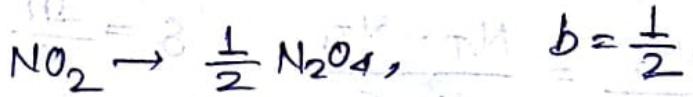
$$P_D = P_{D_0} + \frac{d}{\Delta n} (\pi - \pi_0)$$

$$\text{where } \Delta n = s \cdot a$$

Example

Consider reaction $2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4$

The initial total pressure of NO_2 , $p_{T_0} = 2\text{ atm}$, is decreased by 30% in 10 minutes at 350 K. Determine the rate constant [R = 0.082 L-atm/mole·K]



$$p_A = p_{A_0} - \frac{a(p_T - p_0)}{4n} \quad \text{where } a=1, n=-\frac{1}{2}$$

$$p_A = p_{A_0} + 2(p_T - p_0) \quad \text{as } p_{T_0} = p_{A_0}$$

$$p_A = 2p_T - p_{A_0}$$

$$\frac{d[\text{N}_2\text{O}_4]}{dt} = k_2 [\text{N}_2\text{O}_4]^2 = -\frac{1}{RT} \frac{dp_T}{dt} = k_2 (p_A)^2$$

$$\frac{1}{RT} \frac{dp_T}{dt} = k_2 (2p_T - p_{A_0})^2$$

$$\int \frac{dp_T}{(2p_T - p_{A_0})^2} = -k_2 RT \int dt$$

p_{A_0}

$$\frac{1}{2} \left(\frac{1}{2p_T - p_{A_0}} - \frac{1}{p_{A_0}} \right) = \frac{k_2}{RT} t$$

$$Y = \frac{RT}{2} \left(\frac{1}{2p_T - p_{A_0}} - \frac{1}{p_{A_0}} \right) = k_2 t$$

From Y vs. t plot, k_2 can be estimated

at $t = 10 \text{ min}$ $P_T = 0.7 P_{A_0}$, ($P_{T_0} = P_{A_0} = 2 \text{ atm}$)

$$\frac{1}{2} \left(\frac{1}{1.4 P_{A_0} - P_{A_0}} - \frac{1}{P_{A_0}} \right) = \frac{K_2}{R \times 350} \times 10$$

$$K_2 = 1.07625 \text{ lit mol}^{-1} \text{ min}^{-1}$$

For flow reactor (CSTR, PFR)



Initial
Feed
rate

$$F_A = F_{A_0}$$

$$F_B = \theta_B F_{A_0}$$

$$F_C = \theta_C F_{A_0}$$

$$F_D = \theta_D F_{A_0}$$

Effluent
rate

$$F_A = F_{A_0} (1 - x_A)$$

$$F_B = F_{A_0} \left(\theta_B - \frac{b}{a} x_A \right)$$

$$F_C = F_{A_0} \left(\theta_C + \frac{c}{a} x_A \right)$$

$$F_D = F_{A_0} \left(\theta_D + \frac{d}{a} x_A \right)$$

Effluent con-

$$x_A = \frac{F_A}{F} = \frac{F_{A_0} (1 - x_A)}{V_0}$$

$$x_B = \frac{F_B}{F} = \frac{F_{A_0} \left(\theta_B - \frac{b}{a} x_A \right)}{V_0}$$

$$x_C = \frac{F_C}{F} = \frac{F_{A_0} \left(\theta_C + \frac{c}{a} x_A \right)}{V_0}$$

$$x_D = \frac{F_D}{F} = \frac{F_{A_0} \left(\theta_D + \frac{d}{a} x_A \right)}{V_0}$$

Total feed rate, $F_T = F_{A_0} (1 + \theta_B + \theta_C + \theta_D)$

total effluent rate,

$$F_T = F_{A_0} \left(1 + \theta_B + \theta_C + \theta_D \right) + F_{A_0} \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right) X$$

$$\frac{F_T}{F_{T_0}} = 1 + \frac{F_{A_0}}{F_{T_0}} Sx = 1 + y_{A_0} Sx$$

For bat ch reactor

$$N_T = N_{T_0} + N_{A_0} Sx, \quad \frac{N_T}{N_b} = 1 + \frac{N_{A_0}}{N_{T_0}} Sx = 1 + y_{A_0} Sx$$

Variable volume Reaction

$$PV = Z N_T R T$$

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

$$v = v_0 \left(\frac{P_0}{P} \right) \left(\frac{T}{T_0} \right) \left(\frac{Z}{Z_0} \right) \frac{F_T}{F_{T_0}}$$

for ideal behavior $\frac{Z}{Z_0} = 1$

$$V = V_0 \frac{N_T}{N_{T_0}} = V_0 \left(1 + \frac{N_{A0}}{N_{T_0}} \delta x \right)$$

$$v = v_0 \frac{F_T}{N_{T_0}} = v_0 \left(1 + \frac{F_{A0}}{F_{T_0}} \delta x \right)$$

$$\frac{N_{A0}}{N_{T_0}} \delta = \gamma_{A0} \delta = \epsilon_A \quad V = V_0 (1 + \epsilon_A x)$$

for complete conversion ie $x = 1$

$$\frac{V}{V_0} - 1 = \epsilon = \text{Fractional volume change}$$

$$C_A = \frac{N_A}{V_0 (1 + \epsilon_A x_A)} \quad C_B = \frac{N_B}{V_0 (1 + \epsilon_B x_B)}, \quad C_A = \frac{F_A}{V}$$

$$C = \frac{N_j}{V} = \frac{N_{j0} (0_j + j/a x_A)}{V_0 (1 + \frac{N_{j0} g_s x}{N_{T_0}})}$$

volume

$$v = v_0 (1 + \frac{F_{j0}}{F_{T_0}} \delta x) = v_0 (1 + \epsilon_j x)$$

volume flow rate

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

variable volume reaction in a batch reactor



$$-\frac{1}{V} \frac{dN_A}{dt} = k C_A = k \frac{N_A}{V}$$

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

For 2nd order

$$-\frac{1}{V} \frac{dN_A}{dt} = k \left(\frac{N_A}{V} \right)^2$$

$$\frac{(1 + \epsilon_A) x_A}{1 - x_A} + \epsilon_A \ln(1 - x_A) = k C_{A_0} t$$

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

For n th order $\propto k^n$

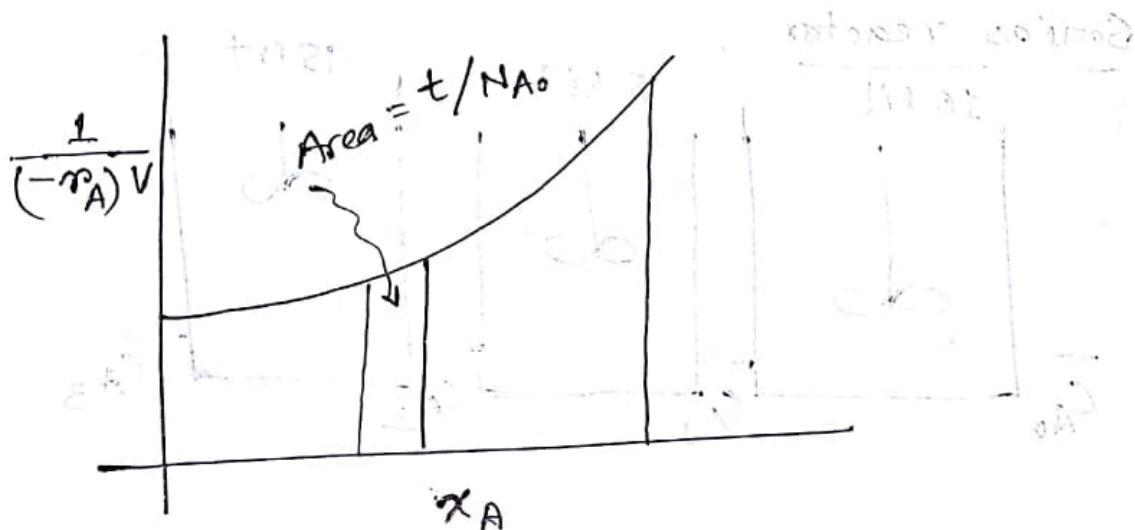
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$$\int_0^{x_A} \frac{(1 + \epsilon_A x_A)^{n-1}}{(1 - x_A)^n} dx_A = N_A o \frac{n^{-1}}{K} t$$

Design ~~use~~ Equation

$$t = N_A o \int_0^{x_A} \frac{dx_A}{\sqrt{(-r_A)}} = N_A o \int_0^{x_A} \frac{dx_A}{V_0(1 + \epsilon_A x_A)(-r_A)}$$

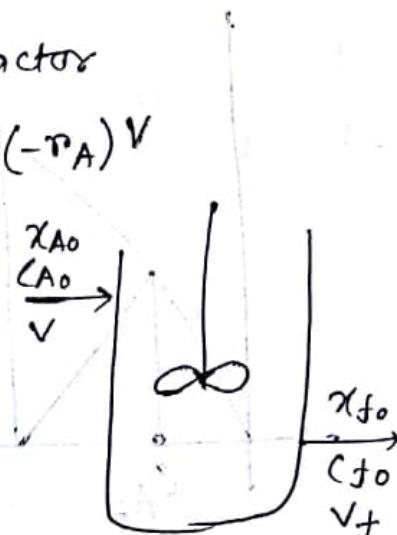
$$t = C_A o \int_0^{x_A} \frac{dx_A}{(1 + \epsilon_A x_A)(-r_A)}$$



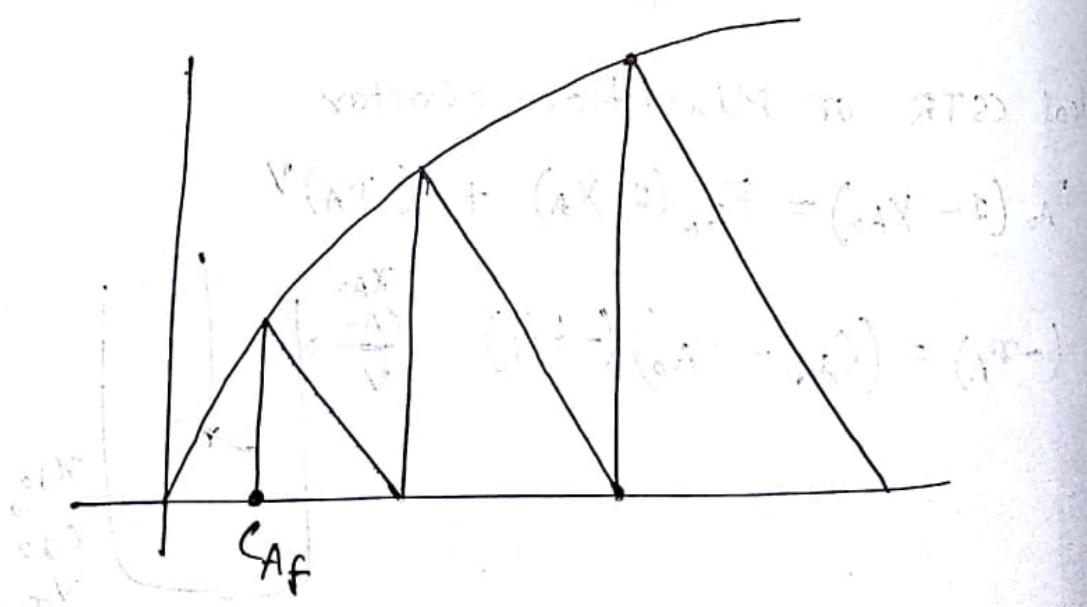
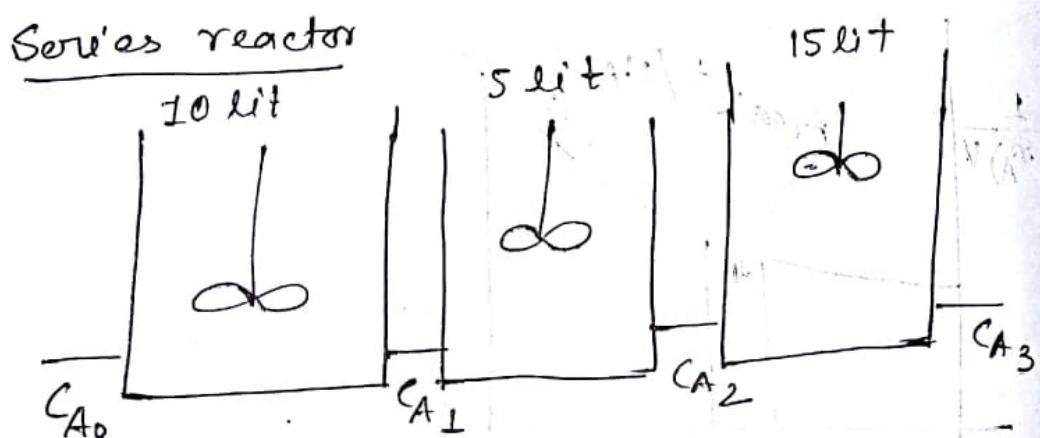
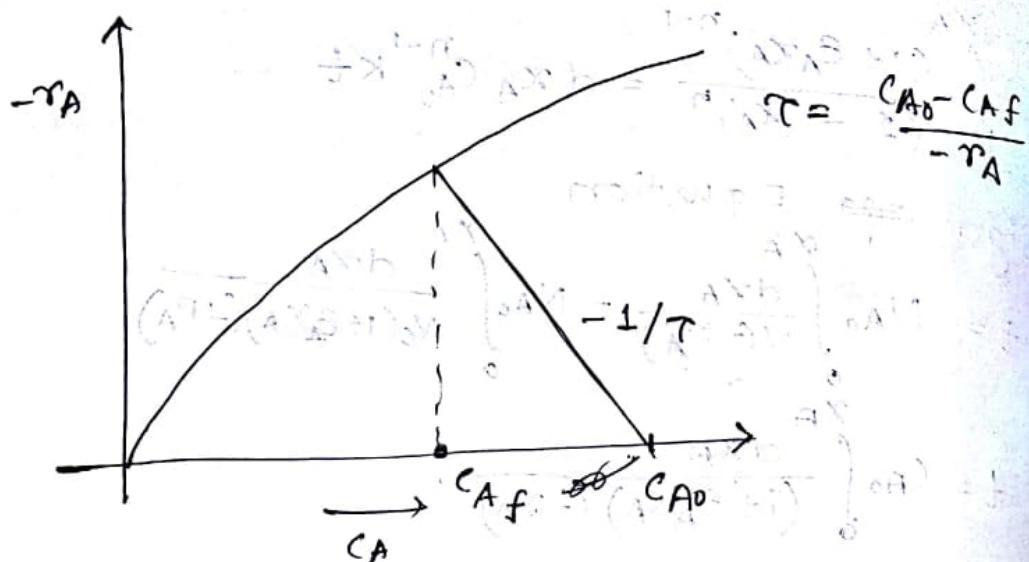
Ideal CSTR or Mixed flow reactor

$$F_{A_0}(1 - x_{A_0}) = F_{A_0}(1 - x_A) + (-r_A)V$$

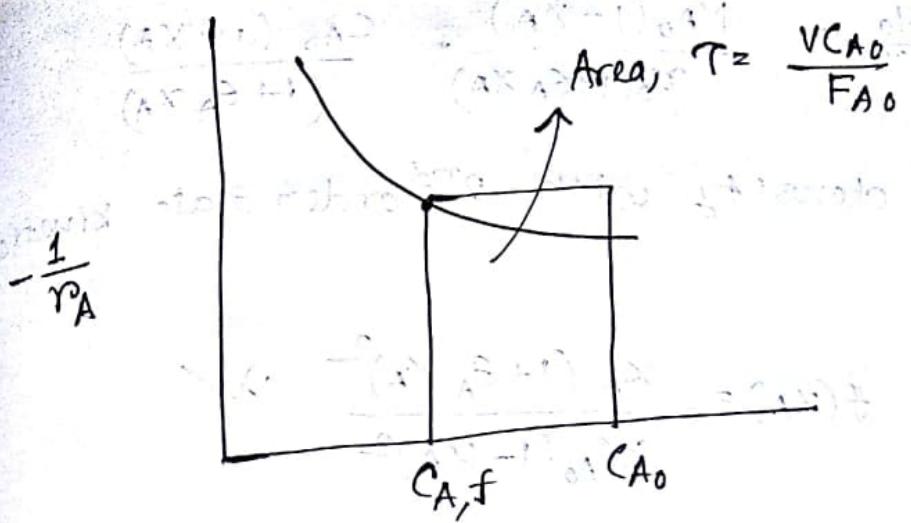
$$(-r_A) = (C_{A_f} - C_{A_0})(-1/\tau)$$



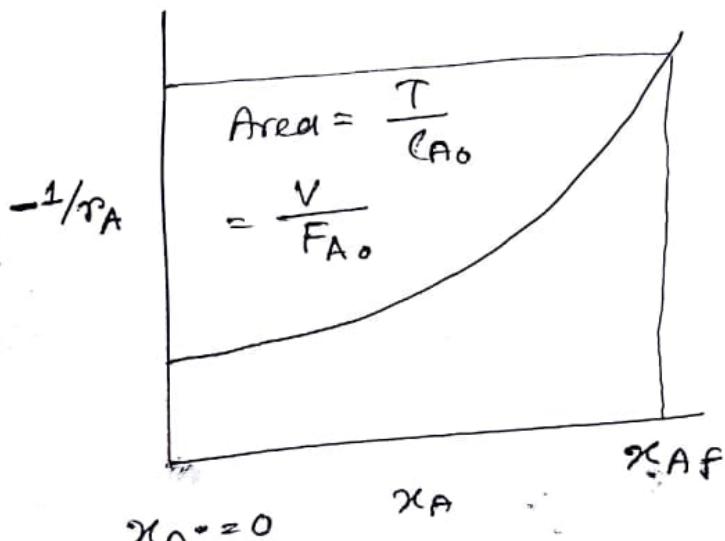
and no volume will be lost in the vessel
assume vessel does not expand like the



usually, τ for all the reactors are same
as all reactors have same volume



$$\text{area} = T = \frac{VCA_0}{FA_0} = (CA_0 - CA_f) \frac{1}{-r_A} = CA_0 \left(\frac{x_{A,f} - x_{A,0}}{-r_A} \right)$$



Variable density with first order rate kinetics

$$\frac{V}{FA_0} = \frac{V_0(1 + \varepsilon_A x_A)}{CA_0 V_0 (1 + \varepsilon_A x_A)} = \frac{x_A}{KCA_0 \frac{(1 - x_A)}{(1 + \varepsilon_A x_A)}}$$

$$kT = \frac{x_A (1 + \varepsilon_A x_A)}{(1 - x_A)} = f(x_A)$$

For various T values, calculate $f(x_A)$ with x_A values and from the slope of straight line k is obtained.

$$C_A = \frac{Nq}{v} = \frac{N A_0 (1 - X_A)}{v_0 (1 + \epsilon_A X_A)} = \frac{C_{A_0} (1 - X_A)}{(1 + \epsilon_A X_A)}$$

Variable density with 2nd order rate kinetic

$$k_T = f(X_A) = \frac{x_A (1 + \epsilon_A X_A)^2}{K C_{A_0} (1 - X_A)^2}$$

$$\left(\frac{C_A}{C_{A_0}} \right) = \frac{V_0 \rightarrow (1 + \epsilon_A X_A)}{C_{A_0} v_0 (1 + \epsilon_A X_A)} = \frac{X_A}{\frac{K C_{A_0}^2 (1 - X_A)^2}{1 + (\epsilon_A X_A)}}$$



start with addition of inhibitor

$$\frac{(A_0 - X_A)}{(A_0 + I)} = \frac{V_0 \rightarrow (1 + \epsilon_A X_A)}{C_{A_0} v_0 (1 + \epsilon_A X_A)} = \frac{V_0}{K C_{A_0}^2 (1 - X_A)^2}$$

$$(A_0 - X_A)^2 = \frac{(A_0 + I)^2 (1 - X_A)^2}{(A_0 + I)^2}$$

if $(A_0 - X_A)$ is small enough then X_A will approach 1
and we can neglect the effect of inhibitor

Problem sheet - 1

Q.1



t, s	0	20	40	60	80	100	140	200	260
P_A, atm	1.0	0.8	0.68	0.56	0.45	0.37	0.25	0.14	0.08
								330	420

t, s	P_A, atm	conversion (X_A)	
		$\frac{X_A}{1-X_A}$	$\ln(1-X_A)$
0	1.0	0	0
20	0.8	0.2	0.25
40	0.68	0.32	0.470588
60	0.56	0.44	0.785714
80	0.45	0.55	1.222222
100	0.37	0.63	1.702703
140	0.25	0.75	2.142857
200	0.14	0.86	2.4
260	0.08	0.92	2.49
330		0.96	
420		0.98	

Plot

$9.59 \times 10^{-3} \equiv \text{slope in case of } 1^{\text{st}} \text{ order rate expression}$

The plug flow reactor

$$\frac{V}{F_{A_0}} = \int_0^{X_A F} \frac{dx_A}{-\tau_A} = \int_0^{0.95} \frac{dx_A}{9.59 \times 10^{-3} C_{A_0} (1-X_A)}$$

$$\frac{V}{V_0} = - \frac{1}{9.59 \times 10^{-3}} \ln(1-X_A) = \frac{2.9957}{9.52 \times 10^{-3}}$$

$$= 312.98$$

$$C_{A_0} = \frac{P_{A_0}}{RT} = 0.0262 \text{ moles/l}$$

$$V_0 = \frac{P_{A_0}}{C_{A_0}} = 0.8481$$

$$V = 0.8481 \times 312.98 \approx 265 \text{ L}$$

Q.2 $A \xrightarrow{k} pR$, zero order
 initial, 0.8 moles of A + 0.2 moles inert = 1.0 moles R
 For const. volⁿ bomb $\Delta n = p - 1$ + 0.2 moles inert

$$-r_A = -\frac{d[A]}{dt} = k \quad a = 1$$

$$-\frac{1}{RT} \int_{P_{A_0}}^{P_A} dP_A = kt$$

$$-\frac{1}{RT} (P_A - P_{A_0}) = kt$$

$$-\frac{1}{RT} (P_A - P_{A_0}) = kt$$

$$P_A - P_{A_0} = -\frac{a}{\Delta n} (\pi - \pi_0)$$

$$\frac{a}{\Delta n RT} (\pi - \pi_0) = kt$$

$$\frac{1}{(p-1)} (1.3 - 1) = k \cdot 2$$

$$\frac{0.15}{(p-1)RT} = k \quad \dots \dots \dots \textcircled{1}$$

const. pressure batch is variable volume reaction

$$C_A - C_{A_0} + M \ln \left(\frac{C_A}{C_{A_0}} \right) = -K_3 C_{E_0} t$$

$$\left[\frac{C_{A_0} - C_A}{t} \right] - \frac{M}{t} \ln \left(\frac{C_A}{C_{A_0}} \right) \leq K_3 C_{E_0}$$

$$\frac{\ln(C_A/C_{A_0})}{t} = \frac{K_3 C_{E_0}}{M} - \frac{1}{M} \left(\frac{C_{A_0} - C_A}{t} \right)$$

$$Y = M'x + C$$

$$Y = \frac{\ln(C_A/C_{A_0})}{t}, M' = -\frac{1}{M}$$

$$\left(\frac{-1}{M} \right)_0$$

~~$$C_A = C_{A_0} + M \ln C$$~~

$$C_{A_0} \int \frac{d\chi_A}{(1 + \epsilon_A \chi_A)(-r_A)} = t \Rightarrow \frac{C_{A_0}}{\epsilon} \ln(1 + \epsilon_A \chi_A) = kt$$

$$\frac{C_{A_0}}{\epsilon_A} \ln \frac{V}{V_0} = kt$$

$0.6 A + 0.4$ inerts $\rightarrow 0.6 \gamma R + 0.4$ inerts

$$\epsilon_A = \frac{0.6(\gamma-1)}{l} = 0.6(\gamma-1)$$

$$P_{A_0} = 0.6 \times P = 1.8 \text{ atm}$$

$$C_{A_0} = \frac{1.8}{RT}$$

$$\frac{1.8}{RT 0.6(\gamma-1)} = \ln \frac{V}{V_0} = kt = \frac{0.15}{(\gamma-1)RT} \times 4$$

$$\ln \frac{V}{V_0} = \frac{0.15 \times 4}{3} = 0.2$$

$$\frac{V}{V_0} = 1.221$$

$$1 - \frac{\Delta V}{V_0} = 0.22$$

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Variable Volume Reactors

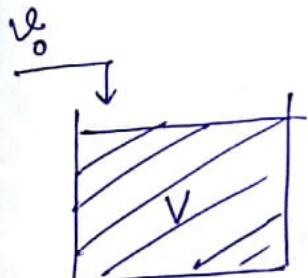
Mole balance:

1) CSTR

$$\frac{V}{V_0 C_{A0}} = \frac{x_{Af} - x_{A0}}{-r_A} = \frac{x_{Af}}{-r_A} - \tau = \frac{V}{V_0}$$

$$-r_A = kC_A = k \frac{C_{A0}(1-x_A)}{1+\epsilon_A x_A}$$

$$\frac{N_A}{V} = \frac{N_{A0}(1-x_A)}{V_0 (1+\epsilon_A x_A)} = \frac{C_{A0}(1-x_A)}{1+\epsilon_A x_A}$$



$$\tau = \frac{V}{V_0}, \quad \tau/C_{A0} = f(x_A)$$

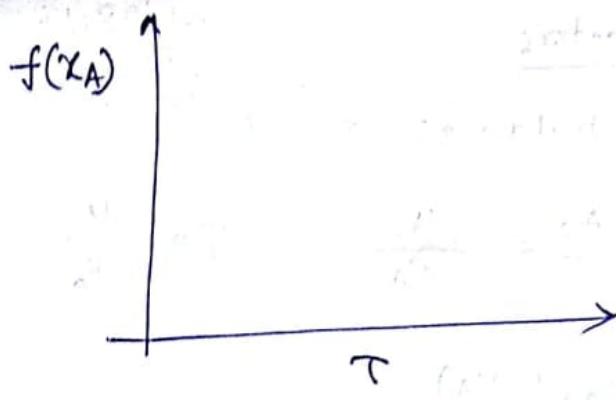
τ			
x_A			
$f(x_A)$			

Variable density with 2nd order kinetics

$$-r_A = k C_A^2$$

$$\frac{V}{F_{A0}} = \frac{V_0(1+\epsilon_A x_A)}{C_{A0} V_0 (1+\epsilon_A x_A)} = \frac{x_A}{k C_{A0}^2 \frac{(1-x_A)^2}{(1+\epsilon_A x_A)^2}}$$

$$K\tau = f(x_A) = \frac{x_A (1+\epsilon_A x_A)^2}{k C_{A0} (1-x_A)^2}$$



For volume basis: $-\frac{dF_A}{dT} = -r_A$

$$F_A = F_{A_0} (1-X_A) \quad \text{then} \quad F_{A_0} \frac{dX_A}{dT} = -r_A$$

$$\frac{V}{F_{A_0}} = \int_0^{X_A f} \frac{dX_A}{-r_A} \quad \text{or} \quad \frac{T}{C_{A_0}} = \int_0^{X_A f} \frac{dX_A}{-r_A}$$

For catalyst basis: $-\frac{dF_A}{dW} = -r'_A$

$$\frac{W}{F_{A_0}} = \int_0^{X_A f} \frac{dX_A}{-r'_A}$$



$$-\frac{dF_A}{dW} = -r'_A = \frac{k' (P_A P_B - \frac{P_C P_D}{K})}{(1 + K_A P_A + K_P P_B + K_C P_C + K_D P_D)^2}$$

$$= F_{A_0} \frac{dX_A}{dW}$$

We can write P_A, P_B, P_C in terms of X_A
And therefore integrating, we get X_A

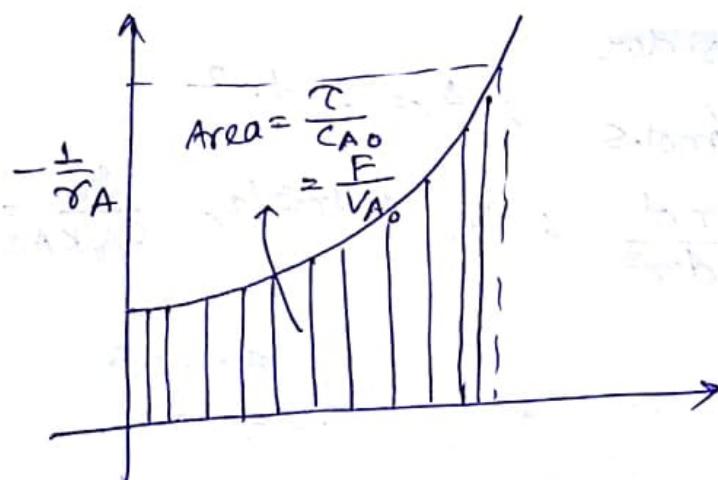
PFR with variable density for 1st order kinetics

$$-r_A = k C_A$$

$$\tau = C_{A0} \int_{X_A i}^{X_A f} \frac{(1 + \epsilon_A X_A) dX_A}{k C_{A0} (1 - X_A)}$$

$$k\tau = \int_0^{X_A} \frac{dX_A}{1 - X_A} + \epsilon_A \int_0^{X_A} \frac{X_A dX}{1 - X_A}$$

$$k\tau = -(1 + \epsilon_A) \ln(1 - X_A) - \epsilon_A X_A = f(X_A)$$



PFR requires lesser volume, so less cost of construction. Thus, PFR is preferred.

For constant volume

$$\epsilon_A = 0; \quad k\tau = -\ln(1 - X_A) = f(X_A)$$

PFR for variable density with 2nd order kinetics

Rate equation: $-r_A = k C_A^2$

Mole balance: $\tau = C_{A0} \int_0^{X_A f} \frac{dX_A}{-r_A}$

with $\tau = C_{A0} \int_0^{X_A f} \frac{X_A (1 + \epsilon_A X_A)^2 dX_A}{k C_{A0}^2 (1 - X_A)^2}$

$$T = C_{A_0} \int_0^{X_A} \frac{X_A(1+\varepsilon_A X_A)^2 dX_A}{K C_{A_0}^2 (1-X_A)^2}$$

$$C_{A_0} K T = 2\varepsilon_A (1+\varepsilon_A) \ln \frac{(1-X_A)\varepsilon_A^2 X_A + (1+\varepsilon_A)^2}{1-X_A}$$

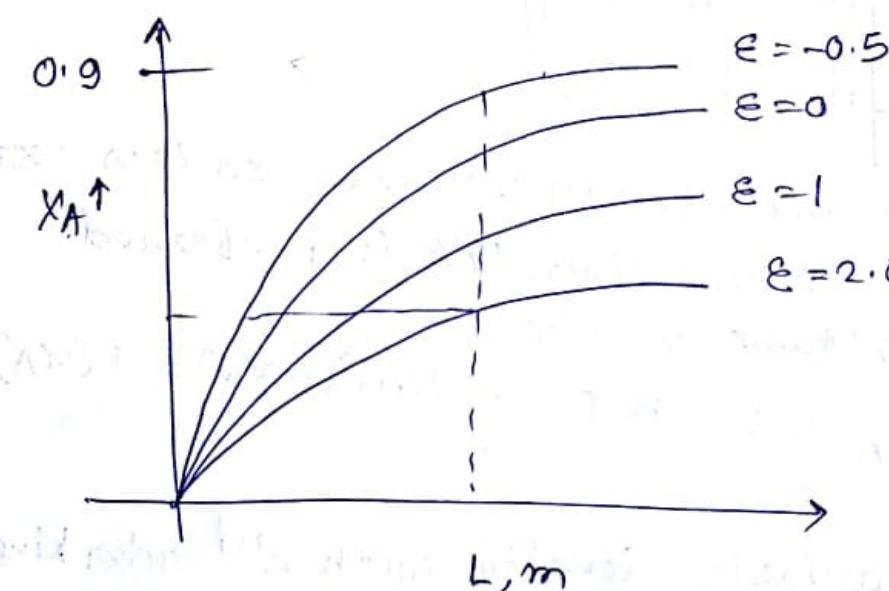
$$T = \frac{A_c L}{v_0}, A_c = \text{the cross sectional area}$$

$$L = \frac{v_0}{C_{A_0} K A_c} \left[2\varepsilon_A (1+\varepsilon_A) \ln \frac{(1-X_A)\varepsilon_A^2 X_A + (1+\varepsilon_A)^2}{1-X_A} \right]$$

let us consider

$$k = 5 \text{ dm}^3/\text{mol.s}, A_c = 1 \text{ dm}^2$$

$$C_{A_0} = 0.2 \frac{\text{mol}}{\text{dm}^3}; v_0 = 1 \text{ dm}^3/\text{s}, \frac{v_0}{C_{A_0} K A_c} = 1$$

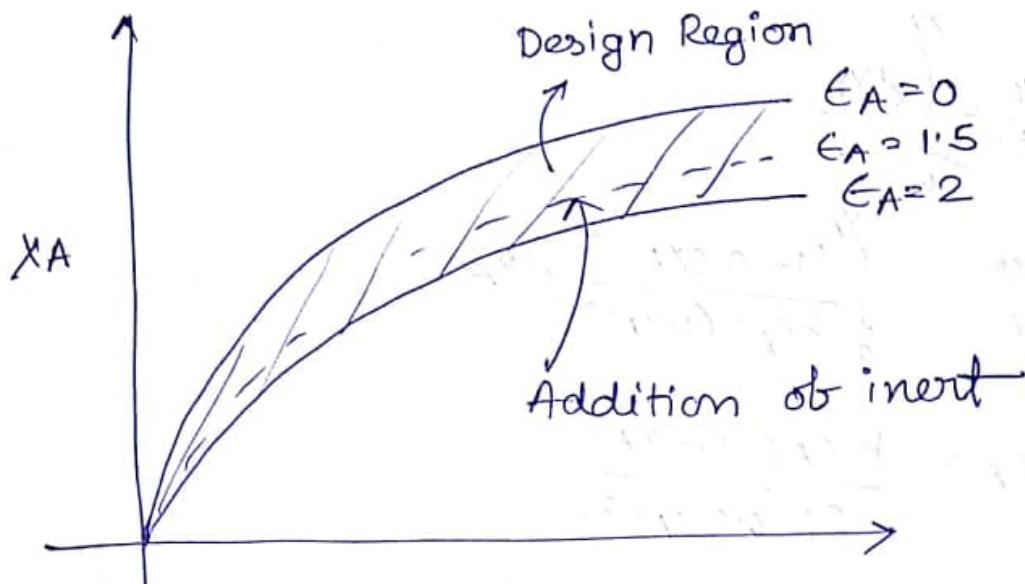


$\epsilon \uparrow, X_A \downarrow$

Case I: with the increase of ϵ_A for same conversion, reactor length increases

Case II: For constant reactor length, with increase in ϵ_A , conversion decreases

- # with addition of inert ϵ decreases
- # without considering ϵ , if reactor is ~~not~~ designed, then conversion reduces.



We will be conducting the dimerisation $2A \rightarrow D$ in a tubular reactor operating at 1.61 atm and total pressure and 400 K.

The feed is pure A vapor (i.e. $C_{A0} = 0.05 \text{ mole/L}$) at this T and P. The reaction rate constant is $K = 0.9 \text{ L/mole.s}$ and the reactor void volume is 25,000 liters.

a) What inlet volumetric flow rate can be used for a desired conversion of 0.85?

b) Give the outlet composition and volumetric flow rate. Estimate the average residence time. How close to the exact answer do you think your guess is?

$$\epsilon = \frac{1/2 - 1}{1} = -0.5$$

$$C_{A_0} = \frac{1.64}{0.082 \times 100} = 0.05 \text{ mole/L}$$

$$\frac{dX_A}{r_A} = \int_0^{X_A} \frac{dx_A}{r_A}$$

$$\frac{dX_A}{r_A} = \int_0^{X_A} \frac{(1 - 0.5X_A)^2}{KC_A^2(1-X_A)^2} dX_A$$

$$-r_A = \frac{KC_A^2(1-X_A)^2}{(1-0.5X_A)^2}$$

$$C_{A_0} kT = 2\epsilon_A(1+\epsilon_A) \ln(1-X_A) + \epsilon_A^2 X_A + (\epsilon_A + 1)^2 \frac{X_A}{1-X_A}$$

$$= 0.25726$$

$$V =$$

Q
At 700°C the rate of decomposition of $\text{A} \rightarrow \text{B} + \text{R}$, on a specific catalyst of given size is found to be

$$-r_A' = -\frac{1}{W} \frac{dN_A}{dt} = \left(10 \frac{\text{litre}}{\text{hr. gram cat}} \right) C_A$$

This is to be a tubular packed bed reactor of 2 cm. I.D using 25% of this active catalyst pellets evenly mixed with 75% of inert pellets to ensure isothermal operations. For 400 $\frac{\text{mol}}{\text{hr.}}$ of feed considering 50% A - 50% inert gas at 8 atm and 700°C , what must be the length of the reactor so that $\frac{P_{A,\text{out}}}{P_{A,\text{in}}} = 0.111$

Data:

Catalyst and inert pellets are porous of